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\(\pi\)-Conjugated Oligomers and Polymers with a Self-Assembled Ladder-like Structure

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Polyarylenes bear great promise as materials for applications in electronic devices.\(^1\) Unsubstituted polyarylenes are insoluble and difficult to process, while substitution of the polymers with solubilizing side chains forces consecutive aromatic units away from coplanarity.\(^2\) In order to solve this dilemma, substituted ladder polymers have been prepared, being both soluble and planar.\(^3\)–\(^6\) Ladder polymers are defined as uninterrupted sequences of fused rings. In the soluble \(\pi\)-conjugated ladder structures described so far, covalent bonds are used to join the \(\pi\) sequences of rings.\(^7\) Following the increasing interest in the use of secondary interactions in supramolecular chemistry, we like to present soluble \(\pi\)-conjugated oligo- and polyarylenes which self-assemble into ladders due to strong intramolecular hydrogen bonding between neighboring rings. Our concept of self-assembled \(\pi\)-conjugated ladder oligomers and polymers is based on the recent finding that strong intramolecular \(N\cdots-H\cdots-N\) hydrogen bonding planarizes the bipyridyl derivative \(1\)\(^8\). From the several options available to incorporate the principle of hydrogen bonding in a six-membered ring in self-assembled ladder-type structures, we selected polymer \(2\) and oligomers thereof, guided by the synthetic feasibility of this option.

The synthetic scheme for the synthesis of oligomers and polymers is depicted in Scheme 1. Crucial steps in the synthesis of both \(2a\) and the more soluble \(2b\) are the Stille coupling of 2,5-dibromopyrazine \(3\) with distannyl compounds \(4a\) and \(4b\), respectively (Scheme 1), and the preparation of the latter reactants. The synthesis of \(4a,b\) is based on the ortho-lithiation of a protected 1,4-phenylenediamine moiety as described by Tour et al.\(^9\) \(^8\). The Stille coupling,\(^10\) as optimized on oligomers, is performed in THF in the presence of \(\text{Pd(PPh}_3\text{)}_2\text{Cl}_2\) in combination with 5 mol % of \(\text{CuBr}\).\(^11\) The addition of \(\text{CuBr}\) is essential to guarantee high yields (over 95%) and high selectivities of the coupling.\(^12\) Under the same conditions, monomers \(3\) and \(4a,b\) were cross-coupled with corresponding monofunctional building blocks to furnish oligomers \(5a,b\), 6, and 7 (Table 1) in reasonable to good yields.\(^13\)

Scheme 1

![Scheme 1](image-url)
Table 1. Spectroscopic Data of Model Compounds and Polymers

<table>
<thead>
<tr>
<th>compd</th>
<th>$\delta_{H-N}^{a}$ (ppm)</th>
<th>$\delta_{H-13C}^{a}$ (ppm)</th>
<th>$\lambda_{\text{UV}}$ (nm)</th>
<th>$\epsilon_{\text{UV}}$ (cm$^{-1}$·mol$^{-1}$·L)</th>
<th>$\epsilon_{\text{IR}}$ (cm$^{-1}$)</th>
<th>$\epsilon_{\text{CV}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>10.7</td>
<td>8.7</td>
<td>440</td>
<td>3281</td>
<td>3285</td>
<td>-1.37</td>
</tr>
<tr>
<td>2b</td>
<td>11.7</td>
<td>9.26</td>
<td>446</td>
<td>3291</td>
<td>3288</td>
<td>-1.32</td>
</tr>
<tr>
<td>3a</td>
<td>11.22</td>
<td>8.73</td>
<td>362</td>
<td>3247</td>
<td>3307</td>
<td>-1.94</td>
</tr>
<tr>
<td>5b</td>
<td>12.56</td>
<td>9.24</td>
<td>362</td>
<td>3239</td>
<td>3263</td>
<td>n.d.$^{a}$</td>
</tr>
<tr>
<td>6</td>
<td>10.52</td>
<td>8.36</td>
<td>360</td>
<td>3290</td>
<td>3266</td>
<td>-1.73</td>
</tr>
<tr>
<td>7</td>
<td>10.59/8.85</td>
<td>399</td>
<td>3287</td>
<td>3246</td>
<td>1.41/1.2</td>
<td></td>
</tr>
<tr>
<td>10.55</td>
<td>8.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.60</td>
</tr>
<tr>
<td>8</td>
<td>8.73</td>
<td>7.34</td>
<td>332</td>
<td>3438</td>
<td>3419</td>
<td>n.d.$^{a}$</td>
</tr>
<tr>
<td>9</td>
<td>8.6</td>
<td>7.8</td>
<td>367</td>
<td>3329/3340</td>
<td>3340</td>
<td>3427</td>
</tr>
</tbody>
</table>

$^{a}$ In CDCl$_3$. $^{b}$ In KBr. $^{c}$ In THF. $^{d}$ vs standard calomel electrode.

From GPC analysis$^{15}$ (PLgel 5 µm/500A, CHCl$_3$), calibrated with oligomers 5a, 6, and 7 and molecular weights of 2a and 2b were determined to be $M_n = 2 \times 10^3$ (approximately 9 aryl units) and $M_w = 5.1 \times 10^3$ (approximately 18 aryl units), respectively. Furthermore, it was found that only odd-numbered oligomers were formed during polymerization. This result is consistent with the finding that 3 is preferably coupled twice in a Stille reaction. Finally, oligomer 8 and the corresponding polymer 9, both with two methyl substituents at the pyrazine moiety, were synthesized to reveal the influence of increased steric hindrance. From GPC analysis of 9, a molecular weight $M_w = 2.8 \times 10^3$ was determined.

Important physical properties of oligomers and polymers discussed are given in Table 1. $^1$H-NMR spectroscopy in CDCl$_3$ showed resonances at low field for the carbamate $N$–H protons of 2a, 5a, 6, and 7 at $\delta_{\text{H}} 10.5$–11.3 ppm and for the amide $N$–H protons of 2b and 5b at $\delta_{\text{H}} 11.7$–12.6 ppm. These data are indicative of strong hydrogen bonding and in correspondence with the donor–acceptor strength of the different units. The carbamate $N$–H protons at $\delta_{\text{H}} 8.7$ and 8.6 ppm for the methyl-substituted pyrazines 8 and 9 point to a much weaker hydrogen bond due to severe steric hindrance. The strength of the hydrogen bonds in 2 is established from NMR experiments at higher temperatures (a $\Delta\Delta T$ of $6.5 \times 10^{-3}$ K$^{-1}$ is measured for 6) and in the presence of acetic acid. However, in the presence of TFA, 2b is protonated and the hydrogen bonds are broken, accompanied by a shift of $\lambda_{\text{max}}$ of the long-wavelength absorption band from 446 to 369 nm.$^{15}$ The downfield anisotropic effect of the carbonyl group is proposed to be due to the coplanar orientation of the amide or carbamate functionality which points to H-3/3’. IR data recorded in chloroform and in the solid state are in agreement with the presence of intramolecular hydrogen bonds.

A gradual red shift of the long-wavelength absorption band in the UV–vis spectra upon increasing the number of repeating units is observed, while the extinction coefficients of oligomers and polymers are comparable. These transitions are explained by the alternating push–pull character of the $\pi$-conjugated system. Furthermore, the large difference in UV between 2a and 9 is in agreement with the $^1$H-NMR and IR data. We also examined the electrochemical properties of oligomers and polymers (Table 1). A reversible reduction potential is found for oligomers and polymers, presumably due to the electron-poor pyrazine rings in the systems under investigation. In contrast to this, we did not observe any reversible oxidations at approximately +1.7 V for 2a or 2b where they were expected on the basis of the band-gap. However, the reduction data clearly demonstrate the extended $\pi$-conjugation of the self-assembled ladder systems.

In conclusion, we have presented the use of intramolecular hydrogen bonds to obtain self-assembled ladder structures. In sharp contrast to the general observation that side groups give rise to steric hindrance and deviation from planarity in polyarylenes, we have used hydrogen bonded acylated amines to turn a repulsive van der Waals interaction between ortho substituents into an attractive hydrogen bond interaction to extend $\pi$-delocalization. Due to the versatility of the approach and the tunability of the structures, we are currently investigating the ultimate optical and electrical properties of this type of structure.

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(15) In oligomer 5b this band moves from 362 nm to a position which is obscured by a strong absorption at 300 nm.