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## Synthesis of Insulated Single-Chain Semiconducting Polymers Based on Polythiophene, Polyfluorene, and $\beta$ -Cyclodextrin

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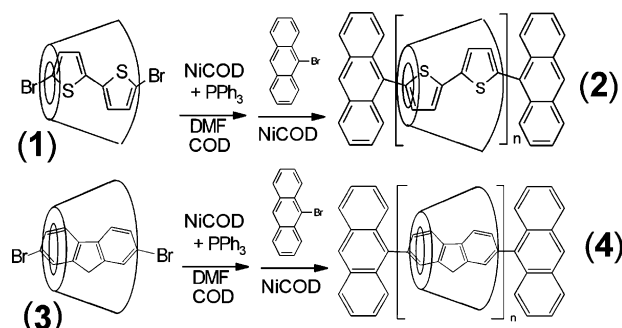
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Synthesis of soluble conjugated polymers is a first priority for their applications in plastics and molecular electronics.<sup>1–5</sup> Various strategies have been used in order to obtain soluble conjugated polymers, such as side chain substitution and precursor routes, just to name a few. Instead of modifying the polymer backbone with substituents, here a strategy based on polyrotaxane with a conjugated polymer as backbone and cyclodextrins (CDs: cyclic oligosaccharides, with a toroidal shape, having complexation properties, due to a hydrophobic interior and a hydrophilic exterior) as complexing rings to form a compact sheath is presented. This strategy not only leads to soluble conjugated polymers but also provides an opportunity to create insulated single-chain semiconducting polymers. Previously, the synthesis of soluble conjugated oligomers using a combination of the polyrotaxane with cyclodextrins and electrolyte side groups has been presented.<sup>6</sup> This elegant

Scheme 1. Reaction Scheme from Complexes to Polyrotaxanes



approach does not offer, however, the possibility to have a maximum coverage with the CDs, an essential requirement for fully insulated single polymer semiconducting chains.

Here, the synthesis and the visualization of two types of insulated semiconducting polymers, based on polythiophene (PT) and polyfluorene (PF), with a high coverage of  $\beta$ -CDs as the insulating sheath is described.

Scheme 1 presents the synthesis of conjugated polyrotaxanes. First, the monomers (5,5'-dibromobithiophene or 2,7-dibromofluorene) were complexed inside  $\beta$ -CD. The complexation has been realized in a mixture of water with a small amount of DMF.<sup>7</sup> The hydrophobic monomer is complexing into the cyclodextrin because its gain in enthalpy is higher than its entropy loss. It was found that complex **1** is more easily formed and isolated than complex **3**. The second step of the synthesis is the polymerization of the monomer complexes **1** and **3**. The Yamamoto<sup>8,9</sup> coupling in DMF with NiCOD as the catalyst, bipyridin or PPh<sub>3</sub> as the ligand, and COD (1,5-cyclooctadiene) as the cosolvent was used. At the end of the polymerization, an excess of 9-bromoanthracene as the bulky group<sup>10</sup> was used to cap the chain ends and prevent unthreading of the CDs.

For the polyfluorene, where the complexation step appears to be more difficult, another procedure has been used. It consists of adding directly the monomer 2,7-dibromofluorene in DMF with an excess of  $\beta$ -CDs.<sup>11</sup>

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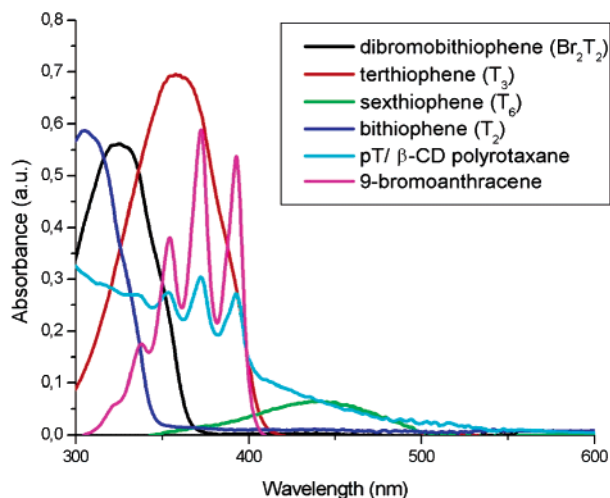
(7) Typically, the ratio DMF/water is around 1/20.

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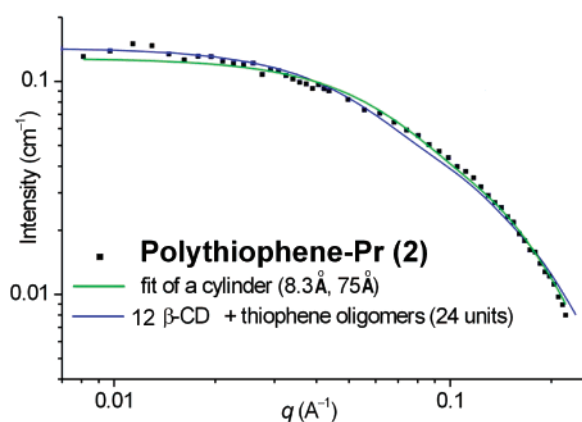
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(10) Experiments were done in a glovebox with dry and oxygen-free solvents and atmosphere. Typically, one uses 1 equiv of catalyst (NiCOD) per dry complex (based on the monomer inside), 2 equiv of COD, and 3 equiv of PPh<sub>3</sub>. The polymerization takes around 24 h at 60 °C. One adds then 1 equiv (compare to the monomer) of 9-bromoanthracene and 1 equiv of catalyst (NiCOD) and maintains a temperature of 60 °C for 16 h.

(11) Workup consists of successive centrifugation and precipitation in acetone and in water to remove non-water-soluble compounds. Yield is typically around 20%.



**Figure 1.** UV-Vis absorption spectra of polyrotaxane, stopper group, some thiophene oligomers, and monomer.

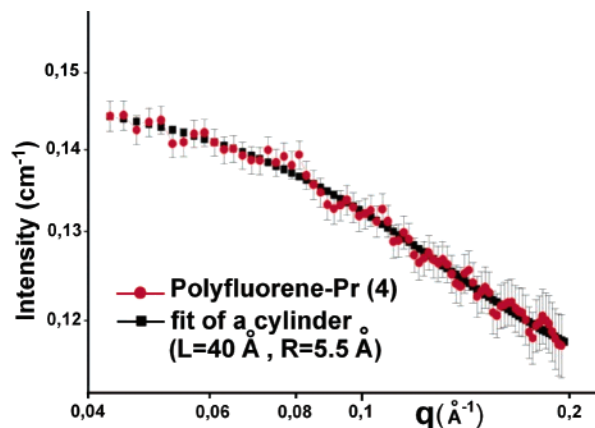


**Figure 2.** SANS of polyrotaxane (2), fitting, and simulations of the experimental data with a cylinder and molecular model, respectively.

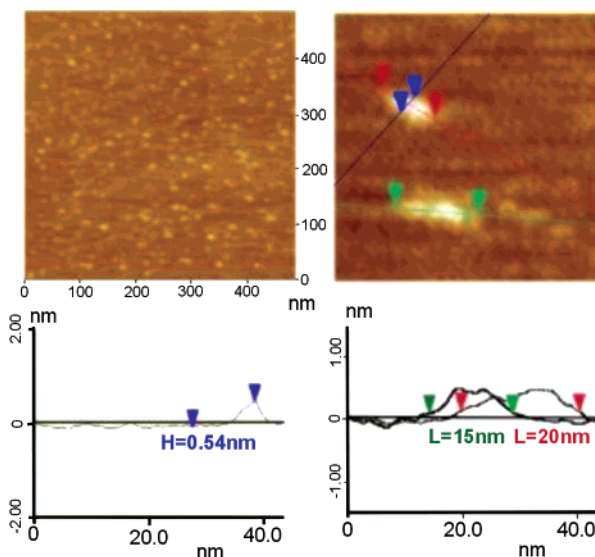
It can be concluded from the UV absorption spectra of **2** and **4** that the anthracene stopper groups are present in the polyrotaxane. The absorption extends to higher wavelengths than that of the oligomers, indicating a higher molecular weight of the conjugated polymer in the polyrotaxane<sup>12</sup> (e.g., **2**) (Figure 1).

Small angle neutron scattering (SANS) measurements have been performed on two types of polyrotaxane. After data reduction, important information about their length, molecular weight, and shape was obtained. The polythiophene data fit to a model cylinder with a length of 75 Å and a radius of 8.3 Å (Figure 2). This length indicates a polythiophene polyrotaxane composed of 12 bithiophene units. The molecular weight of **2** was estimated to be  $9.0 \times 10^3 \text{ g mol}^{-1}$  by extrapolating to  $q = 0$  scattering intensity. A polyrotaxane/CD complex containing 12 bithiophene units and 12 cyclodextrins would result in a molecular weight of  $14 \times 10^3 \text{ g mol}^{-1}$ . The difference in molecular weight can be rationalized by the fact that some cyclodextrins are unthreaded during the polymerization and before the capping reaction, yielding a polyrotaxane containing fewer cyclodextrins but still with a high coverage estimated to be approximately 60%.

(12) See <sup>1</sup>H NMR spectrum of polythiophene polyrotaxane in the Supporting Information.



**Figure 3.** SANS of polyrotaxane (4) and fitting of the experimental data with a cylinder model.



**Figure 4.** AFM measurements of the polyrotaxane (2).

Concerning **4**, the data fit with a cylinder of 40 Å and a radius of 5.5 Å (Figure 3). This length indicates a polyrotaxane composed of 5 fluorene units.

AFM images of **2**<sup>13</sup> agree with the results obtained by UV-Vis and SANS. Elongated features were observed with a length ranging from 15 to 20 nm (Figure 4). The height was found to be 0.54 nm, which is lower than the height of the widest side of the conical shape β-CD (1.5 nm) but higher than the diameter of the polymer. This finding is not surprising since we concluded, from SANS measurements, that the coverage of the conjugated polymer is around 60%, resulting in an average width of **2** between the diameters of the CDs and the polymer chain. The large-scale image (left) indicates an homogeneity in the distribution size of the particles.

Polyrotaxanes of semiconducting polymers/CDs with lengths between 4 and 20 nm have been prepared. Their collective and single molecular sizes were evaluated by SANS and AFM, respectively. Their solubility in solvents such as DMSO and water is only due to a more or less compact CDs sheath instead of the more common addition of solubilizing groups. In addition to providing

(13) This sample was obtained by adding a small amount of NMP to a solution of polyrotaxane in DMSO to break down the aggregates.

solubility to the polyrotaxane and facilitating manipulation at the single molecular level, the CD sheath also insulates the conjugated polymer, making the structure approach that of a molecular wire. These new molecular objects are currently being used to evaluate the semiconducting properties of conjugated polymers at the single-chain level.

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**Supporting Information Available:** Additional figures and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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