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■ Supramolecular Chemistry

Supramolecular Macrostructures of UPy-Functionalized Carbon Nanotubes**

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Abstract: Carbon nanotubes (CNTs) are considered excellent materials for the construction of flexible displays due to their nanoscale dimensions and unique physical and chemical properties. By using the recognition properties of 2-ureido-4[1H]pyrimidinone (UPy), a versatile and simple methodology was demonstrated for the construction of macroscopic structures based on UPy-CNT/polymer composites

prepared by a combination of two functionalization approaches: 1) covalent attachment of UPy pendants on the multiwalled CNT surface (**UPy-MWCNTs**) and 2) directed self-assembly of **UPy-MWCNTs** within polymers bearing UPy pendants (**Bis-UPy 1** and **Bis-UPy 2**) by quadruple complementary DDAA–AADD hydrogen-bond recognition (D = donor, A = acceptor).

Introduction

In the future, display screens are expected to flex or roll during use in various application areas, such as transparent substrates, electrodes, light-emitting devices, dielectrics, coatings, and thin-film transistors.^[1] Carbon nanotubes (CNTs) are considered excellent candidates for this purpose due to their nanoscale dimensions and unique electronic, mechanical, and chemical properties.^[2] However, several processing issues, particularly purification and dispersion, have hindered their commercial uses. Although CNTs can be dispersed in various solvents by using stabilizing agents (e.g., surfactants), they tend to rebundle once the dispersing agents are removed. A successful strategy to address this problem and to attain flexible materials is supramolecular assembly of the CNT constituents.^[3] A variety of hydrogen-bonded supramolecular polymers have been pre-

pared by the recognition between complementary hydrogen-bond donor (D) and hydrogen-bond acceptor (A) moieties, which are directional and predictable noncovalent attractive forces. In particular, the 2-ureido-4[1H]pyrimidinone (UPy) functionality, developed by Meijer and co-workers, has opened the door for many new and exciting applications of quadruple hydrogen bonding due to its facile synthesis and self-complementarity.^[4] UPy strongly dimerizes through DDAA–AADD recognition due to the presence of four primary attractive hydrogen bonds, four attractive secondary interactions, and only two repulsive secondary interactions. The linear array of four hydrogen bonds is preorganized by an intermolecular hydrogen bond that further enhances the stability of the dimer, which results in association constants of 6×10^7 and $6 \times 10^8 \text{ M}^{-1}$ in chloroform and toluene, respectively. Additionally, we have demonstrated that the covalently attached hydrogen-bond moieties are robust enough to guide self-assembly of the supramolecular architecture of the CNTs, impart biodegradability properties to films, or be successfully removed by thermal treatments to recover the electronic properties of pristine CNTs.^[5] By using the recognition properties of UPy we demonstrate a versatile and simple methodology for the construction of macroscopic structures based on UPy–CNTs/polymer composites prepared by a combination of two functionalization approaches: 1) covalent attachment of UPy pendants on the multiwalled (MW) CNT surface to give **UPy-MWCNTs** and 2) directed self-assembly of **UPy-MWCNTs** within polymers bearing UPy pendants (**Bis-UPy 1** and **Bis-UPy 2**) by quadruple complementary DDAA–AADD hydrogen-bond recognition (Scheme 1).

The novel nanohybrid **UPy-MWCNTs** was fully characterized by thermogravimetric analysis (TGA), IR spectroscopy, transmission electron microscopy (TEM), UV/Vis spectroscopy, and ¹H NMR spectroscopy. Subsequently, the self-assembly and recognition properties of nanohybrid **UPy-MWCNTs** and its association with **Bis-UPy 1** and **Bis-UPy 2** (represented in Scheme 1)

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[**] UPy = 2-ureido-4[1H]pyrimidinone.

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Scheme 1. Chemical representation of the interaction of nanohybrid **UPy-MWCNTs** with polymers **Bis-UPy 1** and **Bis-UPy 2**.

were verified by fabrication of a 2D freestanding film and a 3D supramolecular gel by a simple and versatile solution-blending methodology.^[6]

Results and Discussion

MWCNTs were covalently functionalized by a diazonium-salt-based arylation reaction to yield amino-functionalized MWCNTs (NH_2 -MWCNTs (Scheme S1 in the Supporting Information). The UPy moieties were easily introduced by coupling with electrophilic 2-(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (Scheme S2 in the Supporting Information). The Kaiser test was used to quantify the free amino groups before and after the coupling to assess the covalent modification of the NH_2 -MWCNTs. This colorimetric assay gave a final average loading of UPy molecules attached to the MWCNTs of $567 \mu\text{mol g}^{-1}$. TGA confirmed the effective covalent grafting of the UPy moieties on the MWCNTs surface by a weight loss of approximately 24% w/w at 600°C that was not present in the pristine material, as shown in the temperature-modulated plot (Figure S1 in the Supporting Information). The IR spectrum of

UPy-MWCNTs (Figure S2 in the Supporting Information) shows the characteristic band of the pyrimidine carbonyl stretching vibration at $\tilde{\nu} = 1696 \text{ cm}^{-1}$ and the stretching mode of the urea group at $\tilde{\nu} = 1658 \text{ cm}^{-1}$.^[7]

Molecular recognition studies

After complete characterization of the covalent functionalization on the CNTs, we confirmed the noncovalent recognition properties of the UPy pendants of **UPy-MWCNTs**. The interaction between the UPy groups was evaluated by monitoring the dispersibility behavior of the nanohybrid **UPy-MWCNTs**. Nanohybrid **UPy-MWCNTs** was dispersed in polar solvent DMF, which is able to interact with the complementary sites through hydrogen bonds. In a second experiment, nanohybrid **UPy-MWCNTs** was dispersed in $CHCl_3$, which is a noncompeting solvent that is unable to generate hydrogen-bond interactions. The TEM images of **UPy-MWCNTs** always showed good dispersibility in DMF, whereas aggregates were observed in $CHCl_3$ (Figure 1).

As a second confirmation, we probed the ability of **UPy-MWCNTs** to form a strong and selective complex with 2,7-diamido-1,8-naphthyridine (NaPy) through quadruple hydrogen bonds between ADDA–DAAD arrays^[8] (Scheme 2).

The relative values of K_{dim} (UPy) and K_a (UPy–NaPy) in $CHCl_3$ (6×10^7 and $5 \times 10^6 \text{ M}^{-1}$, respectively) show a concentration-dependent selectivity, favoring heterodimer formation at concen-

Figure 1. TEM images of **UPy-MWCNTs** ($c = 0.1 \text{ mg mL}^{-1}$) in DMF (left) and $CHCl_3$ (right).

Scheme 2. Schematic representation of the equilibrium a) between the UPy dimer (blue; DAAD hydrogen-bonding array) and NaPy (red; DAAD hydrogen-bonding array) and b) between the UPy-MWCNTs dimer and NaPy.

trations above 10^{-5} M. Thus, complexation of NaPy with UPy-MWCNTs was followed by UV/Vis and ^1H NMR spectroscopy of samples with concentrations greater than or equal to 10^{-5} M in solution in apolar aprotic solvents (e.g., toluene and benzene) to avoid acidic hydrogen atoms or basic sites, which may interfere with the formation of hydrogen-bond interactions.

UV/Vis monitoring of the titration of NaPy ($c = 2.62 \times 10^{-5}$ M) by UPy ($c = 3.04 \times 10^{-4}$ M) in toluene is shown in Figure S3 (see the Supporting Information). The titration showed a progressive decrease in the absorption intensity of the NaPy band at $\lambda = 347$ nm and formation of a new band at $\lambda = 358$ nm. The UV/Vis spectra collected during titration of a solution of NaPy in toluene ($c = 2.52 \times 10^{-5}$ M) upon progressive addition of aliquots of a solution of UPy-MWCNTs in toluene ($c = 0.54 \text{ mg mL}^{-1}$, 3.08×10^{-4} M in terms of UPy functionalization) are displayed in Figure 2. The UV/Vis absorption during the titra-

tion showed a similar behavior to that for the titration of the pure molecules: a decrease in the absorption intensity of the NaPy band at $\lambda = 347$ nm and formation of a new band at $\lambda = 358$ nm, which clearly indicated binding between the NaPy molecules and UPy-MWCNTs.

The ^1H NMR spectrum of NaPy in $[\text{D}_6]$ benzene was obtained by using an inverse-detection nanoprobe. The spectrum showed two doublets: the first at $\delta = 8.71$ ppm and the second at $\delta = 7.36$ ppm corresponded to the four protons of the naphthyridine ring. A broad singlet at $\delta = 7.84$ ppm was observed for the two amidic protons (Figure 3a). Due to formation of the supramolecular complex NaPy/UPy-MWCNTs, the ^1H NMR spectra of NaPy showed a gradual upfield shift of the signal of the two protons of the naphthyridine ring at $\delta = 7.36$ ppm and a downfield shift of the signal of the two amidic protons from $\delta = 7.84$ ppm to $\delta = 8.19$ and 8.64 ppm in presence of 0.5 and 2 equivalents of UPy-MWCNTs, respectively (Figure 3b and c). Additionally, the shoulder at $\delta = 8.64$ ppm disappeared when deuterated methanol (1 μL) was added, which corroborated that the shoulder corresponded to

Figure 2. UV/Vis spectra collected during the titration of NaPy ($c = 2.52 \times 10^{-5}$ M) by UPy-MWCNTs ($c = 0.54 \text{ mg mL}^{-1}$) in toluene. Inset: NaPy (—), NaPy/UPy-MWCNTs 1:1 (—).

Figure 3. ^1H NMR spectra (500 MHz, C_6D_6): a) NaPy (1×10^{-3} M); b) NaPy (1×10^{-3} M) with UPy-MWCNTs (0.5 equiv, 5×10^{-4} M); c) NaPy (2.5×10^{-4} M) with UPy-MWCNTs (2 equiv, 5×10^{-4} M); d) NaPy (2.5×10^{-4} M) with UPy-MWCNTs (2 equiv, 5×10^{-4} M) and CD_3OD (1 μL).

the amidic protons (Figure 3d). When a UPy molecule was bound to an NaPy molecule a new signal appeared at $\delta = 5.79$ ppm (Figure 4b). This effect is also observed for **UPy-MWCNTs** bound to an NaPy molecule (Figure 4c). In the down-field region of the UPy spectrum three more signals appeared at $\delta = 13.74$, 11.32, and 9.82 ppm due to the complexation with NaPy (Figure 5a and b). These signals are also observed in the spectra of **UPy-MWCNTs** upon the addition of NaPy molecules (Figure 5c–e). Hence, we have unambiguously demonstrated the covalent attachment of UPy moieties to MWCNTs and the noncovalent recognition properties of **UPy-MWCNTs**.

Self-assembled macroscopic structures

The physical and chemical properties induced by the presence of the nanohybrid **UPy-MWCNTs** in two different polymer matrixes were studied. The DDAA–AADD recognition of **UPy-MWCNTs/Bis-UPy 1** (Scheme 1) allows the construction of homogeneous 2D freestanding films, whereas **UPy-MWCNTs/Bis-UPy 2** (Scheme 1) forms a gel stabilized by quadruple hydrogen-bonding interactions. In **Bis-UPy 1** (Scheme 1) the UPy units are attached to trimethylhexane spacers that consist of an equimolar mixture of two regioisomers (2,2,4- and 2,4,4-trimethylhexane) in racemic form. Concentration-dependent ring-chain equilibrium in **Bis-UPy 1** in its racemic form results in characteristic viscosity behavior.^[9] The specific viscosity of **Bis-UPy 1** in CHCl_3 is very low at low concentrations at which **Bis-UPy 1** is present as aggregates, but it increases very rapidly at higher concentrations at which polymeric chains are formed.^[10] Above the critical concentration, chain formation becomes more favorable and polymer growth occurs rapidly.^[11] Knowing this, a stable-blend solution of **UPy-MWCNTs** (1 mg mL^{-1}) and **Bis-UPy 1** (100 mg mL^{-1}) in CHCl_3 was achieved by sonication (Figure S4a in the Supporting Information). Control experiments were carried out by using trimethylhexane diisocyanate

(100 mg mL^{-1}) instead of **Bis-UPy 1** (Figure S4b in the Supporting Information) and, in a second trial, pristine MWCNTs (1 mg mL^{-1}) instead of **UPy-MWCNTs** (Figure S4c in the Supporting Information). Precipitation was always observed in the two different control experiments. These experiments demonstrate that the formation of quadruple hydrogen bonding within the supramolecular polymer significantly increases the dispersibility and stability of **UPy-MWCNTs** in CHCl_3 .

CHCl_3 dispersions of **Bis-UPy 1** (200 mg mL^{-1} , 240×10^{-3} M) and **Bis-UPy 1** (200 mg mL^{-1} , 240×10^{-3} M) premixed with **UPy-MWCNTs** (1 mg mL^{-1}) by ultrasonication were cast on a Teflon mold at room temperature to obtain homogeneous freestand-

Figure 4. ^1H NMR spectra (500 MHz, C_6D_6): a) UPy (5×10^{-4} M); b) UPy (5×10^{-4} M) with NaPy (2 equiv, 1×10^{-3} M); c) UPy-MWCNTs (5×10^{-4} M) with NaPy (2 equiv, 1×10^{-3} M).

Figure 5. ^1H NMR spectra (500 MHz, C_6D_6): a) UPy (5×10^{-4} M); b) UPy (5×10^{-4} M) with NaPy (2 equiv, 1×10^{-3} M); c), d), e) UPy-MWCNTs (5×10^{-4} M) with NaPy (2 equiv, 1×10^{-3} M).

ing membranes (Figure 6a). At this concentration polymeric chains are the predominant form of **Bis-UPy 1**.^[9] The nanocomposite film was characterized by scanning electron microscopy (SEM). The morphological analysis shows an increase in the

number of fibers in the **UPy-MWCNTs/Bis-UPy 1** freestanding film (Figure 6c and e) compared with **Bis-UPy 1** (Figure 6b and d). Higher amounts of fibers form in the composite probes with interconnection between the polymer molecules and **UPy-MWCNTs**.

Finally, the interaction of **UPy-MWCNTs** with a polymer matrix of a triblock polymer of PPG-PEG-PPG (PPG = polypropylene glycol, PEG = polyethylene glycol) (**Bis-UPy 2**) was studied. After sonication of a mixture of **Bis-UPy 2** (5 mg mL^{-1}) in CHCl_3 with **UPy-MWCNTs** (5 % w/w) a stable dispersion was obtained (Figure S5 in the Supporting Information). Control experiments demonstrated the importance of the quadruple hydrogen-bonding interaction.

UPy-MWCNTs (0.2 mg) were solubilized by sonication in a heated solution of **Bis-UPy 2** (50 mg mL^{-1} , 0.4 mL). The gel formed in few minutes at room temperature. To increase the viscosity of the solution in CHCl_3 to obtain a gel the concentration of the **Bis-UPy 2** polymer was raised to 50 mg mL^{-1} . Under these conditions, a homogeneous **UPy-MWCNTs/Bis-UPy 2** composite gel was obtained. The starting dispersion was heated to restructure the viscous solution, and **UPy-MWCNTs** (1 % w/w) was added and dispersed by sonication (Figure 7a). Then, rheology measurements were performed. Figures 7b and c show plots of the storage- (G') and loss modulus (G'') versus the strain amplitude at a frequency of 5 rad s^{-1} at 20°C for the **Bis-UPy 2** gel and **UPy-MWCNTs/Bis-UPy 2** gel, respectively. It was found that both gels present constant moduli between 0.1 and 1 % strain. Importantly, the values of

G' and G'' recovered after application of the strain force were the same for both gels: 2×10^5 and 2×10^4 Pa for the **Bis-UPy 2** and **UPy-MWCNTs/Bis-UPy 2** gels, respectively. However, in the **Bis-UPy 2** gel the moduli were not recovered after the strain

Figure 6. a) Blend-casting process for formation of the homogenous free-standing membranes of **UPy-MWCNTs/Bis-UPy 1**; b), d) SEM images of free-standing **Bis-UPy 1** and c), e) freestanding **Bis-UPy 1/UPy-MWCNTs** film.

breaking (Figure S6 in the Supporting Information). Instead, the **UPy-MWCNTs/Bis-UPy 2** gel was stable after the strain sweep, which made its rheological characterization possible

through a frequency sweep, by using a strain of 0.2% and applying a frequency sweep from 500 to 0.05 rad s^{-1} (Figure 7b and c). These experiments confirm that **UPy-MWCNTs** confer more stability to the gel network. Moreover, the morphological analysis shows that **UPy-MWCNTs** act as a scaffold for the creation of a fibrous network (Figure 6d and Figures S7 and S8 in the Supporting Information).

Conclusions

A new series of supramolecular self-assembled materials were produced by covalently attaching UPy functional groups to MWCNTs to give **UPy-MWCNTs**. Combination of the new nano-hybrid with appropriate Bis-UPy polymers allowed self-assembly of different macroscopic materials. The construction of a freestanding film or a supramolecular gel is achieved by simply changing the spacer between the two UPy functional groups. Morphological and rheological analysis verified that **UPy-MWCNTs** confer more stability to the polymeric networks. The UPy groups promote dispersibility of the **UPy-MWCNTs** in the polymer matrix and increase the contact points between the polymer units growing as fibers rather than aggregates. This work demonstrates that supramolecular motifs comprised of organic molecules covalently grafted to CNT surfaces can control the self-organization of CNTs by hydrogen-bonding recognition. In particular, we demonstrated that self-organization

of functionalized CNTs was a versatile and simple method for the construction of macroscopic structures based on MWCNT-polymer composite structures.

Experimental Section

Materials

All reagents and solvents were obtained from commercial suppliers (Sigma-Aldrich) and were used without further purification. MWCNTs 7000 series were purchased from Nanocyl (lot number MWM P031105, www.nanocyl.com).

Characterization techniques

Thermogravimetric analyses were recorded with a TGA Q500 instrument (TA Instruments) under a nitrogen flow by equilibrating the sample (1 mg) at 100 °C for 20 min and using a heating rate of 10 °C min⁻¹ up to 1000 °C. IR analyses were performed with an FTIR spectrometer (PerkinElmer 2000) on samples formed as KBr pellets. TEM analyses were performed with a TEM Philips EM208 by using an accelerating voltage of 100 kV. The samples were prepared by drop-

Figure 7. a), b) Schematic representation of the formation of the homogeneous **Bis-UPy 2/UPy-MWCNTs** gel; b) storage- (G' ■) and loss modulus (G'' ▼) for the **Bis-UPy 2/UPy-MWCNTs** gel versus strain; c) storage- (G' ■) and loss modulus (G'' ▼) for the **Bis-UPy 2/UPy-MWCNTs** gel versus the shear frequency; d) Atomic-force micrograph (AFM) images obtained on mica from a drop-casting dispersion of **Bis-UPy2/UPy-MWCNTs** (0.005:0.0025 mg mL^{-1}) in CHCl_3 .

ping an aliquot of the dispersion sample in the specified solvent onto a TEM grid (200 mesh, Nichel, carbon only). Absorption experiments were performed with a PerkinElmer Lambda 40 UV/Vis spectrometer at 20 °C in cells with an optical path length of 1 cm. All experiments were carried out at room temperature for solutions of NaPy (2.52×10^{-5} M) in toluene and were recorded from $\lambda = 280$ to 500 nm. The titration of the previous solution (2 mL) was performed by addition of known microvolumes of a solution containing UPy-MWCNTs (0.54 mg mL^{-1}) using an Eppendorf micropipette. The absorption of MWCNTs was subtracted from all UV/Vis titration experiments. ^1H NMR spectroscopy was performed with a Varian Unity Inova 500 spectrometer operating at 500.618 MHz, which was equipped with a 5 mm $^1\text{H}/\text{X}$ inverse-detection probe with a gradient capability and used a spin of 3 kHz. In a typical procedure, weighed amounts of NaPy, UPy-MWCNTs, and *N*-[(butylamino)carbonyl]-6-methylisocytosine were dissolved in D_2O (1 mL). The mixture was sonicated for 20 min then an aliquot (40 μL) of the resulting solutions was injected into an NMR tube. For the SEM measurements the samples were sputter-coated with gold in an Edwards S150A apparatus (Edwards High Vacuum, Crawley, West Sussex, UK) and examined with a Leica Stereoscan 430i scanning electron microscope (Leica Cambridge Ltd., Cambridge, UK). For the rheology measurements, gels were left in the rheometer (MCR Rheometer Series) for a few minutes before starting the measurements. The linear viscoelastic region was determined at 20 °C at a frequency of 5 rad s^{-1} by using strain values of 0.01 to 100%. It was found that the gels gave constant moduli between 0.1 and 1% strain. Frequency-sweep measurements were performed by using a strain of 0.2% and applying a sweep from 500 to 0.05 rad s^{-1} . Atomic-force micrographs were recorded under ambient conditions with silicon cantilever tips (PPP-NCH, 300–330 kHz, 42 N m^{-1} from Nanosensors) with an Asylum Research (Santa Barbara, California) MFP-3D-Bio instrument in noncontact mode under ambient conditions. Samples were prepared by drop-casting solutions of the analyte in CHCl_3 onto freshly cleaved mica surfaces.

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