Supramolecular Assemblies and Materials based on 2,2':6',2''-Terpyridine Metal Complexes

PROEFSCHRIFT

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Chapter I

New Functional Polymers and Materials based on 2,2':6',2''-Terpyridine Metal Complexes

Abstract

New inorganic-organic hybrid structures based on metal-complexes have become of increasing interest over the last few decades in the search for new materials. For this purpose different polypyridyl metal complexes have been used. Recently a strong increase in interest regarding 2,2':6',2''-terpyridine can be observed. In particular, octahedral bis-2,2':6',2''-terpyridine metal complexes offer the advantages of increased symmetry and in the case of ruthenium(III)/ruthenium(II) complexation an entrance to a directed complexation technique. Apart from the combination with polymeric systems, ordered inorganic-organic structures on surfaces are becoming better understood accordingly with the development of sophisticated nanotechnology characterisation techniques. Especially concerning photophysical processes such as solar light to energy conversion, there are many efforts ongoing including terpyridine-complex structures. This chapter deals with the incorporation of terpyridine complexes into polymeric structures such as poly(ethylene glycol), poly(styrene), dendrimers, bio-macromolecules, micelles and resins as well as the combination of terpyridine complexes with surfaces for electrocatalytic, photophysical and self-assembly purposes.

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1.1 Introduction

2,2':6',2''-Terpyridines are among the N-heterocycles which have very high binding affinity towards transition metal ions due to dπ-π* back bonding of the metal to the pyridine rings and the chelate effect.\textsuperscript{[1]} Complexation of one or two 2,2':6',2''-terpyridine (Figure 1.1)\textsuperscript{a} ligands can lead to a metal-complex and in many cases bis-complexes thus formed have octahedral coordination geometries.\textsuperscript{[2]}

\textbf{Figure 1.1:} Left: unfunctionalised 2,2':6',2''-terpyridine. Right: symmetric 4'-functionalised bis-terpyridine-metal complex (charge and anions omitted).

These complexes possess distinct photophysical, electrochemical and magnetic properties.\textsuperscript{[3]} The complex-bonding can be reversed under certain conditions, e.g. varying pH, temperature or applying even stronger competitive ligands, which makes such compounds interesting for the design of new functional materials.\textsuperscript{[4]} However, the application of functionalised terpyridines for these purposes has not been investigated as thoroughly as applications of their sister compounds 2,2'-bipyridines, for which the metal complexes possess similar properties as mentioned above for the terpyridines. The reason for this becomes clear when looking at the history of these two complex ligands. 2,2'-Bipyridines were discovered in 1888 by F. Blau who also synthesised the first bipyridine iron complex.\textsuperscript{[5]} However, 2,2':6',2''-terpyridine was only isolated in the 1930s,\textsuperscript{[6]} and since the synthesis of functionalised terpyridines in many cases requires comparatively more steps than the preparation of functionalised 2,2'-bipyridines, it is not surprising that this compound was investigated first and was also the first to be integrated into polymer structures.\textsuperscript{[7]}

This chapter deals with recent developments of such terpyridine bis- and mono-complexes regarding the incorporation into polymeric structures and the modification of different surfaces. Especially in the search for new functional materials, metallo-supramolecular

\textsuperscript{a} 2,2':6',2''-Terpyridine will be abbreviated as terpyridine or tpy
polymers, dendrimers or micelles have been of great interest for the last few years but also the combination of such stable complexes with "biopolymers" such as DNA/RNA, peptides and enzymes for labelling, intercalation and inhibition purposes is promising.\cite{8} Another field which is rapidly growing due to the technical advances made, is the build-up of ordered structures on a molecular scale on different kinds of surfaces.\cite{9} Also here, terpyridine complexes play an increasing role for applications such as solar cell devices or electrode catalysis. Furthermore, such easily detectable and multi-functional entities are of great use for gaining a more fundamental understanding of self-organisation phenomena of organic or inorganic-organic hybrid materials on surfaces.

An example of a combination of the above mentioned properties for the creation of new functional materials, regarding the more investigated bipyridine complexes, was recently described for the use of a bipyridine ruthenium complex. The complex is homogeneously dispersed in a poly(phenylene vinylene) (PPV) derivative in order to act as an electroluminescent device for the reversible switching between red and green emission.\cite{10} The authors could show that, by applying a bias voltage, at forward bias the excited state of the ruthenium complex is populated, and the characteristic red emission is observed. On reversing the bias, the lowest excited singlet state of the polymer host is populated, with subsequent emission of green light. This example demonstrates the potential uses of such polypyridyl-metal complexes in combination with polymeric materials and surfaces.

Recent advances in the synthesis of functionalised terpyridines have opened new possibilities for the introduction of metal-complexes into polymers and onto surfaces. Especially functionalisation in the 4'-position, by using e.g. substitution reactions with the nowadays commercially available 4'-chloro-terpyridine\cite{11} or the 4'-hydroxy-terpyridine,\cite{12} lead to symmetrical \textit{bis}-complexes with ether bridged functional groups (R, Figure 1.1, right).

First, the most recent advances concerning polymeric structures including terpyridine complex moieties are discussed. For a complete overview over the field the reader is referred to literature.\cite{7,13} Regarding biopolymer-terpyridine complex systems, the focus lies only on systems including terpyridine complexes which are covalently attached to enzymes, peptides or DNA/RNA and will not include simple terpyridine complexes acting as DNA intercalators or ribozyme mimetics, which have been widely discussed elsewhere.\cite{14} Concerning surfaces functionalised with terpyridines, a complete overview is given.
1.2 Polymeric architectures containing 2,2':6',2''-terpyridine metal-complexes

1.2.1 Metallo-polymers from terpyridine-functionalised monodisperse monomers

One way of classifying polymers, which contain terpyridine metal complexes, is to distinguish between metallo-polymers built up from monodisperse or polydisperse monomers. First metallo-polymer systems, starting from monodisperse building blocks, are discussed. In 1995, Constable presented the general concept of bis-terpyridine functionalised telechelics which, upon addition of metal ions, should give coordination polymers (Figure 1.2).[15]

![Polymeric bis-terpyridine-metal complex (charge and anions omitted).](image)

**Figure 1.2**: Polymeric bis-terpyridine-metal complex (charge and anions omitted).

It was mainly work by Kurth *et al.* and Rehahn *et al.* in the late 1990s, who pioneered this concept by using small monodisperse di-terpyridines as monomer in order to create, for example, coordination polyelectrolyte layers. In the last few years, there have been a number of different approaches in this direction, mainly focusing on iron(II) and ruthenium(II) as the "metal glue" for coordination polymerisation. Bis-terpyridine complexes of these two metals possess very high stability constants and regarding heat, only in the case of iron(II) reversibility is known.[16] Firstly, polymerisations using iron(II) chloride as complexing salt are discussed. Recently, Kimura *et al.* gave an example of a chiral structure obtained from twisted enantiomeric bridging ligands (Figure 1.3).[17]
Figure 1.3: Left: chiral bridging ligands in which two terpyridine exo-ligands are linked at 6- and 6’-positions by a chiral binaphthyl spacer. Middle: schematic representation of the stereospecific assemblies of iron(II) and the (R)- and (S)-chiral bridging ligands. Right: (a) effect of iron(II) concentration on the CD spectra of the (R) enantiomer (0.1 mM) in CHCl₃-MeOH at 20 °C: [iron(II)] = 0, 0.02, 0.06, 0.1 mM. Arrows indicate the spectral change. (b) CD spectra of (R)- (⁻⁻⁻⁻⁻⁻) and (S)- (-----) enantiomeric assemblies (0.1 mM) in the presence of iron (II) (0.1 mM) (reprinted from ref. [17]).

The enantiomeric ligands consist of a di-terpyridine functionalised chiral binaphtyl spacer, which are then separately complexed with one equivalent of iron(II) chloride in order to yield the enantiomeric coordination polymers. Upon addition of up to one equivalent of iron(II) chloride, a nearly linear increase in UV/Vis absorption of the Metal-to-Ligand Charge-Transfer (MLCT) band could be obtained. Moreover, circular dichroism (CD) spectroscopy showed an increase in the MLCT band as well, suggesting a chiral induction to the optically inactive Fe(terpyridine)₂-moiety and therefore superstructural chirality. However, characterisation of these novel polymeric or oligomeric species is challenging, and data concerning polydispersity or ring-chain equilibrium is difficult to obtain.

Abruña et al. also reported the synthesis of bridging bis-terpyridine ligands which, in this case, possess inherent chirality (Figure 1.4).[18] Complexation reactions with iron(II) salts were studied in solution with UV/Vis- and CD-spectroscopy in order to confirm the formation of chiral metallo-assemblies.
From the UV/Vis titration with iron(II) tetrafluoroborate it can be seen that especially the isolated MLCT band increases in intensity up to an equivalent of 1:1 but remains unchanged after overtitration (Figure 1.4, bottom). This proves, as reported by Kimura et al., the formation of saturated octahedral bis-complexes. This observation could be confirmed by CD-spectrometry, with additional indication of the formation of an optically active compound upon complexation with iron(II). ESI-mass spectrometry measurements showed that the polymeric assemblies undergo severe fragmentation. However, large fragments with up to 9 ligand-iron(II) repeating units were observed.

Constable et al. recently reported on the separation of different fractions of their polymerisation attempts using a di-terpyridine-tri(ethylene glycol) and iron(II) chloride, by column chromatography. There is great indication according to electrospray mass spectrometry and $^1$H-NMR experiments that the two main products formed are 3+3 and 4+4
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macrocycles (Figure 1.5).\textsuperscript{[19]} Only a smaller fraction which could not be eluted from the silica column is believed to be large macrocycles or linear polymers.

Figure 1.5: Proposed structures of the [3+3] and [4+4] metallo-macrocycles.\textsuperscript{[19]}

Similar observations are discussed in Chapter 4 of this thesis using hexane instead of tri(ethylene glycol) as spacer.\textsuperscript{[20]} For another similar metallo-polymer which consists of bis-terpyridine-di(ethylene glycol) and iron(II) chloride, the reversibility was investigated in a different way. Decomplexation of the iron(II)-polymer system could be shown by addition of the competitive ligand HEEDTA, thus showing full reversibility.\textsuperscript{[21]}
Meijer et al. reported the synthesis of a rigid Fe(II)(terpyridine)$_2$ polymer including oligo-(phenylene vinylene) (OPV) units (Figure 1.6, top).[22] Due to this rigidity, the formation of small cycles in this case is unlikely and the degree of polymerisation was estimated to be DP $\approx 100$ at the applied millimolar concentration, derived from kinetic data obtained from a UV/Vis titration experiment. Such metallo-polymers containing ruthenium(II) as metal centre are of special photophysical interest because of their fluorescence (even at room temperature), provided a conjugated system is attached to the 4'-position. Rehahn et al. recently investigated rodlike bis-terpyridine-Ru(II)-polymers and concluded from $^1$H-NMR-endgroup analysis that these ruthenium-complex polymer chains should have a DP $\geq 20$, which also corresponds to previous results (Figure 1.7).[23] However, in this case a heteroleptic complexation was used, where one of the ligands does not consist of a terpyridine, but of a 2-phenyl-bipyridine. In this case, in addition to the 5 nitrogens, a carbanion completes the complexation to the ruthenium(II) centre.

**Figure 1.6:** Top: combination of a bis-terpyridine-Fe(II)-complex and an oligo(phenylene vinylene) (OPV) unit.[22] Bottom: chiral terpyridine-Ru(II)-complex polymer.[24]
Similar systems containing a chiral pinene moiety attached to the outer terpyridine rings were reported by Barron et al. (Figure 1.6, bottom).[24] Extensive luminescence lifetime studies were carried out on these systems. These showed that the length of the $\pi$-electron delocalisation "box" governs the emission energy at 77 K, where the luminescence lifetimes are not controlled by non-radiative decay in contrast to the situation at room temperature.

A further example using the different approach of first synthesising a 4'-functionalised bis-terpyridine-Ru(II) complex and subsequent polymerisation of this complex to a ruthenium-complex polymer is reported by Constable et al. The bis-complex consisted of thiophene moieties attached to the 4'-positions of the terpyridines in the complex, which could be electrochemically polymerised (Figure 1.8, top).[25]
Figure 1.8: Top: coupling of a bis-4'-thiophene-terpyridine-ruthenium(II) complex resulting in a 2,2'-bithienyl-linked polymer (reprinted from ref. [25]). Bottom: view of the crystal packing of dinuclear platinum(II) terpyridines showing the short Pt-Pt intermolecular interactions (reprinted from ref. [28]).

From semi-empirical calculations (ZINDO/S) it was concluded that, because of the build-up of a positive charge at the thienyl C5 position, the C5 position is the favoured position for coupling to give a linear, rod-like ruthenium-complex polymer. The authors did not determine the degree of polymerisation, but investigated the deep red film (100 nm thick) formed on the electrode surface using AFM and XPS (detection of ruthenium 3d5/2 and S 2p3/2). Furthermore, the red shift of the MLCT-band from 498 nm to 521 nm matches the extended conjugation arising from the bithienyl spacer.

Considering metallo-polymeric structures containing other metal ions, two examples should be mentioned. Perylene bis-imide dyes having two terpyridines attached, give rise to polymerisation upon addition of zinc(II).\textsuperscript{[26]} Comparison of $^1$H-NMR spectra indicated the
formation of polymeric structures, but since the stability of bis-terpyridine-Zn(II) complexes is significantly lower than with ruthenium(II) or iron(II)\textsuperscript{[27]} it might prove difficult to find hard evidence for the formation of long rodlike chains.

A different approach for generating polynuclear heterocyclic assemblies was recently discovered for a dinuclear platinum derivative with the terpyridine acting as a new N,C\textsuperscript{A},C,N bridging ligand.\textsuperscript{[28]} Although only observed in the crystal structure, the formation of infinite monodimensional organoplatinum chains through weak interaction of Pt(II)-Pt(II) contacts (3.283 Å) could be observed, with neighbouring chains being kept together by graphitic (interplanar distance 3.52(2) Å) and van der Waals interactions (Figure 1.8, bottom). The knowledge about the existence of such chains in the crystal might provide helpful information for the utilisation of these phenomena in the build-up of ordered chains or 2-dimensional crystals on different surfaces.

### 1.2.2 Polydisperse systems containing 2,2\textquoteleft;6\textquoteleft;2\textquoteright;\textquoteright;terpyridine metal complexes

The combination of properties of conventional polymers with those of bis-2,2\textquoteleft;6\textquoteleft;2\textquoteright;\textquoteright;terpyridine metal complexes became of increasing interest over the last few years. There are mainly three different approaches to chemically introduce terpyridines and their complexes into polymeric systems: (a) by functionalising properly modified polymers with terpyridine ligands, (b) by using a functionalised terpyridine as an initiator, and (c) by using a terpyridine with a polymerisable group as the monomer or co-monomer (these can be classified as convergent approaches starting from uncomplexed terpyridine). These main approaches also apply to corresponding bis-terpyridine metal complexes (divergent approach in which metallo-polymers are formed starting from the complex). Having a functionalised polymer with non-complexed terpyridine ligands, subsequently allows different combinations upon bis-complexation with different metals, leading to a rich variety of possible new structures. For a detailed insight into these strategies, the reader should turn to recent overviews.\textsuperscript{[7,13]}

The first two approaches are especially appealing for gaining access to extended polymer chains through metal complexation by a terpyridine-functionalised polymer. These polymeric terpyridine starters can be either mono-functionalised or of telechelic nature, possessing more than one terpyridine unit per chain. Having terpyridine units at both ends of each chain allows access to linearly extended chains, containing metal "linkers". Such a system, consisting of a high molecular weight poly(ethylene oxide) polymer endcapped with terpyridines, gave upon
addition of iron(II) or nickel(II) acetate, an extended polymer, which could be shown especially through the increase in viscosity (Figure 1.9).\cite{29,30}

![Figure 1.9: Left: synthesis of a metal-linked poly(ethylene glycol)$_{180}$ (charge and anions omitted). Right: viscosity increase when adding nickel(II) acetate.](image)

In order to investigate a variety of such polymers with different chain lengths, first iron(II) containing polymers were synthesised using a combinatorial approach.\cite{31,32} Another possibility for creating and investigating such systems is to first functionalise only one chain end with terpyridine and then to apply directed as well as undirected coupling methods in order to obtain AA or AB and ABA block copolymer systems (Figure 1.10). Directed coupling can be achieved by first forming a mono-terpyridine metal complex, the most common metal for this strategy being ruthenium(III). Subsequent reduction to ruthenium(II) in the presence of a differently functionalised terpyridine leads to a heteroleptic complex.

![Figure 1.10: Schematic representation of AA-, AB- and ABA type metallo-supramolecular block copolymer systems.](image)
In contrast, undirected couplings use the same ligand for bis-complexation with bivalent metal salts. Looking at AA homopolymer systems this concept was recently realised using poly(ethylene oxide) functionalised with one terpyridine, which, upon complexation with various transition metal ions, gave water soluble polymers with double the mass of the starting polymer ligand plus the metal and counter-ions. These complexes were investigated with respect to their pH sensitivity. It was found that the iron(II)-, cobalt(II)-, zinc(II)- and cadmium(II)-containing polymers showed decomplexation at high and low pH (13 and 1, respectively). Moreover, the copper(II) polymer complex dissociated after the solution was kept at a low pH for a period of a few days. However, the metallo-homopolymers containing ruthenium(II) and nickel(II) as metal centre showed complete insensitivity to pH changes ranging from pH 0 to pH 14, even after stirring for several days. This demonstrates the feasibility of the bis-terpyridine metal(II) linker to be reversed by adjusting the pH in the case of some metal ions. Therefore, new avenues for possible applications of these systems as switchable "smart" materials are opened. As for the characterisation of the described systems using mass spectrometry, only in the case of the cobalt(II) and ruthenium(II), which are among the most stable, the unfragmented bis-polymer complex as well as the fragmented free ligand could be detected. Increasing the laser intensity led to an increase in the ratio of free ligand/bis-polymer complex, which is not unexpected due to the partial dissociation of the complex which is observed upon excitation. Similar AA-type metallo-supramolecular block copolymers were recently synthesised using 4'-hydroxy-methyl functionalised terpyridines as an initiator for the controlled coordinative ring-opening polymerisation of lactides using aluminium alkoxides. Since biodegradable polymers are becoming more and more important, especially in fields such as tissue engineering and waste recycling, the development of new materials in that direction seems appropriate. Using this approach, polylactides end-capped with terpyridine were obtained with very narrow polydispersities. Complexation with iron(II) led to the AA-metallo-polymer which could be characterised by means of GPC and MALDI-TOF-MS. Furthermore, as mentioned earlier, the stability of the Fe(II) complex is temperature dependant. Investigations concerning the temperature sensitivity of iron(II)/polylactide complex films showed disappearance of the typical purple colour at 160 °C. Upon cooling the films, the colour returns. This example also illustrates the principal reversibility of such metallo-supramolecular structures.

Concerning AB or ABA type structures, their preparation requires directed coupling techniques. A well-known strategy for creating such hetero-complexes is the
ruthenium(III)/ruthenium(II) coupling method. First the dark brown mono-terpyridine-Ru(III) complex is formed by refluxing ruthenium(III) chloride in DMF with the ligand. This is then further reacted with a different ligand under reductive conditions (ethanol / cat. N-ethylmorpholine) resulting in the formation of the red ruthenium(II) hetero-complex. Applying this strategy to different terpyridine endcapped polymers led to the hetero-ruthenium-complex polymers (Figure 1.11).

![Synthesised AB-type bis-terpyridine-Ru(II) complexes combining different polymer blocks.][36]

Both of the described metallo-supramolecular block copolymers showed a single signal when analysed using GPC, indicating that no homopolymers were formed. Such AB type structures combining two different polymer chains have up to now only been accessible using living or controlled polymerisation procedures. The same strategy has also been applied for ABA type systems. Here, a bis-terpyridine endcapped poly(propylene oxide) telechelic was first complexed on both ends with ruthenium(III) chloride and subsequently complexed symmetrically on both sides with a 4'-functionalised terpyridine. On the basis of MALDI-TOF mass spectrometry analysis, the existence of each species could be shown with weight averages showing the expected additional masses for each step of the functionalisation. This route opens new avenues for creating such ABA systems, allowing for a wide range of combinations. It should be emphasised again that the stability of these ruthenium-complex polymers is very high as mentioned earlier, so for many applications the complex will not dissociate.
The third main approach for including terpyridines and its complexes in polymeric structures is to use terpyridine (complexes) functionalised with a polymerisable group as the monomer or co-monomer. Concerning the convergent approach, this was demonstrated over 10 years ago utilising vinyl- and acrylic-groups as functional moieties for polymerisation.\cite{7} Recently, Tew et al. prepared a random copolymer using a methyl methacrylate functionalised terpyridine as co-monomer (Figure 1.12, left).\cite{38}

Upon addition of cobalt(II) nitrate the authors observed a rise in viscosity which did not occur in the case of the homopolymer. Even at low concentrations of 4 mg/mL a significant rise in viscosity could be observed, which, when comparing to other non-covalent systems such as hydrogen bonding, had not been the case.\cite{39}

A very similar approach for gaining access to such a copolymer was taken by our own group, with the only difference being the spacer length between the 4’-position of the terpyridine and the polymer backbone.\cite{40} However, this terpyridine copolymer was then used for creating a more complex metallo-polymer. With the ruthenium(III)/ruthenium(II) method, graft copolymers were synthesised where additional terpyridine-Ru(III) end-functionalised poly(ethylene glycol)-chains were attached to the terpyridine on the main polymer backbone via ruthenium(II) complexation. Additionally, a polylactide terpyridine-Ru(III) and a non-polymeric terpyridine-Ru(III) were used as grafting ligand-complexes. For comparing the thermal properties of the grafted copolymers with the starting copolymer, differential scanning calorimetry (DSC) measurements were performed which showed significant differences especially in the glass transition temperatures and therefore demonstrate the influence of the grafting process.
Chapter I

An example for the divergent approach of polymerising bis-terpyridine complexes, which are functionalised on one side with a polymerisable group, was reported recently.\cite{41} Hetero bis-terpyridine-Ru(II) complexes bearing a 4-vinyl-phenyl substituent on one of the 4'-positions and a 4-hydroxymethyl-phenyl on the other 4'-position were copolymerised with styrene using radical polymerisation. The product precipitated from the reaction mixture as an orange solid. The obtained polymer had an $M_n$ (determined by GPC) of 5170 with a polydispersity index (PDI) of 1.62. The fact that no dissociation was observed when passing the GPC column also demonstrates the stability of such hetero bis-terpyridine-Ru(III) complexes. Through possible further functionalisation on the hydroxymethyl function of the ligands, new possibilities for cross-linked or grafted systems become available. Especially the bis-terpyridine-Ru(II) complex offers photophysically interesting properties due to its significant room temperature fluorescence, which is due to the conjugation in the 4'-position of the terpyridine. Cho et al. used the convergent approach to side chain functionalised ruthenium(II) complexes.\cite{42} Here, first a conventional ABA tri-block copolymer was formed by anionic polymerisation to yield poly(CzMA-b-2VP-b-CzMA) with CzMA = 2-(N-carbazolyl)ethyl methacrylate and 2VP = 2-vinylpyridine. The middle block consisting of 0 to 20 2VP units was then complexed with the mixed Ru(II)-terpyridine-(dmbpy)chloride (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) in order to yield the octahedral six-coordinate ruthenium(II) complex as the grafted species (Figure 1.12, right). Investigations were then carried out by electro-luminescence experiments on a polymer layer in a device. Testing polymers with different ruthenium(II) contents led to promising conclusions regarding intra- and inter-molecular energy-transfer and therefore show the possibility to fine-tune the ruthenium(II) complex content via controlled polymerisation techniques for such purposes.

Looking more at mechanical materials properties, the combination of different cross-linking techniques might be of great use e.g. for coating technology. In work originating from our laboratories, an attempt has been made to combine and individually address metal-bis-terpyridine-complexation and the UV-mediated polymerisation of oxetanes.\cite{43} Therefore an acrylate terpolymer was designed bearing a terpyridine as metal complexing unit and an oxetane as a covalent cross-linking unit (Figure 1.13).
The terpolymer obtained through radical copolymerisation had an $M_n$ of 7400 g/mol and an average terpyridine content of 2.8 per polymer chain. It could be shown that by the addition of iron(II) chloride, the typical MLCT absorption (purple colouring) of the bis-complex was observed. Upon subsequent reaction with AlCl$_3$, the ring-opening and thus covalent cross-linking of the oxetane groups took place. Moreover, the order of the cross-linking could also be reverted. In this case, first a rubber-like material was obtained from the covalent cross-
linking by treatment with AlCl₃. The subsequent treatment of the cross-linked polymer to a methanolic solution of iron(II) chloride immediately resulted in a purple colouring of the material, indicating that the additional coordinative cross-linking had taken place. This demonstrates the feasibility of such bis-terpyridine metal complexation as part of a multi-step cross-linking procedure, which might be of interest, for example, for smart coatings with self-healing properties.

1.2.3 Dendrimers, polymer-micelles and -resins including terpyridine metal complexes

Dendrimers, as a special class of macromolecules, possess low polydispersity and are of interest because of their core-shell geometry.[44,45] Especially metal-containing dendrimers are of great current interest because of their potential use as catalysts or molecular carriers for catalysts and light-harvesting antennae. Generally, metallo-dendrimers can be divided into two categories: those having the metal encapsulated within the dendritic envelope and those having the metal located at or near the dendrimer surface. Earlier works on dendrimers containing terpyridine-metal complexes were performed e.g. by Newkome, Balzani, Constable, Chow, Kimura and Hong and are summarised in a recent review.[7] Large polymeric systems or aggregates, such as micelles and cross-linked resin-type structures, offer an alternative to solution chemistry. Examples for this are asymmetric catalytic reductions of carbonyl bonds[46] or different solid phase synthesis approaches demonstrated first impressively by Merrifield in 1965, who anchored reagents to insoluble supports for purposes of solid phase peptide synthesis (SPPS).[47]

Firstly, concerning dendrimers, Chow et al. recently synthesised a series homo- and heteroleptic benzyl-ether dendrimers with a bis-terpyridine ruthenium(II) complex in the core, which is centred for the homoleptic complexes and "off-centred" for the heteroleptic complexes (Figure 1.14).[48]
Cyclic voltammetry (CV) measurements were carried out in order to investigate any influence of the polyether dendritic fragments on the redox potentials of the bis-terpyridine ruthenium(II) core as well as to investigate any influence of the shape of the dendrimer on redox reversibility. No induction effect was observed on the redox potentials of the electrochemically active unit, which could have arose from the electron rich polyethers. In addition, no preferred orientation of the non-spherical different dendrimers towards the electrode could be observed. The redox reversibility decrease correlated with the size exclusion chromatographic data of the ruthenium-complex dendrimer, which is known for spherical dendrimers.
Introducing chirality as well as photoactive bis-terpyridine-Ru(II) complexes into the dendritic sphere is of interest for the creation of macromolecules with new optical properties. Lin et al. functionalised Fréchet-type benzyl bromide dendrons with a binaphtyl-terpyridine which were subsequently complexed to tetrakis(2,2':6',2"'-terpyridinyl-4'-oxymethyl)-methanes by applying ruthenium(III)/ruthenium(II) chemistry (Figure 1.15).[49]

![Figure 1.15: Frechét-type dendrons containing terpyridines which are complexed to a tetrakis-terpyridinyl core.][49]

It was found that the bis-terpyridine-Ru(II) complexes quench the fluorescence of the binaphtyl as well as the dimethoxybenzyl fluorophores, which can be explained by the quenching of the triplet-MLCT states by low-lying metal-centred states. It is believed that the intersystem crossing from the $\pi^*$ bands of the peripheral fluorophores to the triplet-MLCT states is highly efficient, resulting in the emission of the $\pi^*$ system to be quenched. Only for the highest generation dendrimer, a weak luminescence could be observed, which demonstrates the distance dependence of the quenching efficiency. In a similar approach the same authors synthesised a metallo-dendrimer with the same core structure but lacking the dimethoxybenzyl dendron arms.[50] The circular dichroism (CD) spectra for both of these dendrimers showed three cotton effects and were very similar to the spectra of the bis-naphtyl ligands, thus showing no sign of newly formed chirality.
Kim et al. reported the synthesis and characterisation of three different generations of carbosilanes, which included 4, 8 and 16 terpyridines on the dendritic periphery (Figure 1.16).

These dendrimers were also suitable for complexation to other terpyridines using the ruthenium(III)/ruthenium(II) strategy. Characterisation was carried out by MALDI-TOF-mass-spectrometry, NMR as well as UV/Vis absorption. Generally, dendritic carbosilanes are of special interest because they are chemically inert and fluid at high molecular weight in high generation. Therefore, the combination with bis-terpyridine-Ru(II) complexes might lead to unique materials with special photophysical properties.

More complex heteroleptic metallo-supramolecular dendrimers were synthesised by Newkome et al. They applied mixtures of differently functionalised terpyridine-Ru(III) complexes in the reaction with an octa-terpyridinyl polyamide dendritic core, in order to achieve a combinatorial functionalisation approach based on terpyridine-Ru(III)/Ru(II) chemistry (Figure 1.17).
Initially, the terpyridine dendrimer was separately reacted with each of the three terpyridine-ruthenium(III) compounds, which led to dendrimers with different ether functions at the periphery. Subsequently, different mixtures of the three terpyridine-Ru(III) ligands were reacted with the core terpyridine dendrimer. Upon comparison of the $^{13}$C-NMR spectrum of the different species, it could be shown that the three different functionalities were successfully complexed to the dendritic core. Furthermore, the authors could show selective decomplexation of the peripheral tert-butyl esters as well as the selective de-benzylation of the benzyl-ether functionalities of the other complexed ligand. This combinatorial strategy combined with orthogonal decoupling techniques leads to systems with latent or masked regions of reactivity that can be accessed and addressed specifically at a desired time in generational construction. Therefore, an advantageous flexibility between that of a completely directed approach, whereby precise control over monomer attachment is maintained and that of random, uncontrolled mixed monomer attachment to reactants on the surface is achieved.

Concerning micellar aggregates incorporating terpyridine complexes, only our group has reported efforts in this direction up to now. Micelles were formed using the systems reported before which consist of a hydrophilic/hydrophobic block copolymer linked by bis-terpyridine-Ru(II) complexation. As a first example PS$_{20}$–[Ru(II)]–PEO$_{70}$, which represents an amphiphilic block copolymer, was found to aggregate to micelles in water.$^{[53]}$ Concerning the stability of these micelles in terms of bis-terpyridine-Ru(II) connectivity, they were found to be stable upon variation of temperature (20°C – 70°C), ionic strength (pure water – 1 M
NaCl) and pH (0 – 14). However, there were significant influences concerning the hydrodynamic radius ($D_h$).

In a different system including the soft poly(ethylene-co-butylene) core as opposed to the glassy PS core, the ruthenium(II) complexes of the PEB$_{70}$–[Ru(II)]–PEO$_{70}$ could be opened by the addition of the competitive ligand HEEDTA. The solution turned from red to colourless and dynamic light scattering (DLS) measurements confirmed the existence of objects with $D_h = 13$ nm, which are thought to be PEB cores dispersed in water. Moreover, also more complex systems using PS$_{32}$–P2VP$_{13}$–[Ru(II)]–PEG$_{70}$ block copolymers have been prepared.

Up to now, only few reports on terpyridine functionalised polymeric resins or beads have appeared in literature, compared to bipyridine functionalised ones. The main applications of such species lie in the area of heterogeneous catalysis. Yoo et al. functionalised poly(chloromethylstyrene-co-divinylbenzene) (PCD) with a 4’-(4-hydroxyphenyl)-terpyridine (Figure 1.18).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Time/h</th>
<th>Conversion yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene oxide</td>
<td>2</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Cyclopentene oxide</td>
<td>32</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Styrene oxide</td>
<td>48</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>1-Hexene oxide</td>
<td>120</td>
<td>&gt; 99%</td>
</tr>
</tbody>
</table>

**Figure 1.18:** Top: synthesis of polymer-supported poly(chloromethylstyrene-co-divinylbenzene)(PCD)-terpyridine-Fe(III) catalyst. Bottom: hydrolysis of epoxides using PCD-terpyridine-Fe(III) catalyst in a mixture of acetone/H$_2$O (8 : 2 v/v) at room temperature (reprinted from ref. [56]).
Upon complexation with Fe(ClO$_4$)$_3$ they formed terpyridine-Fe(III) \textit{mono}-complexes. The formation of \textit{bis}-complexes seems unlikely because of the terpyridine ligand being attached in a sterically confined, rigid manner. This material was then used to catalyse the ring-opening of different epoxides with methanol and water. They found almost quantitative conversion yields after short reaction times at room temperature.

Buchmeiser \textit{et al.} also investigated the possibility of developing a polymer supported catalyst, in this case for heterogeneous Atom-Transfer Radical Polymerisation (ATRP).\cite{57} However, the terpyridine-Cu(I) grafted PS-DVB (2\% cross-linking) did not lead to any PS which could be isolated.

The loading of different metal-ions (iron(II), cobalt(II), copper(II), ruthenium(III), nickel(II)) on terpyridine functionalised TentaGel (PS/PEO) microbeads ($d = 20\mu m$) is discussed in Chapter 5 and 6 of this thesis.\cite{58} UV/Vis spectroscopic measurements on suspensions of these beads led to the characteristic absorption bands known from the free terpyridine metal complexes, and complexation also becomes apparent in the colouring of the material. Furthermore, the loadings of these beads could be investigated by AAS. The loading rates were found to be in accordance between quantitative \textit{mono}- and \textit{bis}-complexation of the terpyridine on the microbeads. Applying ruthenium(III)/ruthenium(II) chemistry led to the functionalisation of the terpyridine moieties with an anthracene functionalised terpyridine.

In terms of characterisation of terpyridines attached to solid polystyrene supports, Heinze \textit{et al.} developed a new mass spectrometric technique in order to detect the attached terpyridine moieties.\cite{59} Cross-linked polystyrene was first modified with a silyl-ether linker which was then reacted with 4’-(4-hydroxyphenyl)-terpyridine. Dry samples of the resulting material were ground to a fine powder before introduction into the EI mass spectrometer. This method led to the detection of fragments, which could be distinguished from unbound material.

### 1.2.4 Biopolymers and terpyridine metal complexes

Over the last two decades there has been an increasing interest in metal-chelating ligands which can act as DNA/RNA intercalators or as inhibitors for certain enzymes, with the most prominent example being cisplatin.\cite{60} Terpyridines as ligands can also lead to potent intercalators, e.g. it was shown that for Ru(III)Cl$_3$-terpyridine the activity against L1210 leukemia cells is comparable with that of cisplatin.\cite{61} Since there are numerous reviews on the issue of investigating different ligand systems also including terpyridines for such purposes, the focus will be, given the context of this chapter, only on covalently bonded...
systems which have recently attracted attention. As far as the investigation of enzyme-polymer hybrid systems is concerned, recent approaches made include metal-to-ligand complexation using terpyridines ligands.

It has been shown recently, that ruthenium(II) complexes of the type $[\text{Ru}(\text{tpy})(\text{dppz})(\text{CH}_3\text{CN})]^2^+ \text{ (dppz = dipyrido}[3,2-a;2',3'-c]-\text{phenazine)}$, which are tethered to an oligonucleotide (ODN) strand (Figure 1.19), can be specifically photolysed to give a reactive aqua derivative, which can then form a duplex with a DNA target 11mer.$^{[62]}$

![Figure 1.19: Yields of the synthetic terpyridine ruthenium-labelled oligonucleotide conjugates and their target oligo-DNA (reprinted from ref. $^{[62]}$).](image)

<table>
<thead>
<tr>
<th>oligo</th>
<th>yield (%)</th>
<th>solid-phase synthesis</th>
<th>postsynthetic labeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>antisense ODNs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>natural</td>
<td>5'-CTTACCAATC-3'</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>5'-modified</td>
<td>5'-L-pCTTACCAATC-3'</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5'-Ru-pCTTACCAATC-3'</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>3'-modified</td>
<td>5'-CTTACCAATCp-L-3'</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5'-CTTACCAATCp-Ru-3'</td>
<td>69</td>
<td>51</td>
</tr>
<tr>
<td>middle</td>
<td>5'-CTTACp-L-pCAATC-3'</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5'-CTTACp-Ru-pCAATC-3'</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>5'-modified</td>
<td>5'-L-pCTTACCAATCp-L-3'</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5'-Ru-pCTTACCAATCp-Ru-3'</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>target 11mer</td>
<td>5'-TGATTGGTAAG-3'</td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>

This duplex was found to be significantly more stable than the natural, non-ruthenium(II) complex containing a DNA • DNA duplex. Following the hybridisation of the ODN with the
DNA, the nitrogen of a guanine completes the octahedral coordination sphere of the mixed ruthenium(II) complex. However, because of the thus generated steric hindrance, these complexes are again vulnerable to competing ligands such as pyridine and therefore the reactivity and specificity of the resulting aqua-ruthenium(II)-ODN conjugates can be controlled.

Another example for the useful incorporation of a terpyridine complex into an oligonucleotide was shown by Bashkin et al. A 17-mer oligonucleotide probe containing a terpyridine attached to a serinol, which can also act as building block in DNA sequencing, was designed in order to target a 159-mer fragment of the HIV gag gene messenger RNA (Figure 1.20).[^8a]

![Figure 1.20](image)

**Figure 1.20:** *Left: synthesis of the terpyridine modified DNA building block. Middle: target 159-mer fragment of the HIV gag gene mRNA with the 17-mer recognition unit underlined. Right: 17-mer DNA probes (1a-d) with X indicating the serinol-terpyridine residue (reprinted from ref. [^8a]).*

Experiments showed, that upon complexation of the terpyridine probe with copper(II), the target mRNA was specifically cleaved after forming a duplex. Several different 17-mer DNA probe sequences were prepared via automated DNA synthesis with the serinol-terpyridine being included at a different position for each probe. Gel electrophoresis proved upon comparison with RNase T1 and base hydrolysis the specific cleavage of the mRNA according to the position of the serinol-terpyridine in the probe.

An important application in this context is the use of terpyridine complexes as fluorometric sensors. Solid supports bearing immobilised oligodeoxyribonucleotide probes are a useful tool in analysing the base sequence of nucleic acids. Hakala et al. reported a mixture of such particles, each with a given allele-specific oligonucleotide and a reporter group for the specific binding of a fluorescently tagged target.[^63] The fluorescent markers typically consist of covalently linked europium(III) complexes containing a terpyridine unit (Figure 1.21).
fluorescent target itself was made from an oligonucleotide hybrid in such a way that a target oligonucleotide with a 16- or 12-nucleotide sequence at the 3'-terminus, which is complementary to the fluorescently tagged probe oligomer, was first hybridised with a complementary sequence of the target oligonucleotide. This resulting hybrid could then attach to the corresponding particle bound mutation specific probe (target), which had a complementary sequence to the target sequence at the 5'-terminus (8-16 nucleotides long) (Figure 1.21).

**Figure 1.21:** Principle of the sandwich hybridisation assay (reprinted from ref. [63]).

The resulting sandwich type assay was then investigated by microfluorometry of the single particles, which led to the observation of emissions, which were linearly related to the concentration of the target oligomer (over a range of 5 orders of magnitude). The detection of such phenomena is possible because terpyridine-lanthanide chelates have a long-lived fluorescence suitable for time-resolved measurements. Furthermore, the difference between the wavelength of excitation and emission is generally larger, and the emission bands obtained are generally narrow. This is also an example which would fit to the previous section because of the particles used here being uniformly sized (50 μm) porous glycidyl methacrylate/ethylene dimethacrylate beads. The described approach demonstrates the feasibility of such single particle systems for the use in multiparametric assays in order to determine the base sequence of nucleic acids.

Another application of metal-complexes containing terpyridine as ligand is the determination of electron transfer (ET) rates in Azurin from *Pseudomonas aeruginosa*. This protein is
widely studied as a model electron-transfer protein (copper(II) ↔ copper(I)), in particular with respect to the coordination of the copper ion. Gray et al. studied ET tranfer rates of ruthenium(II)-modified azurins \([\text{Ru(II)}(\text{terpyridine})(\text{bpy/phen})(\text{His83})\text{Az}]\)\(^{[64]}\). They could show that the time constants for electron tunneling (copper(I) → ruthenium(III)) in crystals are roughly the same as those measured in solution, indicating very similar protein structures in the two states.

As a means of combining catalytic activity of enzymes with metallo-supramolecular ordering, first experiments with respect to functionalising an enzyme and a protein with a terpyridine unit have been carried out and in case of the enzyme also tested for catalytic activity\(^{[65]}\). A maleimide-functionalised terpyridine was reacted with free thiol groups from lipase B from \textit{Candida antarctica} or to the free thiol groups Bovine Serum Albumin, which were obtained after reduction of exposed disulfide bonds. The functionalised biomolecules were then coupled together through \textit{bis}-terpyridine metal complexation (iron(II), ruthenium(II)) and the success of the reaction was followed by means of UV/Vis-spectroscopy. This approach represents a first step towards the ability to order and aggregate such biomolecules in a specific manner. Future experiments, such as the coupling of biomolecules to polymers should open new possibilities for the development of bio-supramolecular structures.

Recent work from our own group was directed towards sensor applications utilising \textit{bis}-terpyridine metal complexation in combination with the well-known biotin-avidin system\(^{[66]}\). A terpyridine was functionalised with a biotin (vitamin H) unit in the 4' -position with a short pentyl spacer as well as a long PEG\(_{75}\) spacer. This opens possibilities e.g. towards the functionalisation of surfaces with an activated layer of avidin.

1.3 Surfaces modified with 2,2':6',2\(^{\prime}\)-terpyridine metal complexes

1.3.1 Assemblies and layers

Research concerning the modification of surface properties on a molecular level has increased especially since Binnig and Rohrer invented scanning probe techniques like STM (scanning tunnelling microscopy) or AFM (atomic force microscopy) in the mid-1980s. However, there is still much to learn in terms of ordering and orientation of substances on surfaces. Especially metallo-supramolecular structures add a whole range of possibilities, not least because of possible interactions between the complexed metal and a metal surface. Recently, there has been increasing interest in the investigation of adsorbed ordered structures on surfaces.
containing bis-terpyridine metal complexes. For an overview on layer-by-layer self-assemblies containing terpyridine complexes, the reader is referred to a review.\cite{67}

Recently, Abraña et al. described the synthesis of chiral and dendritic multi-terpyridine molecules, which, upon complexation with iron(II) or cobalt(II) and deposition on a surface, led to well-ordered 2-dimensional arrays.\cite{68} In case of a terpyridine functionalised second-generation poly(amido amine) (PAMAM) starburst dendrimer, the authors state that instead of thermodynamically more stable 2-D arrays, chains stacked next to each other ("pearl necklace" formation) were found by STM investigations on highly ordered pyrolytic graphite (HOPG) (Figure 1.22).

![Figure 1.22: Left: structure of the terpyridine dendrimer (dend-8-terpyridine). Right: unfiltered images of dend-8-terpyridine/Fe$^{2+}$ on HOPG, (a) 550 × 550 nm, (b) 200 × 200 nm, (c) 304 × 304 nm, (d) 69 × 69 nm (reprinted from ref.\cite{68}).](image)

Film-deposition and complexation were carried out at the phase boundary of a solution of the dendrimer in CH$_2$Cl$_2$ and an aqueous solution of FeSO$_4$ on the surface of a freshly cleaved HOPG substrate. The resulting STM-images show a quasi-hexagonal structure in which the intermolecular distances are equivalent along two directions, but different (longer) along the third. As mentioned above, this was explained by the 2-D packing of strands, held together by iron(II) complexation. It is believed that this would be the kinetically favoured product, which forms under the applied conditions. Further investigations of these monolayers on HOPG using electrochemical methods such as cyclic voltammetry (CV) and double potential step chrono-amperometry (DPSCA) were also carried out.\cite{69} By comparing the obtained formal potential ($E^\circ$) value of +1.03 V vs. sodium saturated calomel electrode (SSCE) to that of free
Chapter I

[Fe(terpyridine)$_2$]$^{2+}$ ($E^{\text{red}}' = +1.10$ V vs. SSCE), CV experiments indicated that the immobilised species does indeed consist of bis-terpyridine-Fe(II) complexes. Furthermore, by carrying out DPSCA measurements, charge propagation dynamics could be studied. For redox-active films, charge propagation can be described as a diffusional process characterised by an apparent diffusion coefficient. [$^{70}$] By applying the Cottrell equation, values of $D_0$ could be obtained for dend-8-terpyridine/Fe$^{2+}$ ($5 \pm 2 \times 10^{-7}$ cm$^2$/s) as well as for dend-8-terpyridine/Co$^{2+}$ ($1.3 \pm 0.2 \times 10^{-8}$ cm$^2$/s). These results show that the electron-transfer rate for Fe$^{2+}$/Fe$^{3+}$ is more than one order of magnitude faster than of Co$^{2+}$/Co$^{3+}$. A further system described by Abruña et al. consisting of the enantiomeric bis-terpyridine bridging ligands complexed by iron(II), which were already mentioned in section 1 of this chapter, was deposited as a monomolecular film on HOPG. [$^{18}$] As in the case of the dendritic system mentioned above, CV measurements proved the adsorption of a Fe(II)-bis-terpyridine complex containing species. STM-images of films derived from each of the metal-enantiomeric ligand complexes showed mirror symmetric structures. The angles of the features observed in relation to the direction of chain-propagation, were found to be opposite for both enantiomeric films (Figure 1.23).

![Figure 1.23: Top: high resolution STM image of highly ordered metallo-supramolecular arrays. Bottom: energy-optimised structure (MM2) of the (+)-enantiomer and a rendition of the helical structure formed by this bridging ligand and iron(II) (reprinted from ref. [$^{18}$]).](image)

These observations also match energy-minimised geometries derived from molecular mechanics calculations in terms of structure angles as well as the structure length. These facts
together suggest that each of these entities visualised by STM resemble the upper ligand in a chiral strand, which has no direct contact with the surface. In agreement with the findings from the CD spectra described in section 1, it becomes evident that films prepared from (+)-[cterpyridine-x-cterpyridine] form an M helix and the films prepared from (+)-[ctpy-x-ctpy] form the enantiomeric P helix.

Concerning surfaces other than HOPG, metals such as platinum(100) or gold(111) are widely used as substrates for assembling and investigating monolayer structures. Figgemeier and Constable et al. recently reported the self-assembly of a monolayer of heterogeneous bis-terpyridine complexes containing ruthenium(II) or osmium(II) as the metal centre.[71] One of the ligands is an unfunctionalised terpyridine, the other one is a terpyridine bearing a pyridyl function in the 4'-position (Figure 1.24).

![Figure 1.24](image)

**Figure 1.24:** Left: Structural image of [M(tpy)(tpy-py)]^2+, M = ruthenium(II), osmium(II) (counter-ion = PF_6). Right: peak current density as a function of scan rate for a monolayer of [M(tpy)(tpy-py)](PF_6)_2 on a platinum microelectrode (top right), 14 × 45 nm STM image of a of [M(tpy)(tpy-py)](PF_6)_2 monolayer on Pt(100) (bottom right) (reprinted from ref. [71]).

The electron lone pair from the uncomplexed nitrogen in the periphery of the complex should enable adsorption onto a platinum surface. Upon immersing platinum foils or electrodes into an aqueous acetone solution of the complexes for 1 h, spontaneous formation of an adsorbed monolayer was observed. After thoroughly rinsing with the solvent, investigations using STM as well as electrochemistry-techniques were performed. The STM image (ruthenium(II)-complex) shows the formation of a hexagonal array with an average distance between adjacent spots of 2.9 nm while a spot has a radius of approximately 0.55 nm, which indicates
a rather loose packing (surface coverage = 2.2 × 10⁻¹¹ mol cm⁻²). CV measurements on both the ruthenium(II) and osmium(II) containing complexes showed that the peak currents increase linearly with the scan rate, as expected for monolayer formation on the platinum electrode. Comparing with the theoretical value of 90.6 mV for ΔE_p,1/2, calculated for a one electron process, this value is much lower than the measured values for the ruthenium(II) complex as well as the osmium(II) complex monolayers of up to 160 mV. This also indicates the formation of a loosely packed monolayer. Especially when comparing the saturation surface coverages derived from the charge under the oxidation and reduction peaks, a value of 2.5 (± 0.2) × 10⁻¹¹ mol cm⁻² was obtained, which is in good agreement with the STM surface coverage of 2.2 × 10⁻¹¹ mol cm⁻² discussed above.

The immobilisation of ordered terpyridine metal-complexes on gold surfaces via the well-known strong sulfur-gold interaction seems to be even more appealing. Thiols or disulfides are known to be active precursors for such sulfur-gold bonding. Otsuki et al. designed a bis-terpyridine-ruthenium(II) complex which is functionalised on each of the 5- and 5''-positions with 4-thiol-phenylethenyl or 4-acetylthio-phenylethenyl substituents.[72] These ligands are fully conjugated, thus interaction between the surface and the photo- and redox-active ruthenium(II) is theoretically possible. However, when depositing the complexes on a gold(111) surface, only little organisation was observed. CV measurements on a gold electrode which was treated with one of the complexes showed that upon sweeping to a negative potential, only a broad desorption peak at a higher voltage around –0.9 to –1.0 V vs. Ag/AgCl was observed which stands in contrast to a sharper peak observed from a SAM (self assembled monolayer) of octanethiol (–1.02 V).

Another approach with a more complex system was carried out by Kern and Sauvage et al. They reported the deposition of a copper catenane on gold (111). One catenane ring contained a terpyridine and a phenanthroline (phen) moiety on the opposite side of the ring and the other ring accordingly a phenanthroline and a disulfide moiety (Figure 1.25).[73] The ambivalence of the coordination state of the copper centre (copper(I) ↔ copper(II)) has already proven to be useful in similar systems, especially with respect to applications such as molecular motors.
Here, the investigation of both the copper(I) as well as the copper(II)-catenane by CV in solution revealed a complementary behaviour showing that the copper(I)-catenane adopts a tetra coordinated state and that the copper(II)-catenane adopts a penta-coordinated state. This, in turn, indicates that both rings are rotating. Although these observations could not be made for CV measurements on the gold surface, it could be shown that the complex has attached by opening the disulfide upon connecting to the gold surface. Again, a difference between oxidation and reduction peaks of less than 60 mV and no broadening of $\Delta E_p$ was observed when the potential sweep rate was increased. Additionally, polarisation modulation-infrared reflection absorption spectroscopy (PM-IRRAS) revealed information about the relative orientations of the interlocked rings, which were both found to be roughly perpendicular to the surface.

Apart from directly adsorbing and investigating molecules and their layers on surfaces, a recent example of polyelectrolyte multilayer formation should be mentioned. Kurth et al. investigated alternating layers of poly(styrene sulfonate) and a metallo-supramolecular
coordination polyelectrolyte (Co-MEPE) on a poly(ethylene imine) (PEI) modified quartz substrate (Figure 1.26).[74]

Figure 1.26: Left top: metal-ion mediated self-assembly, which leads to a coordination polyelectrolyte (Co-MEPE). Left bottom: multilayer formation by layer-by-layer self-assembly of positively charged Co-MEPE and negatively charged PSS. Right: UV/Vis increase after each double layer addition (reprinted from ref. [74]).

The layers (PSS/Co-MEPE)$_n$ ($n = 1 – 10$) were characterised by UV/Vis spectroscopy, microgravimetry, CV as well as permeability and polarity measurements. UV/Vis spectrometry indicated a linear increase for all the complex bands after each double layer addition. Evidence for multilayer formation is also found from CV measurements, which shows that the anodic and cathodic current peaks rise proportionally to the square root of the scan velocity. This is in contrast to measurements in solution, where a linear rise is observed. Such behaviour is characteristic for layers of electrochemical sites, which possess a semi-infinite electrochemical charge diffusion condition. It could further be shown by comparative CV-measurements that a redox active probe ([Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4+}$) diffuses mostly radially through the layers, which can be explained by the more hydrophobic nature of the PSS/Co-MEPE compared to strong polyelectrolyte layers. The same type of system was also investigated using iron(II) as metal centre which binds more strongly than cobalt(II). Here, it could be shown that the thicknesses of single films, measured in air by surface plasmon spectroscopy, were $18 \pm 3$ Å for the coordination polyelectrolyte and $17 \pm 2$ Å for the PSS respectively. Measuring the thickness at the water-substrate interface resulted in a minimum thickness of $25 \pm 2$ Å for the iron(II) coordination polyelectrolyte and $27 \pm 2$ Å for PSS,
which can be explained by water penetrating the films. Further examples concerning polyelectrolyte assembly and terpyridines are described elsewhere.\[^{67}\]

Together, these examples demonstrate the increasing control that is obtained nowadays in constructing layered structures, here containing the bis-terpyridine metal complex motif. Apart from layer-formation and stabilisation, there is also an increasing interest in controlling and using single molecules or strands of molecules for different applications. In 2002, Park and Pasupathy \textit{et al.} reported on thiol-functionalised bis-terpyridine complexes, which were introduced into a gap of a 200 nm wide gold wire, the gap arising from electromigration by ramping to large voltages at cryogenic temperatures.\[^{75}\] During this process, some of the complexes, which were first bound to the gold wire before breakage, get into the 1-2 nm gap. Utilising complexes with different thiol-to-thiol lengths showed different physical effects on a molecular level (Figure 1.27).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.27.png}
\caption{	extit{Top left: thiol-modified cobalt(II) complexes and their CV in 0.1 M tetra-n-butylammonium-hexafluorophosphate/acetonitrile. Bottom left: I-V curves of a [Co(terpyridine-(CH\textsubscript{2})\textsubscript{S}-SH)\textsubscript{2}\textsuperscript{2+} at different gate voltages \(V_g\) from \(-0.4\) V (red) to \(-1.0\) V (black) with \(\Delta V_g \approx -0.15\) V. Upper inset: topographic AFM image of the electrodes with gap (scale bar, 100 nm). Lower inset: a schematic diagram of the device. Right: differential conductance against V showing temperature and magnetic-field dependence of the Kondo peak (reprinted from ref.\[^{75}\]).}}
\end{figure}
For the "longer" complex, a behaviour corresponding to that of a molecular single-electron transistor could be observed with the gate being the degenerately doped silicon substrate. For the "shorter" complex, a stronger coupling between the ion and the electrons was observed, thus leading to Kondo-assisted tunnelling, which can be described as the formation of a bound state between a local spin in the cobalt(II) centre and the conduction electrons in the electrodes, which leads to the enhancement of conductance at low biases.

In recent work, Gaub and Schubert et al. could show that it is possible to determine binding strengths of bis-terpyridine complexes on a molecular level using single-molecule force spectroscopy.[76]

**Figure 1.28:** *Left: schematic drawing of the experimental setup. Right: histogram of the bond rupture forces (pulling velocity = 118 nm s⁻¹).*[76]

For this purpose a Ru(III)Cl₃-terpyridine bound to a poly(ethylene glycol) spacer in the 4'-position which is end-functionalised with a carboxylic acid was attached to an amino functionalised substrate (Figure 1.28). The same uncomplexed ligand was attached to the tip of the AFM and upon bringing it into close proximity of the surface a bis-terpyridine-Ru(II) complex was formed. Force extension curves were measured upon pulling back the tip until the rupture of the complex bound. This led to a binding force of around 95 pN for a single complex. The histogram of the bond rupture forces in Figure 28 additionally show weaker peaks at 171 and 253 pN which could be attributed, by comparison to superimposed theoretical force versus extension curves, to the rupture of two or three parallel complexes,
respectively. It should be possible to expand this technique to similar systems and therefore this method presents a valuable approach for the characterisation of binding strengths of such systems.

1.3.2 Surface catalysts

An important application of terpyridine complexes on surfaces, which does not necessarily depend on high ordering on a molecular level, is that of electrocatalysis. The first work in this direction, to the best of our knowledge, was presented by Meyer et al. They transferred the use of ruthenium(IV) containing complexes as oxidants for a variety of organic substrates in solution to the electrode surface, using a Ru(IV)-bipyridine-poly-4-vinylpyridine. The same research group bound \([\text{Ru(II)}(\text{tpy})(\text{bpy(PO3H2})2)(\text{OH2})]^{2+}\) to thin films of TiO\(_2\) on glass by phosphonate binding. Upon oxidation with a cerium(IV) derivative, the formation of the catalytically active glass/TiO\(_2\)–Ru(IV)=O\(^{2+}\) is observed. Test oxidations of cyclohexene, benzyl-alcohol, phenol and \textit{trans}-stilbene revealed preferred oxidation to the compound which did not exceed the 2-electron level, because of the surface binding of the oxidant preventing the formation of lower oxidation states than ruthenium(II). The dominant product of the oxidation of cyclohexene, for example, was the alcohol and not the ketone and in the case of \textit{trans}-stilbene, the epoxide was formed. This shows the possibility of limiting reductions to a two-electron process through attaching an oxidant to a surface.

In terms of using ruthenium as reduction catalyst, first experiments have been performed by Chardon-Noblat et al. using a \([\text{Ru(tpy})(\text{CO})\]n complex. The exact structure of this ruthenium-complex polymer is unknown, but based on standard characterisation techniques, the existence of metal-metal binding units could be confirmed. This material was obtained by electrodereuction of isomers of \([\text{Ru(tpy})(\text{CO})\text{Cl2}]\) on the platinum or glassy carbon working electrode surface (Figure 1.29).

![Figure 1.29: Structural formulae of the trans- (left) and cis-[Ru(tpy)(CO)Cl2] complexes (right).][79]
Electrocatalysis performed in pure water containing 0.1 M LiClO$_4$ at $-1.30$ V vs. Ag | AgCl on a carbon felt modified with [Ru(tpy)(CO)$_2$]$_n$. This produced CO and formate with 60% and 15% yield, respectively, after 20 Coulomb had been passed through. However, comparing with the bpy analogue [Ru(bpy)(CO)$_2$]$_n$, [Ru(tpy)(CO)$_2$]$_n$ showed to be less stable under the same experimental conditions. No significant difference was observed between films prepared from the trans- or the cis-isomers.

Regarding the osmium group homologue, an application for the use of PVI-[Os(dmebpy)(tpy)]$^{2+}$ (PVI = poly(N-vinyl imidazole), dmebpy = 4,4′-dimethyl-2,2′-bipyridine) as redox mediator in lacasse-modified electrodes, was recently reported by Barton et al. Lacasses are polyphenol oxidase enzymes which catalyse the oxidation of a variety of inorganic and aromatic compounds, particularly phenols, with the concomitant reduction of molecular oxygen to water. For detailed results, the reader should turn to the literature.

Concerning electrocatalytic reduction with other metals included in bis-terpyridine complexes, two examples exist. Abrúña et al. found that electropolymerised films of vinyl-terpyridine complexes of iron, nickel and cobalt were effective catalysts for CO$_2$ reduction as well as the two- and four-electron reduction of oxygen. These films were found to be quite robust to washings with different solvents and to continuous potential cycling, which, for the latter case, led to a loss of less than 10% after 6 h. The catalytic activity observed for the films was higher when compared to the catalytic activity for the free complexes in solution. Films of [Ni(vinyl-tpy)$_2$]$^{2+}$ [PF$_6$]$^-2$ were found to catalyse both the two- and the four-electron reduction of oxygen, which does not occur when using [Ni(tpy)$_2$]$^{2+}$ [PF$_6$]$^-2$ in homogeneous solution. The reasons for these findings are believed to lie in cooperativity effects between the metal centres, which, in films, are of course more closely packed than in solution. Regarding the differences originating from the use of different metals, cobalt exhibits the highest activity, probably because it acts as a two-electron donor through cobalt(III/I) couples. This cannot be achieved by iron or nickel.

In a similar approach, Elliott et al. used bis-terpyridine ligands, which upon complexation, result in oligo- and/or polymeric materials. The polymerisation was carried out directly on the glassy carbon electrode, resulting in film-coated electrodes. In contrast to the results for [metal(vinyl-tpy)$_2$]$^{2+}$[PF$_6$]$^-2$ films described above, there was no improvement in electroreduction compared to the free metallo-polymer in solution. The authors attribute this fact to the rigidity of the latter system, which possibly does not allow a coordination site to open in order to become catalytically active, which was observed for [Co(vinyl-tpy)$_2$]$^{2+}$[PF$_6$]$^-2$ films in acetonitrile solution. Upon reduction from cobalt(II) to cobalt(I), the terpyridine
ligands are partially and reversibly displaced by two acetonitrile molecules. The examples mentioned here demonstrate the feasibility of terpyridine complexes to act as redoxactive materials.

1.3.3 Photoactive materials

Another major area of research, which includes the study of terpyridine complex-surface interactions, is that of interfacial photophysical processes, especially systems concerning solar light to energy conversion. First examples include photoelectrodes based on electropolymorised molecular ruthenium diads reported by Collin et al.\[^{[83]}\] They described polymer films incorporating molecular diads of the type \(V^{2+} \cdot [\text{Ru(II)-(pterpyridine)}_2]^{2+}\) (\(V = \text{methylviologen}, \text{pterpyridine} = 4'\text{-phenylterpyridine}\)) (Figure 1.30, left).

Figure 1.30: Left: donor-acceptor system DA with a pyrrole (anchor), a ruthenium(II) or osmium(II) bis-terpyridyl complex (photochemical centre) and a methylviologen (MV\(^{2+}\), donor). Right: photocurrent response of an ITO/poly-(DA) modified electrode (reprinted from ref. \[^{[83]}\]).

Thin films were prepared by anodic electropolymorisation of the pyrrole groups on the ligand opposite to the ligand containing the methylviologen on an indium tin oxide (ITO) electrode. Upon irradiation using visible light and in the presence of triethanolamine (TEOA, irreversible electron donor), an anodic photocurrent is observed when the electrode is potentiostated to 0 V. The photoactive centre is first excited by visible light upon which the charge separated state with the methylviologen is formed. Ruthenium(III) then irreversibly oxidises TEOA and the photocurrent is produced by electron-transfer into the polymer and to the electrode. The steady state photoresponse was moderately stable with time (loss of 19%...
after 30 min) in accordance with the stability of the modified electrode (Figure 30, right). The maximum steady state current $I_s$ for different surface concentrations $\Gamma$ was found to be $8 \mu A \text{ cm}^{-2}$ at $\Gamma = 6 \times 10^{-10}$ mol cm$^{-2}$. These results are in good agreement with results obtained for a comparable $V^{2+} [\text{Ru(II)(bpy)}_3]^{2+}$ system, except for the limiting value of $\Gamma$ being lower for the terpyridine case.

These results can be compared to other work carried out by Collin et al., where copolymers which contained monomers of Ru(tpy)$^{2+}$ (photoactive centre) and monomers of a viologen (electron acceptor) were used.$^{[84]}$ For this system, in which the photoactive centre and viologen are not directly covalently linked but only through the polymer backbone, only a moderate maximum $I_s$ of $<1.5 \mu A \text{ cm}^{-2}$ was found, indicating that intramolecular photoelectron transfer is more efficient than intermolecular transfer.

Another example of an electropolymerised system was shown by Hanabusa et al. Using the same basic approach, an aniline modified bis-terpyridine-Ru(II) complex was electropolymerised via a reaction mechanism similar to the electropolymerisation of aniline.$^{[85]}$ The photocurrent response of this polymer film on an ITO electrode in aqueous 0.1 M LiClO$_4$ solution containing 0.5 mmol of methylviologen (MV$^{2+}$) and saturated with oxygen, showed a maximum photocurrent of 1.9 $\mu A \text{ cm}^{-2}$. Because of rapid oxidation of MV$^+$ with oxygen, the unfavourable reverse electron reaction is suppressed.

Further progress in this area was made by choosing nanocrystalline, semiconductor metal oxides, such as TiO$_2$ (anatase modification) on conducting glass as the electrode. Bonhôte et al. investigated charge separation on a donor-sensitiser system (Figure 1.31, top).$^{[86]}$ However, the observed charge separation was not found to be more efficient when comparing to a model sensitiser without the donor system, because of the very fast recombination reaction.

![Figure 1.31: Bonhote's electron donor-sensitiser diads.$^{[86]}$](image)
For a similar system (Figure 1.31, bottom) with a different spacer between the donor and the sensitizer, the photoinduced charge separation was found to be more efficient, because of the electron in the excited state being localized more on the ligand bound to the semiconductor surface.

More recently, Grätzel et al. synthesized the black dye [NHEt₃][RuL(NCS)₃], which exhibits a large red-shift in absorption compared to other compounds from the [Ru(terpyridine)₂]²⁺ family (Figure 1.32).[87] A photovoltaic cell adsorbed monolayer on TiO₂–conducting glass in conjunction with the redox electrolyte LiI/LiI₃ in propylene carbonate showed an incident photon-to-current conversion efficiency (IPCE) of 80% over a broad region with a photocurrent density of 20.5 mA cm⁻². Under standard AM 1.5 sunlight (air mass 1.5 sunlight is the spectrum of sunlight that has been filtered by passing through 1.5 thicknesses of the earth’s atmosphere), an open circuit voltage of 0.72 V is observed which leads to an overall conversion efficiency of over 10%.

This improved system was compared with a bipyridine analogue, which had been up to that point the best performing charge transfer sensitizer (~18 mA cm⁻²). Following that discovery, other research projects were carried out in that direction, which included adsorption and crystallization studies,[88] as well as investigations of interfacial electron-transfer dynamics.[89]

In an attempt to improve the molar extinction coefficient, Huang et al. investigated the analogous 4’-carboxy-phenyl substituted compound, which, probably due to the absence of two carboxy-groups on the outer rings, showed a worse performance in a photovoltaic cell.[90]

![Figure 1.32: Left: salt of the tris-thiocyanato terpyridine ruthenium(II) panchromatic sensitizer. Right: its photocurrent action spectrum comparison with the bipyridine analogue as well as bare TiO₂. L = 4,4’-COOH-2,2’-bipyridine, L’ = 4,4’,4”-COOH-2,2’:6’,2” (reprinted from ref. [87]).](image)

Sugihara and Arakawa et al. tested another analogous compound which incorporated a long alkyl chain on the β-diketonato ligand.[91] Under similar conditions, the photocurrent action
spectrum shows a behaviour similar to that of the mother complex described above. In accordance with the absorption spectra, the alkyl-complex shows higher incident photon to current efficiency (IPCE) values in the 720-900 nm region than the parent compound. By comparing the photocurrents with and without the presence of deoxycholic acid, an indication that the long hydrocarbon chain prevents surface aggregation of the sensitisier was found.

Apart from solar cell research, two other photophysically interesting examples have been reported: photodegradation of organic material and organic light-emitting devices (OLED's). Lam et al. reported on the TiO₂—photodegradation of CCl₄ in aqueous medium (Figure 1.33).[92]

![Figure 1.33: Left: stepwise modification of a TiO₂-surface with terpyridine-Ru(III). Right: visible light mediated photodegradation of CCl₄ in aqueous medium (reprinted from ref. [92]).]

**Figure 1.33:** Left: stepwise modification of a TiO₂-surface with terpyridine-Ru(III). Right: visible light mediated photodegradation of CCl₄ in aqueous medium (reprinted from ref. [92]).

[Ru(tpy-Ph-PO₃H₂)₂][PF₆]₂ was mixed with a suspension of indium tin oxide (ITO) and after filtration, drying and grinding the resulting powder was used for degradation experiments. A 100 W tungsten lamp was used for photolysis in a CCl₄ saturated aqueous solution containing potassium iodide as a reductant. The rate of degradation was found to obey a Langmuir-Hinshelwood rate law, which is expected because only CCl₄ molecules, which are adsorbed to the surface of TiO₂, can be reduced.
Elliott *et al.* investigated an electropolymerised \([\text{Ru(tpy)}_2]^0\) film, which was vapour deposited onto an Alq₃/TPD/ITO (Alq₃ = tris(8-hydroxyquinoline) aluminium(III) complex, emissive and electron transport layer / TPD = triarylamine derivative, hole transport material) substrate in order to create an electroluminescent device.\(^{[93]}\) The \([\text{Ru(terpyridine)}_2]^0\) film acts as a low work function electron-injecting contact and is of special interest because it can be deposited by thermal evaporation, making it easy to handle and to control. OLED's were constructed using \([\text{Ru(tpy)}_2]^0\) as low work-function organic material (LWOM) and the architecture Ag/LWOM/Alq₃(400 Å)/TPD(400 Å)/ITO.

![Figure 1.34: Performance of an OLED with a \([\text{Ru(terpyridine)}_2]^0/\text{Ag}\) cathode (reprinted from ref. \(^{[93]}\)).](image)

Figure 1.34 shows the performance of such a device. Upon reducing the barrier-to-hole injection between ITO and TPD by including the conducting polymer interlayer poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT-PSS), a significant improvement was observed. More current was passed and more light was produced at a given voltage (Figure 1.34). The metal layer covering the LWOM was also varied from Ag to Au, which has a very high work function of 5.2 eV. Devices with different metal layers showed comparable performance, thus indicating that the nature of the metal contact is of secondary importance to the underlying LWOM. This should allow for variation of the metal contact leading to devices which are for example more oxidation resistant and therefore lead to increased device lifetimes.

An example of a blue LED was shown very recently by Che *et al.*\(^{[94]}\) They used *bis*-terpyridine-Zn(II) polymers, with different conjugated and unconjugated spacers, spincoated
on ITO with the device structure: ITO/PEDOT:PSS/zinc-terpyridine-polymer/Ca/Al. The photoluminescence spectra of thin films of some of the zinc-terpyridine polymers are shown in Figure 1.35.

![Photoluminescence Spectra](image)

**Figure 1.35:** Emission spectra of the different terpyridine-Zn(II) polymers as thin films (reprinted from ref. [94]).

For the metallo-polymer, which exhibits an emission maximum of 450 nm, the observed electroluminescence spectrum with the blue EL intensity increases with increasing bias voltage. This example again demonstrates the versatility of terpyridine metal complexes, leading to, in this case, encouraging results towards the search for stable and intense blue light emission, which is currently of particular interest for many photo-optical applications.

### 1.4 Summary and outlook

Terpyridine-metal complexes are gaining increasing interest as a part of new functional materials. Especially their reversibility under certain conditions, as well as their photophysical properties led to a number of research activities combining these complexes with polymers and/or surfaces. Following more extensive research including bipyridine-metal complexes, the C$_{2v}$-symmetric 4'-functionalised bis-terpyridine complexes were included as a linker in terpyridine polymer systems mainly by the groups of Kurth, Rehahn, Hanabusa and Schubert. Especially in terms of future investigation of materials properties, for example rheological behaviour, the defined introduction of such bis-terpyridine complexes into known polymeric systems could be of interest. Chow, Lin, Kim and Newkome recently expanded dendrimer functionalisation to the ruthenium(III)/ruthenium(II) method, allowing for directed coupling
strategies here as well. Larger aggregates and materials, such as micelles and polymeric beads, have also been combined with terpyridine complexes. A clear influence on micelle formation as well as the loading of different metals onto microbeads was shown. A first application for a terpyridine-Fe(II)-microbead heterogeneous catalyst was shown by Yoo et al. The attachment of terpyridine (complexes) to biopolymeric systems found applications such as fluorescent sensors, DNA/RNA cleaving agents as well as a tool for duplex formation enhancer. With the increasing possibilities of investigating ordering on a molecular level, research concerning terpyridine complexes on surfaces has also increased. Especially the deposition and characterisation of chiral complexes and the characterisation of the chiral 2D lattices formed, mainly reported by Abruña et al., show good results concerning supramolecular surface chemistry. Although organic/inorganic approaches to solar cells cannot compete yet with the classic semiconductor materials, significant progress in terms an overall conversion efficiency of over 10% has been made concerning terpyridine ruthenium(II) complexes which convert solar light to energy, mainly described in work by Grätzel et al. This chapter shows that there is still much to be done, also concerning synergisms between the described fields. As an example, it could be imagined that by choosing an adequate polymer and managing to integrate the appropriate terpyridine-metal complex with subsequent precise surface deposition, a better photoactive device could be created.

1.5 Aim and scope of this thesis

Functionalised 2,2′:6′,2′″-terpyridines play an increasing role in scientific research due to the variety of chemical and physical properties of the complexes they form with different transition metal ions. In particular the integration into polymeric structures as well as the modification of different surfaces has become a challenging field for the synthetic chemist. As far as their complexation chemistry is concerned, tridentate mono-terpyridine-complexes and hexadentate symmetric as well as asymmetric bis-terpyridine-complexes are the most common coordination motifs. Especially asymmetric (directed) A-B type bis-complexation with functionalised 2,2′:6′,2′″-terpyridines can lead to valuable chemical building blocks for well-defined structures.

The aims of this thesis were to synthesise and characterise new assemblies and metallopolymers based on terpyridine metal complexation starting from well-defined monodisperse terpyridine building blocks. In addition, the functionalisation of a polymeric microbead
material with terpyridine moieties was a synthetic goal. Subsequently the investigation of metal-complexation, with a particular view to potential applications, was attempted. In this chapter, the growing research fields of 2,2':6',2''-terpyridine-complexes in polymeric architectures and on surfaces have been reviewed. Chapter 2 describes the synthesis of 4'-functionalised 2,2':6',2''-terpyridine building blocks using different methods. Substitution reactions with 4'-chloro-2,2':6',2''-terpyridine and 4'-hydroxy-terpyridine lead to terpyridines bearing chemical functionalities which are connected via alkoxy-spacers to the 4'-position. All of the reported compounds were fully characterised by standard characterisation techniques.

In Chapter 3, examples of functional complexes based on the 4'-functionalised 2,2':6',2''-terpyridines are presented. Among them are an optically active bis-terpyridine-Ru(II)-perylene-bis-terpyridine-Ru(II) triad as well as a coiled coil peptide motif, which is connected via an bis-terpyridine-Fe(II) complex. Furthermore, the investigation of complexation parameters of 4'-chloro-2,2':6',2''-terpyridine and different metal salts using isothermal (micro)calorimetry (ITC) as well as UV/Vis spectroscopy is discussed. Chapter 4 deals with the synthesis of 4'-functionalised chiral and non-chiral (cyclo)alkyl bridged di-terpyridine ligands and complexation studies with iron(II) chloride as well as zinc(II) acetate. Predominantly, the formation of small metallo-supramolecular rings is observed and in the case of the chiral ligands, significant signals in circular dichroism (CD) measurements appear upon metal complexation. The immobilisation of terpyridines via the 4'-position onto cross-linked polymeric microbeads (d = 20 µm) and their subsequent loading with metal ions is described in Chapter 5. UV/Vis- and IR-spectroscopy as well as elemental analysis provide a useful characterisation data for these materials. After loading with different metal ions, AAS-measurements on aqueous solutions of the oxidised beads provide a quantitative determination of the metal content. Sequential functionalisation and potential applications for these terpyridine-beads are discussed in Chapter 6. By applying ruthenium(II)/ruthenium(III) chemistry, the beads can be functionalised via heteroleptic bis-complex formation, leading to different functionalities attached to the microbeads, such as an anthracene or a poly(ethylene glycol). Furthermore, different metal loaded microbeads are investigated regarding their catalytic activity. Finally, in the case of the loading with iron(II) ions, reversible complexation is demonstrated with the help of the competitive ligand HEEDTA. After decomplexation, the microbeads can again take up different metal salts.
1.6 References


New Functional Polymers and Materials based on 2,2':6',2''-Terpyridine Metal Complexes


Chapter II

Synthesis of Terpyridines Functionalised in the 4'-Position

Abstract

The synthesis of 2,2':6',2''-terpyridines functionalised in the 4'-position is shown. Different chemical groups can be introduced in a one step reaction by the nucleophilic aromatic substitution of 4'-chloro-2,2':6',2''-terpyridine with alcoholates or thiolates as well as by the reaction of 2,6-bis-(pyrid-2-yl)-4-pyridone with different electrophiles. This leads to terpyridines having an ether- or a thioether-function in the 4'-position to which a functional group is attached via an alkyl-spacer. Using this approach terpyridines bearing functionalities such as amines, carboxylic acids, hydroxides, thiols, bromo- and epoxide-functions have been synthesised. Further sequential functionalisation leads to a chloride, an isocyanate and a disulfide attached via alkoxy spacers to the terpyridine. Additionally, a terpyridine with alkynyl functionality in the 4'-position is reacted with a bromo-functionalised oligo-phenylene-vinylene (OPV) in a Sonogashira coupling. The synthetic pathways reported here offer an easy access to a multitude of 4'-functionalised terpyridines, which represent valuable building blocks for new metallo-supramolecular structures.

2.1 Introduction

Terpyridines, which form metal complexes with a variety of transition metal ions,\(^1\) have many potential applications in fields such as macromolecular chemistry, nanoscience, biochemistry and photophysics, as already discussed for 2,2':6',2''-terpyridine regarding metallo-polymers and surfaces in Chapter 1. 2,2':6',2''-Terpyridine and its derivatives have also been subject to the use as building blocks for novel supramolecular structures, such as double helicates,\(^2\) dendrimers,\(^3\) micelles,\(^4\) or others.\(^5\) They are also used in nanoscience, an example being the formation of ordered architectures on surfaces\(^6\) (see also Chapter 1) or of functional molecular devices.\(^7\) Biochemical applications include the potential use of terpyridine complexes as sensors in tumor research\(^8\) and as DNA/RNA binding agents.\(^9\) In particular, the use of 2,2':6',2''-terpyridines functionalised in the 4'-position in the above described fields is of great interest.\(^{3c,5a,10b}\) For this purpose compounds which are easily accessible in large scale and high yields are a prerequisite. Utilising terpyridines with functionality in the 4'-position as building blocks for back-to-back metallo-oligomeric or -polymeric systems offers the advantage of creating linear systems in which the octahedral metal complex is located in the backbone of the metallo-polymer. Also no additional diastereomeric metal complex centres are added because of a terpyridine having \(C_{2v}\) symmetry with a rotation axis through the 4'-position (Figure 2.1, right), thus leading to no fac or mer (bis-terpyridine) diastereomers upon complexation of 4'-functionalised terpyridines.

![Figure 2.1](image)

**Figure 2.1:** Left: unfunctionalised 2,2':6',2''-terpyridine. Right: 4'-functionalised terpyridine with rotation axis.

Since the work in this thesis is mainly related to 4'-functionalised terpyridines, their complexation and further potential applications, the basics of terpyridine synthesis, especially regarding functionalisation in the 4'-position, will be elaborated in somewhat more detail at this point.

Generally, the synthesis of functionalised terpyridines can be classified into three basic categories: ring assembly reactions, the directed cross-coupling of functionalised pyridines
Synthesis of Terpyridines Functionalised in the 4'-Position

and the sequential functionalisation of activated terpyridine intermediates. In terms of ring assembly, the most common reaction is the well-known Kröhnke condensation (Scheme 2.1, top).[10] A N-heteropyridinium salt is synthesised and subsequently reacted by ammonia condensation with an enone. A variation of this methodology starting from 2,6-diacetylpyridine was recently reported by Sasaki et al.[11] The iodide salt of the bis(pyridinium) derivative was obtained from 2,6-diacetylpyridine in a yield of 85% and was subsequently reacted with various α,β-unsaturated aldehydes in the presence of ammonium acetate in order to yield different symmetric terpyridines functionalised in the 4', the 4,4''- and the 5',5''-positions (Scheme 2.1, bottom).

![Scheme 2.1](image)

Scheme 2.1:  Top: Kröhnke-method: i) R²CHO, NaOH, EtOH, 0 °C, 60-95%. ii) N-{1-(2'-pyridyl)-1-oxo-2-ethyl}pyridinium iodide, [NH₄⁺][AcO⁻], EtOH: overall yield 30-80%. Bottom: Sasaki-method: Step 1: 85%, step 2: 80-90%.

Directed cross-coupling leading to functionalised terpyridines was carried out using the Stille methodology (Scheme 2.2).[12] This Pd⁰/PdⅡ based coupling procedure requires a 2,6-dihalopyridine and two equivalents of 2-(trialkylstannyl)pyridine (Scheme 2.1, top). The reaction to the terpyridine is carried out with palladium(0) catalysts in toluene for at least 24 hours. Depending on the functionalisation of the starting material, terpyridines functionalised at almost every desired position, also on a multi-gram scale, can be obtained.[13]
The Stille reaction can also be carried out using 2,6-bis(trimethylstannyl)pyridines as the central ring units and coupling them with the corresponding 2-bromo-pyridines (Scheme 2.2, bottom).\[^{[14]}\] Other cross-coupling reactions based on the Pd\(^{0}/\)Pd\(^{II}\) cycle have not been used yet for terpyridine synthesis, but have been proven to work for terpyridine-related compounds in excellent yields, such as the Negishi cross-coupling for 2,2'-bipyridines.\[^{[15]}\]

Concerning the synthesis of functionalised terpyridines by the reaction with a terpyridine intermediate, in particular functionalisation in the 4'-position has been carried out.\[^{[16]}\] Prominent examples are the use of the alcolholate of the 4'-hydroxy-terpyridine (tautomeric form of 2,6-bis-(pyrid-2-yl)-4-pyridone) as nucleophile and the aromatic nucleophilic substitution of 4'-chloro-terpyridine or 4'-bromo-terpyridine in order to yield terpyridines bridged by an ether function (Scheme 2.3). Both of these intermediates are also accessible via the Kröhnke methodology.\[^{[17]}\]
Also the 4'-carbaldehyde terpyridine, synthesised by the Stille methodology, was proven to be a valuable intermediate. The functionalisation of these ligands leads to a variety of different 4'-modified terpyridines in one functionalisation step. The only requirements are good nucleophiles (in the case of 4'-chloro-terpyridine) or electrophiles (in the case of 4'-hydroxy-terpyridine). Of course, a suitable work-up procedure is also required. A key feature of most of these compounds is their insolubility in water, thus the crude products can be obtained by simple precipitation of the DMSO reaction mixture in water. Some examples for $R^{1,2}$ are depicted in Table 2.1. For the functionalisation of the 4'-hydroxy-terpyridine, different substituents $R^1$ such as a diethylene-glycol$^{[18]}$ a sugar$^{[19]}$ or an alkyl functionality were described. The nucleophilic substitution of 4'-chloro-terpyridine led to a carboxylic acid$^{[3b]}$ a phenyl-alkyl$^{[20]}$ or for example a norbornene$^{[21]}$ function, upon reaction with the corresponding alcohols.

**Table 2.1:** Selected literature examples for $R^1$, $R^2$ and $R^3$ from Scheme 2.3.

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<tr>
<th>$R^1$</th>
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<td>O O H</td>
<td>C H O</td>
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<td>O O Ac</td>
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The 4'-carbaldehyde terpyridine leads, upon reaction with a C=O nucleophile, for example to an imine$^{[22]}$, a ferrocene or a ferrocene-ethylene$^{[23]}$ bridged derivative (Table 2.1). In this part of the work, the objective was to synthesise new 4'-functionalised terpyridine-building blocks, mainly utilising the above mentioned direct functionalisation *via* the 4'-chloro-2,2':6',2''-terpyridine and its precursor 2,6-bis-(pyrid-2-yl)-4-pyridone (Scheme 2.4). These starting materials were first reported by Ward et al.$^{[17]}$ and have recently been synthesised by our group on large scale.$^{[24]}$
Scheme 2.4: Synthesis of 4’-chloro-2,2’:6’,2’’-terpyridine (overall yield: 35%) and its precursor 2,6-bis-(pyrid-2-yl)-4-pyridone (overall yield: 60%).

For this reaction sequence, the Kröhnke methodology used for the preparation of 1,5-diketones was extended to the 1,3,5-trione. The 2,6-bis-(pyrid-2-yl)-4-pyridone 1 is prepared in two steps by Claisen condensation of acetone with ethyl picolinate. Subsequently the 4’-chloro-2,2’:6’,2’’-terpyridine 2 can be obtained by reaction with PCl₅/POCl₃.

2.2 Direct functionalisation from 4’-chloro-terpyridine

A variety of new terpyridines functionalised in the 4’-position, utilising the substitution reaction of alcoholates and thiolatesa with 4’-chloro-2,2’:6’,2’’-terpyridine[25,26] (first described by Newkome et al. for the case of the alcoholates),[27] were synthesised. The introduction of different functionalities into the 4’-position of the 2,2’:6’,2’’-terpyridine was carried out in one reaction step starting from the 4’-chloro-2,2’:6’,2’’-terpyridine 2 (Scheme 2.4). Utilising the base supported nucleophilic substitution of the chloro-function with functional alcoholates in an aprotic medium such as DMSO led to the formation of 4’-functionalised terpyridines with an alkoxy spacer. In the case of using diols as starting material (for obtaining hydroxy-functionalised terpyridines), these had to be applied in excess in order to obtain mainly monofunctionalisation (Scheme 2.5).

Scheme 2.5: Synthesis of hydroxy-alkoxy-functionalised terpyridines.

a Alcoholates and thiolates, formed in situ under the strong basic conditions (KOH/DMSO) are in contrast to the corresponding alcohols good nucleophiles.
Purification was carried out by first precipitating *bis*-functionalised material from MeOH and subsequent recrystallisation from THF. Sampath and co-workers also carried out these reactions in the same time-period.[28] They used less excess of the hydroxy functionalised starting material with the other reaction conditions being the same. The yields were similar to the ones reported here, except for the C$_3$-spaced compound, where the yield reported here was significantly lower. This was due to repeated recrystallisation and precipitation, which was necessary in order to remove the *bis*-functionalised by-product.

Several amino- and carboxy-functionalised 2,2':6',2''-terpyridines were prepared by the reaction of the corresponding alcoholates with 4'-chloro-2,2':6',2''-terpyridine 2 (Scheme 2.6). The amino functionalised terpyridines were obtained by addition of the amino-alcohols to a KOH-basic DMSO suspension and the subsequent addition of 4'-chloro-2,2':6',2''-terpyridine.[26] Amines 5 and 6 were isolated in yields of 89% and 88%, respectively. In the case of 5, which has already been known from literature,[29] the yield could be increased as well as the work-up procedure simplified. Lowering the reaction temperature still resulted in 100% conversion after 4 h reaction time. Moreover, decomposition of the starting material or formation of a *bis*-terpyridine functionalised material could not be observed in this case. Simple precipitation of the product by pouring the reaction mixture into a 10-fold excess of water, followed by filtration and chemical as well as physical drying yielded the pure product.

**Scheme 2.6:** Synthesis of 4'-amino-alkoxy- and 4'-carboxy-alkoxy-functionalised 2,2':6',2''-terpyridines. All reactions were performed in DMSO / KOH.

For the functionalisation of 4'-chloro-terpyridine 2 with alkoxy-carboxy chains we recently developed a new route. Up to now the only functionalisation route known is the reaction of
the \( \alpha, \omega \)-hydroxy-carboxy-alkanes,\(^{[27]} \) for which only the 1-hydroxybutyric acid is commercially available. Following the same strategy as described above, but making use of the \textit{in situ} ring opening reaction of lactones to the alcoholate nucleophiles under the basic reaction conditions, the 4'-alkoxy-carboxy functionalised terpyridines 8 and 9 with different alkyl spacer lengths were obtained (Scheme 2.6). For final purification of these compounds, recrystallisation from THF was found to be the most convenient method. The reaction conditions of the experiments as well as melting points of the obtained compounds are listed in Table 2.2. The given reaction time resembles the time of the reaction until at least \( >95\% \) conversion of the 4'-chloro-2,2':6',2''-terpyridine 2 has been reached (measured by \( ^1\text{H-NMR} \)).

**Table 2.2: Reaction data of the amino- and carboxy-functionalised terpyridines.**

<table>
<thead>
<tr>
<th>no.</th>
<th>X</th>
<th>reagent</th>
<th>time (h)</th>
<th>temp. (°C)</th>
<th>mp (°C)</th>
<th>yield [%]</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>pentyl-NH(_2)</td>
<td>5-amino-1-pentanol</td>
<td>4</td>
<td>40</td>
<td>104</td>
<td>89</td>
<td>([29]) [71], [25] [75]</td>
</tr>
<tr>
<td>6</td>
<td>piperidine</td>
<td>4-hydroxy-piperidine</td>
<td>4</td>
<td>70</td>
<td>181</td>
<td>88</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>((S)-2\text{-amino}-4\text{-methyl}-pentyl)</td>
<td>L-leucinol</td>
<td>10</td>
<td>40</td>
<td>–</td>
<td>31</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>butyl-COOH</td>
<td>( \delta \text{-valerolactone} )</td>
<td>48</td>
<td>75</td>
<td>175</td>
<td>72</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>pentyl-COOH</td>
<td>( \varepsilon \text{-caprolactone} )</td>
<td>48</td>
<td>60</td>
<td>205</td>
<td>83</td>
<td>([25]) [65]</td>
</tr>
</tbody>
</table>

Typically, higher melting points are observed for the alkyl-carboxy-terpyridines 8 and 9 as well as for the more rigid piperidine functionalised terpyridine. Having an alkyl chain or even a branched chain between the amine and the terpyridine decreases the melting point from 6 (181 °C) to 5 (104 °C) to 7 (liquid at room temperature). Concerning the reaction times and the reaction temperatures, conditions of 4 h and 40 °C are required for the full conversion of the unbranched 5-amino-1-pentanol to the amino-pentoxy terpyridine 5. Increasing values for reaction temperature and/or reaction time are required for the secondary alcohol 4-hydroxy-piperidine (leading to 6) and the sterically more hindered L-leucinol (leading to 7). The longest reaction times of 48 h are observed for the ring-opening of the lactones (leading to 8 and 9). For all of these compounds yields of 70 to 90% could be obtained except for the chiral amine 7 (31%). The reason for the low yield in the latter case can be found in the high water-
solubility of the product. Thus, 7 cannot be precipitated in water which required extensive column chromatography for purification (furthermore, proof for complete retention of configuration under the basic reaction conditions could not be obtained yet). However, a clear increase in the yields for the already reported amino-pentoxy terpyridine 5 from 75% to 89% and for the carboxy-pentoxy terpyridine 9 from 65% to 83% could be observed. Additionally, the synthesis of the stilbene functionalised terpyridine 10 was carried out utilising the same chemistry as described above (Scheme 2.7). In particular, regarding the combination of photo-physically interesting moieties such as terpyridine complexes with stilbene and/or its copolymers, the stilbene-functionalised terpyridine 10 could be an interesting compound.

Scheme 2.7: Synthesis of the stilbene-oxy-functionalised 2,2':6',2''-terpyridine 10. The reaction was performed in DMSO / KOH.

Reacting 4'-chloro-2,2':6',2''-terpyridine 2 with half an equivalent of R,R-dihydrobenzoin does not lead to a ditopic bis-terpyridyl ligand, but partially to the stilbene-functionalised terpyridine 10. Here the reaction was stopped before full conversion was reached in order to avoid by-product formation or degradation. The appearance of the typical absorption shoulder at 320 nm as well as only one signal for the double-bond proton of the stilbene moiety in the $^1$H-NMR spectrum indicated the formation of the thermodynamically favoured trans-isomer. This indication was subsequently proven by X-ray structure analysis (Figure 2.2).
It is apparent that in the trans-stilbene moiety the phenyl rings do not lie in one plane, as one would expect because of π-conjugation. This is reflected in the torsion angles of 14.3 at C(20)-C(21)-C(22)-N(27) and 31.6 at C(21)-C(20)-N(28)-C(29). In addition, the terpyridine rings are slightly twisted (e.g. torsion angle of 13.9 at N(1)-C(6)-C(13)-C(18)). The main reason for this rather complicated geometry lies probably in the oxygen-bridge, which connects the two conjugated systems and forces them into this position.

The reaction of an excess of di-thiols to terpyridine 2 (as described above for the diols) presents a route for the synthesis of thiol-alkyl-thioxy functionalised terpyridines. Such terpyridines are of interest for the creation of functional self-assembled monolayers or the supramolecular manipulation of gold nanoparticles. It was found that the base catalysed reaction of the thiols with the chloro-terpyridine 2 occurs quantitatively within 30 min at room temperature (Scheme 2.8).

Scheme 2.8: Synthesis of the thiol-alkylthioxy-functionalised 2,2':6',2''-terpyridines 11-13.
This faster reaction at lower temperatures becomes understandable when taking the lower $pK_a$ value of thiols compared to alcohols and the higher nucleophilicity of thiolates compared to alcoholates into account.\cite{30} Due to extensive purification which is needed in order to separate the product from the excess of high-boiling dithiol as well as to separate from disulfide by-products formed, the yields range from only 2\% to 24\%. Nevertheless, in the case of the thiol-terpyridine with a C$_{10}$-linker, single crystals suitable for X-ray crystal structure determination could be obtained (Figure 2.3).

**Figure 2.3:** Left: ORTEP view of 13 (thermal ellipsoids are at the 50\% probability level). Right: elementary cell in the crystal.

The crystal structure is dominated by alkyl-chain interactions, as can be seen when looking at the unit cell. All atoms of one molecule lie nearly in one plane and for the terpyridine ring, the thermodynamically favoured all-trans conformation regarding the nitrogens is observed. Due to its long alkyl spacer, this compound is an ideal candidate for the fabrication and investigation of new self assembled monolayer (SAM) structures on gold (111).

An alternative route was described recently in literature, which led to similar terpyridine thiols in very good overall yields of around 90\% by reacting thioacetate-alkyl-bromides with 2,6-bis-(pyrid-2-yl)-4-pyridone and subsequent cleavage to the thiols with NaOMe.\cite{31}
2.3 Direct functionalisation from terpyridone

As already mentioned in the introduction, apart from functionalisation in the 4’-position using 4’-chloro-2,2’:6’,2”-terpyridine \( \text{2} \) also its precursor, the \( 2,6\text{-bis-}\left(\text{pyrid-2-yl}\right)\text{-4-pyridone 1} \) can be used. Here the synthesis of two new ligands by direct functionalisation of the \( 2,6\text{-bis-}\left(\text{pyrid-2-yl}\right)\text{-4-pyridone 1} \) is described.\(^{[32]}\)

The alcoholate of the tautomeric form of the \( 2,6\text{-bis-}\left(\text{pyrid-2-yl}\right)\text{-4-pyridone 1} \), the 4’-hydroxy-terpyridine, can be prepared \textit{in situ} in a \( \text{K}_2\text{CO}_3\)-basic DMF suspension in order to act as nucleophile for \( S_\text{N}2\)-type nucleophilic substitutions (Scheme 2.9). For a nucleophilic attack onto alkyl chains, good anionic leaving groups such as halides or tosylates are required. Two functionalised terpyridines were synthesised using this route, starting from 1,10-dibromodecane and \( R\)-epichlorohydrin. For obtaining the bromo-decaneoxy functionalised terpyridine \( \text{15} \), a 10-fold excess of the di-functionalised starting material had to be used in order to minimise di-substitution (Scheme 2.9). After precipitation in a 10-fold excess of water, purification including column chromatography and crystallisation was necessary for the separation from the di-terpyridyl by-product.

\[ \text{Scheme 2.9: Synthesis of the epoxy (14)- and the bromo (15)-terpyridines from the 2,6-bis-(pyrid-2-yl)-4-pyridone 1.} \]

In the case of the epoxy-methoxy-terpyridine \( \text{14} \) special measures had to be taken for purification. Utilising standard column chromatography on alox N with \( \text{CHCl}_3/\text{MeOH} \) (99/1) as eluent resulted in a quantitative ring opening by nucleophilic attack of the methanol. However, filtration on alox N with dry \( \text{CHCl}_3 \) as eluent, followed by careful crystallisation
from THF, yielded the pure product. The reaction temperature was kept below 50 °C in order to avoid by-product formation or degradation. For both compounds 14 and 15, characterisation was carried out using standard techniques. In the case of the epoxy-methoxy-terpyridine 14 a crystal structure could be obtained, showing the expected chirality. Although gas chromatography (GC) operates at high temperatures, it was possible to obtain a signal corresponding to the terpyridine-epoxide from chloroform solution. Furthermore, no additional peaks from fragmentations or impurities can be observed (Figure 2.4).

![Figure 2.4](image)

It should be mentioned that the introduction of such sensitive groups as bromides or epoxides has not been possible using the functionalisation route via the 4'-chloro-2,2':6,2''-terpyridine. Apart from the availability of nucleophilic starting material in the latter case, this also has to do with the stronger basic system KOH/DMSO, which is required for the nucleophilic aromatic substitution compared to K₂CO₃/DMF for the Sₘ₂-type reaction used here.

### 2.4 Sequential terpyridine functionalisation

Some of the above-described terpyridines were used for sequential functionalisation resulting in the synthesis of a thiolan-functionalised terpyridine 16, an isocyanate-terpyridine 17 as well as a chloro-propoxy-terpyridine 18 (Scheme 2.10). The first two compounds were obtained through sequential functionalisation of the amino-pentoxy-terpyridine 5 and the latter from the hydroxy-propoxy-terpyridine 3, respectively.
Scheme 2.10: Sequential synthesis of a dithiolan (16)- and an isocyanate (17)-terpyridine from the amino-terpyridine 5 and of a chloro-propoxy-terpyridine 18 from the hydroxy-terpyridine 3.

The terpyridine functionalised with an alkoxy-halide, here a propoxy-chloride, which could serve as an important intermediate for further terpyridine functionalisation, could be obtained through functional group interconversion reaction of the hydroxy-alkoxy functionalised terpyridine 3, which was obtained through reaction of 4’-chloro-2,2’:6’,2”-terpyridine 2 with an excess of 1,3-dihydroxy propanol (see Scheme 2.5). Reaction of 3 in refluxing SOCl₂ led to the chloro-propoxy-terpyridine 18, which, after recrystallisation, was obtained as a pure compound in 66% yield. An approach towards a metal-surface active terpyridine was made by functionalising the above mentioned amino-terpyridine 5 by reaction with the racemic DL-thioctic acid utilising the well-known DCC method in order to yield the dithiolan functionalised terpyridine 16 in 35% yield (Scheme 2.10). The pure product was obtained after column chromatography and repeated recrystallisation from diethyl ether. These measures of purification were necessary in order to separate the product from the main by-product dicyclohexylurea. Applying other coupling methods which, e.g., include the activation with CDI (N,N’-carbonyldiimidazole), could maybe increase the yield. Again, a useful tool for the detection of such higher mass molecules and possible higher molecular
weight by-products is MALDI-TOF mass spectrometry. Figure 2.5 (left) shows the spectrum of pure 16 after the described purification procedure.

**Figure 2.5:** Left: MALDI-TOF mass spectrum (matrix: dithranol) of 16. Right: $^1$H-$^1$H-COSY-NMR-spectrum of 16.

Apart from the molecule isotope distribution plus hydrogen from the matrix dithranol, the only major species detected is the molecule plus sodium, which is typical for MALDI-TOF-MS. A good proof for the detection of the desired molecule is also provided by the simulation of the isotopic distribution, which is shown in the top inset of Figure 2.5 (left). The $^1$H-NMR spectrum of this compound shows a complex signal pattern, which could be completely assigned by an $^1$H-$^1$H-COSY experiment (Figure 2.5, right). Characteristic is the broad –NH– signal around 5.6 ppm.

The introduction of an isocyanate function can be carried out by the reaction with phosgene, which is very poisonous and therefore not easy to handle. Additionally, problems regarding purification could occur due to the protonation of the basic terpyridine rings by the HCl formed during the reaction. Utilising di-tert-butyltricarbonate\[33\] (tri-carb), the conversion from an amino-group into an isocyanate-group can simply be carried out at room temperature in CH$_2$Cl$_2$ (Scheme 2.10).\[34\] After evaporation of the solvent, the product can be crystallised from $n$-pentane at low temperatures in order to obtain compound 17 in a yield of 73%. X-ray structure analysis led to the crystal structure and elementary cell in the crystal (Figure 2.6). The terpyridine ring and the alkyl chain lie in one plane, starting with the nitrogen of the
isocyanate group the plane angle changes. This is reflected in the torsion angles of 64.9 at C(22)-C(23)-C(24)-N(25) and 68.7 at C(23)-C(24)-N(25)-C(26) and leads to a "box-type" arrangement in the crystal.

Figure 2.6: Left: ORTEP view of 17 (thermal ellipsoids are at the 50% probability level). Right: elementary cell in the crystal.

Such a compound that can easily be further reacted quantitatively with alcohols (urethane bond) or amines (urea bond) is of good use when trying to functionalise macromolecules or polymers, where purification can be more difficult.

An alternative route for the modification with a hydroxy-butoxy functionality was investigated as well by using a protection group methodology (performed in collaboration with O. Hien[35]). 4'-Chloro-terpyridine was functionalised with tert-butoxy-butanol and subsequently the deprotection to the alcohol was performed (Scheme 2.11).

Scheme 2.11: Synthesis of the hydroxy-butoxy-terpyridine 20 utilising protection group methodology.
This route leads to the hydroxy-butoxy-terpyridine 20 in an overall yield of 84% and does not involve the difficulty of separating from di-functionalised by-product, when using the diols in excess (see Scheme 2.5).

Additionally, utilising a different approach, an alkinyl terpyridine was coupled to a bromo-functionalised chiral oligo-phenylene-vinylene (OPV) in a Sonogashira-type coupling,[36] thus opening avenues to energy/electron donor acceptor systems upon metal-complexation with appropriate systems (Scheme 2.12).

![Scheme 2.12: Synthesis of the oligo-phenylene-vinylene (OPV)-terpyridine 23 via Sonogashira-type coupling.](image)

This coupling makes use of the catalytic Pd⁰/PdⅡ cycle,[37] in which first oxidative addition of the aromatic bromide takes place. Subsequently, the halide is exchanged for the alkylnyl anion with the driving force being the scavenging of the proton by the basic solvent. Reductive elimination leads to the coupled product with the catalyst restored as palladium(0) species. The palladium(0) species used here was not created in situ from a palladium(II) salt, but directly applied in form of pure Pd(0)(PPh₃)₄. The UV/Vis spectrum shows the typical absorption of the OPV unit around 450 nm as well as the bands of terpyridine from 260 to 340 nm in chloroform (Figure 2.7).

![Figure 2.7: UV/Vis spectrum of 23 in CHCl₃.](image)
The difficulty regarding purification in this case was to separate the product from unfunctionalised starting material. The MALDI-TOF mass spectra were recorded before and after column chromatography using the same instrument settings. The latter spectrum, recorded with the same measurement parameters and preparation procedure, showed no unfunctionalised Br-OPV4 suggesting that, at least to the largest extent, the column chromatography separation was successful (Figure 2.8).

![MALDI-TOF mass spectra of OPV4-terpyridine 23, left: crude product, right: after column chromatography (matrix: dithranol).](image)

**2.5 Conclusion**

The functionalisation of 2,2':6',2''-terpyridines in the 4'-position is of importance for gaining access to bis-complexes, which do not give additional chiral products upon complexation and also provide directionality, since the complexation direction is generally located at 180° to the functionality starting from the 4'-position. Using the readily available 2,6-bis-(pyrid-2-yl)-4-pyridone 1 and 4'-chloro-2,2':6',2''-terpyridine 2, a series of new terpyridines was synthesised which are linked via an ether or a thioether bridge to different functional groups. In this way, amino-, carboxylic acid-, alcohol-, thiol- and stilbene-modified terpyridines were obtained by the nucleophilic substitution of 2 and bromo- and epoxy-functionalised ones were obtained by reaction with 1. A new convenient route for the introduction of alkyl-carboxylic acids in the 4'-position of the terpyridine has been established, using the *in situ* ring opening of lactones under the basic reaction conditions and thus leading to the subsequent reaction of the alcoholate with the chloro-terpyridine. The sequential functionalisation of the amine-functionalised terpyridine 5 with DL-thioctic acid led to a dithiolan-functionalised terpyridine 16. Other further functionalisation of some of the obtained compounds led to a chloro- as well as an isocyanate-terpyridine. Finally, the combination of a terpyridine with an OPV-unit *via* the Sonogashira-type coupling resulted in a terpyridine bonded in a conjugative way to a
photophysically active unit. The easy availability of all of the reported compounds and starting materials, except for the thiols 11-13 (considering the yields), opens new possibilities for the design of different types of 4'-functionalised terpyridine building blocks, in some cases with different alkyl-spacer lengths. As a result, tailor-made ligands for macromolecular and nanoscience applications, where metal complexation is of importance, are accessible.

2.6 Experimental

General remarks and instruments used: Basic chemicals were obtained from Sigma-Aldrich. The solvents used were supplied by Biosolve (AR grade). $^1$H- and $^{13}$C-NMR were recorded on a Varian Mercury 400 (or 300) spectrometer and the chemical shifts were calibrated to the solvent peaks. For more clarity, the carbons and hydrogens of the alkyl spacers are numbered using Greek symbols starting from the first carbon at the functionality and ending at the carbon next to the 4'-ether function at the terpyridine. UV/Vis spectra were recorded on a Perkin Elmer Lambda-45 (1 cm cuvettes). MALDI-TOF mass spectra were recorded on a Perseptive Biosystems Voyager-DE STR Biospectrometry and EIMS were obtained from a Shimadzu GCMS-QP5000. Elemental analyses were measured on a Perkin Elmer Series II 2400 and melting points were obtained from a Büchi Melting Point B-540. For X-ray crystallographic data, selected crystals were mounted on a Bruker-AXS APEX diffractometer with a CCD area detector. Graphite-monochromated Mo-K radiation (71.073 pm) was used for the measurements. The nominal crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different angle for the crystal, and each exposure took 20 s and covered 0.3° in. The data were corrected for polarisation and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structures were solved by direct methods (SHELXS-97). Refinement was carried out with the full-matrix least-squares method based on $F^2$ (SHELXL-97) with anisotropic thermal parameters for all non-hydrogen atoms. These X-ray measurements were done by Guido Kickelbick (Institute of Materials Chemistry, Vienna University of Technology). Tert-butoxy-butanol was used as prepared after a known literature procedure.

2,6-Bis(pyrid-2-yl)-4-pyridone (1) and 4'-chloro-2,2':6',2''-terpyridine (2) were synthesised by the BASF AG and our own research group (see also ref.[24]).

3-(2,2':6',2''-Terpyridin-4'-yloxy)-propan-1-ol (3): To a stirred suspension of powdered KOH (4.4 g, 77 mmol) in water free DMSO (150 mL) at 40 °C 1,3-propandiol (31 g, 0.41 mol) was added. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (10.44 g, 39.00 mmol) and the mixture was stirred for 20 h at 50 °C and then poured into deionised water (400 mL). The aqueous phase was then removed by filtration and the crude product was washed with deionised water and dried in vacuo. The product was purified by precipitating the by-product in MeOH (2x) followed by recrystallisation from THF (2x) yielding 3 as a white solid (4.9 g, 41%, Lit.: 85%[28]). M.p. 143 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.09$ (tt, $J = 5.7, 6.0$ Hz, 2 H, H$_6$), 3.87 (dt, $J = 5.7, 5.7$ Hz, 2 H, H$_4$), 4.37 (t, $J = 6.0$ Hz, 2 H, H$_5$), 7.31 (m, 2 H, H$_{5,5''}$), 7.82 (m, 2 H, H$_{4,4''}$), 7.99 (s, 2 H, H$_{3,3''}$), 8.59 (m, 2 H, H$_{3,3''}$), 8.66 (m, 2 H, H$_{6,6''}$). $^{13}$C NMR (300 MHz, CDCl$_3$): $\delta = 31.9$ (C$_6$), 59.5 (C$_8$), 65.5 (C$_7$) 107.3 (C$_{5,5''}$), 121.3 (C$_{4,4''}$), 123.8 (C$_{3,3''}$), 136.8 (C$_{3,5''}$), 148.9 (C$_{6,6''}$), 156.0 (C$_{2,2''}$), 156.9 (C$_{2,6''}$), 167.0 (C$_4$).
MALDI-TOF-MS (Matrix: dithranol) *m/z* = 308 (MH⁺). C₂₁H₂₃N₃O₂ (307.35): calcd. C 70.34, H 5.58, N 13.67; found C 70.06, H 5.49, N 13.48.

6-(2,2',6',2''-Terpyridin-4'-yloxy)-hexan-1-ol (4): To a stirred suspension of powdered KOH (1.0 g, 18 mmol) in water free DMSO (25 mL) at 40 °C, 1,6-hexanediol (4.43 g, 37.5 mmol) was added. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (1.00 g, 3.74 mmol) and the mixture was stirred for 4 h at 40 °C and then poured into distilled water (400 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried *in vacuo*, yielding 4 as a white solid (937 mg, 72%, Lit.: 76%[28]). M.p. 111 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.43-1.67 (m, 7 H, H₅,₇,₉,₁₀), 1.87 (tt, J = 5.8, 5.8 Hz, 2 H, H₁₀), 3.67 (t, J = 5.9 Hz, 2 H, H₉), 4.24 (t, J = 5.8 Hz, 2 H, H₇), 7.32 (ddd, J = 1.1, 4.7, 7.1 Hz, 2 H, H₅,₇), 7.84 (ddd, J = 1.6, 7.1, 7.1 Hz, 2 H, H₄,₆), 8.01 (s, 2 H, H₃,₅), 8.61 (d, J = 7.1 Hz, 2 H, H₃,₅), 8.70 (d, J = 4.7 Hz, 2 H, H₆,₆'). ¹³C NMR (300 MHz, CDCl₃): δ = 25.8 (C₇), 32.7 (C₀), 25.5 (C₃), 29.0 (C₉), 68.1 (C₅), 107.4 (C₅,₇), 121.4 (C₄,₆), 123.8 (C₃,₅), 136.8 (C₃,₅), 149.0 (C₆,₆'), 156.2 (C₂,₂'), 157.1 (C₂',₆), 167.3 (C₄). EIMS (70 eV) *m/z* = 349 (M⁺). C₂₁H₂₂N₃O₂ (349.43): calcd. C 72.18, H 6.63, N 12.03; found C 72.13, H 6.58, N 12.16.

5-(2,2':6',2''-Terpyridin-4'-yloxy)-pentylamine (5): To a stirred suspension of powdered KOH (2.82 g, 50.3 mmol) in DMSO (250 mL), 5-aminopentanol (9.4 g, 91 mmol) was added drop wise at 40 °C. After 20 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (5.58 g, 20.8 mmol) and the mixture was stirred for 2.5 h at 40 °C and then poured into deionised water (1.75 L). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried *in vacuo*, yielding 5 as a light yellow solid (6.20 g, 89%, Lit.: 71%,[29] 75%[25]). M.p. 104 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.19 (s, 2 H, –NH₂), 1.52-1.57 (m, 4 H, H₄,₅), 1.87 (tt, J = 5.9, 6.1 Hz, 2 H, H₆), 2.73 (t, J = 6.1 Hz, 2 H, H₅), 4.23 (t, J = 6.10 Hz, 2 H, H₅), 7.32 (ddd, J = 1.0, 4.6, 7.2 Hz, 2 H, H₄,₅), 7.83 (ddd, J = 4.9, 7.2, 7.2 Hz, 2 H, H₄,₅), 8.03 (s, 2 H, H₃,₅), 8.60 (d, J = 7.2 Hz, 2 H, H₃,₅), 8.69 (d, J = 4.6 Hz, 2 H, H₆,₆'). ¹³C NMR (300 MHz, CDCl₃): δ = 23.4 (C₇), 28.9 (C₁), 33.6 (C₃), 42.2 (C₀), 68.1 (C₅), 107.4 (C₅,₇), 121.3 (C₄,₆), 123.8 (C₃,₅), 136.8 (C₃,₅), 149.0 (C₆,₆'), 156.2 (C₂,₂'), 157.1 (C₂',₆), 167.3 (C₄). MALDI-TOF-MS (Matrix: dithranol) *m/z* = 335 (MH⁺). EIMS (70 eV) *m/z* = 334 (M⁺). C₂₀H₂₂N₄O (334.42): calcd. C 71.83, H 6.63, N 16.75; found: C 71.70, H 6.27, N 16.80.

4'-(2-Piperidin-4-yloxy)-2,2':6',2''-terpyridine (6): To a stirred suspension of powdered KOH (297 mg, 5.29 mmol) in DMSO (60 mL), 2-(4-piperidine)ethanol (0.823 g, 6.37 mmol) was added at 70 °C. After 20 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (0.56 g, 2.11 mmol) and the mixture was stirred for 4 h at 70 °C and then poured into deionised water (600 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried *in vacuo*, yielding 6 as a white solid (664 mg, 88%). M.p. 181 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.56 (s, 1 H, –NH–), 1.75 (m, 4 H, H₆,₇,₈,₉), 2.07 (m, 2 H, H₁₀), 2.80 (m, 2 H, H₄,₅), 3.15 (m, 2 H, H₆), 4.78 (m, 2 H, H₇), 7.33 (ddd, J = 1.0, 4.5, 7.1 Hz, 2 H, H₅,₇), 7.83 (ddd, J = 4.9, 7.2, 7.2 Hz, 2 H, H₄,₅), 8.01 (s, 2 H, H₃,₅), 8.60 (d, J = 7.2 Hz, 2 H, H₃,₅), 8.72 (d, J = 4.5 Hz, 2 H, H₆,₆'). ¹³C NMR (300 MHz, d₆-THF): δ = 32.1, 43.7 (C₃), 72.9 (C₇), 108.2, 121.3, 123.8, 136.8, 149.0, 156.2, 165.9 (C₂,₂', C₃,₃', C₄,₄', C₅,₅', C₆,₆', C₂',₆', C₃,₃', C₄'). EIMS (70 eV) *m/z* = 332 (M⁺). C₃₈H₃₂N₆S₂ (332.40): calcd. C 72.27, H 6.06, N 16.85; found: C 72.20, H 6.15, N 16.90.
3-Methyl-1-(S)-(2,2''6,2''-terpyridin-4'-yloxy)methyl)butylamine (7): To a stirred suspension of powdered KOH (377 mg, 6.72 mmol) in DMSO (50 mL), S-leucinol (1.31 g, 11.2 mmol) was added drop wise at 30 °C. After 30 min 4'-chloro-2,2':6,2''-terpyridine 2 was added (600 mg, 2.24 mmol) and the mixture was stirred for 10 h at 30 °C and then poured into deionised water (500 mL). The aqueous phase was then extracted with DCM (3 x 150 mL), the organic fractions were combined and the solvent was evaporated to give the crude product as a yellow oil. Further purification was carried out by column chromatography (Alox N, eluent dichloromethane, gradient with MeOH 5% → 10%). After removal of the solvent in vacuo 7 was isolated as a light yellow oil (240 mg, 31%). \(R_l\) = 0.58 (alox N, \(CH_2Cl_2\)/MeOH, 92/8). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 0.96\) (m, 6 H, 2 -CH\(_3\)), 1.37 (m, 2 H, -CH-CH\(_2\)-CH\(_2\)-), 1.50 (b, 2 H, -NH\(_2\)), 1.81 (m, 1 H, -CH\(_2\)-CH\(_2\)-(CH\(_3\))\(_2\)), 3.30 (m, 1 H, -CH\(_2\)-NH\(_2\)), 3.96, 4.17 (2 x dd, \(J = 7.6, 8.9\) Hz, \(J = 3.8, 9.0\) Hz, 2 x 1 H, -O-C\(_{H_2}\)-), 7.32 (ddd, \(J = 1.1, 5.0, 4.2\) Hz, 2 H, \(H_5\), 7.84 (ddd, \(J = 1.8, 5.0, 7.3\) Hz, 2 H, \(H_4\)), 8.01 (s, 2 H, \(H_3\)), 8.61 (d, \(J = 3.7\) Hz, 2 H, \(H_3\), \(H_5\)). EIMS (70 eV) \(m/z = 350\) (M\(^+\)). C\(_{21}\)H\(_{21}\)N\(_3\)O\(_3\) (349.38): calcd. C 68.75, H 5.48, N 12.03; found C 68.54, H 5.30, N 11.99.

5-(2,2':6,2''-Terpyridin-4'-yloxy)-pentanoic acid (8): To a stirred suspension of powdered KOH (0.74 g, 11 mmol) in DMSO (50 mL), \(\delta\)-valerolactone (0.52 g, 5.2 mmol) was added drop wise at 75 °C. After 30 min 4'-chloro-2,2':6,2''-terpyridine 2 was added (696 mg, 2.60 mmol) and the mixture was stirred for 48 h at 75 °C and then poured into deionised water (175 mL). To the transparent solution, concentrated hydrochloric acid was added drop-wise until precipitation of a white solid (pH ≈ 6). The aqueous phase was then removed by filtration and the crude product was washed with ethanol and dried in vacuo, yielding 8 as a white solid (654 mg, 72%). M.p. 205 °C. \(^1\)H NMR (400 MHz, d\(_8\)-THF): \(\delta = 1.78\) (m, 2 H, \(H_6\)), 1.87 (m, 2 H, \(H_7\)), 2.32 (t, \(J = 7.2\) Hz, 2 H, \(H_0\)), 4.22 (t, \(J = 6.3\) Hz, 2 H, \(H_3\)), 7.29 (ddd, \(J = 1.2, 4.6, 7.4\) Hz, 2 H, \(H_3\)), 7.82 (ddd, \(J = 1.8, 7.9, 7.9\) Hz, 2 H, \(H_4\)), 8.07 (s, 2 H, \(H_3\)), 8.56 (m, 4 H, \(H_3\)), 8.61 (b, 1 H, \(HOOC–\)). \(^1\)C NMR (300 MHz, d\(_8\)-THF): \(\delta = 22.7, 29.7\) (\(C_\gamma\)), 34.1 (\(C_\phi\)), 68.9 (\(C_\varepsilon\)), 108.2, 111.8, 121.9, 124.8, 137.6, 150.2, 157.3, 158.3 (\(C_{2,2'}\), \(C_{3,3'}\), \(C_{4,4'}\), \(C_{5,5'}\), \(C_{6,6}\), \(C_{2,6}\), \(C_{3,5}\), \(C_\phi\)), 168.4 (\(C_\varepsilon\)). MALDI-TOF-MS (Matrix: dithranol) \(m/z = 350\) (M\(^+\)). C\(_{21}\)H\(_{21}\)N\(_3\)O\(_3\) (349.38): calcd. C 68.75, H 5.48, N 12.03; found C 68.54, H 5.41, N 11.96.

6-(2,2':6,2''-Terpyridin-4'-yloxy)-hexanoic acid (9): To a stirred suspension of powdered KOH (7.40 g, 132 mmol) in DMSO (50 mL), \(\epsilon\)-caprolactone (5.97 g, 52.3 mmol) was added drop wise at 60 °C. After 30 min 4'-chloro-2,2':6,2''-terpyridine 2 was added (6.96 g, 26.0 mmol) and the mixture was stirred for 48 h at 60 °C and then poured into deionised water (1.6 L). To the transparent solution, concentrated hydrochloric acid was added drop-wise until precipitation of a white solid (pH ≈ 6). The aqueous phase was then removed by filtration and the crude product was recrystallised from THF and dried in vacuo, yielding 9 as a white solid (7.85 g, 83%). M.p. 187 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.61\) (tt, \(J = 6.1, 6.7\) Hz, 2 H, \(H_6\)), 1.79 (tt, \(J = 6.7, 6.7\) Hz, 2 H, \(H_7\)), 1.91 (tt, \(J = 6.1, 6.1\) Hz, 2 H, \(H_7\)), 2.42 (t, \(J = 6.7\) Hz, 2 H, \(H_6\)), 4.27 (t, \(J = 6.1\) Hz, 2 H, \(H_2\)), 7.35 (ddd, \(J = 1.1, 3.9, 4.9\) Hz, 2 H, \(H_5\)), 7.84 (ddd, \(J = 1.6, 4.9, 7.3\) Hz, 2 H, \(H_4\)), 7.99 (s, 2 H, \(H_3\)), 8.61 (d, \(J = 7.3\) Hz, 2 H, \(H_3\)), 8.70 (d, \(J = 3.9\) Hz, 2 H, \(H_6\)). \(^1\)C NMR (300 MHz, d\(_8\)-THF): \(\delta = 26.8, 30.1\) (\(C_\gamma\)), 34.5 (\(C_\varepsilon\)), 43.7 (\(C_\phi\)), 69.1 (\(C_\varepsilon\)), 108.2, 109.9, 121.9, 124.9, 137.6, 150.2, 157.3, 158.3 (\(C_{2,2'}\), \(C_{3,3'}\), \(C_{4,4'}\), \(C_{5,5'}\), \(C_{6,6}\), \(C_{2,6}\), \(C_{3,5}\), \(C_\phi\)), 168.4 (\(C_\varepsilon\)). EIMS (70 eV) \(m/z = 362\) (M\(^+\)–H). C\(_{21}\)H\(_{21}\)N\(_3\)O\(_3\) (363.41): calcd. C 69.41, H 5.82, N 11.56; found C 69.07, H 5.79, N 11.50.
4'-(1,2-Diphenyl-vinyloxy)-2,2':6',2''-terpyridine (10): To a stirred suspension of powdered KOH (224 mg, 3.99 mmol) in DMSO (30 mL), hydrobenzoin (202 mg, 0.943 mmol) was added at 40 °C. After 20 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (505 mg, 1.89 mmol) and the mixture was stirred for 4 h at 40 °C and then poured into deionised water (300 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried in vacuo. The crude product was dissolved in ethyl acetate and an insoluble by-product was filtered off. Recrystallisation from ethyl acetate yielded colourless crystals of 10 (96 mg, 15%). M.p. 192 °C. 1H NMR (400 MHz, CDCl3): δ = 6.82 (s, 1 H, =C–H), 7.18 (dd, J = 1.1, 1.1, 7.4 Hz, H3′,H5′), 7.31 (m, 3 H, Haryl), 7.67 (m, 4 H, Haryl), 7.81 (dd, J = 1.8, 7.8, 7.8 Hz, 2 H, H4′,H6′), 8.14 (s, 2 H, H3,5′), 8.57 (dd, J = 1.0, 1.0, 8.0 Hz, 2 H, H3,5′), 8.65 (dd, J = 0.8, 1.7, 4.7 Hz, 2 H, H6,6′). 13C NMR (300 MHz, CDCl3): δ = 107.4 (C5,5′), 113.5, 117.4 (Cstilbeneic), 121.3 (C4′), 123.8 (C3,3′), 125.8, 127.6, 128.6, 128.7, 129.2, 134.2, 135.2 (Cstilbeneic), 136.8 (C3′), 144.1, 148.5 (Cstilbeneic), 149.0 (C6,6′), 155.8 (C2,2′), 157.5 (C2,6′), 165.2 (C6′). MALDI-TOF-MS (Matrix: dithranol) m/z = 427 (M+). EIMS (70 eV) m/z = 354 (MH+). C20H22N4O (427.50): calcd. C 81.48, H 4.95, N 9.83; found: C 81.71, H 4.83, N 9.82.

4-(2,2':6',2''-Terpyridin-4'-ylsulfanyl)-butane-1-thiol (11): To a stirred suspension of powdered KOH (281 mg, 4.00 mmol) in water free DMSO (40 mL) at 30 °C, 4-(2,2':6',2''-Terpyridin-4'-ylsulfanyl)-butane-1-thiol (10) was added (536 mg, 2.00 mmol) and the mixture was stirred for 1 h at 30 °C and then poured into deionised water (2 L). The reaction mixture was neutralised with HCl dil,aq and extracted with CH2Cl2, 2,2':6',2''-terpyridine powder and the mixture was stirred for 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added drop wise. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (536 mg, 2.00 mmol) and the mixture was stirred for 1 h at 30 °C and then poured into deionised water (2 L). The reaction mixture was neutralised with HCl dil,aq and extracted with CH2Cl2 and with n-pentane (3 × 200 mL). Further purification was carried out by column chromatography (alox N, eluent: CH2Cl2 and recrystallisation from THF (3x) yielding 11 as a white solid (16 mg, 2%). M.p. 85 °C. 1H NMR (300 MHz, CDCl3): δ = 1.42 (t, J = 7.3 Hz, 1 H, –SH), 1.80-1.96 (m, 4 H, Hβγ), 2.51 (dt, J = 6.9, 7.9 Hz, 2 H, Hα), 3.19 (t, J = 6.9 Hz, 2 H, Hα), 7.34 (dd, J = 1.2, 4.8, 7.5 Hz, 2 H, H5,5′), 7.86 (dd, J = 1.8, 1.8, 7.7 Hz, 2 H, H4,4′), 8.33 (s, 2 H, H3,5′), 8.60 (d, J = 1.0, 1.0, 7.9 Hz, 2 H, H3,5′), 8.70 (d, J = 0.9, 1.8, 4.8 Hz, 2 H, H6,6′). MALDI-TOF-MS (Matrix: dithranol) m/z = 354 (MH+). C19H19N3S2 (353.49) + ½ H2O: calcd. C 57.15, H 4.49, N 11.37; found: C 57.14, H 4.34, N 11.76. Crystallographic data (C20H22N4O): monoclinic, space group P2(1)/n, a = 14.446(8), b = 11.372(5), c = 14.463(8) Å, β = 90°, γ = 90°.

6-(2,2':6',2''-Terpyridin-4'-ylsulfanyl)-hexane-1-thiol (12): To a stirred suspension of powdered KOH (0.6 g, 11 mmol) in water free DMSO (40 mL) at 30 °C, 6-(2,2':6',2''-Terpyridin-4'-ylsulfanyl)-hexane-1-thiol (11) was added drop wise. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (1.00 g, 3.74 mmol) and the mixture was stirred for 1 h at 30 °C and then poured into deionised water (2 L). The precipitate was extracted with CH2Cl2 (3 × 200 mL) and the solvent was removed. Excess 1,6-dimercaptohexane was removed by "Kugelrohr"-distillation and the remaining crude oil was recrystallised from diethyl ether yielding 12 as a white solid (302 mg, 21%). M.p. 87 °C. 1H NMR (300 MHz, CDCl3): δ = 1.33 (t, J = 7.3 Hz, 1 H, –SH), 1.43-1.67 (m, 4 H, Hβα), 1.65-1.80 (tt, J = 7.1, 7.1 Hz, 2 H, Hα), 1.80 (tt, J = 6.9, 6.9 Hz, 2 H, Hα), 2.54 (td, J = 7.1, 7.1 Hz, 2 H, Hα), 3.18 (t, J = 6.9 Hz, 2 H, Hα), 7.32 (dd, J = 1.1, 5.0, 4.2 Hz, 2 H, H5,5′), 7.84 (dd, J = 1.8, 5.0, 7.3 Hz, 2 H, H4,4′), 8.01 (s, 2 H, H3,5′), 8.61 (d, J = 7.3 Hz, 2 H, H3,5′), 8.70 (d, J = 4.2 Hz, 2 H, H6,6′). 13C NMR (CDCl3): δ = 25.8 (Cβ), 32.7 (Cγ), 25.5 (C5), 26.9 (C6′), 29.0 (C6), 68.1 (C4), 107.4 (C5,5′), 121.4 (C4′′), 123.8 (C3,3′), 136.8 (C3,5′), 149.0 (C6,6′), 156.2 (C2,2′), 157.1 (C2,6), 167.3 (C6′). EIMS (70 eV) m/z = 382 (M+). C21H22N6S2 (381.55): calcd. C 66.06, H 6.21, N 11.07.
10-(2,2':6',2''-Terpyridin-4'-ylsulfanyl)-decane-1-thiol (13): To a stirred suspension of powdered KOH (129 mg, 2.30 mmol) in water free DMSO (50 mL) at 30 °C 1,6-dimercaptohexane (3.08 g, 14.9 mmol) was added drop wise. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (399 mg, 1.49 mmol) and the mixture was stirred for 1 h at 30 °C and then poured into deionised water (1 L). The precipitate was extracted with CH2Cl2 (3 x 200 mL), the solvent was removed and the crude product was purified by column chromatography (alox N, eluent: CH2Cl2 and recrystallisation from THF (3x) yielding x as colourless crystals (24 mg, 4%). M.p. 83 °C. 1H NMR (300 MHz, CDCl3): δ = 1.32 (t, J = 7.7 Hz, 1 H, –SH) 1.22-1.40 (m, 10 H, H 1,5,5''), 7.84 (ddd, 1 H, H 5,5''), 8.60 (d, J = 1.1, 1.1 Hz, 2 H, H 5,5''), 7.33 (ddd, J = 1.1, 4.8, 7.4 Hz, 2 H, H 3,3''), 8.69 (d, J = 1.0, 1.8, 4.8 Hz, 2 H, H 6,6''). 13C NMR (CDCl3): δ = 24.6, 28.3, 28.4, 28.8, 29.0, 29.1, 29.4, 29.4, 30.9 (C 3,3''), 83.3 (s, 2 H, H 3,3''), 8.60 (d, J = 1.1, 1.1 Hz, 2 H, H 3,3''). MALDI-TOF-MS (matrix: dithranol) m/z = 438 (MH+). 1H (pyridone) C25H31N3S2 (437.66) +¼ H2O: calcd. C 67.91, H 7.18, N 9.50; found: C 67.70, H 6.81, N 9.86. Crystallographic data (C25H31N3S2): orthorhombic, space group Pbcn, a = 9.3691(8), b = 17.3353(14), c = 28.8572(2) Å, α = 90°, β = 90°, γ = 90°.

(R)-4'-Oxiranmethoxy-2,2':6',2''-terpyridine (14): To a stirred suspension of powdered K2CO3 (5.5 g, 40 mmol) in DMF (120 mL) at room temperature 2,6-bis-(pyrid-2-yl)-4-pyridone 1 (5.00 g, 201 mmol) was added. After 30 min, (R)-epichlorohydrin (5.55 mg, 60.0 mmol) was added and the mixture was stirred for 23 h at 50 °C and then poured into deionised water (350 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried in vacuo. The crude white product was filtered over alox N and recrystallised from THF to yield 14 as a white crystalline material (3.74 g, 61%). Rf = 0.92 (alox N, CH2Cl2). IR (ATR): 1598, 1582, 1562 (C=C, C=N, terpyridine), 1254 (C=O, epoxide), 827 cm⁻¹. M.p. 129 °C. 1H NMR (300 MHz, CDCl3): δ = 2.83 (dd, J = 2.4, 2.6 Hz, 1 H, Hα), 2.94 (dd, J = 4.1, 4.2 Hz, 1 H, Hβ), 3.43 (m, 1 H, Hγ), 4.22 (dd, J = 5.7, 5.7 Hz, 1 H, Hγ), 4.51 (dd, J = 2.9, 2.9 Hz, 1 H, Hβ), 7.33 (dd, J = 1.2, 4.7, 7.5 Hz, 2 H, H3,3''), 7.85 (dd, J = 1.8, 7.6, 7.6 Hz, 2 H, H4,4''), 8.05 (s, 2 H, H3,3''), 8.60 (dd, J = 1.1, 1.1 Hz, 2 H, H3,3''), 8.62 (dd, J = 1.1, 1.1 Hz, 2 H, H6,6''). 13C NMR (300 MHz, CDCl3): δ = 44.5 (C 1), 49.8 (C 2), 68.6 (Cγ), 107.3 (C5,5''), 121.3 (C4,4''), 123.9 (C 3,3''), 136.8 (C 3,3''), 149.0 (C 6,6''), 155.9 (C 2,2''), 157.2 (C 2,2''), 166.6 (C 1). UV/Vis (CHCl3), λmax (λ, ε, M⁻³cm⁻¹) = 279 (22000), 241 nm (24500). MALDI-TOF-MS (Matrix: dithranol) m/z = 306 (MH+). EIMS (70 eV) m/z = 305 (M⁺). C18H15N2O2 (305.33): calcd. C 70.81, H 4.95, N 13.76; found: C 70.78, H 4.97, N 13.70. Crystallographic data (C18H15N2O2): orthorhombic, space group Pbcn, a = 11.3013(8), b = 16.0780(12), c = 16.3808(12) Å, α = 90°, β = 90°, γ = 90°.

4'-(10-Bromo-decylxyo)-2,2':6',2''-terpyridine (15): To a stirred suspension of powdered KOH (680 mg, 12.1 mmol) in DMF (100 mL) at room temperature 2,6-bis-(pyrid-2-yl)-4-pyridone 1 (1.00 g, 4.01 mmol) was added. After 20 min, 1,10-dibromo-decane (7.63 g, 25.4 mmol) was added and the mixture was stirred for 80 min at RT and then poured into deionised water (600 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and then precipitated in 50 mL n-pentane. The crude white product was recrystallised from ethanol, yielding 15 as a white crystalline material (1.125 g, 60%). M.p. 78 °C. 1H NMR (300 MHz, CDCl3): δ = 1.41 (m, 12 H, H-alkyl), 1.85 (m, 4 H, Hα), 3.41 (t, J = 6.9 Hz, 2 H, Hβ), 4.22 (t, J = 6.4 Hz, 2 H, Hβ), 7.32 (dd, J = 1.2, 4.8, 7.5 Hz, 2 H, H3,3''), 7.84 (dd, J = 1.8, 7.5, 8.0 Hz, 2 H, H4,4''), 8.01 (s, 2 H, H3,3''), 8.62 (dd, J =
5-(1,2)Dithiolan-3-yl-pentanoic acid (5-(2,2′,6′,2″-terpyridin-4′-yloxy)-pentyl)-amide (16): Amino-pentoxy-terpyridine 5 (334 mg, 0.998 mmol), racemic thioctic acid (412 mg, 2.00 mmol), DCC (0.23 g, 1.1 mmol) and a catalytic amount of DMAP (~4 mg) were stirred in dry CHCl₃ for 10 h at room temperature. The insoluble residue was filtered off and washed with 2 × 10 mL of dry CHCl₃. The filtrate was evaporated and the remaining crude residue was purified by column chromatography (Alox N, eluent: dichloromethane, 0.5% MeOH). Further purification was carried out by recrystallisation from diethyl ether (2 ×) in order to yield 16 as a light yellow solid (183 mg, 35%). 

4′-(5-Isocyanato-pentyloxy)-2,2′;6′,2″-terpyridine (17): To a stirred solution of di-tert-butyltricarbonate (40 mg, 0.15 mmol) in CH₂Cl₂ (8 mL) under argon, a solution of 5 (40 mg, 0.12 mmol) was added slowly (over a period of 5 minutes) at room temperature. After 15 min, the solvent was evaporated and the oily residue dissolved in pentane at room temperature in order to obtain a saturated solution. Crystallisation at −25 °C yielded 17 as colourless crystals. (31 mg, 73%, still approximately a few mol% by-product di-terpyridine urea observed in MALDI-TOF). 

M. 4′-(5-Isocyanato-pentyloxy)-2,2′;6′,2″-terpyridine (18): Hydroxy-propoxy-terpyridine 3 (3.00 g, 9.76 mmol) was carefully added to 10 mL of SOCl₂ (heat development!) and refluxed for 5 h. The remaining SOCl₂ was removed in vacuo and the residue was neutralised with saturated NaHCO₃ solution. The crude product was filtered off and dried in vacuo. The product was...
then purified by recrystallisation from ethanol in order to yield 18 as a colourless crystalline solid (2.10 g, 66%). M.p. 105 °C. $^1$H NMR (300 MHz, CDCl₃): δ = 2.30 (m, 2 H, H₂β), 3.78 (t, J = 6.3 Hz, 2 H, H₂α), 4.39 (t, J = 5.8 Hz, 2 H, H₂γ), 7.36 (ddd, J = 1.2, 4.8, 7.5 Hz, 2 H, H₅,⁵'), 7.85 (ddd, J = 1.8, 7.5, 7.5 Hz, 2 H, H₄,₄'), 8.03 (dd, 2 H, H₃,₃'), 8.61 (ddd, J = 1.1, 2.1, 2.1 Hz, 2 H, H₃,₃'). 13C NMR (70 eV) of 1-tert-butyloxytetramethylene (19): To a stirred suspension of powdered KOH (6.0 g, 0.11 mol) in water free DMSO (40 mL) at 60 °C a solution (~ 40%aq.) of 1-tert-butoxy-4-butanol was added. After 30 min 4'-chloro-2,2':6',2''-terpyridine 2 was added (3.01 g, 11.3 mmol) and the mixture was stirred for 24 h at 60 °C and, after cooling to room temperature, poured into distilled water (500 mL) at 0 °C. The aqueous phase was then removed by filtration and further purification was carried out by column chromatography (alox N, eluent hexane/ethyl-acetate v/v: 9/1), yielding 19 as a white crystalline solid (3.90 g, 92%). M.p. 87 °C. R₁ = 0.39 (alox N, eluent hexane/ethyl-acetate v/v: 9/1). $^1$H NMR (200 MHz, CDCl₃): δ = 1.19 (~CH₂, 9 H, s) 1.75 (m, 2 H, H₂β), 1.94 (m, 2 H, H₂α), 3.44 (t, J = 7.1 Hz, 2 H, H₂α), 4.25 (t, J = 6.9 Hz, 2 H, H₂β), 7.33 (dd, J = 5.0, 4.2 Hz, 2 H, H₅,⁵'), 7.83 (t, J = 7.2, 4.9 Hz, 2 H, H₄,₄'), 8.00 (s, 2 H, H₃,₃'), 8.64 (d, J = 7.29 Hz, 2 H, H₃,₃'), 8.69 (d, J = 4.27 Hz, 2 H, H₆,₆'). 13C NMR (200 MHz, CDCl₃): δ = 25.98 (Cγ, C-2), 26.95 (Cβ, C-3), 27.46 (~CH₂), 61.37 (Cα), 68.03 (Cδ), 72.48 (~C(CH₃)₂), 107.36 (C₅,₅'), 121.25 (C₄,₄'), 123.65 (C₃,₃'), 136.68 (C₅,₅'), 143.89 (C₆,₆'), 156.10 (C₄,₄'), 167.24 (C₃'). EIMS (70 eV) m/z = 377 (M+). C₁₉H₁₈ClN₃O₂ (377.38): calcd. C 66.36, H 4.95, N 13.0. 4-(2,2':6',2''-Terpyridin-4'-yloxy)-butan-1-ol (20): 3.01 g (8 mmol) 4-(4'-oxo-(2,2':6',2''-terpyridinyl)-butoxytetramethylene 19 was dissolved in water free dioxyane (200 mL). 4 N hydrochloric acid (50 mL) was added drop wise and the mixture was refluxed for 6 h. After removal of the dioxyane, NaHCO₃-solution (260 mL) was added (1 mol/L) and the mixture was extracted with CH₂Cl₂ (3 times with 200 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed in vacuo yielding 20 as a white solid (2.35 g, 92%). M.p. 121 °C. $^1$H NMR (300 MHz, CDCl₃): δ = 1.79 (s, 9 H, H₂β), 1.94 (m, 2 H, H₂α), 3.75 (t, J = 7.1 Hz, 2 H, H₂α), 4.32 (t, J = 6.9 Hz, 2 H, H₂β), 7.36 (dd, J = 5.0, 4.2 Hz, 2 H, H₅,⁵'), 8.06 (s, 2 H, H₃,₃'), 8.62 (d, J = 7.3 Hz, 2 H, H₃,₃'), 8.70 (d, J = 4.3 Hz, 2 H, H₆,₆'). 13C NMR (300 MHz, CDCl₃): δ = 25.5 (Cγ), 29.3 (Cβ), 62.4 (Cα), 68.0 (Cδ), 107.5 (C₅,₅'), 121.4 (C₄,₄'), 123.8 (C₃,₃'), 136.9 (C₃,₃'), 149.0 (C₆,₆'), 156.1 (C₂,₂'), 157.1 (C₂,₂'), 167.2 (C₃'). EIMS (70 eV) m/z = 321 (M+). C₁₉H₁₉N₃O₂ (321.38): calcd. C 71.01, H 5.96, N 13.07; found C 70.67, H 5.72, N 13.00.

OPV4-Br (21): 21 was first reported and synthesised by Dr. Emiel Peeters.[41]

4'-Alkynyl-2,2':6',2''-terpyridine (22): 22 was first reported by Grosshenny et al.[42] and synthesised by Dr. Abdelkrim El-Ghayoury.
4′-OPV4-alkinyl-terpyridine (23): To a mixture of OPV4-Br 21 (223 mg, 0.191 mmol), the 4′-alkinyl-2,2’:6’,2’-terpyridine 22 (59 mg, 0.23 mmol) and Pd(PPh₃)₄ (15 mg, 0.01 mmol) 10 mL of N-propylamine was added and stirred for 60 h under reflux. After evaporation of the N-propylamine, the crude product was purified by column chromatography (alox N, eluent: hexane/CHCl₃ as 3/2) and dried under high vacuum in order to yield 23 as an orange solid (102 mg, 40%). M.p. 213 °C. 1H NMR (300 MHz, CDCl₃): δ = 0.95-1.18 (m, 48 H, –C₃H₃), 1.30-1.44 (m, 8 H, H aliph), 1.56-1.75 (m, 8 H, H aliph), 1.85-2.10 (m, 8 H, H aliph), 2.24 (s, 3 H, Haliph), 3.70-4.03 (m, 16 H, H aliph), 6.73 (s, 1 H), 7.07 (s, 1 H), 7.10 (s, 1 H), 7.17-7.22 (m, 5 H), 7.32-7.38 (m, 2 H), 7.45-7.57 (m, 2 H), 7.84-7.91 (m, 2 H), 8.59 (s, 2 H, H₃,5'), 8.61-8.63 (m, 2 H, H₃,3''), 8.69 (m, 2 H, H₆,6''). 13C NMR (300 MHz, CDCl₃): δ = 26.3, 35.0, 35.1 (C aliph.), 66.0, 74.3 (C triple-bond), 121.2, 121.7, 123.0, 123.9, 124.8, 133.3, 134.7, 135.0 (COPV-system), 107.4 (C₅₁5'), 121.3 (C₄₄'), 123.8 (C₃₃'), 136.8 (C₃,5'), 149.2 (C₆₆'), 156.2 (C₂₂'), 157.0 (C₂,6'), 167.5 (C₄). UV/Vis (CHCl₃), λₘₐₓ (ε, M⁻¹cm⁻¹) = 453 (40300), 280 nm (19300). MALDI-TOF-MS (Matrix: dithranol) m/z = 1342 (M +).

C₈₈H₁₁₅N₃O₈ (1342.89) + 3 H₂O: calcd. C 75.66, H 8.73, N 3.01; found: C 75.70, H 8.76, N 2.91.

2.7 References


Chapter III

4'-Functionalised bis-Terpyridine Metal Complexes

Abstract
The complexation of 2,2’:6’,2”-terpyridines with transition metal ions can lead to mono- or bis-terpyridine complexes. Here, bis(4’-functionalised terpyridine)-cadmium(II) and -cobalt(II) model complexes were synthesised in good yields. Ruthenium(III)/ruthenium(II) chemistry leads to heteroleptic bis-complexes, where first a ruthenium(III) mono-complex is synthesised and subsequently reacted with another ligand in order to form the bis-complex in a directed manner. Using this methodology, several heteroleptic model complexes with 4’-functionalised ligands from Chapter 2 as well as a photoactive triad including two Ru(II)-bis-terpyridine complexes and a perylene core could be realised. The functionalisation of a coiled coil peptide motif and subsequent complexation with iron(II) led to a de novo designed metallo-protein, which shows defined aggregation behaviour, depending on solvent, temperature and concentration. Thiol functionalised terpyridines open possibilities to influence the arrangement of gold nanoparticles via terpyridine-metal complexation. Furthermore, the complexation behaviour of 4’-chloro-2,2’:6’,2”-terpyridine with different metal ions, studied by UV/Vis spectroscopy and isothermal titration microcalorimetry (ITC), gave insights into the thermodynamics of terpyridine-metal complexation.

3.1 Introduction

Metal complexes of 2,2':6',2''-terpyridines have been known since the isolation of 2,2':6',2''-terpyridine by Morgan and Burstall\[^1\]\ and have since been studied to a wide extent regarding synthesis and characterisation.\[^2\] More recently such complexes have been applied in fields such as metallo-supramolecular chemistry, where the metal centres are used to control self-organisation processes\[^3\]\ or are used for photophysical purposes, where energy or electron transfer processes to or from the photoactive complex leads to molecular light to energy conversion systems\[^4\]\ (see also Chapter 1). Metal ions suitable for the build-up of such metallo-assemblies are transition metals such as iron(II), ruthenium(II) or nickel(II), which lead to (pseudo-)octahedral bis-terpyridine complexes with high stability constants.\[^5\]\ In this context, the well-known directed coupling method utilising ruthenium(III)/ruthenium(II) chemistry is of special interest (Scheme 3.1).

Scheme 3.1:  *Left:* examples for undirected bis-terpyridine metal complexation. *Right:* directed complexation using ruthenium(III)/ruthenium(II) chemistry (counterions omitted).

Ligand A is first complexed with ruthenium(III) in order to form a *mono*-terpyridine complex and subsequently free terpyridine ligand B is added under reductive conditions in order to form A-terpyridine-Ru(II)-terpyridine-B systems. This coupling methodology was first applied by Stone *et al.* in 1981\[^6\]\ in order to prepare an unfunctionalised *bis*-terpyridine-Ru(II) complex for charge-transfer luminescence investigations and has since been applied by numerous groups in order to create new photophysically interesting systems as well as new materials. A literature example which impressively demonstrates the possibilities using such ruthenium coupling in order to create molecularly well-defined complex assemblies was
4'-Functionalised *bis*-Terpyridine Metal Complexes

reported by Sauvage *et al.* in 1993.[7] With this type of directed coupling reaction, they synthesised heteronuclear ruthenium- and osmium-containing dyads, which upon investigation of the photophysical properties gave a good insight into electron and energy transfer of such molecularly well-defined systems.[8]

Concerning the reversibility of such metallo-supramolecular complex structures, only little is known about the exact thermodynamic and kinetic processes up to date. As already mentioned in Chapter 1, complexes with stronger binding metal ions such as *bis*-terpyridine-Fe(II) complexes start to exchange at higher temperatures of over 100 °C.[9] Among the metal ions which have significantly lower association constants with terpyridines are zinc(II), cadmium(II) or manganese(II).[5] Therefore these metal ions should prove to be interesting for metallo-supramolecular structures which can be reversed by applying less severe conditions than e.g. in case of iron(II) ions.

Further applications of such complexes, in particular concerning 2,2':6',2''-terpyridines with a synthetic handle in the 4'-position, lie in the fields of metallo-dendrimers, surface science and biochemistry (see Chapter 1). For example, in collaboration with the group of Roeland Nolte, we made first attempts to combine and control large biomolecules such as enzymes with the help of using the amino-pentyl-functionalised terpyridine 5 described in Chapter 2.[10] Since these studies are in the very first stages and still ongoing, they will not be discussed here further.

In this chapter the synthesis of functionalised symmetric and asymmetric metal complexes, using the methodologies mentioned above, are described. Among the synthesised assemblies are a photophysically interesting triad built up of two *bis*-terpyridine-Ru(II) complexes and a perylene as well as a synthetic coiled coil peptide strand complexed together by iron(II) ions. Moreover, first experiments towards functionalising and connecting gold-nanoparticles with thiol-functionalised terpyridine (complexes) were carried out. Additionally, attempts were made in order to gain a better insight into the thermodynamics of undirected terpyridine-metal complex formation using isothermal microcalorimetry (ITC) and UV/Vis spectroscopy.

### 3.2 Synthesis of 4’-functionalised *bis*-terpyridine model complexes

#### 3.2.1 Undirected, symmetric complexation

Two complexes using ligands described in Chapter 2 were prepared in an undirected manner, leading to functionalised *bis*-terpyridine complexes with functional groups in the 4'-positions.
This approach can lead to valuable building blocks for extended metallo-supramolecular assemblies where the metal ion is already specifically bound to functionalised ligands and the further covalent linkage can take place after metal-complexation (divergent approach). The often-applied alternative pathway is a convergent approach where first the ligands are covalently attached to their final destination and metal-complexation to the final structure is the last step.\[3a,11\] Here, the challenge in the divergent approach applied was to perform complexation reactions without the modification of the functional groups in the 4'-position of the ligands. Both complexes presented here could be characterised by means of NMR- and UV/Vis spectroscopy, MALDI-TOF mass spectrometry as well as elemental analysis. However, crystals suitable for X-ray structure analysis could not be obtained up to date. First the cadmium(II) bis-terpyridine complex 24 was synthesised by reacting the terpyridine ligand 4 and cadmium(II) acetate in a 2:1 ratio (Scheme 3.2).

\textbf{Scheme 3.2:} Synthesis of the pseudo-octahedral cadmium(II)-complex 24.

The reaction conditions were chosen according to standard literature procedures involving this type of bis-terpyridine complexation with transition metal ions.\[^{[2,12]}\] First, complexation takes place in methanol solution at 70 °C using the soluble acetate salt of cadmium(II). Through addition of a large excess of NH\textsubscript{4}PF\textsubscript{6} the bis-complex could be precipitated from the reaction mixture. The pure product was then obtained by crystallisation of the crude product utilising diffusion of diethyl ether into an acetone solution of the complex. The diamagnetic nature of cadmium(II) ions allows for characterisation of the complex with NMR. The \textsuperscript{1}H-NMR spectrum showed significant differences when compared to the spectrum of the free ligand 4 (Figure 3.1).
Figure 3.1: Comparison of the low-field $^1H$-NMR regions of the ligand 4 (top spectrum) with its cadmium(II) complex (bottom spectrum) in CD$_3$CN.

The shifts of the signals are mainly due to the influence of the electrons of the metal centre on the magnetic field and due to the fact that the terpyridines are locked in a pseudo-octahedral position in which some of the ligand protons "feel" the magnetic fields created by the opposite lying terpyridine. Especially the protons in the 6,6"-positions show a significant shift, because additionally their position lies next to the complexed nitrogen. The UV/Vis absorption behaviour will be discussed later. Apart from bis-complexes, mono-complexes are also readily formed by applying only one equivalent of the metal salt, which was shown for [Cd(tpy)Cl$_2$] by Pickardt et al.$^{[13]}$ This fact should also be reflected in the binding constants, which will be discussed later for the group-homologue zinc.

As an example for a symmetric terpyridine-complex with a more reactive functionality we chose to react the epoxide-terpyridine (Chapter 2) with cobalt(II) acetate. The symmetric complex 25 was formed by the reaction of two equivalents terpyridine-epoxide 14 with one equivalent of cobalt(II) acetate (Scheme 3.3). Cobalt(II) can be reduced to lower oxidation states, which preferably form mono-terpyridine complexes.$^{[14]}$ Therefore, cobalt could be a metal ion suitable for reversible metallo-supramolecular structures.
Scheme 3.3: Synthesis of the cobalt(II)-complex 25.

Because of the vulnerability of the epoxide group to methanol, the reaction was carried out by stirring at room temperature for 30 min. The addition of excess NH₄PF₆ then immediately produced quantitative precipitation of the crude product. After filtration and washing with MeOH and water, the pure complex was obtained. The shifts in the ¹H-NMR are influenced by the paramagnetism of cobalt(II) (Figure 3.2). Due to the hyperfine interaction of the unpaired cobalt(II) electrons with the ligand protons, a low-field shift is observed with the signals still being sharp enough for integration. Through comparison with similar complexes reported by Constable et al., the spin-state of the cobalt(II) can be assigned as low-spin.

Figure 3.2: ¹H-NMR of the cobalt(II)-complex 25 (in CD₃CN).
The existence of the complex 25 was proven by MALDI-TOF mass spectrometry. Figure 3.3 shows the spectrum obtained for the Co(II)-bis(epoxide-terpyridine) complex 9, recorded with the matrix DHB (dihydroxy benzoic acid).

![MALDI-TOF-MS spectrum](image)

**Figure 3.3**: MALDI-TOF-MS of the bis(epoxide-terpyridine)Co(II) complex 25 (matrix: 2,5-dihydroxybenzoic acid (DHB)).

The spectrum shows four isotope distributions which could all be assigned. All fragments refer to singly positive charged compounds. The peaks at m/z 814 and 669 represent the complex without one and none counter-ions, respectively. These fragment types are often observed for bis-terpyridine complexes.\(^{[17]}\) The fragment at m/z 517 refers to the complex without the counter-ions and without one ligand plus matrix minus a proton. At m/z 1033 the dimer of the latter fragment minus one proton is detected as can be shown through comparison with the simulated spectrum. Another method for the detection of successful terpyridine-metal complexation is UV/Vis spectroscopy. Especially the ligand-centred (LC) absorptions and, in some cases, metal-to-ligand charge-transfer (MLCT) absorptions are significant for terpyridine-metal complexes (Figure 3.4).\(^{[2]}\)
Figure 3.4: UV/Vis spectra of ligand 14 (—) and cobalt(II) complex 25 (⋯) (in CD$_3$CN).

The shift of the ligand centred (LC) absorption band to lower energy is typical for terpyridine complexation and can also be seen for the above discussed cadmium(II) complex (not shown here). Additionally, in the case of the cobalt(II) complex a weak MLCT absorption becomes visible when compared to the spectrum of the free ligand (Figure 3.4). There was also an attempt made to complex the amino-pentyl functionalised terpyridine 5 (see Chapter 2) with zinc(II). Using the same basic procedure as for the above described cadmium(II)-complex did not lead to the pure bis-terpyridine zinc complex. In particular when looking at the elemental analysis data, there was a strong indication for the amino group playing a role in the complexation because of the value for zinc being more than 1.5-fold above the calculated value. A more detailed insight regarding the thermodynamics and kinetics of the complexation of 4′-chloro-terpyridine with cobalt(II), zinc(II) and manganese(II) will be presented at the end of this chapter.

3.2.2 Directed complexation via ruthenium(III)/ruthenium(II) chemistry

The already mentioned, directed coupling with ruthenium(II) leads to extremely stable bis-terpyridine complexes which have photophysically interesting properties. In collaboration with Harald Hofmeier, several functional complexes were synthesised.$^{[18]}$ First, unsubstituted terpyridine was used for the synthesis of a symmetric model complex, which was prepared following known literature procedures.$^{[6]}$ After the reaction of ruthenium(III) chloride with terpyridine in ethanol, in order to form the 1:1 Ru(III)-mono-terpyridine complex, the second
ligand and catalytic amounts of N-ethyl-morpholine were added and the mixture refluxed for additional 4 hours. A well-known feature of such terpyridine-Ru(II) complexes is their fluorescence, which is usually deactivated at room temperature if no electron accepting substituent is attached directly to the terpyridine.\cite{19} Figure 3.5 shows the temperature dependent fluorescence of complex 26.

**Figure 3.5:** Temperature dependent fluorescence of complex 26.

It is known that the lowest excited state, which is a triplet metal-to-ligand charge-transfer state (3MLCT), undergoes a fast thermally activated radiation-less decay to an upper lying triplet metal-centred state (3MC) of the ruthenium ion.\cite{20} Thus, only at low temperatures excitation within the absorption bands of these complexes leads to the 3MLCT emission around 625 nm.\cite{19,21} In contrast to previously reported examples, where rigid-glass-matrices were utilised, a confocal setup equipped with a helium cryostat was used for this experiment.\cite{12} The sample was measured in solid state on a quartz glass substrate and the measurement setup was cooled down to 5 K in steps of 50 K. The observed low temperature fluorescence for the *bis*-terpyridine-Ru(II) was not observed with the free ligand nor the *mono*-terpyridine-Ru(III) complex.

Regarding the (from a supramolecular standpoint) more appealing concept of asymmetrical complexation, we attempted the synthesis of terpyridine end-capped *bis*-complexes with a
synthetic handle on one side, using some of the ligands presented in Chapter 2 (Scheme 3.4).\textsuperscript{[22]}

Scheme 3.4: Schematic drawings of the asymmetric bis-terpyridine complexes (PF\textsubscript{6}\textsuperscript{−} counter-ions omitted).

The yields for these complexes range between 61\% and 79\% and therefore demonstrate the feasibility of successful directed complexation, which is not hindered by the functionalities of the 4'-functionalised terpyridines. In the case of the carboxy-functionalised complex, this could be proven by X-ray analysis (Figure 3.6).

Figure 3.6: X-ray analysis of complex 27 (thermal ellipsoids are at the 50\% probability level).\textsuperscript{[22]}
Since these types of complexes are very stable,[23] it should be possible to further react them without destroying the asymmetric complex. Therefore, they present valuable model compounds as building blocks for novel metallo-supramolecular structures. The combination of energy/electron deficient moieties with energy/electron rich moieties on a molecular level has gained much interest over the last decade, especially in search of good charge separation for new organic solar cells.[24] We sought to synthesise a molecular triad containing a room-temperature-fluorescent perylene moiety and two bis-terpyridine-Ru(II) complexes. Perylenetetracarboxylic dianhydride (PTCDA) 30 has been reacted with the amino-functionalised 2,2':6',2"-terpyridine 5 in quinoline yielding the bis-terpyridine-terminated perylene dye 31 in 87% yield (Scheme 3.5). Compound 31 could be characterised in detail using NMR, elemental analysis and MALDI-TOF mass spectrometry.

Scheme 3.5: Synthesis of the Ru(II)-bis-terpyridine-perylene-Ru(II)-bis-terpyridine triad.

Due to the low solubility of 31 in chloroform (~ 2 × 10⁻⁵ mol/L), NMR spectroscopy was carried out in d-trifluoroacetic acid (d-TFA). This leads to protonation of the terpyridine rings and results all the expected signals with the corresponding integral values. The addition of the preformed terpyridine-Ru(III) complex 32 to ligand 31 gave the ruthenium(II)-bis-terpyridine complex 33 in 44% yield (after anion exchange with hexafluorophosphate
counter-ions). The complex 33 with a molar mass of 2273 g/mol could be detected by MALDI-TOF mass spectrometry. Moreover, NMR proved the existence of the *bis*-complex 33 (for a different approach towards such perylene-terpyridine compounds see ref.[25]). A qualitative comparison of the UV/Vis spectra of the ligand 31 with the ruthenium complex 33 shows the shift of the ligand centred band to 320 nm for the complex 33 (Figure 3.7).

![UV/Vis-spectra of the terpyridine-perylene ligand 31 (—) and its bis-Ru(II)-terpyridine complex 33 (----) (in DMSO).](image)

The typical perylene absorption is seen for both compounds from 400-550 nm. It should be mentioned though that the MLCT absorption, which occurs for Ru(II)-*bis*-terpyridine complexes at around 500 nm, lies underneath the perylene absorption for complex 33. First investigations regarding electron/energy transfer processes in this triad point towards an energy transfer process from the ruthenium(II)-terpyridine complex moiety to the perylene. However, due to the lack of reproducibility of the experiments, mainly because of solubility problems, this could not be unequivocally proven up to date.

### 3.3 "Coiled coil"-peptide motifs and terpyridine-metal complexation

In order to gain a better insight into structure-property relationships of metallo-proteins, which are of importance e.g. in DNA-binding zinc finger proteins,[26] we designed and investigated a minimalistic model system of a metallo-protein including terpyridine-metal complexation. The synthesised structure consists of two terpyridine modified α-amino acid
sequences held together by iron(II) ions. Generally, such de novo designed α-amino acid sequences are known to induce folding into dimeric and tetrameric superstructures.\textsuperscript{[27]} The terpyridine modified coiled-coil apoproteins were prepared by standard Fmoc solid-phase peptide synthesis, using the carboxy-hexoxy-terpyridine 9 as the N-terminal capping agent. Upon addition of 0.5 equivalents of iron(II) sulphate heptahydrate and subsequent precipitation with an excess of ammonium hexafluorophosphate, the purple complex 35 was obtained (Figure 3.8).

![Figure 3.8: Schematic drawing of the metallo-protein 35.](image)

Characterisation was done by means of MALDI-TOF mass spectrometry, reverse phase HPLC as well as UV/Vis spectroscopy (Figure 3.9). Upon comparing the UV/Vis spectra of the apoprotein with the iron(II) complex, the typical shift of the LC band to 329 nm as well as the appearance of the MLCT absorption at 561 nm, which is typical for Fe(II)-bis-terpyridine complexes, can be observed (Figure 3.9).

![Figure 3.9: UV/Vis-spectra of terpyridine-apoprotein 34 (---) and its bis-iron(II) complex 35 (-----) (in PBS, pH 7.4).](image)
According to UV/Vis spectroscopy, metal complexation yields bis-complexes which are rather insensitive to changes in concentration, solvent and pH. Evidence for decomplexation was only found in aqueous solution above pH 11 and at very high pressures during RP-HPLC, which is a known phenomenon for iron(II)-terpyridine complexes. MALDI-TOF mass spectrometry confirmed the formation of a bis-complex (Figure 3.10).

**Figure 3.10:** MALDI-TOF mass spectrum of the metallo-protein 35 (matrix: DHB).

The signal observed at m/z = 5750 corresponds to the sum of the masses of two terpyridine-containing apopeptides and one iron(II) ion. The isotope pattern could not be resolved, as can also be seen from the simulated spectrum (Figure 3.10, inset). Further characterisation could be done by gel permeation chromatography (GPC), which showed a reduced elution time, thus a higher mass for the complex when compared to the apopeptide. The folding behaviour of the metallo-protein and the apopeptide as well as the native coiled coil (without terpyridine) was then studied by circular dichroism (CD) spectroscopy and analytical ultracentrifugation (AUC); the native coiled coil peptide has already been investigated. Varying concentration, solvent and temperature indicated equilibria of different aggregates (Scheme 3.6). AUC-measurements proved the formation of unimeric, dimeric and tetrameric metallo-protein aggregates. In addition, large aggregates, which sedimented even at low rotor speeds, were found. From CD-measurements, it was found that at low concentrations (< 50 μM) the helix content does not decrease as in the case of the apopeptide and the native coiled coil. This is in accordance with the AUC result for this low concentration which still shows unimers, dimers and tetramers with a decrease in the large aggregate fraction.
Scheme 3.6: Proposed equilibria of the different aggregations of the metallo-protein.

When adding 50% ethanol to the phosphate-buffered saline (PBS) solution, only unimeric species could be found by AUC. CD spectroscopy, however, showed that the α-helical character is retained upon disruption of the tertiary structure. Finally, an increase in temperature (90 °C) resulted in both dissociation and unfolding, i.e. full denaturation, of the metallo-protein. For a more detailed insight into aggregate formation, first non-contact mode AFM measurements were performed on a bulk layer of the terpyridine-apopeptide and the metallo-terpyridine-peptide (approximately 0 to 1 microns thickness, prepared by drop-casting (Figure 3.11)). In the case of the apopeptide extended linear strands with a diameter of approximately 20 nm, which lie on top of the bulk material, could be visualised.

Figure 3.11: Left: AFM phase images of terpyridine-apopeptide. Right: metallo-terpyridine-peptide (right) measured from the bulk.
An explanation for such strands would be the aggregation of the apopeptide through parallel interaction of the coiled coil peptide sequence, resulting in a horizontal aggregation in one direction. Aggregation of the apopeptide is also found in solution. AUC measurements confirmed the formation of unimeric, dimeric, tetrameric and octameric aggregates. Thus, crystallisation to larger aggregates seems to be reasonable upon solvent evaporation. For the metallo-protein the mainly observed structures are ill-defined, hard, flat domains on top of the bulk material with a diameter of 500 to 1000 nm alternating with softer domains. This observation corresponds well to the formation of large aggregates as seen in the AUC measurements. It should be mentioned that this phase contrast never appeared for the terpyridine-apopeptide. These hard, flat domains could also have to do with crystallisation of the terpyridine complex salt.

3.4 Assembly of gold-nanoparticles by thiol-terpyridine

In the last decade there has been an increasing interest in the manipulation of different metal nanoparticles, since their fabrication as well as the required techniques for characterisation have made significant progress. The interplay of such particles with electromagnetic radiation, which involves quantum effects, opens avenues for many potential applications. Therefore the synthesis of well-defined 1-dimensional (1D)-, 2D- and 3D-arrays of such nanodots is a logical step in this research field.\[^{30}\] As already described above, properly functionalised terpyridine complexes can act as building blocks for new supramolecular structures. Applying this to gold nanoparticles, terpyridine complexes could act as a linker and, depending on the metal ion used for the terpyridine complex, the complex could influence the photophysical properties of the gold-nanoparticles. Rotello \textit{et al.} first reported on attempts to combine terpyridine-metal complexation with small gold nanoparticles (d = 2 nm).\[^{31}\] They could prove the formation of large aggregates due to bis-terpyridine-metal complexation (metal = iron(II), zinc(II), copper(II), silver(II)) by UV/Vis spectroscopy and small angle X-ray scattering (SAXS). Here, the attempt was somewhat different. Using commercially obtained gold nanoparticles (d = 20 nm), which are stabilised with citrate in water solution in order to prevent agglomeration, first studies were carried out on the influence of the addition of the 4'-mercaptophexylsulfide-terpyridine \textbf{12} (see Chapter 2) and cobalt(II) and iron(II) ions. It was envisioned that the terpyridine should bond to the gold particle \textit{via} the thiol moiety, with the terpyridine groups still having enough freedom to form a bis-complex with other terpyridines of other gold-particles in the presence of free metal ions (Scheme 3.7).
It is known that also unfunctionalised terpyridine moieties form organised domains on gold(111) surfaces. These domains consist of parallel periodic chains of terpyridines, which interact through π-stacking and which are adsorbed vertically on the surface via the free electron pairs of the nitrogens.[32] However, this dipole adsorption-interaction is much weaker than the sulphur-gold bond (145-174 kJ/mol[33]). In addition, the chain length of the spacer between thiol and terpyridine consists of only six methylene groups, which should, at least to a large extent, prevent the terpyridine from back-folding onto the nanoparticle.

First, the influence of 4'-mercaptohexylsulfide-terpyridine 12 on the gold nanoparticles was investigated by UV/Vis spectroscopy and atomic force microscopy (AFM). As references the 4'-hydroxy-hexaoxy-terpyridine 4 (see Chapter 2) as well as 1-mercaptodecane, which roughly represent the separated functionalities of the 4'-mercaptohexylsulfide-terpyridine 12, were used. Upon the addition of a 1000-fold excess of the compounds to aliquots of the purchased gold nanoparticle solution, only the sample with 4'-mercaptohexylsulfide-terpyridine 12 showed a significant difference in UV/Vis absorption, measured 1 h after preparation (Figure 3.12).
Untreated, citrate functionalised nanoparticles exhibit an UV/Vis absorption spectrum with a maximum absorption band at 525 nm, which is typical for the excitation of the plasmon resonance for gold nanoparticles with a 20 nm diameter. The shift of the absorption maximum to lower energies (here to 700 nm) is significant for the formation of larger aggregates. In this case, the formation of such aggregates could be explained by the disturbance of the protective citrate layer by terpyridine moieties attached to other gold particles (via their thiol group), which are located in close proximity. Subsequently, this could trigger the aggregation of the nanoparticles. This seems to be a reasonable explanation when comparing representative AFM height images of the reference without addition of any ligand and the sample with 4'-mercaptohexylsulfide-terpyridine 12 (Figure 3.13).
Figure 3.13: Top: non-contact mode height AFM images of citrate-stabilised particles (as purchased, left) and particles + ligand 12 (right). Bottom: corresponding typical height cross-sections.

The reference sample shows as expected particles of approximately 20 nm in height. In contrast, the sample treated with 4'-mercaptohexylsulfide-terpyridine 12 gives mostly rather large aggregates of 50-60 nm in height, where the particles seem to be agglomerated together. When choosing a lower concentration of the ligands (100-fold), the effect of agglomeration due to the 4'-mercaptohexylsulfide-terpyridine ligand 12 could be almost completely suppressed. However, when adding cobalt(II) acetate in order to induce complexation of the terpyridine nanoparticles, a blank measurement containing only the particles and cobalt(II) acetate also showed the formation of agglomerates, which made it impossible to distinguish and study the subsequent terpyridine-cobalt complexation of the nanoparticles. Obviously, the cobalt(II) acetate also disturbs the protecting citrate layer and mediates agglomerate formation. Therefore iron(II) chloride, which is well-known for its capability of forming stable iron(II)-bis-terpyridine complexes, was chosen for a further investigation. Again, a
100-fold excess of ligand was used and three measurements were performed. From the UV/Vis absorption spectra it can be seen that in this case only the sample with iron(II) chloride and the ligand 12 showed a significant shoulder in an absorption range around 640 nm (Figure 3.14).

![UV/Vis-spectra of particles + ligand 12 (---), particles + iron(II) chloride (----) and particles + iron(II) chloride + ligand 12 (· · ·) (in H$_2$O/EtOH).](image)

**Figure 3.14:** UV/Vis-spectra of particles + ligand 12 (---), particles + iron(II) chloride (----) and particles + iron(II) chloride + ligand 12 (· · ·) (in H$_2$O/EtOH).

A significant difference to the measurements concerning the free ligand is observed in terms of agglomeration. The shoulder that arises is at around 640 nm in contrast to the large aggregate formation for the free ligand experiments, where a maximum of 700 nm can be observed. This could present a first indication that, for the iron(II) chloride, complexation of the nanoparticles due to terpyridine complexation does take place. A shift to a wavelength of 640 nm instead of 700 nm indicates the formation of smaller aggregates. However, AFM-images did not reveal any significant differences, again only spots with a height of 20 nm could be observed and further distinguishing between one, two or even more particles aggregating together in a 2-dimensional fashion was not possible. Nevertheless, also the iron(II) chloride without the ligand seems to have an effect on agglomeration as can be seen from Figure 3.14, but in this case it is not as pronounced as reported for the cobalt(II) acetate.

### 3.5 Metal binding studies

Thermodynamic and kinetic data of terpyridine-complexation with transition metal ions have been obtained up to date mainly by stopped flow measurements.$^{[5,35]}$ Isothermal titration
Microcalorimetry (ITC) has been proven to be a useful method for the study of complexation parameters of other metal-to-ligand complexation systems such as human serum albumin with nickel(II)$^{[36]}$ or a lignin derivative with copper, lead and manganese.$^{[37]}$ Here, it was attempted to determine the stability constants for the complexation of 4'-chloro-terpyridine $2$ with manganese(II), zinc(II) and cobalt(II) by ITC.

Briefly, the method works as follows. Aliquots of one binding partner (here the metal salt) are titrated to the other binding partner (here the 4'-chloro-terpyridine). Upon each titration the machine monitors and reports the amount of heat it has to add (endothermic) or release (exothermic) of the measuring cell in order to keep it at the same temperature as the reference cell (in the present case: 26 °C). The titration syringe simultaneously acts as a stirrer in order to minimise diffusion effects in the cell. The obtained data can then be fitted to a binding model, using the association constant(s) and the enthalpy(s) of complexation as fitting parameters. The Gibbs free energy of complexation can be calculated using $\Delta G = -RT\ln(K)$ (Arrhenius equation), after which the complexation entropy is calculated using $\Delta G = -RT\ln(K)$ (Second Law of thermodynamics). Most known attempts in literature, which concern thermodynamics (and kinetics) of terpyridine-metal complexation, focus on one reaction step at a time, using e.g. a large excess of the metal ion with the focus on 1:1 metal to ligand complexation thus pseudo-first order kinetic equations to derive the thermodynamic stability constants may be applied. The following equations are of importance for fitting the experimental data according to a sequential binding sites model, which, in this case, takes into account two sequential binding sites for the guest (chloro-terpyridine ligand) on the host (apo-metal ion). Here, it was attempted to obtain $K_1$ (1:1 complex) and $K_2$ (2:1 complex) from one titration experiment. Concerning the statistics of complexation, the following assumption was made: based on what is known from literature, all the investigated metal ions are believed to coordinate in a hexacoordinate fashion with the terpyridine ligand.$^{[2]}$ Thus, there is the possibility of coordinating one and/or two terpyridines per metal ion (Scheme 3.7).

![Scheme 3.7](image)

**Scheme 3.7:** Complexation of one and/or two terpyridines per metal ion (counter-ions omitted).
Chapter III

It should be mentioned though, that lower coordination modes could also be possible, which would reflect in the dependency of the binding-sites towards each other. Since this question cannot be answered with complete certainty, it will not be taken further into account here. In Equation 1, \( F_n \) is the fraction of total apo-metal having \( n \) bound ligands. \( F_n \) contains the fitting parameters \( K_n \) and the free concentration of ligand (for details see manual of MicroCal ITC\(^{[38]}\)). The heat content for the \( i^{th} \) injection is then determined from Equation 1.

**Equation 1:** \[ Q = M V_0 (F_1 \Delta H_1 + F_2 [\Delta H_1 + \Delta H_2]) \]

**Equation 2:** \[ \Delta Q(i) = Q(i) + \frac{dV_i}{V_0} \left[ \frac{Q(i) + Q(i-1)}{2} \right] - Q(i-1) \]

with: \( Q \) = total heat content of the solution contained in \( V_0 \); \( M_t \) = bulk concentration of metal-salt in \( V_0 \); \( V_0 \) = active cell volume; \( \Delta H_n \) = free enthalpy for reaction step \( n \); \( F_n \) = fraction of metal-salt having \( n \) bound ligands; \( Q(i) \) = total heat released after the \( i^{th} \) injection; \( \Delta Q(i) \) = heat released from completion of the \((i-1)^{th}\) to the \(i^{th}\) injection.

This heat content is then used for the expression for heat released \( \Delta Q(i) \), from the \( i^{th} \) injection (Equation 2), which then leads to a Marquardt minimisation routine.

In parallel, UV/Vis titrations were performed for these systems. The fitting of the data in these cases was done using the equilibrium equations and the mass balance equations in combination with the Lambert-Beer equation.\(^{a}\) Data were fitted using a spreadsheet methodology described previously.\(^{[39]}\) The choice of the ligand used was 4'-chloro-terpyridine 2 for which no thermodynamic and kinetic investigations whatsoever have been performed up to now. Cobalt(II) acetate-tetrahydrate, zinc(II) chloride and manganese(II) chloride were the metal salts used in the investigations. These metal ions are known to show significant differences in association constants.\(^{[5b, 35c]}\) The choice of metal salts had also to do with purity, availability and good working experience. All experiments were performed in distilled and dried methanol due to the low solubility of the ligand 4'-chloro-terpyridine in water.

\(^{a}\) The fitting was done with the help of Dr. Jasper Michels, TNO, Eindhoven.
The first system discussed here is cobalt(II) acetate-tetrahydrate / 4'-chloro-terpyridine. For the reaction of unfunctionalised terpyridine with excess cobalt(II) acetate (pseudo first order, assuming only 1:1 complex formation) in water a complexation constant $K_1$ of $2.5 \times 10^8$ L/mol, measured by stopped flow, was obtained.$^{[5b]}$ Here, the titration of 4'-chloro-terpyridine with cobalt(II) acetate-tetrahydrate by ITC revealed a similar result (Figure 3.15).

![ITC-titration of cobalt(II) acetate to 4'-chloro-terpyridine (cell conc.: 0.09 mM, in MeOH, with the fitted N (complexation ratio), K (M$^{-1}$), $\Delta H$ (kcal/mol) and calculated $\Delta S$ (kcal/molK) values).](image)

**Figure 3.15:** *ITC-titration of cobalt(II) acetate to 4'-chloro-terpyridine (cell conc.: 0.09 mM, in MeOH, with the fitted N (complexation ratio), K (M$^{-1}$), $\Delta H$ (kcal/mol) and calculated $\Delta S$ (kcal/molK) values).*

On the upper left of Figure 3.15 the actual titration can be seen as recorded by the ITC machine (heat flux versus time). The graph below shows the integral heat per injection, normalised for concentration and cell volume, plotted against the molar ratio. The raw data has been corrected for heat of dilution, by subtracting a heat-of-dilution measurement, where the metal salt solution is titrated into the pure solvent methanol (titration of pure solvent to the ligand solution was not taken into account, because there is no significant heat effect). This data could only be fitted using a simpler fitting model, which only considers one type of identical sites (in principal the same as the above described site model without the condition of sequential order). This model only leads to one $K = K_1 = K_2$ for both reaction steps but nonetheless a rough estimate of the range of the binding constants is obtained. The fit clearly
shows a sharp transition at a molar ratio of 0.5 cobalt(II) to 4'-chloro-terpyridine (N = 2.00, 2 ligands to 1 metal ion), which proves the formation of a 2:1 bis-complex. Since no distinction could be made between the two reaction steps, because of the identical sites fitting model, the values obtained for the enthalpy (which is as expected negative) and the entropy (which is also clearly positive - 4 hydrated waters are set free) are only average values. Lowering the concentration might lead to more data points around the ratio of 0.5, thus leading to a curve which could be fitted by the sequential binding sites model. However, such attempts did not prove to be successful up to date also because of the signal to noise ratio getting too high at lower concentrations. Values found in literature (terpyridine / cobalt(II) in water) for separate measurements of $K_1$ and $K_2$ by stopped flow show that $K_1 (2.5 \times 10^8 \text{ L/mol}) < K_2 (7.9 \times 10^9 \text{ L/mol})$. This indicates positive cooperativity since $K_2$ is significantly larger than $K_1$. This could also be the case for the system measured above, since also at lower concentrations than the one shown here a sudden change around the metal to ligand ratio of 0.5 was observed, meaning that preferably the 2:1 complex is formed, also on overtitration with cobalt(II) ions. One has to be careful though when comparing systems measured in water and methanol since both the salt (ions) and the ligand will have very different solvation behaviour in these solvents.

These findings may now be compared with data obtained from an UV/Vis titration. Generally, it has to be noted that the UV/Vis titration requires much smaller concentrations (between 1 and 2 orders of magnitude). Figure 3.16 shows the UV/Vis titration as well as the rise in absorption at 329 nm upon addition of cobalt(II) acetate-tetrahydrate including the fitting curve.

**Figure 3.16:** Left: UV/Vis-titration of cobalt(II) acetate to 4'-chloro-terpyridine (conc.: $2.5 \times 10^{-5} \text{ mM, in MeOH}$). Right: absorption at 329 nm as a function of molar ratio.
A good fit could be achieved for a 2:1 ligand to metal binding model. The K-values obtained by this method were found to lie in the range of \((8.5 \pm 1.5) \times 10^6\) M\(^{-1}\) for \(K_1\) as well as \(K_2\). These results are found to be over one order of magnitude lower than the result obtained from ITC. Influences from water contaminations (influence on hydration layer), which cannot be completely excluded since the ITC machine could not be run under inert gas condition, might play a role here. Again, lowering the concentration further might possibly, but not necessarily, give results that are more precise. Nevertheless, the combined range of the ITC and UV/Vis titration experiments in terms of the binding constants lies in the range of \(7 \times 10^6\) M\(^{-1}\) to \(2.5 \times 10^8\) M\(^{-1}\) for both \(K_1\) and \(K_2\), which is higher than for the following investigated systems. In terms of synthesis and isolation, the most similar compound to the one investigated here which is known from literature (in particular regarding the acetate counter-ions) is a \(bis\)-4'\-para-tolyl-terpyridine cobalt(II) di-acetate complex.\(^{[40]}\) Apart from that, also the above described 4'-methoxy-epoxy-terpyridine was reacted with cobalt(II) acetate, but precipitated and purified as PF\(_6\)\(-\) salt. For the best of our knowledge, no evidence whatsoever has been found in literature for the existence of a comparable cobalt(II) acetate - terpyridine complex in a 1:1 metal to ligand ratio, which does indicate that complexation with cobalt(II) acetate occurs with positive cooperativity (\(K_1 < K_2\)).

The next system investigated was zinc(II) chloride / 4'-chloro-terpyridine (Figure 3.17). Again, the data points have been corrected for dilution as described above.

**Figure 3.17:** \(ITC\)-titration of zinc(II) chloride to 4'-chloro-terpyridine (cell conc.: 0.10 mM, in MeOH, with the fitted \(K (M^{-1})\), \(\Delta H \) (kcal/mol) and calculated \(\Delta S \) (kcal/molK) values).

The experimental data can be fitted well with the above described sequential binding sites model. The value of \(4.6 \times 10^6\) L/mol for \(K_1\) is in good agreement with the value of \(1.0 \times 10^6\)
obtained for unfunctionalised terpyridine with excess zinc(II) by stopped flow measurements (pseudo first order) in water.[5b] To the best of our knowledge, no measurements in methanol are known from literature. Furthermore, the ITC measurement gives a value for $K_2$, which lies significantly below the value for $K_1$ ($K_2$ for a Zn-terpyridine system has up to date not been reported in literature). This negative cooperativity would suggest that the 1:1-complex is the favoured product upon reacting metal and ligand in a 1:1 ratio as opposed to the above discussed cobalt case. It should be mentioned though, that the $K_2$ value discussed here (thus the mentioned cooperativity) also includes further processes like the decomplexation of the chlorides attached to the Zn(II)-terpyridine. The enthalpies are, as expected, again negative for both reaction steps. The entropy for the first step is slightly negative, which seems reasonable considering the formation of one product (the mono-complex) out of two educts (chloro-terpyridine and zinc(II) chloride) and indicates that at least one of the chlorides is still bound to the zinc(II). This is supported by the finding that the entropy for the second step is highly positive, which could be explained by the displacement of the two chloride anions by the second terpyridine.

The UV/Vis titration for the zinc(II) system indicates a more complicated behaviour than the UV/Vis spectrum of the cobalt(II) acetate titration. Up to the equivalence of zinc(II) to chloro-terpyridine of 1 to 2, a linear increase in the arising ligand centred (LC) band is observed. However, after further titration, the maximum of the LC band starts to shift significantly and remains unchanged after a 1:1 ratio is reached (Figure 3.18).

![Figure 3.18](image)

**Figure 3.18:** Left: UV/Vis-titration of zinc(II) chloride to 4'-chloro-terpyridine (conc.: $2.2 \times 10^{-5}$ M, in MeOH). Right: rise in maximum absorption between 325 nm and 335 nm of the LC band with indication of the slopes.

Because of the shift in the absorption maximum around 0.5 equivalents, one can conclude that in this case at least more than one species is present. This observation is in agreement with the
finding of negative cooperativity from the ITC experiment. It seems likely that upon further titration after a 1:2 zinc to ligand ratio is reached, the formation of mono-complexes immediately starts taking place. Hence, this indicates, that the final maximum of the LC band belongs to the 1:1 complex, in contrast to the maximum observed up to a titration of a 1:2 zinc to ligand ratio, which belongs to the 2:1 complex (bis-complex). Because of this shift, no fitting of the rise in absorbance was attempted. A crystal structure for the 1:1 complex with unsubstituted terpyridine as the chloride salt has been reported. Furthermore, a bis-complex of a 5,5''-methyl substituted terpyridine with PF$_6^-$ counter-ions was reported by our group. This demonstrates that, in contrast to the cobalt(II) acetate system, 1:1-complexes can be isolated by reaction of a 1:1 ratio of metal to ligand, which matches the indication of negative cooperativity. A higher concentration had to be used in this case because of the lower enthalpy (at 26 °C), when compared to the other systems.

The last investigated system is that of manganese(II) chloride / 4'-chloro-terpyridine. The fit of the experimental data, using the sequential binding sites model obtained by ITC resulted in a value of $5.0 \times 10^4$ L/mol for $K_1$ (Figure 3.19), which can be compared to the value $1.0 \times 10^5$ L/mol found for terpyridine with excess manganese(II) perchlorate (pseudo first order), measured by the stopped flow method in anhydrous methanol.

![Figure 3.19: ITC-titration of manganese(II) chloride to 4'-chloro-terpyridine (cell conc.: 1.0 mM, in MeOH, with the fitted $K$ (M$^{-1}$), $\Delta H$ (kcal/mol) and calculated $\Delta S$ (kcal/mol/K) values).](image)

Using the same method Holyer et al. found $K_1$ to be $2.5 \times 10^4$ L/mol for terpyridine and manganese(II) measured by stopped flow in water. However, a recent study using the ITC method and 4'-hydroxy-terpyridine / manganese(II) chloride in water solution gave a much higher value for $K_1$ of $2.0 \times 10^7$ L/mol. Except for the last mentioned system, where the
hydroxy-group in the 4’-position may have a considerable influence on complexation (see tautomerism of 4’-hydroxy-terpyridine in Chapter 2), all other known values from literature for similar systems lie in the same range as the value measured in this work. The value obtained for $K_2$ lies over two orders of magnitude lower at $2.6 \times 10^2$ L/mol. Again, this could indicate negative cooperativity (as defined above), and does seem reasonable, when taking into account, that mono-complexes with manganese(II) chloride have been prepared using a nearly 1:1 metal to ligand ratio (X-ray crystal structure determination).[43]

The corresponding UV/Vis titration is displayed in Figure 3.20. Unlike for the zinc(II) and the cobalt(II) cases, a significant rise in the absorption of the band at 330 nm was still observed at ratios above 2 (manganese) to 1 (4’-chloro-terpyridine), while at the same time the initial part of the curve is straight. Thus, modelling with a 1:2 model as in the case for cobalt(II) acetate was not possible.

![Figure 3.20](image)

**Figure 3.20:** Left: UV/Vis-titration of manganese(II) chloride to 4’-chloro-terpyridine (conc.: $3.5 \times 10^{-5}$ M, in MeOH). Right: rise in absorption at 330 nm.

Since the change in the UV/Vis-spectra still occurs in accordance with the isosbestic point at 305 nm and the reference measurement of manganese(II) chloride alone did not give a significant absorption, an unknown coordination mode of terpyridine with manganese(II) might be the reason for the observed behaviour. It could also be imagined that the formation of negatively charged manganese(II) chloro-complexes which are formed upon overtitration have an influence on the binding behaviour of the terpyridine ligand. Manganese(II) chloride and the chloride counter-ions of the complexes are well known to form $[\text{MnCl}_3]^{-}$ complexes.[44] These questions, however, remain to be answered.
In conclusion the same tendency can be found for the association strength of the investigated metal ions with 4'-chloro-terpyridine (cobalt(II) > zinc(II) > manganese(II)) compared to what is known from literature for unfunctionalised terpyridine. However, the influence of solvent and the counter-ions also seem to play crucial roles and more into detail studies should prove to give a better understanding.

3.6 Conclusions

The complexation of terpyridines may be carried out in the presence of functional groups. For example, a 4'-methoxy-epoxy-terpyridine could be complexed with cobalt(II) under mild conditions to the symmetric bis-complex. Also directed complexation could be performed, utilising ruthenium(III)/ruthenium(II) chemistry, in order to yield asymmetric terpyridine complexes with a synthetic handle on one side, which consisted of amino-, carboxy- or hydroxy-functionalities. Functionalisation of a perylene-core with the amino-pentyl functionalised terpyridine and subsequent complexation with RuCl$_3$-mono-terpyridine led to a photophysically interesting model-compound for a donor-acceptor-donor triad. The combination of terpyridine-metal complexation and a de novo designed coiled coil sequence was realised and investigated using CD spectroscopy, analytical ultracentrifugation (AUC) and AFM regarding superhelical coil formation in dependence of temperature, solvent and concentration. In particular at low concentrations, evidence for a more pronounced coiled coil formation was found when comparing to the apopeptide and the native coiled coil sequence. 4'-Thiol-functionalised terpyridine complexes have the potential to influence the arrangement of gold nanoparticles. First experiments show that an effect can be seen by UV/Vis spectroscopy upon treatment of gold particles with a thiol functionalised ligand and iron(II) chloride. Finally, complexation parameters of the weaker binding metal ions cobalt(II), zinc(II) and manganese(II) have been studied using ITC and UV/Vis spectroscopy with the ligand 4'-chloro-terpyridine. The results obtained are comparable to what is known from literature for unfunctionalised terpyridine, despite the different solvents used for parts of these measurements. The ITC-titrations for zinc(II) chloride and manganese(II) chloride are somewhat indicative of a negative cooperativity leading to the almost quantitative formation of 1:1 complexes after overtitration over the 2:1 ligand to metal ratio. The investigated metal salts cobalt(II) acetate-tetrahydrate, zinc(II) chloride and manganese(II) chloride all show, despite the similar charge of the metal ions, remarkably different association behaviour with terpyridine ligands.
3.7 Experimental part

**General remarks and instruments used:** Basic chemicals were obtained from Sigma-Aldrich. In addition to the instruments and chemicals mentioned in Chapter 2, the following instruments and chemicals were used. Citrate stabilised gold colloids (d = 20 nm, approx. 0.01% HAuCl₄) were purchased from Sigma-Aldrich. ITC experiments were carried out on a VP-ITC isothermal titration calorimeter from MicroCal (distilled methanol was used for all experiments, cell temperature was set to 26 °C). AFM imaging in non-contact mode was done on a Solver P47H (NTMDT) using NSG11-B tips from NTMDT. Samples were prepared by drop-casting from methanol solutions (1.3 – 1.8 × 10⁻⁵ mol/L for the coiled coil experiments) and from ethanol/water solution (1 – 2 × 10⁻⁵ mol/L for the gold nanoparticle experiments) onto a silicon-wafer.

Compounds 26 and 32 were synthesised according to a standard literature procedure. Compounds 27, 28, 29 were synthesised as described elsewhere. Compound 30 was donated by the BASF AG.

**Bis{6-(2,2':6',2''-terpyridine-4'-yloxy)-hexan-1-ol}-cadmium(II)-di-hexafluorophosphate (24):** 6-(2,2':6',2''-Terpyridine-4'-yloxy)-hexan-1-ol (4) (191 mg, 0.55 mmol) was dissolved in 20 mL methanol and cadmium(II) acetate hydrate (627 mg, 0.27 mmol) was added and the mixture stirred under reflux for 2 h. NH₄PF₆ (3.90 g, 23.9 mmol) in 3 mL H₂O was added to the hot reaction-mixture and it was stirred for another 10 min. After 12 h at 4 °C the precipitate was filtered off and washed with water (3 × 20 mL), methanol (3 × 20 mL), diethyl ether (3 × 20 mL) and again with water (3 × 20 mL). The crude product is purified by recrystallisation from diethyl ether / acetone to yield 24 (225 mg, 75%) as colourless crystals. D.p. = 258 °C. ¹H NMR (300 MHz, d-TFA): δ = 1.66-1.85 (m, 16H, H₅₆,₅₇,₆₅,₆₆,₆₇,₆₈), 4.68 (t, J = 6.19 Hz, 4H, H₂), 7.44 (m, 4H, H₅₅'), 7.99 (d, J = 4.01 Hz, 4H, H₆₆'), 8.12 (m, 4H, H₃₃'), 8.15 (m, 4H, H₃₄'), 8.55 (d, J = 7.65 Hz, 2H, H₃₃'), ¹³C NMR (300 MHz, d-TFA): δ = 26.4 (C₅₅'), 26.4 (C₇₇'), 29.6 (C₈₈'), 33.5 (C₉₉'), 62.5 (C₁₀₁), 71.3 (C₁₂₁), 111.4, 124.4, 128.2, 142.2, 144.8, 150.4, 170.5, 178.9 (C₅₅', C₄₄', C₃₃', C₃₃', C₆₆', C₂₂', C₂₂', C₆₆'). MALDI-TOF-MS (matrix: dithranol) m/z = 957 (M – PF₆⁻ – dihydroxy benzoic acid – H⁺), 669 (M – 2 PF₆⁻). C₄₂H₄₆F₁₂N₆O₄P₂Cd (1101.20): calcd. C 45.81, H 4.21, N 7.63; found: C 45.63, H 4.28, N 7.62. UV/Vis (CH₃CN), λₘₐₓ (ε, M⁻¹cm⁻¹) = 320.5 (23443), 307.0 (24590), 273.0 (41639), 243.0 nm (54426).

**Bis{4'-oxiranylmethoxy-2,2';6',2''-terpyridine}-cobalt(II)-di-hexafluorophosphate (25):** To a stirred suspension of 14 (60 g, 0.20 mmol) in MeOH (10 mL) Co(OAc)₂ × 4 H₂O (16 mg, 0.064 mmol) was added at room temperature. After 30 min NH₄PF₆ (95 mg, 0.58 mmol) in 10 mL MeOH was added upon which an orange-brown precipitate was formed. The mixture was stirred for another 10 min and the precipitate was filtered off and washed with MeOH (3 × 30 mL) and CHCl₃ (3 × 30 mL). Solvent rests were evaporated under reduced pressure. The crude product was then washed with water (3 × 30 mL), subsequently dried under high vacuum and further purified by crystallisation from slow diffusion of diethyl ether into acetone to yield 25 (44 mg, 71%) as dark red crystals. ¹H NMR (300 MHz, CH₃CN): δ = 5.98, 7.04, 8.95, 14.09, 14.56 (10 H, H-alkyl-epoxide), 6.19, 14.59, 34.43, 69.90, 73.90 (20 H, H-terpyridine). MALDI-TOF-MS (Matrix: dithranol) m/z = 517 (M – ligand – 2 PF₆⁻ + dihydroxy benzoic acid – H⁺), 669 (M – 2 PF₆⁻ + e⁻), 814 (M – PF₆⁻), 1033 (2 × (M – ligand – 2 PF₆⁻ + dihydroxy benzoic acid – H⁺) – H⁺), IR (ATR): 1/λ (cm⁻¹): 1614, 1603, 1572, 1559 (C=C, C=N, terpyridine); 1253 (C=O, epoxide); 827 (P=O, PF₆⁻). UV/Vis (CH₃CN), λₘₐₓ (ε, M⁻¹cm⁻¹) = 501 (8200), 322 (27500), 285 nm (29200). C₃₆H₃₆CoF₁₂N₆O₄P₂ (959.53): calcd. C 45.06, H 3.15; found: C 44.76, H 3.16, N 8.59.
**N,N'-Bis[6-[4'-oxy(2,2':6,2''-terpyridine)-pentyl]-3,4:9,10-perylenedibisaxamide (31):**

To a mixture of 3,4:9,10-perylenetetracarboxylic dianhydride 30 (0.050 g, 1.127 mmol) and 5-(2,2':6,2''-terpyridine-4'-yloxy)-pentylamine 5 (0.170 g, 0.508 mmol) quinoline (15 mL) was added. The mixture was stirred for 38 h at 120 °C and after cooling to room temperature, the reaction mixture was suspended in ethanol and the dark green precipitate was filtered off. After washing with ethanol (3 × 50 mL) and chloroform (3 × 50 mL), the product was dried in vacuo, yielding 31 (0.114 g, 87%) as a dark green solid. M.p. > 300 °C. 1H NMR (300 MHz, d-/G37/G29/G24/G0C/G1D/G03/G37/G29/G24/G0C/G1D/G03/G2F/G03/G20/G03/G14/G11/G1C/G18/G03/G0B/G50/G0F/4 H, H,G16), 2.13 (m, 4 H, H,G15), 2.26 (m, 4 H, H,G2F), 4.58 (m, 8 H, H,G2E/G0F/G30), 8.21, 8.34, 8.93 (m, 20H, H 3,3'', H3',5', H4,4'', H5,5'', H6,6''), 8.93 (m, 8H, H IV,V). 13C NMR (300 MHz, d-/G37/G29/G24/G0C/G1D/G03/G2F/G03/G20/G03/G15/G17/G11/G1C/G0F/G03/G15/G1C/G11/G14/G0F/G03/G16/G13/G11/G13/G03/G0B/G26/G16, C,G15, C,G2F), 43.56 (C,G2E), 72.1 (C,G30), 102.6, 112.7, 114.8, 115.2, 116.8, 118.7, 119.8, 123.6, 126.5, 132.8, 137.7, 138.7, 139.0 (C,2,2'', C,3,3'', C,3,5', C,4,4'', C,5,5'', C,6,6'', C,2',6', C III, C IV, C V, C VI, C VII, C VIII), 156.5, 160.7 (C,4', C II). MALDI-TOF-MS (matrix: dithranol) m/z = 1025 (MH+). UV/Vis (CH3CN), G1C max (G30, M−1cm−1) = 526.0 (3730), 493.0 (4450), 316.5 (7880), 237.5 nm (8650). C64H48N8O6 + 1 H2O (1043.39): calcd. C 73.69, H 4.83, N 10.74; found: C 73.99, H 4.58, N 11.01.

**[(2,2':6',2''-Terpyridin-4-yloxy-pentyl)-perylenetetracarboxylic-diimide] [2,2';6',2''-terpyridine] ruthenium(II)-hexafluorophosphate (33):** This compound was synthesised as described elsewhere.[18] Analytical data: M.p. > 300 °C. 1H NMR (300 MHz, CD3CN), δ = 1.82 (m, 4 H, CH2), 2.10 (m, 4 H, CH2), 4.20 (m, 2 H, CH2N), 4.59 (t, J = 6.49 Hz, 2 H, CH2O), 7.13 (m, 4 H, H 5,5''), 7.29 (d, J = 4.96 Hz, 2 H, H6,6''), 7.43 (d, J = 5.34 Hz, 2 H, H6,6''), 7.9 (m, 6 H, H-perylene), 8.30 (s, 2 H, H3,3''), 8.32 (s, 2 H, H 3',5'), 8.36 (t, J = 8.01 Hz, 1 H, H4), 8.46 (d, J = 8.01 Hz, 4 H, H3,3''), 8.72 (d, J = 8.39 Hz, 2 H, H3,3''). 13C NMR (300 MHz, d-/G37/G29/G24/G0C/G1D/G03/G2F/G03/G20/G03/G15/G17/G11/G1C/G0F/G03/G15/G1C/G11/G14/G0F/G03/G16/G13/G11/G13/G03/G0B/G26/G16, C,G15, C,G2F), 43.56 (C,G2E), 72.1 (C,G30), 102.6, 112.7, 114.8, 115.2, 116.8, 118.7, 119.8, 123.6, 126.5, 132.8, 137.7, 138.7, 139.0 (C,2,2'', C,3,3'', C,3,5', C,4,4'', C,5,5'', C,6,6'', C,2',6', C III, C IV, C V, C VI, C VII, C VIII), 156.5, 160.7 (C,4', C II). MALDI-TOF-MS (matrix: dithranol) m/z = 1694 (M+–4 PF6). C94H70N14O6Ru2P4F24 + 2 diethyl ether (4971.96): calcd. C 50.80, H 3.89, N 7.97; found: C 50.41, H 4.01, N 7.63. UV/Vis (CH3CN), G1C max (G30, M−1cm−1) = 217 (196500), 258 (110600), 303 (89330), 486 (62250), 521 nm (66540).

**Apoprotein (34):** This compound was synthesised as described elsewhere.[27] Analytical data: MALDI-TOF-MS (matrix: dithranol) m/z = 2867 (M+ + Na). UV/Vis (PBS, pH 7.4), G1C max (G30, M−1cm−1) = 217 (196500), 258 (110600), 303 (89330), 486 (62250), 521 nm (66540).

**Bis(aipoprotein)-iron(II)-hexafluorophosphate (35):** This compound was synthesised as described elsewhere.[27] Analytical data: MALDI-TOF-MS (matrix: DHB) m/z = 5750 (M+–PF6). UV/Vis (PBS, pH 7.4), G1C max (G30, M−1cm−1) = 291, 329, 561 nm (3790).

**Gold-nanoparticle experiments:** The functionalisation experiments were carried out in 5 mL glass jars, which were thoroughly cleaned (as were the magnetic stirrers and the glassware for preparation of the solutions) before usage with KOH/isopropanol, HCl_dil. and ultrasonification with HPLC-grade ethanol. For all experiments first 1 mL of citrate stabilised gold colloid was added and subsequently 0.5 mL of metal salt in ethanol and/or ligand 4 or ligand 12 or mercaptodecane were added as described in the appropriate concentrations. In the cases where multiple additions were made, all samples were brought to the same concentration by addition of pure ethanol.
3.8 References


4′-Functionalised bis-Terpyridine Metal Complexes


Chapter IV

Formation of Metallo-Assemblies through Complexation of Di-Terpyridines

Abstract
The complexation of bridged di-terpyridine ligands with metal ions leads to new metallo-supramolecular assemblies. The corresponding terpyridine ligands were synthesised using the nucleophilic substitution of 4'-chloro-2,2':6',2"'-terpyridine with different dialcoholate-alkyl and dithiolate-alkyl nucleophiles. Upon the addition of metal-salt the formation of metallo-polymeric assemblies consisting of low molar mass, achiral and chiral di-terpyridine ligands could be observed. For both cases, characterisation utilising NMR- and UV/Vis-spectroscopy revealed complex formation. Additionally, for the di-terpyridine with a hexadecyl-spacer, a viscosity experiment was used to prove metal-mediated metallo-assembly. For the chiral system, circular dichroism (CD) experiments showed the formation of optically active compounds, with the spectra of the enantiomeric assemblies being mirror-symmetric.

Chapter IV

4.1 Introduction

In the search for new functional materials, the formation of inorganic-organic polymeric structures has been of increasing interest over the last decade. Particularly, the controlled, supramolecular build-up of such structures is of special interest in this context. Functionalised 2,2':6',2''-terpyridines as metal-complexing ligands are well-suited candidates for this purpose because two 2,2':6',2''-terpyridines are able to form stable bis-complexes with a series of transition metal ions. The concept of the metallo-polymerisation of stiff di-2,2':6',2''-terpyridine telechelics with transition metal ions such as iron(II) or ruthenium(II) was first presented by Constable et al. and has since been applied in different works (see Chapter 1). In general, utilising terpyridines with functionality in the 4'-position as building block offers the possibility of creating linear systems in which the octahedral metal complex is located in the backbone of the metallo-polymer or assembly. This provides the main advantage that (as already mentioned in Chapter 2) no additional diastereomeric metal complex centres are formed. A basic classification can be made between the di-terpyridine ligands themselves either being polymeric or non-polymeric. Especially when doing the complexation in dilute solution, which is sometimes required due to the bad solubility of the ligand, larger systems such as polymeric di-terpyridines will preferably form the [1+1] intramolecular complex (macrocycle) instead of extended chains. Nevertheless, successful attempts have been carried out on the directed coupling of terpyridine modified, polymeric telechelics, leading to extended, well characterised metal-containing polymers. There has also been a lot of attention directed to monodisperse rigid chains, which cannot form [1+1] complexes or smaller macrocycles. Abruña et al. reported on the synthesis of chiral metallo-polymers containing bis-terpyridine-Fe(II) complexes and their deposition on a highly ordered pyrolytic graphite surface (HOPG). The synthesis and characterisation of molecular rods containing bis-terpyridine-Ru(II) complexes was described by several groups, the first experiments having been carried out by Ziessel et al. With respect to controlled macrocycle formation, a rigid [6+6] macrocycle using a non-linear rigid di-terpyridine system has been synthesised. More recently, Constable et al. described the formation of metallo-macrocycles by the complexation of di-terpyridines separated by a tri(ethylene glycol) chain in the 4'-positions of the terpyridine. All of the mentioned systems could be expanded in the future with chiral terpyridine ligands, for which synthetic routes have recently been described. Here, the synthesis and metal-complexation of a family of 4'-functionalised di-
terpyridines with the spacer consisting of \(\alpha,\omega\)-dialcoholate and \(\alpha,\omega\)-dithiolate chains of different lengths is described (Figure 4.1).

![Diagram](image)

**Figure 4.1:** General structure of the investigated ligands.

The described compounds were synthesised by reacting two equivalents of 4’-chloro-2,2’:6’,2″-terpyridine with different alkane-dialcoholates and alkane-dithiolates. Other approaches included sequential functionalisation of the amino-functionalised terpyridine 6 introduced in Chapter 2. Complexation studies were carried out by the addition of metal salts to some of these ligands. The products were studied by the means of UV/Vis- and \(^1\)H-NMR-spectroscopy as well as MALDI-TOF mass spectrometry. A viscosity titration could be performed for the di-terpyridine ligand with a hexadecanyl spacer, because of its sufficiently high solubility. For the chiral di-terpyridine-metal systems circular dichroism (CD) spectroscopy was found to be an important tool for characterisation. For all the reported complexations, ring-formation was found to be dominant over the formation of long polymeric chains.

### 4.2 Ligand synthesis

The nucleophilic substitution of 4’-chloro-2,2’:6’,2″-terpyridine with different \(\alpha,\omega\)-alkyl-di-alcohols and \(\alpha,\omega\)-alkyl-di-thiols led to telechelic di-terpyridines bridged by alkanedioxy- or alkanedithioxy-chains of different lengths (Scheme 4.1).\(^{[20]}\)
Scheme 4.1: Synthesis of the achiral di-2,2':6',2''-terpyridine ligands. All reactions were performed in DMSO / KOH.

The chain lengths range from 6 methylene-units for the diether 36, the dithioether 39 and the mixed ether-sulfide 38 to 10 methylene-units for the dithioether 40 and to 16 methylene-units for the diether 37. The reaction in a DMSO/KOH mixture and subsequent precipitation steps in water or recrystallisation gave all products in moderate yields between 43-75%. Reactions were carried out at temperatures between 60 °C and 70 °C over the course of four hours. In the case of the C_{10}-spacer connected via sulfide linkages (40), a study of the reaction conditions showed that the substitution can be performed at room temperature and complete conversion was achieved after 30 minutes. By-products, especially the mono-functionalised alcohols and thiols could be quantitatively removed by precipitation in methanol. The precursors for these compounds are all commercially available. Moreover, 4'-chloro-2,2':6',2''-terpyridine (2) has been synthesised on a large scale in our own lab.\(^{[10]}\) Given the fact that all of the relevant alkyl diols are commercially available, it would be possible to prepare a whole series of di-terpyridines bridged by 3 to 16 methylene groups,\(^{[a]}\) which could subsequently be

\(^{[a]}\) The reaction using ethylene glycol did not lead to the nucleophilic substitution.
used in a systematic study of metallo-polymer and/or -assembly formation. Here, we first concentrated on reactions using the short, but flexible di-terpyridine 36 with the O-C₆H₁₂-O-spacer in order to investigate polymer and/or assembly formation (see section 4.2). A similar strategy was applied in order to yield the chiral di-terpyridines 41 and 42, bridged by the 1,2-cyclohexandioxy spacer (Scheme 4.2).

Scheme 4.2: Synthesis of the chiral di-2,2';6',2''-terpyridine ligands. All reactions were performed in DMSO / KOH.

These reactions could only be performed in low yields, which is believed to be mainly due to steric hindrance. In addition, the parallel competitive substitution reaction of hydroxide (from KOH) becomes significant when reacting for longer periods of time. Therefore, a more extensive work-up procedure was required. The resulting enantiomeric ligands were used for first complexation experiments. When comparing the ¹H-NMR-shifts of the ether and the thioether compounds, significant differences can be found in the chemical shift for H₃₅₃₅₅₅ of the terpyridine ring and for H₃₅ of the bridging chain (Table 4.1). For the thioethers in 38, 39 and 40, the terpyridine signal (H₃₅₃₅₅₅) is shifted to lower and the bridging chain signal (H₃₅) is shifted to higher field.

Table 4.1: Comparison of the ¹H-NMR shifts (in CDCl₃) and melting points.

<table>
<thead>
<tr>
<th>ligand</th>
<th>δ H₃₅₃₅₅₅</th>
<th>δ H₃₅</th>
<th>M.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>4.26 (4 H)</td>
<td>8.01 (4 H)</td>
<td>224</td>
</tr>
<tr>
<td>37</td>
<td>4.22 (4 H)</td>
<td>8.00 (4 H)</td>
<td>112</td>
</tr>
<tr>
<td>38</td>
<td>4.24 (2 H) + 3.20 (2 H)</td>
<td>8.01 (2 H) + 8.34 (2 H)</td>
<td>197</td>
</tr>
<tr>
<td>39</td>
<td>3.18 (4 H)</td>
<td>8.32 (4 H)</td>
<td>199</td>
</tr>
<tr>
<td>40</td>
<td>3.18 (4 H)</td>
<td>8.32 (4 H)</td>
<td>160</td>
</tr>
</tbody>
</table>
The melting points are all above 100 °C and the smaller the bridging ligands (less alkyl-chain part) are, the higher are the melting points (up to 224 °C). It should be mentioned that the more polar, smaller ligands showed inclusion of water, which was found to be ½ of an equivalent for the C₆-spaced ligands 36 and 38, and ¼ of an equivalent for the chiral ligands, even after having applied standard chemical and physical drying procedures. Figure 4.2 shows MALDI-TOF-mass spectrometry graphs of the one of the non-chiral ligands (36) and one of the chiral ligands (R-enantiomer 41), which were used for metal complexation studies. The isotopic distribution observed (+ 1 H from the matrix) was consistent with the simulated distributions.

Figure 4.2: MALDI-TOF-MS of the achiral ligand 36 (left) and the chiral ligand 41 (right).

Using the above-described approach a new family of di-terpyridines, bridged by alkyl-dioxy and alkyl-dithioxy chains, could be synthesised. A further possibility for the synthesis of monodisperse di-terpyridine ligands is to first functionalise terpyridine in the 4’ position with a spacer attached to a chemical handle. Two of these ligands can then be connected using an appropriate chemical building block. A model compound regarding this approach was synthesised using the 4’-(2-piperidin-4-yloxy)-2,2’:6’,2”-terpyridine 6 presented in Chapter 2. Two equivalents of the ligand were reacted with one equivalent of hexamethylene diisocyanate in refluxing chloroform (Scheme 4.3).
Formation of Metallo-Assemblies through Complexation of Di-Terpyridines

Scheme 4.3: Sequential synthesis of di-2,2’:6’,2”-terpyridine ligand 43.

Repeated crystallisation/precipitation from THF yielded the pure model compound. Applying this stepwise synthesis could lead to well-defined di-terpyridines with longer spacers between the two terpyridine moieties. This methodology could prove to be important for the creation of new metallo-polymeric systems with integrated bis-terpyrdine complexes, since starting from a monodisperse di-terpyridine ligand is a major advantage in terms of characterisation and fine-tuning of the final material properties.

4.3 Complexation of the non-chiral ligands with iron(II) ions

Ligand 36, which, according to molecular modelling studies, cannot form a [1+1] intramolecular complex, was reacted with one equivalent of iron(II) chloride (Scheme 4.4). Iron(II) chloride can be obtained commercially as pure beads (Aldrich) which are moderately hygroscopic and oxidise only slowly to iron(III) in air. The complexation was carried out in a CHCl3/MeOH (1/1) mixture. The solvent mixture is necessary because while the ligand is insoluble in methanol, the iron(II) chloride, by contrast, is readily soluble. Since it is known that the formation of Fe(II)-bis-terpyridine complexes occurs fast at room temperature,[21] the reaction was carried out by simply mixing one equivalent of iron(II) chloride and ligand 36 at room temperature (Scheme 4.4).
Scheme 4.4: Schematic drawing of the complexation of di-terpyridine ligands with iron(II) (counter-ions omitted).

An UV/Vis titration experiment showed a linear increase in the metal-to-ligand charge-transfer (MLCT) band around 557 nm up to the addition of one equivalent iron(II) chloride (addition of $10 \times 0.1$ eq.) (Figure 4.3).

Figure 4.3: UV/Vis titration of 36 with iron(II) chloride in CHCl$_3$/MeOH (1:1 mixture), inset: rise of the MLCT band at 557 nm in relation to the equivalents iron(II) titrated.

Overtitration does not result in any further increase or other changes in the spectrum, suggesting the formation of bis-complexes. Similar results have been reported in
Formation of Metallo-Assemblies through Complexation of Di-Terpyridines

literature,[12,22] thus there is strong indication for the formation of "saturated" bis-complexes upon mixing together one equivalent of each reactant. When looking at the room temperature $^1$H-NMR spectrum after complex formation, the typical shifts in the low-field region between 7 and 9 ppm for the terpyridine signals can be observed. However, additional signal groups at higher field are present (e.g. around 7.1 and 7.8 ppm) next to the expected ones (Figure 4.4, 45a).

Figure 4.4: Change of the $^1$H-NMR spectrum of metallo-assembly 45a upon heating (in CD$_3$OD).

A significant change was observed upon refluxing the sample for 24 hours in methanol/chloroform. The additional signals become larger and the original signal groups lose intensity (Figure 4.4, 45b). After further refluxing for 48 hours, no further change in the signal intensities is observed. When heating the mixture upon which metal-exchange of the complexes is expected to occur,[23] the entropy-driven formation of smaller cycles could be envisioned. Smaller cycles are expected to yield a significant shift in the NMR-signals.[18] An attempt was made to separate the mixture by column chromatography using silica as column material and a polar acetonitrile/water/KNO$_3$ aq (20/2/1) mixture as eluent.[24] Applying this method, two main fractions of the mixture 45b, prepared through the refluxing procedure, could be obtained and purified by precipitation as the PF$_6^-$ salt in a yield of 46% for the first and 25% for the second fraction (Figure 4.5). In total, six fractions were visible on the column
of which only the first two were isolated and purified, because reasonable amounts for characterisation could not be obtained from the other fractions. The $^1$H-NMR-spectra of the first two fractions showed significant differences in the terpyridine region of their spectra (Figure 4.5, Table 4.2). For the second fraction, all of the terpyridine signals are shifted slightly to lower field, with the value of the shift varying for the different signals (Figure 4.5).

![Figure 4.5](image)

**Figure 4.5:** Left: picture of the separation of the coloured complex-assemblies. Right: $^1$H-NMR spectra (in CD$_3$CN) of the corresponding separated compounds 46 and 47.

**Table 4.2:** Relative difference in the $^1$H-NMR shifts for metallo-macrocycles 46 and 47 (from low field to high field).

<table>
<thead>
<tr>
<th>$^1$H-NMR signal</th>
<th>3',5'</th>
<th>3,3''</th>
<th>4,4''</th>
<th>6,6''</th>
<th>5,5''</th>
<th>−CH$_2$−</th>
</tr>
</thead>
<tbody>
<tr>
<td>difference in chemical shift [ppm $\times 10^3$]</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

In contrast, the H$_a$-signals of the bridging hexyl-chain have almost the same chemical shift. A confirmation of the formation of macrocycles with three iron(II) ions and three ligands ([3+3] macrocycle) and four iron(II) ions and four ligands ([4+4] macrocycle) is found on the basis of MALDI-TOF mass spectrometry data in combination with the $^1$H-NMR spectra. The most significant peak in the MALDI-TOF spectrum for compound 46 (first fraction) corresponds to the [3+3] macrocycle minus one counter-ion (Figure 4.6).
Figure 4.6:  **MALDI-TOF-MS of the metallo-macrocycles 46 (left row) and 47 (right row).** Top: spectra of 46 and 47. Middle: expansions of the signals. Bottom: simulations.

Figure 4.7:  **MALDI-TOF-MS of a mixture of 46 and 47.**

For compound 47 (second fraction), the [4+4] macrocycle minus one counter-ion plus H is observed (Figure 4.6). It is important to note that the spectrum of 46 does not contain any
signal of the [4+4] macrocycle. If any [4+4] macrocycle would be present it would show up in
the spectra according to a test measurement of a mixture of both fractions. A clear proof for
the existence of [3+3]- and [4+4]-structures results from these MALDI-TOF-MS data.
Furthermore, the simulations of the isotope patterns for both the [3+3]- and the [4+4]-signals
match the experimental findings exactly. It should be noted that only using the "soft" matrix
"malononitrile" (trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene] malononitrile) led to
ionisation and detection of the compounds 46 and 47. In case of the common matrix dithranol
no signals were obtained. The existence of open chains can be ruled out when looking at the
NMR-spectra (Figure 4.5). An open chain would contain an uncomplexed terpyridine, which
would yield additional signals in the terpyridine region, which is clearly not the case. The
formation of smaller macrocycles seems very unlikely, since a [1+1]-assembly is sterically
not possible and a [2+2]-assembly, which is sterically very tense, should give an even more
significant shift in the $^1$H-NMR when compared to the spectra of the obtained [3+3]- (46) and
the [4+4]- (47) macrocycles. Moreover, such smaller macrocycles should be easier to detect
in MALDI-TOF-MS in comparison with the larger ones obtained, which is not the case.
Therefore the compound, which was isolated as the first fraction from the column, is believed
to be the [3+3]-macrocycle 46. It cannot be ruled out that the second fraction ([4+4], 47) still
contains a small impurity of 46, as indicated by the signal corresponding to 46 in the MALDI-
TOF spectrum. On the other hand this signal could also result from fragmentation during
ionisation. A mixture of both macrocycles 46 and 47, resembling the weight percentage as
found after column separation, was also investigated with MALDI-TOF-MS (Figure 4.7). The
finding is, that the spectrum approximately looks like the addition of the spectra shown in
Figure 4.6. That means that, as expected, the [3+3] signal is higher than the [4+4] signal. Figure
4.8 shows schematic drawings of the proposed structures of the [3+3]- as well as the [4+4]-
macrocycle. Attempts to further purify especially the [3+3]-macrocycle for elemental analysis
and to grow crystals suitable for X-ray diffraction are still ongoing.
Formation of Metallo-Assemblies through Complexation of Di-Terpyridines

Regarding the stability of the [3+3] macrocycle 46, a first experiment has been performed. Figure 4.9 shows the comparison of the spectra of 46 (left, sample was measured after stirring in acetonitrile solution for 1 h at room temperature) and after heating to reflux in acetonitrile for 1 h (right). Both spectra were recorded using exactly the same instrument settings and preparation procedures.

After refluxing the signal of the [4+4] macrocycle can be seen again, which indicates rearrangement of the macrocycle equilibrium due to exchange processes (decomplexation / recomplexation). A sodium adduct plus another PF$_6^-$ counter-ion can be seen appearing as well at m/z = 2802. Sodium adducts often appear in MALDI-TOF-MS and their appearance in
this case might have to do with different crystallisation behaviour of the heated sample on the MALDI-MS-target.

A drawback of these rather small alkyl-bridged di-terpyridines is their poor solubility in common solvents. Therefore, for the above-mentioned system it has not been possible to investigate polymer properties such as the viscosity behaviour. However, for the ligand with the C\textsubscript{16}-spacer the solubility was sufficient. First, one equivalent of ligand \textit{37} was reacted in a first experiment at room temperature with one equivalent of iron(II) chloride in a MeOH/CHCl\textsubscript{3} mixture (1/1 ratio). The originating typical purple coloured solution indicated the formation of \textit{bis}-terpyridine-Fe(II) complexes.\textsuperscript{[4]} This mixture was then precipitated by the addition of an excess of ammonium-hexafluorophosphate and filtered off leading to the purple coloured coordinated species. Due to the long flexible alkyl spacer of the di-terpyridine ligand, intramolecular as well as intermolecular ring-formation has to be considered. Especially the [1+1] intramolecular ring formation has proven to be possible for a similar system, containing a ditopic ligand based upon a 2,7-disubstituted naphthalene bearing two terpyridine-terminated ethylene-oxy substituents.\textsuperscript{[25]} This 1:1 (iron(II) chloride : ligand \textit{37}) mixture was also investigated by MALDI-TOF mass spectrometry (Figure 4.10).

\textbf{Figure 4.10: } \textit{MALDI-TOF} mass spectrometry of one equiv. ligand \textit{37} with one equivalent of iron(II) chloride (in CHCl\textsubscript{3} / MeOH, 1:1 mixture).
Using the "soft" matrix "malononitrile", which allows a low energy ionisation when compared to other common matrices such as e.g. dithranol, aggregates of different sizes corresponding to the metallo-supramolecular rings minus one PF$_6^-$ could be observed, with the largest being a [10+10]-aggregate with a mass of over 10,500 Dalton. It seems likely that these aggregates are macrocycles, since open linear structures should not exist due to the stability of the bis-terpyridine-Fe(II) complex moiety. Moreover, uncomplexed terpyridine moieties of small species would be easily visible by $^1$H-NMR, which is not the case (the possible macrocycle ring formation has already been discussed for similar systems). On the other hand these signals could, at least partially, also consist of fragments of even larger structures (metallo-polymers, oligomers or large cycles). As can be seen from the simulation, the isotope pattern for the [4+4] aggregate with a mass of 4,122 Dalton can still be well resolved. However, by far the most prominent signal observed is the [2+2] aggregate. If formed, the [1+1] aggregate should give an even much more prominent signal in MALDI-TOF-MS, compared to what is known for such complexes from literature. Since no separation of the single macrocycles has been attempted up to date, not much can be said about the weight percentages of the fractions formed, but there is a strong indication that the [2+2] aggregate is the favoured product. The formation of the [1+1] intramolecular complex could still be sterically hindered as in the case for the C$_6$-ligand described before. The naphthalene-bridged system described in literature consists of a spacer which is just one spacer unit longer as in the present case. Additionally, the angle of which the chains protrude from the naphthalene unit favours mono-cyclisation. Another fact, which should be taken into consideration for this ligand with a C$_{16}$-spacer, is the possibility of catenation, which becomes sterically possible even for smaller ring sizes.

As already mentioned, a drawback of most of these rather small alkyl-bridged di-terpyridines is their poor solubility in common solvents. However, in contrast to the metallo-polymers/cycles formed by a C$_6$-ligand the ligand with the C$_{16}$-spacer revealed a solubility which was sufficient to perform a viscosimetric titration in the solvent mixture CHCl$_3$/MeOH mixture (1/1 ratio, Figure 4.11).
Figure 4.11: Viscosimetric titration of ligand 37 with iron(II) chloride in CHCl$_3$ / MeOH (1:1 mixture).

A rise in the relative viscosity value up to 1.0 equivalents of iron(II) chloride, which is the value for saturated *bis*-complexation (one ligand having two terpyridines binding one iron(II)), could be observed. A test measurement with the directly synthesised compound (1 to 1 ratio) revealed the same viscosity value as observed in the titration experiment at the 1 to 1 ratio. This indicates the formation of larger aggregates due to *bis*-terpyridine metal complexation. After overtitration, the viscosity decreases again to a value still above half of the maximum increase. As known from literature for metal-complexes with cobalt(II), zinc(II) and manganese(II), this could indicate negative cooperativity of the first (1:1, *mono*-complexation) and the second (2:1, *bis*-complexation) complexation steps. That would lead to $K_1 > K_2$ and therefore, after overtitration over the 1:1 (one metal : 1 ligand (= two terpyridine moieties)) ratio, *mono*-complexes are being formed. However, if this assumption would be correct, the viscosity value at 2.0 equivalents of iron(II) chloride should be the same as at the beginning of the titration. Several considerations could play a role here. From what is known from literature ($\log K_1 = 7.1$, $\log K_2 = 13.8$)$^{[21]}$ and from the fact that there is no evidence found in literature for the isolation of *mono*-terpyridine-Fe(II) complexes, a highly positive cooperativity should be expected for terpyridine-Fe(II) complexes. On the other hand, the entropically favoured formation of smaller structures as well as the growing shear forces with longer chain length could still, to a certain extent, favour the formation of Fe(II)-*mono*-complexes, especially in the presence of an excess of iron(II) chloride, thus leading to the break-up of the chains and the lowering of the viscosity. Nevertheless, the rise in viscosity up
to the equivalent of one iron(II) to one ligand indicates the formation of larger metallo-polymeric architectures (oligomers and polymers, but probably also large cycles and catenanes, etc.).

### 4.4 Metal-complexation of the chiral ligands 41 and 42

On a smaller scale, the enantiomeric ligands 41 and 42 were complexed with iron(II) chloride under the same conditions as described above (Scheme 4.4). An UV/Vis titration revealed a similar behaviour as described for the achiral metallo-assembly, thus suggesting quantitative Fe(II)-bis-terpyridine complexation. Additionally, circular dichroism (CD) spectroscopy was carried out by performing a titration experiment (Figure 4.12).

![Figure 4.12: Left: CD-titration. Right: plots of the CD and UV/Vis intensities around 321 nm of the chiral metallo-assembly 49 (solvent: CHCl₃/MeOH, 1:1 mixture).](image)

Through addition of iron(II) chloride to 42, leading to metallo-polymer 49, different bands become visible in the CD spectra. The strongest band around 321 nm belongs to the ligand centred (LC) absorptions. CD effects were observed for the metal centred (380 nm) and the MLCT bands (558 and 274 nm). When looking at the change in the ligand centred band, different slopes can be observed up to the addition of one equivalent of iron(II) chloride, after which no change is observed anymore. The steady negative increase after the addition of about 0.75 eq. iron(II) might suggest that after this point, where on average three metals are complexed to four ligands, ring closure and the formation of [4+4] rings starts taking place (due to sterical hindrance, the smallest possible ring size here would be [4+4], according to molecular modelling). These observed CD effects have, as expected, the opposite sign for the enantiomeric system 41, leading to metallo-polymer 48 (Figure 4.13).
A further strong indication for the preferred formation of [4+4] rings in this case is given by MALDI-TOF mass spectrometry (Figure 4.14).

**Figure 4.14:**  *MALDI-TOF-MS of the chiral metallo-polymer 48 (R,R-enantiomer).*

In this case, the only visible metallocycle is the [4+4] cycle. Especially the absence of a signal corresponding to a [3+3] macrocycle which should be visible by this technique (see above the [3+3] of ligand 36 (46)), fits to the above assumption based on CD-spectroscopy. All other signals visible could not be assigned and may result from other fragmented aggregates. Figure

![Schematic drawings of the proposed structures of the main products in the chiral metallo-polymers](image)

**Figure 4.15:** Schematic drawings of the proposed structures of the main products in the chiral metallo-polymers 48 (R,R-enantiomer) and 49 (S,S-enantiomer) (counter-ions omitted).

A further investigation was carried out with zinc(II) acetate, which is known to form mono- as well as bis-terpyridine complexes, when reacted in a 1:1,[28] and 1:2[29] ratio (metal to ligand), respectively. An UV/Vis- as well as a CD-titration was performed with the S,S enantiomer 42. The UV/Vis titration shows two different slopes in the rise in absorption at 325 nm (Figure 4.16).
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Figure 4.16: UV/Vis titration of ligand 42 (S,S-enantiomer) with zinc(II) acetate.

This result differs from the titration of zinc(II) acetate to unfunctionalised terpyridine, where only one slope is observed as a steady rise up to the equivalent of 1.0 for the mono-terpyridine-Zn(II) complex. The absorption band at 325 nm rises up to the equivalent of 2.0 (two zinc(II) acetate to one di-terpyridine ligand) indicating mono-complexation which remains unchanged after further titration. The same behaviour is found for the before-mentioned model-titration. However, there is a significant change observed in the slope around 0.5 equivalents zinc(II) acetate. This could be explained by the formation of bis-complexes as long as an excess of terpyridine moieties is present (Figure 4.17).

Figure 4.17: Left: schematic drawing of the proposed bis-complexation up to 0.5 eq. zinc(II) acetate with ligand 42 (S,S-enantiomer). Right: proposed complexation after addition of 2 eq. zinc(II) acetate (mono-complexes), with indication of exciton coupling (counter-ions omitted).
Further addition (between 0.5 and 2.0 eq.) of zinc(II) acetate does not lead to the formation of further bis-complexes with the formation of polymeric structures, but rather to an equilibrium between mono- and bis-complexes, which is reflected in the lower steepness of the slope. These considerations may be compared to results obtained from the CD-titration (Figure 4.18).

**Figure 4.18:** CD titration of ligand 42 (S,S-enantiomer) with zinc(II) acetate.

Upon addition of zinc(II) acetate, a negative increase at the wavelengths 327 nm and 294 nm can be observed between 0.5 and 2.0 equivalents. The observed CD effect in this case might be due to exciton coupling\(^{30}\) as in the case for the bis-terpyridine-Fe(II) complexes, which in this case could result from the two mono-complexed terpyridines in one ligand (Figure 4.18, right). In the beginning where only two ligands are coupled together, no such effect can be observed, because no exciton coupling to an intramolecular complexed ligand can take place. This explanation fits the above findings for the UV-titration well. It is important to note that in the case of the above discussed iron(II) macrocycles the negative increase flattens off at 1.0 equivalents (Figure 4.12). Thus for the zinc(II) acetate case exciton coupling between mono-complexed ligands takes place in contrast to the coupling in the macrocycles for the iron(II) chloride case. It has to be mentioned, however, that the above-discussed interpretations are still somewhat speculative and are open for further discussions.

### 4.5 Conclusions

A new family of di-2,2':6',2''-terpyridine ligands bridged by alkyl-oxy- or alkyl-thioxy-chains has been synthesised by nucleophilic substitution of 4'-chloro-2,2':6',2''-terpyridine with the
corresponding alkoholates or alkyl-thiolates. Such ligands are of importance for the creation and study of extended assemblies and polymeric structures using metal complexation. Moreover, the enantiomeric di-terpyridines bearing a cyclohexane-dioxy spacer were synthesised using the same strategy. Chiral and achiral macrohexane-dioxy spacer macrocyclic metallo-assemblies have been synthesised in dilute solution. UV/Vis titrations indicated the quantitative formation of bis-terpyridine complexes. In the case of the achiral system consisting of the hexyl-di-oxy bridged di-terpyridine ligand and iron(II), the thermodynamically preferred product seems to be a [3+3] macrocycle. The [4+4] macrocycle could also be isolated and both products were characterised by 1H-NMR-, UV/Vis-spectroscopy as well as MALDI-TOF mass spectrometry. This methodology presents a simple approach towards the formation and also separation of metallo-macroyclic ring structures including di-terpyridines and iron(II). For the chiral system first investigations using circular dichroism (CD) spectroscopy showed chirality transfer to the LC- and the MLCT-absorption bands. A CD-titration indicated the possible formation of a [4+4] macrocyclic ring. Additionally, the typical behaviour of preferred mono-complex formation was shown by experiments with zinc acetate. Finally, for the first time a viscosity measurement on the metallo-polymerisation using an apolar monodispers di-terpyridine ligand could be performed, which indicated the formation of metallo-assemblies.

4.6 Experimental Section

**General remarks and instruments used**: Basic chemicals were obtained from Sigma-Aldrich. In addition to the instruments and chemicals used in the Chapter 2, the following instruments and chemicals were used. Iron(II) chloride was obtained as anhydrous beads from Aldrich. 1H- and 13C-NMR spectra were recorded on a Varian Mercury 400 spectrometer and the chemical shifts were calibrated to the solvent peaks. For more clarity, the carbons and hydrogens of the alkyl spacers are numbered using Greek symbols starting from the first carbon next to the 4'-ether functions at the terpyridine (as indicated in Scheme 4.1). CD spectra were recorded on a Jasco J-600 spectropolarimeter. Viscosimetric measurements were performed on a Lauda PVS 1 viscosity measuring system. Luminescence emission spectra were recorded on a Perkin-Elmer LS 45 luminescence spectrometer.

1,6-**Bis(2,2':6',2''-terpyridin-4'-yloxy)hexane** (36): To a stirred suspension of powdered KOH (482 mg, 8.60 mmol) in water free DMSO (25 mL) at 70 °C 1,6-hexandiol (254 g, 2.15 mmol) was added. After 30 min 4'-chloro-2,2':6',2''-terpyridine was added (1.15 g, 4.31 mmol) and the mixture was stirred for 4 h at 70 °C and then poured into water (500 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water, dried in vacuo and recrystallised from CH2Cl2 yielding 36 as a white solid (1.67 g, 66%). M.p. 224 °C. 1H NMR (300 MHz, CDCl3): δ = 1.62 (m, 4 H, Hγ,γ'), 1.91 (tt, J = 5.8, 5.8 Hz, 4 H, Hβ,β'), 4.26 (t, J = 5.8 Hz, 4 H, Hα,α), 7.32 (ddd, J = 1.1, 4.7, 7.1 Hz, 4 H, H5,5',5''',5'''''),
7.84 (dd, J = 1.6, 7.1, 7.1 Hz, 4 H, H_{4,4',5',5''}), 8.01 (s, 4 H, H_{3,3',3',3''}), 8.61 (d, J = 7.1 Hz, 4 H, H_{3,3',3',3''}), 8.70 (d, J = 4.7 Hz, 4 H, H_{6,6',6',6''}). {^{13}}C \text{ NMR (300 MHz, CDCl}_3): \delta = 44.5 (C_{\beta,\beta}), 49.8 (C_{\alpha,\alpha}), 68.6 (C_{\gamma,\gamma}), 107.3 (C_{5,5',5',5''}), 121.3 (C_{4,4',4',4''}), 123.9 (C_{3,3',3',3''}), 136.8 (C_{3,3',3',3''}), 149.0 (C_{6,6',6',6''}), 155.9 (C_{2,2',2',2''}), 157.2 (C_{2,2',2',2''}), 166.6 (C_{4,4''}). MALDI-TOF-MS (matrix: dithranol) m/z = 581 (MH^+). IR (ATR): 1/\lambda (cm^{-1}): 2941, 2870 (C–C); 1598, 1581, 1562 (C=C, C=N, terpyridine). C_{36}H_{32}N_{6}O_{2} (580.68 + 1/2 H_{2}O): calced. C 73.33, H 5.64, N 14.25; found: C 73.55, H 5.25, N 14.32.

1,6-Bis(2,2';6',2''-terpyridine-4'-yloxy)hexadecane (37): To a stirred suspension of powdered KOH (415 mg, 7.40 mmol) in water free DMSO (25 mL) at 60 °C, 1,6-hexadecanol (478 mg, 1.85 mmol) was added. After 20 min 2 was added (1.04 g, 3.90 mmol), the mixture was stirred for 24 h at 60 °C and then poured into water (600 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water and dried in vacuo yielding 37 as a white solid (1.00 g, 75%). M.p. 112 °C. {^1}H \text{ NMR (300 MHz, CDCl}_3): \delta = 1.33 (m, 20 H, H_{3,3',3',3''}), 1.49 (m, 4 H, H_{3,3,3,3}), 1.82 (m, 4 H, H_{3,3,3,3}), 4.22 (t, J = 6.4 Hz, 4 H, H_{3,3,3,3}), 7.32 (dd, J = 1.3, 4.8, 7.5 Hz, 4 H, H_{5,5',5',5''}), 7.84 (ddd, J = 1.9, 7.9, 7.9 Hz, 4 H, H_{4,4',4',4''}), 8.00 (s, 4 H, H_{5,5',5',5''}), 8.61 (ddd, J = 1.0, 1.0, 7.9 Hz, 4 H, H_{3,3',3',3''}), 8.69 (d, J = 0.9, 1.7, 4.8 Hz, 4 H, H_{6,6',6',6''}). {^{13}}C \text{ NMR (300 MHz, CDCl}_3): \delta = 25.9, 29.0, 29.3, 29.6, 29.6, 29.7, 29.7 (C_{\alpha,\alpha,\alpha,\alpha}), 68.2 (C_{0,0}), 107.4 (C_{5,5',5',5''}), 121.3 (C_{4,4',4',4''}), 123.7 (C_{3,3',3',3''}), 136.7 (C_{3,3',3',3''}), 149.0 (C_{6,6',6',6''}), 156.2 (C_{2,2',2',2''}), 157.0 (C_{2,2',2',2''}), 167.4 (C_{4,4''}). MALDI-TOF-MS (matrix: dithranol) m/z = 721 (MH^+). IR (ATR): 1/\lambda (cm^{-1}): 2918, 2853 (C–C); 1601, 1584, 1563 (C=C, C=N, terpyridine). C_{36}H_{32}N_{6}O_{2} (720.95): calced. C 76.63, H 7.27, N 11.66; found: C 76.41, H 7.16, N 11.58.

1-(2,2';6',2''-Terpyridine-4'-ylsulfanyl)-6-(2,2';6',2''-terpyridine-4'-yloxy)hexane (38): To a stirred suspension of powdered KOH (107 mg, 1.91 mmol) in water free DMSO (20 mL) at 70 °C 6-mercapto-1-hexanol (0.05 g, 0.37 mmol) was added. After 20 min 2 was added (0.204 g, 0.763 mmol), the mixture was stirred for 4 h at 70 °C and then poured into deionised water (200 mL). The aqueous phase was subsequently removed by filtration and the product was washed with deionised water and dried in vacuo to yield 38 as a white solid (0.16 g, 71%). M.p. 197 °C. {^1}H \text{ NMR (300 MHz, CDCl}_3): \delta = 1.59-1.64 (m, 4 H, H_{3,3,3,3}), 1.80-1.94 (m, 4 H, H_{3,3,3,3}), 3.20 (t, J = 6.6 Hz, 2 H, H_{3,3}), 4.24 (t, J = 5.91 Hz, 2 H, H_{3,3}), 7.31 (m, 4 H, H_{3,3,3,3}), 7.84 (m, 4 H, H_{4,4',4',4''}), 8.01 (s, 2 H, H_{3,3,3}), 8.34 (s, 2 H, H_{3,3,3}), 8.61 (m, 4 H, H_{3,3,3,3}), 8.70 (m, 4 H, H_{6,6',6',6''}). {^{13}}C \text{ NMR (300 MHz, CDCl}_3): \delta = 25.9 (C_{3,3}), 28.4 (C_{3,3}), 28.6 (C_{3,3}), 28.9 (C_{3,3}), 30.8 (C_{3,3}), 68.0 (C_{3,3}), 107.4 (C_{3,3,3}), 117.8 (C_{3,3,3}), 121.3, 121.4 (C_{3,3,3}), 123.7, 123.8 (C_{3,3,3}), 136.7, 136.8 (C_{4,4',4',4''}), 149.0, 149.1 (C_{6,6',6',6''}), 151.7 (C_{4,4''}), 155.0, 156.0 (C_{2,2',2',2''}), 156.2 (C_{2,2',2',2''}), 167.4 (C_{4,4''}). MALDI-TOF-MS (matrix: dithranol) m/z = 598 (MH^+). IR (ATR): 1/\lambda (cm^{-1}): 2940, 2863 (C–C); 1598, 1576, 1558 (C=C, C=N, terpyridine). C_{36}H_{32}N_{6}O_{2} (596.74 + 1/2 H_{2}O): calced. C 71.38, H 5.49, N 13.87; found: C 71.76, H 5.42, N 13.64.

1,6-Bis(2,2';6',2''-terpyridine-4'-ylsulfanyl)hexane (39): To a stirred suspension of powdered KOH (482 mg, 12.0 mmol) in DMSO (10 mL) at 70 °C 1,6-hexandithiol (0.38 g, 2.5 mmol) was added. After 30 min 2 was added (669 mg, 2.50 mmol) and the mixture was stirred for 4 h at 70 °C and then poured into water (500 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water, dried in vacuo and recrystallised from THF yielding 39 as a white solid (0.41 g, 53%). M.p. 199 °C. {^1}H \text{ NMR (300 MHz, CDCl}_3): \delta = 1.59 (m, 4 H, H_{3,3}), 1.82 (m, 4 H, H_{3,3}), 3.18 (t, J = 7.23 Hz, 4 H, H_{3,3}), 7.31 (m, 7.07 Hz, 2 H, H_{3,3,3}), 7.84 (m, 2 H, H_{4,4',4',4''}), 8.32 (s, 2 H, H_{3,3,3}), 8.60 (m, 2 H, H_{3,3,3}), 8.71 (m, 2 H, H_{6,6',6',6''}). {^{13}}C \text{ NMR (300 MHz, CDCl}_3): \delta = 28.3
1,10-Bis(2′,6′,2′′-terpyridin-4′-ylsulfanyl)decane (40): To a stirred suspension of powdered KOH (878 mg, 15.7 mmol) in DMSO (40 mL) at room temperature 1,6-decandithiol (542 g, 2.62 mmol) was added. After 30 min 2 was added (1.33 g, 4.97 mmol), the mixture was stirred for 1 h at room temperature and then poured into water (500 mL). The aqueous phase was then removed by filtration and the product was washed with deionised water, dried in vacuo, redissolved in CH₂Cl₂ and dried with sodium sulfate. The crude product was precipitated from THF yielding 40 as a white solid (0.76 g, 46%). M.p. 160 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.50 (m, 4 H, H₂γ), 1.77 (m, 4 H, H₂β), 3.18 (t, 4 H, H₆α,δ), 1.32 (m, 8 H, H₂β), H₂α,δ), 7.32 (m, 7.07 Hz, 4 H, H₃,5,5′,5″-m), 7.84 (m, 4 H, H₄,4′,4″-m), 8.32 (s, 4 H, H₃,3′,3″,3″″-m), 8.60 (m, 4 H, H₃,3′,3″,3″″-m), 8.69 (m, 4 H, H₆,6′,6″,6″″-m). ¹³C NMR (300 MHz, CDCl₃): δ = 28.4 (C₆α,δ), 28.8 (C₆γ), 29.1 (C₆β), 29.3 (C₆α,δ), 30.8 (C₆δ,β), 117.7 (C₃,5,5′,5″-m), 121.4 (C₃,3′,3″,3″″-m), 123.8 (C₅,5′,5″-m), 136.8 (C₄,4′,4″-m), 149.0 (C₆,6′,6″,6″″-m), 151.6 (C₄,4″-m), 154.9 (C₂,6,6′,6″,6″″-m), 156.0 (C₂,2′,2″,2″″-m). MALDI-TOF-MS (matrix: dithranol) m/z = 669 (MH⁺). IR (ATR): 1/λ (cm⁻¹): 2932, 2862 (C–C); 1575, 1557, 1538 (C=C, C=N, terpyridine). C₄₀H₄₀N₆O₁₂ (668.91): calcd. C 71.82, H 6.03, N 12.56; found: C 71.79, H 5.99, N 12.45.

(1R,2R)-trans-1,2-Bis(2′,6′,2′′-terpyridin-4′-oxyloxy)-cyclohexane (41): To a stirred suspension of powdered KOH (96 mg, 1.7 mmol) in DMSO (20 mL) at 60 °C (1R,2R)-trans-1,2-cyclohexanediol (50 mg, 0.43 mmol) was added. After 20 min 2 was added (225 mg, 0.840 mmol), the mixture was stirred for 3 d at 60 °C and then poured into water (180 mL). After adjusting the pH to 6-7 with HCl, the aqueous phase was removed by filtration and the product was washed with deionised water and dried in vacuo. The crude product was recrystallised from MeOH yielding 41 as colourless crystals (34 mg, 12%). M.p. 205 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.54, 1.82, 2.31 (m, m, d, J = 11.81 Hz, 8 H, Hα,β,γ,δ₁,₂), 4.91 (t, J = 3.69 Hz, 2 H, Hγ₂), 7.29 (ddd, J = 1.2, 4.8, 6.3 Hz, 4 H, H₃,5,5′,5″-m), 7.81 (ddd, J = 1.8, 7.8, 7.8 Hz, 4 H, H₄,4′,4″-m), 8.02 (s, 4 H, H₃,3′,3″,3″″-m), 8.55 (d, J = 8.0 Hz, 4 H, H₃,3′,3″,3″″-m), 8.64 (d, J = 4.8 Hz, 4 H, H₆,6′,6″,6″″-m). ¹³C NMR (300 MHz, CDCl₃): δ = 22.6 (Cγ₁,₂), 28.8 (Cβ₁,₂), 77.2 (Cγ₂), 108.3 (C₃,5,5′,5″-m), 121.3 (C₃,3′,3″,3″″-m), 123.6 (C₅,5′,5″-m), 136.6 (C₄,4′,4″-m), 149.0 (C₆,6′,6″,6″″-m), 156.2 (C₄,4″-m), 157.2 (C₂,6,6′,6″,6″″-m), 166.2 (C₂,2′,2″,2″″-m). MALDI-TOF-MS (matrix: dithranol) m/z = 579 (MH⁺), UV/Vis (CH₃CN), λmax(ε, M⁻¹cm⁻¹) = 279 nm (48720). IR (ATR): 1/λ (cm⁻¹): 2939, 2863 (C–C); 1599, 1580, 1560 (C=C, C=N, terpyridine). C₃₉H₄₀N₈O₂ (578.67 + ½H₂O): calcd. C 74.14, H 5.27, N 14.41; found: C 74.27, H 4.91, N 14.50.

(1S,2S)-trans-1,2-Bis(2′,6′,2′′-terpyridin-4′-oxyloxy)-cyclohexane (42): To a stirred suspension of powdered KOH (96 mg, 1.7 mmol) in DMSO (50 mL) at 60 °C (1S,2S)-trans-1,2-cyclohexanediol (144 mg, 1.24 mmol) was added. After 20 min 2 was added (528 mg, 1.97 mmol), the mixture was stirred for 3 d at 60 °C and then poured into water (450 mL). After adjusting the pH to 6-7 with HCl, the aqueous phase was removed by filtration and the product was washed with deionised water and dried in vacuo. The crude product was recrystallised from MeOH and filtrated through a layer (3 cm) of neutral aluminium oxide yielding 42 as white solid (68 mg, 8%). M.p. 205 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.50 (m, 4 H, H₂γ), 1.77 (m, 4 H, H₂β), 3.18 (t, 4 H, H₆α,δ), 1.32 (m, 8 H, H₂β), H₂α,δ), 7.32 (m, 4 H,
H_{5,5',5''',5''''}, 7.84 (m, 4 H, H_{4,4',4'',4''''}), 8.32 (s, 4 H, H_{3,5',3''',5''''}), 8.60 (m, 4 H, H_{3,3',3''',3''''}), 8.69 (m, 4 H, H_{6,6',6'',6''''}). ^{13}C NMR (300 MHz, CDCl3): δ = 28.4 (C_{6,6'',6''',6''''}), 28.8 (C_{7,7'}), 29.1 (C_{7,7''}), 29.3 (C_{6,6''}, 30.8 (C_{6,6'''}), 117.7 (C_{5,5',5''',5''''}), 121.4 (C_{3,3',3''',3''''}), 123.8 (C_{5,5',5''',5''''}), 136.8 (C_{5,5',5''',5''''}), 156.0 (C_{2,2',2''',2''''}), 157.3 (C_{2',6',2''',6''''}), 157.7 (>C=O), 166.6 (C 4',4'''''). MALDI-TOF-MS (matrix: dithranol) m/z = 669 (MH^+). UV/Vis (CH3CN), λ_{max} (e, M^{-1} cm^{-1}) = 279 nm (48720). IR (ATR): 1/λ (cm^{-1}): 2939, 2863 (C–H). 1H NMR (CD3OD): δ = 1.32 – 1.43 (m, 4 H, H_{3,3',3''',3''''}), 1.58 – 1.94 (m, 4 H, H_{2,2',2''',2''''}), 1.85 – 2.08 (m, 8 H, >CH2–CH2–), 3.20 – 3.28 (m, 4 H, H_{6,6''',6''''}). 13C NMR (300 MHz, CDCl3): δ = 25.5 (C_{6,6''''}, 30.1 (>CH–CH2–), 40.4 (C_{7,7''}), 40.6 (C_{6,6''''}, 58.5 (~CH2–N~), 71.6 (~O–CH~), 108.1 (C_{5,5',5''',5''''}), 121.3 (C_{4,4',4'',4''''}), 123.8 (C_{3,3',3''',3''''}), 136.8 (C_{3,3',3''',3''''}), 149.0 (C_{6,6',6'',6''''}), 157.3 (C_{2,6',2''',6''''}), 167.6 (>C=O), 166.6 (C_{4,4''''}). MALDI-TOF-MS (matrix: dithranol) m/z = 833 (MH^+). C_{36}H_{32}N_{6}O_{2} (833.00 + 1/2) = 834 (MH^+). C_{36}H_{32}N_{6}O_{2} (CH_{3}CN): calcd. C 74.1, H 5.3, N 14.4; found: C 74.1, H 5.3, N 14.7.

N,N’-Bis{4’-(2-Piperidin-4-yloxy)-2,2’:6’,2’’-terpyridine}-1,6-hexanediisocyanate (43): 4’-(2-Piperidin-4-yloxy)-2,2’:6’,2’’-terpyridine (6) (101 mg, 0.303 mmol) was dissolved in CHCl3 (10 mL) as was hexamethylene diisocyanate (0.023 mL, 0.64 mmol). The hexamethylene diisocyanate solution was added dropwise to the solution of 6 and the solution was refluxed for 12 h. The solvent was evaporated and the crude orange oil was recrystallised twice from THF and washed with methanol in order to yield 43 as white solid (65 mg, 51%). M.p. 224°C.

1H NMR (300 MHz, CDCl3): δ = 1.32 – 1.43 (m, 4 H, H_{3,3',3''',3''''}), 1.58 – 1.94 (m, 4 H, H_{2,2',2''',2''''}), 1.85 – 2.08 (m, 8 H, >CH2–CH2–), 3.20 – 3.28 (m, 4 H, H_{6,6''',6''''}). 13C NMR (300 MHz, CDCl3): δ = 25.5 (C_{6,6''''}, 30.1 (>CH–CH2–), 40.4 (C_{7,7''}), 40.6 (C_{6,6''''}, 58.5 (~CH2–N~), 71.6 (~O–CH~), 108.1 (C_{5,5',5''',5''''}), 121.3 (C_{4,4',4'',4''''}), 123.8 (C_{3,3',3''',3''''}), 136.8 (C_{3,3',3''',3''''}), 149.0 (C_{6,6',6'',6''''}), 157.3 (C_{2,6',2''',6''''}), 167.6 (>C=O), 166.6 (C_{4,4''''}). MALDI-TOF-MS (matrix: dithranol) m/z = 833 (MH^+).

Metallo-polymerisation of 2 with iron(II) chloride (45a): Di-terpyridine ligand 36 (46.3 mg, 0.080 mmol) was dissolved in CHCl3/MeOH (1/1, 100 mL), anhydrous iron(II) chloride (10.1 mg, 0.080 mmol) was added and the reaction mixture was stirred for 10 h at room temperature. The solvent was evaporated and the resulting dark-violet material dried in vacuo. 1H NMR (CD3OD): δ = 1.99 (m, 4 H, H_{7,7'}), 2.28 (m, 4 H, H_{6,6''}, 4.81 (m, 4 H, H_{6,6''}), 7.20 (m, 4 H, H_{5,5',5''',5''''}), 7.31 (m, 4 H, H_{4,4',4'',4''''}), 7.95 (s, 4 H, H_{3,3',3''',3''''}), 8.74 (m, 4 H, H_{3,3',3''',3''''}), 8.82 (m, 4 H, H_{6,6',6'',6''''}). 45b: a solution of 45a was heated to reflux in CHCl3/MeOH as 1/1 (100 mL) for 24 h, which, after evaporation of the solvent resulted in the same product as 45a, but with different intensities in the 1H NMR (CD3OD) spectrum. 1H NMR (CD3OD): δ = 1.70-2.32 (m, 4 H, H_{7,7'}), 2.01-2.61 (m, 4 H, H_{6,6''}, 4.61-4.93 (m, 4 H, H_{6,6''}), 7.09-7.35 (m, 8 H, H_{5,5',5''',5''''}), 7.76-8.01 (m, 4 H, H_{4,4',4'',4''''}), 8.65-8.77 (m, 4 H, H_{3,3',3''',3''''}), 8.78-8.84 (m, 4 H, H_{3,3',3''',3''''}).

Metallo-macrocyles 46 and 47: 28 mg of the metallo-polymer-mixture 45b was dissolved in CH3CN/H2O/KNO3 aq,sat (20/2/1 mixture) and eluted with the same solvent mixture from a silica column. Two fractions could be isolated and precipitated through addition of NH4PF6. The products were filtered off and dried in vacuo, in order to yield both substances as purple solids.

46 [3+3]: Yield: 46%(wt). 1H NMR (CD3CN): δ = (H_{7,7'} are hidden under residual solvent peak 1.82-2.22 ppm), 4.67-4.77 (m, 4 H, H_{6,6''}, 6.90-7.00 (m, 4 H, H_{5,5',5''',5''''}), 7.07-7.19 (m, 4 H, H_{6,6',6'',6''''}), 7.59-7.69 (m, 4 H, H_{4,4',4'',4''''}), 8.37-8.47 (m, 4 H, H_{3,3',3''',3''''}), 8.53 (s, 4 H, H_{3,3',3''',3''''}). MALDI-TOF-MS (matrix: malononitrile) m/z = 2634.25 (M^-PF6). UV/Vis (CH3CN), λ_{max} (e, M^{-1} cm^{-1}) = 557 (23770), 367 (6110), 316 (58780), 273 nm (82550). IR (ATR): 1/λ (cm^{-1}): 2926 (C–C); 1617, 1563, 1550 (C=C, C=N, terpyridine); 831 (P–F, PF6).

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Chapter IV

47 [4+4]: Yield: 25%(wt). $^1$H NMR (CD$_3$CN): $\delta = (H_{\gamma \beta}$ are hidden under residual solvent peak 1.82-2.22 ppm), 4.67-4.77 (m, 4 H, H$_{4\alpha \alpha'}$), 6.93-7.03 (m, 4 H, H$_{5,5',5''',5''''}$), 7.09-7.21 (m, 4 H, H$_{6,6'',6''',6''''}$), 7.64-7.74 (m, 4 H, H$_{3,3'',3''',3''''}$), 8.42-8.52 (m, 4 H, H$_{3',5',3''',5'''}$). MALDI-TOF-MS (matrix: malononitrile) m/z = 3561.31 (MH$^+$–PF$_6$). UV/Vis (CH$_3$CN), $\lambda_{\text{max}}$ (e, M$^{-1}$cm$^{-1}$) = 557 (33345), 367 (7410), 316 (93600), 273 nm (134100). IR (ATR): $1/\lambda$ (cm$^{-1}$): 2925 (C–C); 1615, 1562, 1549 (C=C, C=N, terpyridine); 832 (P–F, PF$_6$).

Metallo-polymer synthesis with ligand 37: 200 mg (0.277 mmol) of 37 were dissolved in 15 mL of a MeOH / CHCl$_3$ mixture (1 / 1 ratio). A solution of 35.1 mg (0.277 mmol) iron(II) chloride was added to the solution and the mixture was stirred at room temperature for one hour. A 40-fold of ammonium-hexafluorphosphate (1.8 g) dissolved in 20 mL of a MeOH / CHCl$_3$ mixture (1 / 1 ratio) was added. After precipitation, the purple solid was collected by filtration and washed with MeOH (3 × 10 mL) and water (3 × 10 mL). $^1$H NMR (CD$_3$CN): $\delta$ = 1.0-1.9 (m, 24 H, H$_{\gamma \gamma}$), 1.9-2.2 (m, 4 H, H$_{\beta \beta'}$), 4.5-4.8 (m, 4 H, H$_{\alpha \alpha'}$), 6.9-7.5 (m, 8 H, H$_{5,5',5''',5''''}$), 7.7-8.1 (m, 4 H, H$_{6,6'',6''',6''''}$), 8.5-9.0 (m, 8 H, H$_{3,3'',3''',3''''}$). UV/Vis (CH$_3$CN), $\lambda_{\text{max}}$ (e, M$^{-1}$cm$^{-1}$) = 557 (33330), 362 (15430), 317 (93650), 274 nm (63170).

Viscometric titration of ligand 37: 200 mg (0.277 mmol) of 37 were dissolved in 15 mL of a MeOH / CHCl$_3$ mixture (1 / 1 ratio). This solution was poured into the Ubbelohde capillary viscometer and equivalents of iron(II) chloride were added as solid beads according to Figure 4.10. The Ubbelohde was equipped with a stirring mechanism, which therefore allowed stirring of the mixture during all of the titrations. After the addition of each equivalent of iron(II) chloride, the mixture was stirred for 30 min prior to the measurement. 10 measurements were performed after each addition and the mean value was taken (standard deviations < ±4%).

Chiral metallopolymers 48 and 49: Di-terpyridine ligands 41 and 42 (5 mg, 0.009 mmol) were dissolved in CHCl$_3$/MeOH as (1/1, 10 mL), anhydrous iron(II) chloride (1.1 mg, 0.080 mmol) was added and the reaction mixture was stirred for 10 h at room temperature. The solvent was evaporated and the resulting dark-violet material dried in vacuo. UV/Vis (CH$_3$CN), $\lambda_{\text{max}}$ (e, M$^{-1}$cm$^{-1}$) = 558 (13760), 362 (6080), 317 (43090), 274 nm (63170).

Iron(II) chloride UV/Vis- and CD-titrations of 36 and 42. The ligand was dissolved in CHCl$_3$/MeOH (1/1, 2.0 × 10$^{-5}$ M in 100 mL) and aliquots of 0.2 × 10$^{-5}$ mol iron(II) chloride in CHCl$_3$/MeOH (1/1) were then titrated into the stirred solution. An UV/Vis spectrum was recorded after each addition in 20 min time intervals. For the CD-titration of 42, the aliquots were changed according to Figure 4.12.

Zinc(II) acetate UV/Vis- and CD-titrations of 42: 2.9 mg (5.0 × 10$^{-6}$ mol) of 42 were dissolved in CHCl$_3$/MeOH as (1/1, 100 mL) and aliquots iron(II) chloride according to Figure 4.16 in CHCl$_3$/MeOH (1/1) were then titrated into the stirred solution under Argon gas. After each titration the solution was stirred for 10 min and then a sample was taken and the UV/Vis and the CD-spectra were measured. The sample was then placed back into the titration flask and the titration continued.
4.7 References


Chapter V

Terpyridine-Functionalised TentaGel® Microbeads: Synthesis and Metal Chelation

Abstract

2,2′:6′:2″-Terpyridines bound to a polymer microbead support allow the complexation of transition metal ions. The functionalisation of hydroxy-modified TentaGel® microbeads with 4′-chboro-terpyridine occurs readily in a basic DMSO suspension, leading to the chelating microbead material. An important means of characterisation of this partially soluble crosslinked polymer is UV/Vis spectroscopy, which can be carried out on a suspension of the material. The loading process with different transition metal ions leads to differently coloured materials for which loading values can be determined by atom absorption spectroscopy (AAS). More advanced characterisation using atomic force microscopy and scanning electron microscopy revealed specific changes in the surface morphology upon terpyridine functionalisation and metal complexation.

5.1 Introduction

Functional polymeric microspheres are used especially in medical and biochemical applications such as adsorbents, latex diagnostics, affinity bioseparators as well as drug and enzyme carriers.\textsuperscript{[1]} But also the capability of such solid supports to complex metal ions via metal complexing ligands has been of great interest for decades.\textsuperscript{[2]} Besides the utilisation in the development of new catalysts with specific activities, the simple isolation and recycling properties of such functionalised support materials are of importance. Therefore such beads play also an important role in combinatorial chemistry.\textsuperscript{[3]} Moreover, the selective uptake of certain transition metal ions is attractive for environmental purposes.\textsuperscript{[4,5]} Finally, new functional materials can be envisioned by the combination of metal complexes with special electrochemical or photochemical properties and solid support materials.

Polymeric microspheres are prepared chemically by heterogeneous polymerisations (emulsion-, suspension- and precipitation-polymerisation) and by physical methods such as emulsification, coacervation and spray-drying.\textsuperscript{[6,7]} These different methods lead to a variety of microspheres in terms of size, surface chemistry, composition, surface texture and morphology. More features are depicted in Table 5.1.

Table 5.1: Features of polymeric microspheres (-beads).

<table>
<thead>
<tr>
<th>Feature</th>
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<tr>
<td>Small size and volume</td>
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<tr>
<td>Large specific surface area</td>
</tr>
<tr>
<td>Ability to diffuse</td>
</tr>
<tr>
<td>Stable dispersion</td>
</tr>
<tr>
<td>Uniform size, surface chemistry, morphology</td>
</tr>
<tr>
<td>Variation of size, surface chemistry, morphology</td>
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</table>

Among the most important features is the surface area to volume ratio, which is in general inversely proportional to the diameter of the microsphere. The total surface area of 1 g microspheres having a diameter of 0.1 µm is about 60 m\(^2\).

However, regarding metal-complexation or -loading of such microspheres or microbeads, a well-known problem for such heterogeneous systems is leaching of the metal ions, e.g. in the case of phosphines as ligands.\textsuperscript{[8]} Therefore, recent approaches include the use of poly(pyridine)s as chelating ligands. 2,2'-Bipyridine and 2,2':6',2''-terpyridine units present
two of the most prominent types of $N$-heterocyclic ligands for transition metal ions and are widely used in analytical and supramolecular chemistry as well as material science.\cite{9} In particular, terpyridine ligand systems offer a wide range of specific properties, such as complexation of a variety of interesting transition metal ions (such as cobalt, nickel, ruthenium, copper, manganese, zinc, etc.) leading to very high stability constants and interesting physical properties of the corresponding metal complexes.\cite{9} Besides the free ligand systems or closely related substituted or functionalised compounds, the incorporation into linear copolymers has been described recently.\cite{10} However, the immobilisation of the terpyridine ligand onto solid supports would open additional opportunities for applications, such as in catalysis, removal of metal ions by chelation from contaminated solutions, combinatorial chemistry, functional materials or the selective grafting of compounds or nano-objects. In particular, the combination with polymer-based beads is of interest, and surprisingly little has so far been explored in this direction.

Most of the examples described use low molar mass derivatives or ligands bound to linear soluble polymers. In the case of bipyridine, also several examples are described where the ligand is bound to a solid substrate.\cite{11} In particular, poly(styrene) beads are utilised for this immobilisation. However, the recent strongly growing interest in the utilisation of terpyridine ligands and their corresponding metal complexes is at present not actively displayed regarding heterogenisation. Only very few papers describe the immobilisation onto planar substrates (e.g. via layer-by-layer self-assembly processes\cite{12}) or beads. In the latter case, only three examples have been published: The copolymerisation of norbornene-terpyridine derivatives and subsequent immobilisation on silica particles\cite{13} and the functionalisation of poly(styrene) beads with terpyridine ligands.\cite{14,15} Yoo et al.\cite{14} used a direct reaction of the styrene moieties and the corresponding terpyridine derivative (Scheme 5.1).
Scheme 5.1: Yoo's synthesis of a polymer-supported PCD-terpyridine-Fe(III) catalyst.

The authors claim to have established a very rigid connection, which did not allow the formation of the typical octahedral bis-complexes upon addition of transition metal salts. These two known examples use both a rather rigid connection to the poly(styrene) bead material, where the functionalised chloromethyl-styrene or silyl-chloride-styrene units are reacted with the phenyl-terpyridine or terpyridine in the 4'-positions. Such a stiff connection should prevent the formation of octahedral bis-complexes to a great extent. Therefore uncommon and usually not stable mono-complexes can be isolated and utilised for catalytic purposes, such as the Fe(III)-mono-terpyridine complex.\[14\] In order to allow a high loading rate with transition metal ions through the formation of bis-complexes, a different connection approach was selected in the present thesis, starting from hydroxy-functionalised TentaGel® microbeads (Figure 5.1).\[16,17\]
Figure 5.1: Chemical architecture of a TentaGel®-OH microbead.

TentaGel® microbeads consist of a cross-linked poly(styrene) core with grafted-on hydroxy-terminated poly(ethylene glycol) side chains and combine the advantages of gelatinous resins (such as the well-known 1% cross-linked poly(styrene) resins or cross-linked poly(acrylamides) and macro-porous resins (Kieselgur, glass or highly cross-linked poly(styrene)). These hybrid type resins therefore allow to some extent solid-phase chemistry under liquid-phase conditions. Nishide et al. also applied this strategy for a bipyridine functionalised microbead material in 1982 (Scheme 5.2).[18] Polystyrene beads (here: cross-linked with 20 mol% divinylbenzene, DVB) were grafted with poly(ethylene oxide) in order to obtain better solvation.

Scheme 5.2: 2,2′-Bipyridines linked to a polystyrene core via a solubility-enhancing poly(ethylene oxide).[18]

The reaction with the chloromethyl functionalised bipyridine then led to the bipyridine functionalised resin. From absorption measurements in a buffered water solution they found a
stability constant of 4700 L/mol for the complexation of copper(II) chloride dihydrate, which is, however, lower than for free bipyridines in solution.\[19\]

Here, a new immobilisation route for terpyridine ligands onto poly(ethylene glycol) grafted poly(styrene) beads resulting in flexible and highly accessible metal complexing resins is reported. The 4’-chloro-2,2’:6’,2”-terpyridine\[20,21\] was chosen as functionalised terpyridine unit which can be easily synthesised in multi-gram quantities and is also commercially available. The loading properties of the commercially available hydroxy-functionalised microbeads used are depicted in Table 5.2.

<table>
<thead>
<tr>
<th>Table 5.2: Properties of TentaGel® M-OH microbeads.</th>
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<tbody>
<tr>
<td>Beads</td>
</tr>
<tr>
<td>TentaGel® M-OH (cap.: 0.23 mmol/g and 0.27 mmol/g)</td>
</tr>
</tbody>
</table>

The reason for using material with two different OH-loading capacities was the lack of commercial availability of sufficient material having the same capacity.

### 5.2 Functionalisation of TentaGel®-beads with 2,2’:6’,2”-terpyridine

In order to obtain a high degree of functionalisation of the resin with the N-heterocyclic ligand, the hydroxy-functionalised TentaGel® microbeads 50 were reacted with an excess of 4’-chloro-2,2’:6’,2”-terpyridine 2 in DMSO in the presence of KOH (Scheme 5.3). The reaction conditions were optimised earlier for the reaction of 50 with small hydroxy-terminated organic entities\[22\] (see also Chapter 2) as well as linear poly(ethylene glycol)s.\[10\]
Scheme 5.3: Schematic representation of the functionalisation of the hydroxy-functionalised microbeads 50 (capacity: 0.23 and 0.27 mmol –OH / g) with 4'-chloro-2,2':6',2''-terpyridine 51.

The resulting oxo-ether bridged 2,2':6',2''-terpyridine functionalised resin 51 was thoroughly washed several times with a mixture of CHCl₃/MeOH (1:1) to remove the excess of unreacted 4'-chloro-2,2':6',2''-terpyridine. Subsequently, the terpyridine-functionalised beads were characterised by standard techniques. The UV/VIS spectrum revealed a strong intense band around 280 nm, which can be assigned to the π*⁻→π bands of the terpyridine ligand. The IR-spectrum showed the typical pyridine valence vibrations around 1570 and 800 cm⁻¹ (Figure 5.2, the OH-band is visible in both cases due to the large water-uptake of the TentaGel® beads).

Figure 5.2: Comparison of the FT-IR spectra of the hydroxy-functionalised microbeads 50 (starting material, ······) and the 2,2':6',2''-terpyridine-functionalised microbeads 51 (———).
Moreover, addition of iron(II) chloride to the beads immediately resulted in an intense purple colouring of the beads typical for the Fe(II)-bis-terpyridine complexes. In order to avoid any misinterpretation by eventually non-covalently included terpyridine ligands, a test reaction was performed (see experimental part).

There was also an attempt made to functionalise simple cross-linked hydroxy-modified PS-microbeads (1% divinylbenzene, DVB) with 4'-chloro-terpyridine (Scheme 5.4). Though having a higher loading capacity (0.7 – 1.0 mmol/g) these microbeads had a lower swelling capability in more polar solvents\cite{117} and solvent mixtures such as MeOH/CHCl₃ than the TentaGel® beads \textbf{50}. Another advantage of the TentaGel® microbeads is their constant swelling, which is nearly independent of the polarity of the solvent utilised.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{scheme54.png}
\caption{Scheme 5.4: Schematic representation of the functionalisation of the hydroxy-functionalised PS microbeads \textbf{52} (capacity: 0.7 – 1.0 mmol –OH / g) with 4'-chloro-2,2':6',2''-terpyridine \textbf{2}.}
\end{figure}

A test-complexation with iron(II) chloride also resulted in the typical purple-colouring. However, results obtained from elemental analysis clearly indicated non-quantitative functionalisation (Table 5.3, top). First, when looking at the values for the commercially obtained poly(styrene)-OH beads \textbf{52}, a close match can only be obtained when taking into account a certain weight percentage of water (2.5%wt). By then comparing the measured values for the terpyridine functionalised microbeads \textbf{53} to the calculated ones on the same basis of water uptake (2.5%wt), a reasonable value is only obtained when taking into account non-quantitative terpyridine functionalisation of the poly(styrene)-O-terpyridine beads \textbf{53} (25%).
Table 5.3: Elemental analyses of the starting materials "Bead-OH" (50 and 52) and the functionalised "Bead-O-tpy" (51 and 53).

<table>
<thead>
<tr>
<th></th>
<th>PS-OH (calc. + 2.5% wt H₂O)</th>
<th>PS-OH (found)</th>
<th>PS-O-tpy (calc. + 2.5% wt H₂O, 100% tpy)</th>
<th>PS-O-tpy (calc. + 2.5% wt H₂O, 20% tpy)</th>
<th>PS-O-tpy (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>87.6</td>
<td>87.6</td>
<td>85.8</td>
<td>87.7</td>
<td>87.7</td>
</tr>
<tr>
<td>% H</td>
<td>7.6</td>
<td>7.9</td>
<td>7.1</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>% N</td>
<td>0.0</td>
<td>0.0</td>
<td>3.5</td>
<td>1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>TentaGel®-OH (calc. + 4% wt H₂O)</th>
<th>TentaGel®-OH (found)</th>
<th>TentaGel®-O-tpy (calc. + 4% wt H₂O, 100% tpy)</th>
<th>TentaGel®-O-tpy (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>63.1</td>
<td>63.1</td>
<td>63.9</td>
<td>64.5</td>
</tr>
<tr>
<td>% H</td>
<td>8.8</td>
<td>8.8</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>% N</td>
<td>0.0</td>
<td>0.0</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Taking similar considerations for the TentaGel® microbeads into account, two major differences can be observed. First, the commercial TentaGel®-OH microbeads 50 (loading capacity: 0.23 mmol/g) seem to have a larger water uptake of 4%wt (which seems reasonable for a PEG-grafted system). On this basis the measured values for the TentaGel®-terpyridine 51, especially for nitrogen, match the calculated values for quantitative terpyridine functionalisation. However, here it has to be taken into account that the calculated values are based on the bead manufacturers maximum poly(ethylene glycol) weight percentage of 70% poly(ethylene glycol) for TentaGel®-OH 50. Nevertheless, even taking other percentages of PEO/PS, slightly different water contamination and errors of measurement into account, a degree of terpyridine functionalisation larger than 95% can be concluded for the TentaGel®-terpyridine 51 in contrast to the 25% in the case of the poly(styrene)-O-terpyridine beads 53. Because of the PS-terpyridine system having the major disadvantages of lower swelling capability and the discussed low terpyridine functionalisation of 25 mol% (compared to available HO-functionality), this system was not investigated further concerning metal-complexation experiments.

5.3 Metal ion loading of the TentaGel®-terpyridine beads

The prepared terpyridine-functionalised microbeads should be suitable for the complexation of a wide range of transition metal ions in a solution-like behaviour, whereby the poly(ethylene glycol) spacers would enable a high flexibility of the metal complexing unit. To investigate the complexation properties, the microbeads were treated with several metal salts (Scheme 5.5).
Scheme 5.5: Loading with different metal-salts: Fe-beads (54a), Co-beads (54b), Cu-beads (54c) and Ni-beads (54d).

For this purpose, beads were suspended in CHCl$_3$/MeOH (1:1) and an excess of the metal salt (Fe(OAc)$_2$, Co(OAc)$_2$, Cu(OAc)$_2$ and Ni(OAc)$_2$, respectively) was added. After mixing with the help of an ultrasonic bath for 1 h in order to ensure complete swelling and mixing$^{[16,17]}$ (the reactions of these metal ions with terpyridine in homogeneous systems occurs instantaneously$^{[9a]}$), the beads were filtered off, washed and dried. Depending on the metal salt utilised, the corresponding typical colour of the corresponding terpyridine metal complex was observed (Figure 5.3). There was no colour change observed for the nickel(II)-loaded beads when compared to the colourless TentaGel$^\text{®}$-terpyridine 51.

In order to verify that no leaching of the metal-complex species has taken place, the iron(II) loaded beads 54a were stored for several days in a CHCl$_3$/MeOH mixture and compared to the TentaGel$^\text{®}$-terpyridine 51 as well as a solution of free terpyridine plus iron(II) in the same concentration (Figure 5.4).
Figure 5.3: Pictures of the different metal ion loaded beads. Left: Fe(II)-beads (54a). Middle: Cu(II)-beads (54c). Right: Co(II)-beads (54b).

Figure 5.4: Left: TentaGel®-tpy without iron(II) chloride. Middle: TentaGel®-tpy + iron(II) chloride. Right: free tpy-Fe-tpy with an identical concentration (all in CHCl₃/MeOH, 1/1 mixture).

The comparison clearly shows the typical purple colour of the MLCT band for the cases where iron(II)-terpyridine complexes are present. For the case of the complexes being bound to the bead material, a purple sediment of the iron(II)-loaded TentaGel®-terpyridine 54a can be observed as opposed to the deep purple solution of free iron(II)-terpyridine complexes and the white precipitate of the TentaGel®-terpyridine 51. This optical observation could be further confirmed by UV/VIS spectroscopy. As an example, the comparison of the iron-loaded bead 54a with the hydroxy- (50) and terpyridine-functionalised (51) beads are shown in Figure 5.5 (the spectra were recorded in a suspension which was prepared by mixing in an ultrasonic bath, see also ref.[23] for a similar procedure).
Figure 5.5: Left: UV/VIS spectra of Fe(II)-loaded terpyridine-beads 54a (-----), terpyridine-beads 51 (----) and hydroxy-beads 50 (·········), all measured in CHCl₃/MeOH (1:1, suspension, approx. 0.5 mg/L). Right: Pictures of suspensions of iron(II) acetate loaded beads in CHCl₃/MeOH (1/1), one minute after shaking (left), 10 minutes after shaking (right).

The red-shift of the π*→π band and the appearance of the metal-to-ligand-charge-transfer (MLCT) band at 559 nm clearly indicated the successful formation of the bis-terpyridine-Fe(II) complex. Figure 5.5 (right) gives an impression of the sedimentation behaviour of the iron-loaded beads in the cuvette used for UV/Vis measurements. 30 Seconds after the mixing in the ultrasonic bath, the beads are still distributed regularly over the whole liquid volume. After ten minutes some of the material has already sedimented, with a significant amount still being in suspension. Accordingly, the MLCT signal loses intensity (not shown here). Finally, a filtrate of the suspension used for the UV/Vis measurements does not show any signal anymore, thus confirming no leaching of iron(II)-terpyridine complexed material into the solution. This example demonstrates the high flexibility and accessibility of the terpyridine ligands attached to the microbead via poly(ethylene glycol) spacer units in contrast to the recently described direct coupling of the terpyridine units onto poly(styrene) moieties.[14]

UV/Vis spectra were also recorded for the beads loaded with other metal ions (Figure 5.6). It should be noted that although the same amount of material was weighed for a measurement, the absolute values of the absorption bands differ to an extent larger than known from the corresponding soluble free complexes. This may be related to the different swelling behaviour of the different metal-loaded beads.
For the nickel(II)-, cobalt(II)- and copper(II)-TentaGel®-terpyridines (54 b-d) again the typical shift in the $\pi^* \leftarrow \pi$ band, as compared to the uncomplexed TentaGel®-terpyridine 51 can be seen.

In order to further investigate the loading capabilities of the terpyridine-functionalised beads, the metal contents of the beads after the loading reactions were determined by atom absorption spectrometry (AAS) for the cases of loading with iron(II), cobalt(II) and copper(II) acetates as well as for the corresponding chlorides (55a-c). In first experiments, an indirect method of measuring the metal content complexed onto the beads was applied. The beads were treated with a defined amount of metal-salt solution and subsequently the metal content in the filtrate was measured. However, this method resulted in values with large errors and poor reproducibility. Therefore, a direct measuring method was developed. Applying a destructive sample preparation method led to measurable water solutions. The loaded beads were oxidised in a mixture of sulfuric acid and peroxide. Subsequently a water solution leading to a suitable metal concentration for the AAS measurements was prepared (Table 5.4).

Additionally, in order to exclude unspecific binding of metal acetate to the bead material, test loadings with the TentaGel®-HO bead and preparation of AAS samples were performed in the same way.
Table 5.4: Loading of the microbeads with metal salts as determined by AAS (all \( R^2 > 0.996 \)), bead capacities: 0.23 mmol/g for the acetates, 0.27 mmol/g for the chlorides.

**in mg metal / g bead:**

<table>
<thead>
<tr>
<th>Metal-salt</th>
<th>Loading of terpyridine-beads 51</th>
<th>Test loading of HO-bead 50</th>
<th>Expected amount for only bis-complexation</th>
<th>Expected amount for only mono-complexation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OAc)₂</td>
<td>5.8</td>
<td>0</td>
<td>6.4</td>
<td>12.8</td>
</tr>
<tr>
<td>Co(OAc)₂</td>
<td>7.1</td>
<td>0</td>
<td>6.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Cu(OAc)₂</td>
<td>14.4</td>
<td>0</td>
<td>7.6</td>
<td>15.1</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>6.8</td>
<td>0</td>
<td>7.6</td>
<td>15.1</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>8.4</td>
<td>0</td>
<td>8.0</td>
<td>15.9</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>13.0</td>
<td>0</td>
<td>8.6</td>
<td>17.2</td>
</tr>
</tbody>
</table>

**in 10⁻³ mmol / g bead:**

<table>
<thead>
<tr>
<th>Metal-salt</th>
<th>Loading of terpyridine-beads 51</th>
<th>Test loading of HO-bead 50</th>
<th>Expected amount for only bis-complexation</th>
<th>Expected amount for only mono-complexation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OAc)₂</td>
<td>104</td>
<td>0</td>
<td>115</td>
<td>230</td>
</tr>
<tr>
<td>Co(OAc)₂</td>
<td>128</td>
<td>0</td>
<td>115</td>
<td>230</td>
</tr>
<tr>
<td>Cu(OAc)₂</td>
<td>220</td>
<td>0</td>
<td>115</td>
<td>230</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>122</td>
<td>0</td>
<td>135</td>
<td>270</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>150</td>
<td>0</td>
<td>135</td>
<td>270</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>233</td>
<td>0</td>
<td>135</td>
<td>270</td>
</tr>
</tbody>
</table>

These measurements proved that no unspecific binding of metal acetate to the bead took place (Table 5.4). For the iron(II) and cobalt(II) salts, the values were around the expected amount for bis-complexation. The iron(II) values were a bit below (almost only bis-complexes present) and the cobalt(II) values a bit above (some more mono-complex formation) the expected bis-complexation value (for both salts). This is in accordance to complexation behaviour described in literature, where for soluble systems the difference between the two formation constants (\( K_1 \) for mono-complex formation and \( K_2 \) for bis-complex formation) is larger for the iron(II) system. This means that for a given concentration the tendency towards mono-complexation is larger for the cobalt(II) case. Furthermore, it is obvious that copper(II) acetate as well as the copper(II) chloride seem to form preferably mono-complexes as opposed to the copper(II) and iron(II) acetate, which is also known for non-heterogeneous systems.\(^{9a,24}\) These first loading results indicate that also such beads can selectively form mono or bis-complexes, depending on the metal salt utilised.
5.4 Surface characterisation

Further characterisation attempts were made by surface analysis techniques. X-ray photoelectron spectroscopy (XPS) was carried out in order to identify the different metals by measuring their significant electron binding energies. A problem with this surface oriented technique is that the surface density of metal ions has to be high enough to obtain usable results. One major problem was preparing the samples on the indium stamp. A complete, homogeneous surface coverage was not easy to obtain also due to the lack of material. However, in the case of the cobalt(II) acetate loaded beads 54b, a clear proof for the existence of cobalt was found (Figure 5.7).

![XPS measurement of the cobalt(II) acetate loaded microbeads 54b with fit (upper curve) and baseline (lower curve).](image)

The observed binding energy of the 2p-electron of 779.6 eV as well as the 2p-splitting (2p\(_{3/2}\) - 2p\(_{1/2}\)) of 15.6 eV correspond well to values known from other cobalt complexes.\(^{[25]}\)

The prepared terpyridine-functionalised as well as metal loaded microbeads were also investigated regarding their microscopic and nanoscopic morphology. For this purpose, scanning electron microscope (SEM) and atomic force microscope (AFM) measurements were performed. Figure 5.8 shows representative SEM-images of some of the functionalised beads. Comparing the hydroxy functionalised TentaGel\(^{\circledR}\) microbeads 50 (Figure 5.8a) with the terpyridine-functionalised microbeads 51 (Figure 5.8b) and the Co(OAc)\(_2\)-loaded terpyridine-microbeads 54b (Figure 5.8c), a trend to a smoother surface can be observed.
Moreover, the hydroxy functionalised beads revealed a stronger adhesion to each other. The fact that metal containing beads showed a much smoother surface compared to the more wrinkled one of a ligand functionalised bead has already been reported for a similar system involving 4-vinyl-pyridine/1-vinylpyrrolidone grafted crosslinked polystyrene beads (20 mol% divinylbenzene) and copper(II) chloride.\textsuperscript{[18]} It must be taken into account though that the observed differences could also result from the sputtering of the beads with gold, which is required for the SEM measurement.

Figure 5.8: Left: SEM-micrographs of the commercial hydroxy functionalised bead 50 (a), the terpyridine-functionalised bead 51 (b) and the Co(II)-loaded terpyridine-bead 54b (c). Right: AFM images of the commercial hydroxy functionalised beads 50 (a), terpyridine functionalised beads 51 (b) and the Co(II)-loaded terpyridine-beads 54b (c). The images on the left side are height images; the images on the right represent the corresponding phase images.

Nevertheless, the observed features are characteristic for the different types of investigated beads, also regarding the fact that all the samples have been prepared according to the same procedure (spreading on glass plates from a droplet of deionised water and evaporation of the
water in vacuo for 20 h). The Atomic Force Microscopy image (phase image) for the hydroxy-functionalised microbeads showed a lamellar like structure, which is well-known for poly(ethylene glycol)s (Figure 5.8a). Upon functionalisation with terpyridine units these lamellae are not visible anymore, which could be due to a steric disturbance induced by the rather bulky terpyridine into the poly(ethylene glycol) phase. In case of the metal loaded beads (cobalt(II) acetate, 54b), a different surface (granular structure) can be observed. At present we are not able to present a reasonable interpretation for these findings. However, the effect might be related to the crystallinity of the metal complex salt.

5.5 Conclusion

Metal complexing 2,2'-6',2''-terpyridine functionalised microbeads have been prepared by reaction of 4'-chloro-2,2'-6',2''-terpyridine with hydroxy functionalised TentaGel® microbeads. The success of the reaction could be proven by UV/VIS spectroscopy (in suspension), IR spectroscopy as well as by metal complexing tests. Moreover, the terpyridine-modified beads were complexed with several metal-acetate and -chloride salts (iron(II), copper(II), cobalt(II), nickel(II)). The loading of the beads was qualitatively characterised by UV/VIS and IR spectroscopy, optical microscopy as well as quantitatively by AAS. The AAS results illustrate that the binding of metal ions to the beads is specific; it could be shown that no unspecific complexation with the starting material, the HO-functionalised bead, takes place. Moreover, the uptake of the different metal ions (iron(II), cobalt(II) and copper(II)) leads to values which relate to the complexation characteristics of free terpyridine complexation. For iron(II) and cobalt(II), the "intrabead" bis-complexation is favoured, as opposed to copper(II), where significantly more mono-complex is formed. In addition, surface characteristics have been investigated utilising SEM and AFM indicating significant differences. A more flat surface can be observed after metal complexation in contrast to a more wrinkled one for the non-metal-salt loaded microbeads. These first characterisation results of metal complexing microspheres based on terpyridine-complexation present a valuable basis for further complexation studies, using for example other metal ions and solvent systems.
5.6 Experimental section

Materials: Hydroxy-functionalised TentaGel® microbeads 50 (d = 20 μm, capacity: 0.23 mmol/g) and 52 (d = 20 μm, capacity: 0.7 – 1.0 mmol/g) were purchased from Rapp-Polymer. 2,2’-6’,2”-Terpyridine (98%), cobalt(II) acetate tetrahydrate (99.999%), nickel(II) acetate tetrahydrate (99.998%), copper(II) acetate monohydrate (99.994%), iron(II) acetate (99.995%) and ruthenium(III) chloride were purchased from Aldrich. KOH (85%) was obtained from Merck. Chloroform and methanol were purchased from Biosolve LTD (both AR-quality). DMSO (99.7%) was obtained from Acros and dried over molsieves (3Å) before use. 4’-Chloro-2,2’:6’,2”-terpyridine 2 was synthesised as described elsewhere.[21]

Instruments: UV/VIS spectra were recorded on a PerkinElmer Lambda 45 UV/VIS spectrometer. AFM measurements and optical microscopy were performed on a NT-MDT Solver P7LS (with integrated optical microscope). SEM images were obtained using a Jeol 840a. FT-IR spectra were recorded on a PerkinElmer Spectrum One. AAS measurements were performed on a Shimadzu AA 6200. XPS spectra were measured on a VG Escalab 200 MK spectrometer equipped with an AlKα source and a hemispherical analyser connected to a five-channel detector. Energy correction was performed by using the In 2p peak of In2O3 at 444.5 eV as a reference.

Functionalisation of the TentaGel® resin: The resin 50 (499 mg, 0.10-0.15 mmol hydroxy-functionality) was suspended in DMSO (50 mL), an excess of KOH (84 mg, 1.5 mmol) was added and the mixture was stirred at 60 °C. After 20 min 4’-chloro-2,2’:6’,2”-terpyridine 2 (203 mg, 0.768 mmol) was added and stirring was continued for 48 h at 60 °C. The reaction mixture was poured into water (450 mL) and the microbeads were filtered off. The product was washed with deionised water (5 × 40 mL), chloroform (5 × 40 mL) and dried in vacuo to yield 51 as a yellow solid material. UV/VIS (suspension CHCl3/MeOH as 1/1): λmax = 277 nm. FT-IR: 1583, 1564, 798 cm⁻¹ (P–F). Elemental analyses 50: calcd. (+ 4%wt H2O) C 63.1, H 8.8, N 0.0; found: C 63.1, H 8.8, N 0.0, 51: calcd. (+ 4%wt H2O) C 64.0, H 8.6, N 1.1.; found: C 64.5, H 8.6, N 1.1.

In order to prove the successful removal of free terpyridine, small amounts of the filtrate were treated with iron(II) chloride, whereby no formation of coloured iron(II) terpyridine complexes could be observed.

Functionalisation of the poly(styrene) resin: The resin 52 (500 mg, 0.35-0.50 mmol hydroxy-functionality) was suspended in DMSO (50 mL), an excess of KOH (112 mg, 2.00 mmol) was added and the mixture was stirred at 60 °C. After 20 min 4’-chloro-2,2’:6’,2”-terpyridine 2 (535 mg, 2.08 mmol) was added and stirring was continued for 48 h at 60 °C. The reaction mixture was poured into water (450 mL) and the microbeads were filtered off. The product was washed with deionised water (5 × 40 mL), chloroform (5 × 40 mL) and dried in vacuo to yield 53 as a yellow solid material, UV/VIS (suspension CHCl3/MeOH as 1/1): λmax = 277 nm. FT-IR : 1583, 1564, 798 cm⁻¹ (P–F). Elemental analysis 52: calcd. (+ 2.5 %wt H2O) C 87.6, H 7.6, N 0; found: C 87.6, H 7.9, N 0; 53: calcd. (+ 2.5%wt H2O, 20 mol% tpy) C 87.7, H 7.4, N 1.0; found: C 87.7, H 7.5, N 1.1.

In order to prove the successful removal of free terpyridine, small amounts of the filtrate were treated with iron(II) chloride, whereby no formation of coloured iron(II) terpyridine complexes could be observed.

The bead functionalisation reaction described above was performed in the absence of the base KOH as well. In this case, the nucleophilic aromatic substitution reaction cannot work.
However, any inclusion or adsorption of the terpyridine moieties inside the TentaGel® microbeads should still take place. After the work-up, no terpyridine signals in UV/VIS spectroscopy or FT-IR spectroscopy could be detected. Moreover, no colouring of the bead material upon addition of iron(II) chloride was observed, proving that indeed no inclusion or adsorption of terpyridines took place.

**General preparation of the loading with metal ions.** The terpyridine functionalised beads 51 (50.0 mg) were suspended in CHCl₃/MeOH (2.5 mL/2.5 mL) and an excess of metal-salt was added as follows: 54a: Fe(OAc)₂ (3.7 mg, 0.021 mmol), 54b: Cu(OAc)₂ × H₂O (4.0 mg, 0.020 mmol), 54c: Co(OAc)₂ × 4 H₂O (5.0, 0.024 mmol), 54d: Ni(OAc)₂ (6.2 mg, 0.025 mmol), 55a: FeCl₂ (5.4 mg, 0.042 mmol), 55b: CuCl₂ (5.8 mg, 0.043 mmol), 55c: CoCl₂ (5.2, 0.040 mmol). The loading was carried out by mixing with the help of an ultrasonic bath for 1 h at room temperature. The beads were then filtered off and washed carefully (no vacuum) with CHCl₃/MeOH (1:1, 4 × 5 mL) and dried in vacuo to result the differently coloured microbeads. 54a: FT-IR: 1615 cm⁻¹; UV/VIS (suspension CHCl₃/MeOH, 1:1): λₘₐₓ = 559 nm (MLCT), 319 nm (π* ← π). 54b: UV/VIS (suspension CHCl₃/MeOH, 1:1): λₘₐₓ = 326(π* ← π), FT-IR: 1616, 1573 cm⁻¹. 54c: UV/VIS (suspension CHCl₃/MeOH, 1:1): λₘₐₓ = 312 (π* ← π), FT-IR: 1615 cm⁻¹; XPS: Eₐ(2p3/2): 779.6 eV, Eₐ(2p1/2): 795.2 eV, 54d: UV/VIS (suspension CHCl₃/MeOH, 1:1): λₘₐₓ = 326 (π* ← π); FT-IR: 1614, 1573 cm⁻¹. 55a: FT-IR: 1615, 1590 cm⁻¹; UV/VIS (suspension CHCl₃/MeOH, 1:1): λₘₐₓ = 559 nm (MLCT), 319 nm (π* ← π). 55b: FT-IR: 1617, 1590 cm⁻¹. 55c: FT-IR: 1617, 1589 cm⁻¹.

**AAS measurements:** General procedure for sample preparation (54a-c and 55a-c): Between 6 and 8 mg of the loaded beads (as well as the HO-beads for the test experiments) were oxidised in 1 mL H₂SO₄ and 0.5 mL H₂O₂. After complete oxidation, the solution was diluted with deionised water to an expected metal concentration of exactly 2.5 ppm (systematical errors caused by the preparation procedure were not taken into concern). For the preparation of the calibration curves a solution containing the same concentration H₂SO₄ / H₂O₂ was utilised. The calibration curves (5 calibration points, 1 to 5 ppm) of all measurements as well as the test measurements revealed an R²-value of ≥ 0.996.

**SEM measurements:** For the SEM measurements samples were prepared by depositing microbeads on carbon tape on the sample holder.

**XPS measurements:** XPS measurements were done on an indium stamp (d = 1 cm), which was covered with the sample as homogeneously as possible.

**AFM measurements:** For the AFM measurements samples were prepared by depositing a drop of a water suspension of the microbead material on a silicon plate. The samples were measured after drying in vacuo.
Chapter V

References


Chapter VI

Directed Functionalisation and Potential Applications of Terpyridine-TentaGel® Microbeads

Abstract

Functionalised polymeric microbeads have widespread applications in fields such as catalysis, solid phase synthesis or affinity chromatography. The terpyridine functionalised microbeads presented in Chapter 5 were investigated regarding their potential use as catalytic material as well as reversible metal-chelating material. First, the feasibility of further functionalisation via bis-terpyridine-Ru(II) complexation is shown. Ruthenium(III)/ruthenium(II) chemistry can also lead to heteroleptic bis-terpyridine-Ru(II) complexes on a polymeric TentaGel® supported material as shown in Chapter 3 for non-solid-supported complexes. The catalytic activities of terpyridine-Ru(III)- and terpyridine-Cu(II)-functionalised microbeads were tested for the ring-opening of styrene oxide with methanol. Reversible binding of iron(II) is shown by decomplexation with the help of the highly competitive ligand HEEDTA. The recomplexation with iron(II) proved to be quantitative, as measured by AAS.

Part of this work has been published: U. S. Schubert, A. Alexeev, P. R. Andres, Macromol. Mater. Eng. 2003, 288, 852-860.
6.1 Introduction

Polymeric microspheres, such as the TentaGel® beads presented in Chapter 5, have in addition to the already briefly mentioned medical, biochemical and catalytic applications, potential uses due to their unique optical, opto-electrical and rheological properties.\[1\] Particles in the range from 100 nm to 1000 nm, which can form colloidal crystals, can for example act as Bragg diffraction gratings. Such gratings have been shown to be temperature sensitive with possible applications as thermally tunable optical filters.\[2\] The tunability of the swelling behaviour in a very defined manner makes polymeric lattices interesting as modifiers of dispersion viscosity, which may be influenced by temperature or changes in pH.\[3\] Further potential applications lie in the field of electrorheological fluids (ERF), where the rheological properties can be controlled by an electric field.\[4\] These ERFs, which may lead to novel switches, clutches or actuators, consist of particles (from 1 to 100 µm diameter in size) suspended in a non-conducting liquid. Upon applying a high voltage on such a suspension placed between electrodes, the particles show alignment into strings stretching from one electrode to the other. These potential applications justify the demand for polymeric microspheres, which possess new properties. In Chapter 5, metal loading experiments using unspecific complexation strategies (e.g. formation of the bis-complexes utilising two identical ligands or mono-complexes) were described. However, the directed coupling method utilising ruthenium(III)/ruthenium(II) terpyridine chemistry allows the selective construction of A-[Ru]-B type complexes. For this purpose, mono-terpyridine-Ru(III) complexes represent the key intermediates. This route has been applied to discrete organic\[5\] as well as polymeric systems (see Chapter 3). An application of this selective construction principle to microbeads could allow the design of a new platform for the immobilisation of a wide range of compounds utilising directed terpyridine-ruthenium complexation. Due to the high stability of the complexes (e.g. no exchange with competing ligands takes place over 24 h in a pH-range of 0-14\[6\]), they can act as a stable linker for chemically modifying solid supports and therefore selectively change the properties. This could also open new routes for the development of novel heterogeneous catalytic systems.

Here, different functionalities attached to the subsequently added terpyridine moiety could be grafted via ruthenium(III)/ruthenium(II) terpyridine chemistry onto the TentaGel® microbead, such as different polymers or an anthracene dye. The obtained functional microbeads were characterised by means of UV/Vis- and IR-spectroscopy as well as atomic force microscopy. First tests concerning their catalytical activity have been performed, using the mono-
complexed terpyridine-Ru(III) and terpyridine-Cu(II) functionalised microbeads 54c and 55c. Furthermore, the reversible complexation of iron(II) chloride onto terpyridine-TentaGel® beads is shown.

6.2 Directed complexation via Ru(III)/Ru(II)-terpyridine chemistry

In a first experiment regarding these investigations, the terpyridine-functionalised TentaGel® microbeads 51 were treated with ruthenium(III) chloride (Scheme 6.1). The resulting material 56 revealed the typical dark brown colour known from terpyridine-Ru(III) mono-complexes.[7]

![Scheme 6.1](image)

Scheme 6.1: Functionalisation of terpyridine-functionalised TentaGel® microbeads 51 with Ru(III)Cl₃ leading to compound 56 and subsequent directed functionalisation to 57 and 58.

Subsequently, 56 was reacted with uncomplexed 2,2'-6',2''-terpyridine as well as with free anthracene functionalised terpyridine[8] under reducing conditions, leading to beads 57 and 58 (Scheme 6.1). The reaction conditions were chosen according to known reactions, utilising ethanol as solvent as well as reducing agent and N-ethyl-morpholine as catalyst.[7] The success of the reaction could be followed visually by the change in colour from brown (terpyridine-Ru(III)) to red (bis-terpyridine-Ru(II)), also under the optical microscope (Figure 6.1).
Figure 6.1: Optical microscope images of single beads of the Ru(III)Cl₃-terpyridine microbeads 56 (left) and the terpyridine graft 57 (right).

The UV/Vis spectra of 57 and 58 (Figure 6.2) clearly revealed the typical metal-to-ligand-charge-transfer (MLCT) absorption around 490 nm (measured from suspension as described in Chapter 5). In addition, the anthracene functionalised material 58 showed the typical absorption bands for anthracene between 350 nm and 400 nm, which match the absorption bands of the uncomplexed terpyridine-anthracene ligand. Furthermore, the IR-signals of the amide function of the anthracene-terpyridine ligand could be observed.

Figure 6.2: Left: UV/Vis spectra of the terpyridine graft 57 (—), hydroxy-functionalised microbeads 50 (-----) and terpyridine functionalised microbeads 51 (---). Right: UV/Vis spectra of the anthracene-grafted microbeads 58 (—) and free anthracene-terpyridine (all measured in CHCl₃/MeOH (1/1) in suspension).

All UV/Vis measurements of the functionalised microbead materials were cross-checked with UV/Vis measurements of the filtrates, which showed no absorption band at around 490 nm. Encapsulation of unbound complexes could also be ruled out by earlier test measurements with the hydroxy-functionalised microbeads 50 (Chapter 5). This proves that the measured
signals do indeed originate from the functionalised microbead material. Additionally, for the terpyridine-grafted microbeads a settling experiment monitored by UV/Vis spectroscopy was performed (Figure 6.3).

![Figure 6.3: UV/Vis spectroscopic evolution of the MLCT absorption of the terpyridine-grafted microbeads 57 over time (in CHCl₃/MeOH (1/1) suspension).](image)

The suspension, which was prepared with the help of an ultrasonic bath (1 min), was measured after defined time intervals with the cuvette staying in the measurement chamber. Over time the MLCT-signal disappeared, proving that the absorbing species are attached to the microbeads, which slowly precipitate.

The data obtained from the initial experiments prove that to some extent functionalisation to asymmetric Ru(II)-bis-terpyridie-complexes has been successful. However, up to now it was not possible to obtain quantitative data for the ruthenium(III) loading or the grafting via ruthenium(II). ICP-AES (Inductive Coupled Plasma - Atom Emission Spectrometry) measurements were attempted, however, errors when measuring a defined solution of ruthenium(III) chloride were found to be above 30%, with the source of the error being unknown up to date. Nevertheless, further functionalisation experiments were carried out by trying to attach terpyridine functionalised polymers via directed ruthenium(III)/ruthenium(II) coupling reactions (Scheme 6.2). Again, UV/Vis spectroscopy confirmed the formation of ruthenium(II) complexes, which should result from directed complexation reactions.


Scheme 6.2: Synthesis of the PS$_{2000}$-graft 59 and the PEO-grafts 60 and 61 via directed Ru(III)/Ru(II)-terpyridine coupling.

The IR-spectrum of the PEO$_{3000}$ functionalised microbead 60 was compared with the model complex Ru(II)-bis-PEO$_{3000}$-terpyridine. This model complex is identical with the attached bis-complex, since the "PEO arms" on the microbead have a molecular weight $M_n$ of about 3000 g/mol (Figure 6.4).

Figure 6.4: Comparison of the IR-spectra of the PEO$_{3000}$-graft 60 (----) with the terpyridine microbeads 51 (-----) and the model complex Ru(II)-bis-PEO$_{3000}$-terpyridine (—).

The appearing bands of the complexed species are very similar and moreover, all of the bands in the model complex also appear in the PEO$_{3000}$-graft 60. Especially the disappearance of the
terpyridine valence vibration bands at 1583 cm$^{-1}$ and 1564 cm$^{-1}$ for 51 and the appearance of the band at 1610 cm$^{-1}$ for the complexed bead material 60 are characteristic. The spectra for the other graft materials 59 and 61 showed no additional significant bands. An indication for differences between the PEO$_{3000}$-graft 60 and the PS$_{2000}$-graft 59 can be found from the aggregation behaviour of the beads, when preparing samples for optical microscopy by suspending the materials in water and drop-casting on silicon wafers (Figure 6.5).

![Figure 6.5](image)

**Figure 6.5:** Microscope images (grey scale) of the PEO$_{3000}$-graft 60 (left) and the PS$_{2000}$-graft 59 (right).

The representative images show a slight tendency for stronger agglomeration in the case of the PS$_{2000}$-graft 59, which could be explained through the hydrophobic nature of the polystyrene in contrast to the poly(ethylene glycol). Especially regarding the polymer-grafted materials, one could expect to observe differences on the microbead-topography. Therefore, as already shown for the cobalt-loaded microbead in Chapter 5, non-contact mode AFM measurements were performed (Figure 6.6).
As already observed in Chapter 5 for the cobalt(II)-loaded microbeads, the ruthenium(III) functionalised microbeads 56 show a relatively hard surface with no defined features in contrast to the commercial hydroxy-functionalised microbeads 50. When looking at a
representative image of the PS\textsubscript{2000}-microbeads 59 (Figure 6.6, (c)), also no features can be found. However, for the PEO\textsubscript{17000}-microbeads 61 lamellae-like structures can be observed in the phase contrast image. This observation corresponds to the findings of the unfunctionalised HO-microbead, where lamellae-formation is believed to originate mainly from the HO-PEO-chains. Further significant differences could not be observed. Also different SEM techniques, including environmental SEM did not reveal any typical topographic features.

### 6.3 Potential use of metal-loaded microbeads as catalysts

Polymeric microbeads are already known for their use as transition metal catalysts (see introduction of Chapter 5). One requirement is that the substrate needs to have the possibility to access the complexed metal ion site. Most of the here reported complexes were found to preferably exist as pseudo-octahedral bis-terpyridine complexes. However, as reported in Chapter 5, the copper(II)-loaded microbeads 54b and 55b showed a loading value which corresponded to, at least partial, mono-complexation. The Ru(III)-loaded terpyridine-microbeads 56 reported before should also be in a mono-complexed state. Therefore, these two materials were tested as heterogeneous catalysts for different common reactions. From literature two examples were found where terpyridine-metal complexes are known to successfully act as catalysts. One of them is cyclopropanation\textsuperscript{[10]} and the other one the ring-opening of styrene-oxide.\textsuperscript{[11]} Especially cyclopropanation (where diazoacetate reacts with styrene) is catalysed starting from copper(II) acetate terpyridine mono-complexes. However, transferring the reaction conditions to the microbead material was not successful. No catalytic effect at all, measured by GC-MS, was observed using the copper(II)-loaded microbead material 55b. The reaction was allowed to continue for 3 days (samples were taken each day). Following that, the mixture was allowed to run under refluxing conditions for 1 day. After refluxing, the reaction slowly started (a few percent conversion), but without any difference between the sample with and without the catalyst. Therefore, this route was not investigated further. The ring-opening of styrene-oxide with methanol (Scheme 6.3) or water has already proven to be successful for a different type of bead material with terpyridine-iron(III) mono-complexes (see also introduction of Chapter 5).\textsuperscript{[11]} Here, tests were performed using the three metal-loaded beads mentioned before (Table 6.1).
Scheme 6.3: Schematic representation of the catalysed ring-opening of styrene-oxide.

Table 6.1: Results of catalysis with different metal-loaded microbeads (in % conversion).

After 1 h stirring, room temperature, MeOH

<table>
<thead>
<tr>
<th></th>
<th>without cat</th>
<th>CuCl₂tpy-bead</th>
<th>Cu(OAc)₂tpy-bead</th>
<th>RuCl₃tpy-bead</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene-oxide</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>99.2</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

After further 1 h stirring, reflux, MeOH

<table>
<thead>
<tr>
<th></th>
<th>without cat</th>
<th>CuCl₂tpy-bead</th>
<th>Cu(OAc)₂tpy-bead</th>
<th>RuCl₃tpy-bead</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene-oxide</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>89.7</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10.3</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

After further 100 h stirring, reflux, MeOH

<table>
<thead>
<tr>
<th></th>
<th>without cat</th>
<th>CuCl₂tpy-bead</th>
<th>Cu(OAc)₂tpy-bead</th>
<th>RuCl₃tpy-bead</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene-oxide</td>
<td>54.3</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>36.2</td>
<td>-</td>
<td>-</td>
<td>91.2</td>
</tr>
<tr>
<td>B</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>8.8</td>
</tr>
</tbody>
</table>

The results show that there is a catalytic effect for the ruthenium(III)-loaded microbeads, although it seems to be rather weak. Isomer A is the favoured product, which is expected due to sterical and electronic reasons. Nevertheless, by comparing with the results obtained without catalyst, complete conversion for the ruthenium(III)-loaded material is already reached after a total of 102 hours, while stirring under reflux. Since no activity was found for the copper(II) acetate microbeads after 1 hour of refluxing it was concluded that this system is inactive. The most significant backdraw for these microbeads concerning their use as catalyst...
is the relatively low degree of metal-loading. Yoo et al. had a 6-7 times higher metal-loading value in their system.\textsuperscript{[11]} Due to lack in sufficient amounts of material, these first tests could only be performed by using smaller amounts of the microbead material.

### 6.4 Reversible metal-complexation

Apart from selective binding,\textsuperscript{[12]} the reversible binding of transition metal ions to adsorbents is of interest, i.e. for the cleaning of industrial effluents. Since terpyridine-transition-metal complexes reveal strong association constants (as described and discussed in the former chapters), terpyridine functionalised TentaGel\textsuperscript{®} microbeads might be suitable for such purposes. Especially in terms of reusing such a material for the above-mentioned purpose, the decomplexation or the extraction of the metal ions would be of special interest. One of the easiest ways to realise this is to apply a highly competitive ligand, which has an even stronger complexation to the metal ions than the terpyridine ligand. HEEDTA (N-(2-hydroxyethyl)-ethylenediamine-triacetic acid) is known for its very strong association with iron(II) ions\textsuperscript{[13]} and was therefore chosen as metal-extracting reagent (Figure 6.7).

![Molecular formula of HEEDTA](image)

**Figure 6.7:** Molecular formula of HEEDTA (N-(2-hydroxyethyl)-ethylenediamine-triacetic acid).

The complexation of iron(II) chloride has been discussed in Chapter 5, which showed nearly quantitative formation of bis-complexes on the microbeads. Therefore iron(II) chloride was chosen as the metal salt. Different solvent systems were tested, such as mixtures of DMF/CHCl\textsubscript{3}/H\textsubscript{2}O or CHCl\textsubscript{3}/MeOH. Apart from the complexing ability of the competitive ligand HEEDTA, two conditions have to be satisfied for successful extraction experiments: first, the HEEDTA has to be soluble and second the TentaGel\textsuperscript{®} microbeads should be able to swell sufficiently in the solvent system in order to ensure the accessibility of the metal complexes by the HEEDTA on a reasonable time-scale. For this purpose the above-mentioned solvent systems were not useful because of the low HEEDTA-solubility. The best system found was H\textsubscript{2}O/THF, which ensured the solubility of the ligand throughout the extraction.
time as well as good swelling behaviour of the TentaGel® microbeads.\cite{14} The experiments were carried out by stirring defined amounts of the microbeads \textit{51} in a glass beaker and adding a 300-fold excess of the dissolved HEEDTA (H$_2$O/THF). After stirring the mixture for 24 hours at 50 °C, the typical violet colour of the microbeads suspension disappeared (Figure 6.8, left).

![Figure 6.8: Left: decomplexation of iron(II)-loaded microbeads (50 °C, H$_2$O/THF (1/1)). Right: recomplexation with iron(II) chloride (50 °C, H$_2$O/THF (1/1)).](image)

After filtration, washing with H$_2$O/THF and drying under reduced pressure, the microbeads were complexed again by stirring the microbeads in H$_2$O/THF and adding an excess of 4 equivalents of iron(II) chloride. Again the purple colouring of the material could be observed (Figure 6.8, right). Figure 6.9 shows samples of the isolated and dry microbeads after complexation, decomplexation and again recomplexation.

![Figure 6.9: Left: dried samples of Terpyridine-TentaGel® \textit{51}: complexation with iron(II)chloride. Right: decomplexation with HEEDTA (middle) and recomplexation with iron(II) chloride.](image)

The colours of the complexed microbeads are deep purple, which is typical for terpyridine-iron(II) complexation. The decomplexed material has an orange-brownish colour, which is
comparable to the colour of the terpyridine functionalised TentaGel® microbead (yellow-brownish). This visual observation could also be confirmed by IR spectroscopy (Figure 6.10).

![IR-spectra of the iron(II) chloride - complexed (---), - decomplexed (----) and - recomplexed (-----) terpyridine microbeads 51.](image)

**Figure 6.10:** *IR-spectra of the iron(II) chloride - complexed (---), - decomplexed (----) and - recomplexed (-----) terpyridine microbeads 51.*

For both the complexed and recomplexed microbeads the typical bands and shifts in intensities could be observed. The spectrum of the decomplexed microbeads is similar to the spectrum taken for the terpyridine-functionalised microbeads 51. In order to obtain quantitative values for de- and recomplexation, AAS measurements (as already described in Chapter 5) were carried out. Samples of 4-5 mg of the *in vacuo* dried materials were taken after each step and solutions suitable for AAS were prepared by first oxidising the microbeads with sulphuric acid / peroxide and then diluting the solution with water. Table 6.2 shows the results.

**Table 6.2:** *AAS results of the iron(II) chloride - complexed, - decomplexed and - recomplexed terpyridine microbeads 51.*

<table>
<thead>
<tr>
<th>Metal-salt</th>
<th>Loading of terpyridine-beads</th>
<th>after decomplexation (HEEDTA)</th>
<th>after recomplexation</th>
<th>Expected amount for only mono-complexation</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₂</td>
<td>128</td>
<td>6</td>
<td>144</td>
<td>135</td>
</tr>
</tbody>
</table>
The first loading of the beads results in a value of 0.128 mmol/g, which is identical within the error range with the value reported in Chapter 5 for the solvent system chloroform / methanol (0.122 mmol/g). After decomplexation with HEEDTA a value of 0.006 mmol/g was found. This means that 5% of the iron(II) still remained in the microbeads. Choosing longer decomplexation times, slightly higher temperatures or different volume percentages of the H$_2$O/THF mixture could help to further improve the efficiency. Apart from recomplexation with iron(II) chloride, first test-complexations were carried out with other chloride salts (Figure 6.11).

![Figure 6.11](image)

Figure 6.11: Dried samples of the recomplexation of the HEEDTA decomplexed microbeads with iron(II) chloride (left), copper(II) chloride (middle) and cobalt(II) chloride (right).

1 mg of the decomplexed microbeads was added to a 2 mL-solution of each copper(II) chloride and cobalt(II) chloride (iron(II)-complexation shown for comparison). The suspensions were mixed at room temperature for 1 hour and, after settling of the materials, the solutions were carefully removed. The same procedure was repeated two times with H$_2$O/THF solutions in order to make sure that the colouring is not influenced by free metal salt. Again, as described in Chapter 5, the typical blue-greenish colour for the copper-loaded microbeads 55c and the orange colour for the cobalt-loaded microbeads 55b could be observed.

### 6.5 Conclusions

2,2’-6’,2”-Terpyridine functionalised TentaGel® microbeads can be functionalised in a directed manner using ruthenium(III)/ruthenium(II) chemistry. Different ligands such as unfunctionalised terpyridine, an anthracene-functionalised terpyridine or polymer-functionalised terpyridines were grafted to the microbead material. In particular UV/Vis...
characterisation in case of the anthracene-functionalised microbead could prove the successful grafting process. Optically, a colour change from black (terpyridine-Ru(III)-bead or compound) to red (bis-terpyridine-Ru(II)-bead) could be observed for all the experiments. In case of the PEG\textsubscript{17000}-grafted microbead, AFM investigations revealed lamellae-like structures, which are typical for poly(ethylene glycol)s. First experiments on the use of metal-loaded microbeads showed only weak catalytic activity in the case of the ruthenium(III)-loaded microbeads in the ring-opening of styrene-epoxide. Reversible complexation could be performed in the case of the terpyridine-TentaGel\textsuperscript{®} microbeads 51 loaded with iron(II) chloride. More than 95% of the iron(II), according to AAS measurements, could be extracted by applying the highly competitive ligand HEEDTA. Upon recomplexation with iron(II) chloride, no decrease in loading ability was observed. The results described in this chapter open new routes for the selective functionalisation of beads by various polymers, biomaterials and nano-objects, with the potential of leading to new types of heterogeneous catalysts. The successful decomplexation and recomplexation of iron(II) chloride on the terpyridine-TentaGel\textsuperscript{®} microbeads presents a promising starting point for further research on reusable metal scavenger resins.

6.6 Experimental Section

**General remarks and instruments used**: Apart from the instruments and chemicals used in the previous chapters the following materials were used. The Cl\textsubscript{3}Ru(III)-terpyridine-PS\textsubscript{2000}, the terpyridine-PEO\textsubscript{3000} and the terpyridine-PEO\textsubscript{17000} were synthesised by Bas G. G. Lohmeijer and are described elsewhere.\[^{[9]}\] The anthracene functionalised terpyridine was synthesised by Richard Hoogenboom and is described elsewhere.\[^{[8]}\] Ruthenium(III) chloride (waterfree) was purchased from Aldrich. HEEDTA (39%-41% water-solution, Trilon\textsuperscript{®} D) was supplied by the BASF AG.

**Terpyridine-Ru(III) functionalised beads 56**: The terpyridine functionalised beads 51 (50.0 mg) were suspended in CHCl\textsubscript{3}/MeOH (2.5 mL/2.5 mL) and an excess of ruthenium(III) chloride (8.1 mg, 0.033 mmol) was added. The loading was carried out by mixing with the help of an ultrasonic bath for 1 h at room temperature. The beads were then filtered off and washed carefully (no vacuum) with CHCl\textsubscript{3}/MeOH (1:1, 4\(\times\)5 mL) and dried in vacuo to result the black microbeads 56: FT-IR: 1613, 1556 cm\(^{-1}\) (C=C, C=N, terpyridine), UV/VIS (suspension CHCl\textsubscript{3}/MeOH, 1:1): \(\lambda_{\text{max}} = 416\) nm (MLCT), 309 nm (\(\pi^* \rightarrow \pi\)).

**General preparation of the grafting experiments**: The terpyridine-Ru(III) functionalised beads 56 (10.0 mg, capacity 0.002 – 0.003 mmol terpyridine-Ru(III)) or the terpyridine functionalised beads 51 (10.0 mg, capacity 0.002 – 0.003 mmol) were suspended in ethanol (10 mL). Subsequently a drop of N-ethyl morpholine and a 10-fold excess of the terpyridine ligand or the terpyridine-Ru(III) complex (0.025 mmol) were added and the mixture was gently stirred under reflux for 24 h. The grafted beads were then filtered off and washed with...
ethanol, methanol and dichloromethane (each $3 \times 30$ mL). The terpyridine complex grafted beads 57, 58, 59, 60 and 61 were isolated as a red material. 57: FT-IR: 1615, 1545 cm$^{-1}$ (C=C, C=N, terpyridine), UV/VIS (suspension CHCl$_3$/MeOH, 1:1): $\lambda_{\text{max}} = 483$ nm (MLCT), 305 nm ($\pi^* \rightarrow \pi$, terpyridine), 58: FT-IR: 1716, 1662, 1610, 1543 cm$^{-1}$ (C=C, C=N, terpyridine), UV/VIS (suspension CHCl$_3$/MeOH, 1:1): $\lambda_{\text{max}} = 498$ nm (MLCT), 386, 367, 347 ($\pi^* \rightarrow \pi$, anthracene), 310 nm ($\pi^* \rightarrow \pi$, terpyridine), 59: FT-IR: 1716, 1662, 1610, 1543 cm$^{-1}$ (C=C, C=N, terpyridine), UV/VIS (suspension CHCl$_3$/MeOH, 1:1): $\lambda_{\text{max}} = 498$ nm (MLCT), 310 nm ($\pi^* \rightarrow \pi$, terpyridine), 60: FT-IR: 1716, 1662, 1610, 1543 cm$^{-1}$ (C=C, C=N, terpyridine), UV/VIS (suspension CHCl$_3$/MeOH, 1:1): $\lambda_{\text{max}} = 498$ nm (MLCT), 310 nm ($\pi^* \rightarrow \pi$, terpyridine), 61: FT-IR: 1716, 1662, 1610, 1543 cm$^{-1}$ (C=C, C=N, terpyridine), UV/VIS (suspension CHCl$_3$/MeOH, 1:1): $\lambda_{\text{max}} = 498$ nm (MLCT), 310 nm ($\pi^* \rightarrow \pi$, terpyridine).

**General procedure of the catalysis experiments:** 4 mg (calculated to determine the actual amount of the catalysts to ~0.001 mmol) of the metal-loaded microbeads were suspended in 1 mL of MeOH and 20 mg (0.17 mmol) styrene-oxide was added. Samples for GC-MS were taken according to the times mentioned in the text. Sample-preparation was done by taking 0.05 mL out of the reaction mixture and diluting it in 1 mL of chloroform.

**Decomplexation – recomplexation experiment:**

**Complexation:** 100 mg terpyridine functionalised beads 51 were suspended in a mixture of H$_2$O/THF (1/1, 120 mL) in a beaker equipped with a suspended stirring bar (Aldrich). 14 mg (~4 equivalents) of iron(II) chloride were added and the mixture was stirred at 50 °C for 24 h. The beads were then filtrated off and dried under reduced pressure (high vacuum) overnight. 4-5 mg of the dried material was taken for AAS measurements (sample preparation: see Chapter 5).

**Decomplexation:** 66 mg of the complexed beads were suspended in a mixture of H$_2$O/THF (1/1, 80 mL) and a 300-fold of HEEDTA (~7 g Trilon D solution) was added and the mixture was stirred at 50 °C for 24 h. The beads were then filtrated off and dried under reduced pressure (high vacuum) overnight. 4-5 mg of the dried material was taken for AAS measurements (sample preparation: see Chapter 5).

**Recomplexation:** 33 mg of the complexed beads were suspended in a mixture of H$_2$O/THF (1/1, 50 mL) and 4-5 mg (~4 equivalents) of iron(II) chloride were added. Subsequently, the mixture was stirred at 50 °C for 24 h. The beads were then filtrated off and dried under reduced pressure (high vacuum) overnight. 4-5 mg of the dried material was taken for AAS measurements (sample preparation: see Chapter 5).

The calibration curves (5 calibration points, 1 to 5 ppm) of all AAS measurements revealed an $R^2$-value of $\geq 0.995$. 
6.7 References

Summary

The research described in this thesis deals with the construction of new metallo-polymeric assemblies and materials based on terpyridine-metal complexation. First the synthesis of 4'-functionalised 2,2':6',2''-terpyridine building blocks is discussed, followed by the synthesis of different assemblies using some of these building blocks. Finally the modification of a polymeric bead-like material containing terpyridine units and its complexation behaviour towards different metal ions is described.

In the beginning of this thesis a family of molecular building blocks of terpyridines functionalised in the 4'-position was synthesised. The 4'-position was chosen in order to avoid more complex chiral structures upon subsequent complexation. Two major strategies were chosen for functionalisation. The first being the functionalisation from 4'-chloro-terpyridine via nucleophilic substitution reactions and the second being the functionalisation from its precursor, the 2,6-bis-(pyrid-2-yl)-4-pyridone, via electrophilic substitution. Using these strategies, a multitude of alkoxy-bridged functionalities, examples being chloro-, bromo-, carboxy-, amino-, thiol- or epoxy-moieties, could be attached to the terpyridine. All of the reported compounds were fully characterised by standard techniques including NMR- and UV/Vis-spectroscopy, MALDI-TOF- and/or EI-mass spectrometry as well as elemental analysis. Additionally, in some cases x-ray crystal structure determination could be carried out.

The organic synthesis of terpyridine building blocks was followed by complexation studies of 4'-functionalised terpyridines leading to novel assemblies. Two model-complexes of the above-mentioned functional terpyridines, leading to 4'-functionalised transition bis-terpyridine-metal complexes were synthesised and fully characterised, showing that complexation can be carried out in presence and without modification of the functional groups. On a more application-oriented level, different assemblies were synthesised. Using ruthenium(III)/ruthenium(II) chemistry, a di-terpyridine-perylene which was synthesised by using the amino-pentyloxy-terpyridine described previously, was complexed in a directed manner with unfunctionalised terpyridine units leading to a photophysically active triad where heteroleptic bis-terpyridine-Ru(II) complexes are spaced by a perylene moiety. Furthermore the combination of coiled coil peptide sequences and bis-terpyridine-Fe(II) has been investigated. Therefore a de novo designed coiled coil sequence was first functionalised with
the 4’-carboxy-alkoxy-terpyridine described previously. Subsequently complexation with iron(II) ions was studied in dependence of temperature, solvent and concentration. Methods like CD-spectroscopy and analytical ultracentrifugation (AUC) gave valuable insights into association behaviour and tertiary structure formation. A somewhat different approach towards coordination assemblies was the functionalisation and manipulation of gold-nanoparticiles by terpyridine-metal complexation. First experiments showed a significant change in the plasmon absorption depending on the addition of the thiol-functionalised terpyridine and iron(II). Additionally, metal binding studies were carried out by isothermal microcalorimetry (ITC) and UV/Vis titrations using different transition metal salts and 4’-chloro-terpyridine. The results could be compared to similar systems known from literature.

Focussing on the formation of coordination polymers, back-to-back di-terpyridines, bridged by non-chiral and chiral alkyl-dioxy and -thioxy chains of different lengths were synthesised by nucleophilic substitution of 4’-chloro-terpyridine using the same chemistry as described above. Subsequent complexation with metal salts led to the formation of larger assemblies, which could be proven by MALDI-TOF mass spectrometry as well as viscosimetry measurements. For the di-terpyridine monomers with a hexyl-dioxy spacer, metallo-macrocyclic rings could be separated and isolated. Similar observations were made for the chiral di-terpyridines where CD-spectroscopy could give additional valuable information concerning ring size and chirality transfer to the metal centre.

Finally, a hydroxy functionalised TentaGel® microbead material was functionalised with 4’-chloro-terpyridine, leading to a transition metal ion absorbing material. Complexation studies were carried out using different transition metal ions leading to differently coloured bead materials. The metal loading of the beads could be determined quantitatively by AAS measurements, which led to a significant difference in the case of copper ions. Preferably mono-terpyridine complexation instead of bis-terpyridine complexation as for the other investigated metal ions could be observed. Using ruthenium(III)/ruthenium(II) chemistry the terpyridine beads could be functionalised by heteroleptic complex formation with different 4’-functional terpyridines, bearing e.g. anthracene or polymer functionality. Finally, in the case of the loading with iron(II) chloride, the complexed iron(II) ions could be removed almost quantitatively by the reaction with the soluble competitive ligand HEEDTA. This led to the uncomplexed microbeads, which could be recomplexed nearly quantitatively with iron(II) chloride again, which was again proven by AAS measurements.
The investigations described in this work may add crucial experimental knowledge to the field of metallo-supramolecular assemblies and materials built up from 2,2':6',2"-terpyridines and should provide a solid basis for future investigations regarding such metallo-supramolecular species in bulk and on surfaces.
Zusammenfassung


Abschließend wurde ein hydroxy-funktionalisiertes Microbead-Material mit 4'-Chlor-Terpyridin funktionalisiert, welches zu einem Übergangs-Metall absorbierenden Material führte. Komplexierungs-Versuche mit verschiedenen Übergangs-Metall-Ionen führten zu verschieden-farbigen Materialien. Der Metal-Gehalt der Beads konnte mittels AAS-Messungen quantitativ bestimmt werden was zu einem deutlichen Unterschied für den Fall der Kupfer-Ionen führte. Es wurde bevorzugt mono-terpyridin Komplexierung statt bis-

Die in dieser Arbeit beschriebenen Untersuchungen könnten entscheidendes experimentelles Wissen zum Bereich der metallo-supramolekularen Assemblies und Materialien basierend auf 2,2':6',2''-Terpyridinen hinzufügen und sollten eine solide Basis für zukünftige Untersuchungen in Bezug auf solche metallo-supramolekulare Spezies im Bulk und auf Oberflächen bilden.
Curriculum Vitae

Philip R. Andres was born on September 8th 1971 in Summit, New Jersey (USA). After obtaining his high school degree (Abitur) in Neubiberg bei München in 1992, he studied chemistry at the Technische Universität München from 1992-2000. His diploma thesis dealt with the synthesis of 4’-functionalised terpyridines as building blocks for novel metallo-supramolecular assemblies and polymers. In 2000, he started working on his Ph.D. thesis at the Technische Universität München in the group of Prof. U. S. Schubert on supramolecular assemblies and materials based on terpyridine complexes. In 2001, he followed Prof. U. S. Schubert to Eindhoven University of Technology (Netherlands) to complete his Ph.D. work. The most important results of his research are presented in this thesis.
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Completing my PhD-thesis at the TU Eindhoven has brought me a lot of experience, not only on the scientific side of things but also in terms of getting to know a different culture and many nice and interesting individuals. Therefore I guess I was really fortunate to have had the chance of coming to Eindhoven and being able to do research in such a modern and pleasant environment.

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Philip
Publications

refereed


*non-refereed*


