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A Self-Threading Polythiophene: Defect-Free Insulated Molecular Wires Endowed with Long Effective Conjugation Length

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Abstract: Herein, we report on a self-threading polythiophene whose conjugated molecular wire is sheathed within its own cyclic side chains. The defect-free insulating layer prevents electronic cross-communication between the adjacent polythiophene backbone even in the solid film. Notably, the covalently linked cyclic side chains extend the effective conjugation length of the interior polythiophene backbone, which results in an excellent *intrawire* hole mobility of 0.9 cm^2 V^{-1} s^{-1}.

Insulated molecular wires (IMWs) are conjugated polymers molecularly covered with an insulating layer, which are structurally analogous to electric cords in nanoscale.[1,2] Due to the "insulation" of the π-conjugated backbones, IMWs are expected to be applied to various optoelectronic applications and nanotechnology.[2,3] As recently reviewed by Frampton and Anderson,[1a] IMWs have mostly been prepared through polyrotaxane formation[4] or polymer wrapping approaches,[5] both of which depend on intermolecular interactions. Although a facile preparation procedure (i.e., just mixing two components) is a great advantage, the formation of structural defects is unavoidable because the supramolecular processes are governed by the thermodynamic equilibrium. To address this issue, synthetic approaches that afford defect-free IMWs have recently attracted much attention.[6] Particularly intriguing are the examples based upon *semiconducting* polymers such as polypyrroles and polythiophenes, which are as of yet scarcely developed.[7,8] A charge carrier confined within such one-dimensional transporting pathways not only leads to various electronic applications but also enables elucidation of the mechanisms of conduction.[1,6a] Herein, we report on a unique polythiophene whose conjugated molecular wire is sheathed within its own cyclic side chains. Notably, the covalently linked cyclic side chains enhance the effective conjugation length (ECL) of the interior polythiophene backbone, which results in an excellent intrinsic hole mobility.

A synthetic strategy has been implemented that allows access to a new class of sterically hindered thiophene derivatives. The unique three-dimensional architecture of our monomer is reminiscent of rotaxanes; however, the "ring" and "axis" are covalently connected. In other words, the molecular axis (i.e., bithiophene) is threading through its *own* cyclic side chain; accordingly, we prefer to refer to the monomer as a self-threading bithiophene (**1HSTB** and **1STB**).

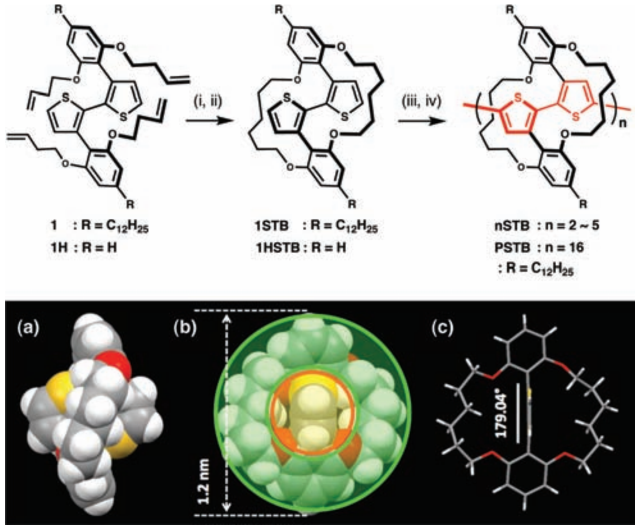

Figure 1. Synthetic route toward a self-threading polythiophene (**PSTB**): (i) second generation Grubbs catalyst, DCM, RT; (ii) H$_2$ gas, Pd/C, DCM/MeOH, RT; (iii) NBS, CHCl$_3$/AcOH, 0 °C; (iv) Ni(COD)$_2$, bipy, PhMe/DMF, 80 °C. (a) Lateral and (b and c) axial views of a self-threading bithiophene monomer (**1HSTB**) in crystallized form.

The monomers are sashed with alkyl chains that doubly crossover the two resorcinol units. Such a three-dimensional architecture is expected to prevent $\pi-\pi$ stacking interactions between adjacent polythiophene backbones. **1HSTB** was prepared in five steps (overall yield $\sim$60%) from commercially available materials and unambiguously characterized.[9] A double ring closing olefin metathesis (RCM) reaction is the key step that results in the cyclic side chain production exclusively, which was monitored by a ^{1}H NMR spectroscopic method (Figure S1).[9] In addition, this reaction is highly *trans*-selective as confirmed by the ^{1}H NMR spectrum and X-ray crystal structure.[9] The quantitative and regiospecific reaction suggests the perfect fit of the insulating layer to the girth of the bithiophene backbone.[10]

X-ray crystallographic analysis of **1HSTB** (after hydrogenation) shows that about a half of the bithiophene surface is indeed concealed (Figure 1a). Remarkably, the bithiophene backbone is nearly planar (torsional angle = 179.04°). This is noteworthy that ordinary β-substitutions cause dihedral twists, which in turn decrease the ECL.[11] From **1STB** as a monomer having solubilizing dodecyl groups, we have synthesized regioregular (head-to-head) insulated thiophene oligomers (**nSTB**, $n = 2-5$) and a polymer (**PSTB**) through bromination using NBS followed by Yamamoto reductive coupling. Using the isolated **nSTB**s as standards for analytical GPC, the molecular weight of **PSTB** was determined to be 14.4 kD (PDI

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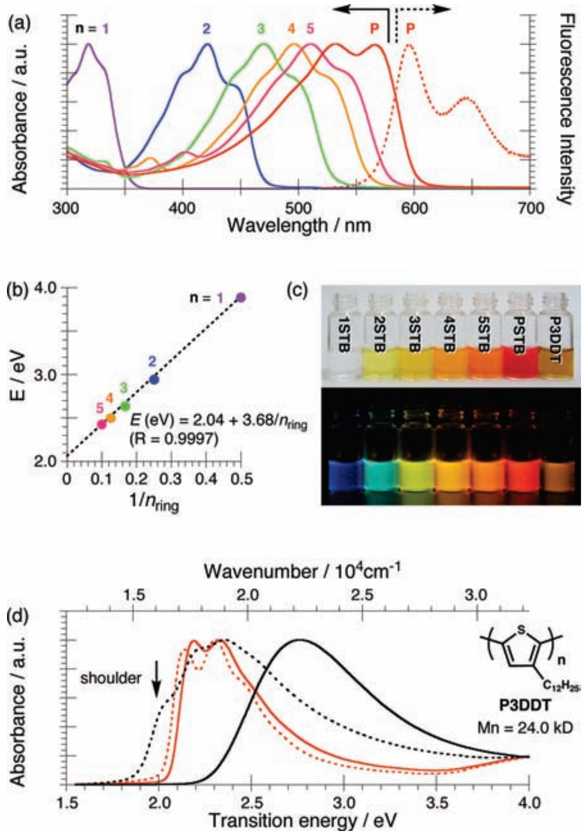

Figure 2. (a) Normalized absorption spectra of **nSTB**s ($n = 1-5$), **PSTB** (red), and fluorescence spectrum of **PSTB** (dotted red line). (b) Correlation between electronic transition energies (E) and inverse ring numbers ($1/n_{\mathrm{ring}}$) of **nSTB**s. (c) Photographs of the solutions of **nSTB**s ($n = 1-5$), **PSTB**, and **P3DDT** from left to right under room (top) and UV (bottom) light. (d) Absorption spectra of **PSTB** (red lines) and **P3DDT** (black lines) in solutions (solid lines) and spin-coated films (dotted lines).

= 1.4), which corresponds to 32 repeating thiophene rings (DP = 16).[9] A computer generated model of **PSTB** revealed its rod-like structure with a diameter of 1.2 nm, which shows good agreement with the height profiles of its AFM images (Figure S8).[9]

Figure 2a displays absorption spectra of **STB** derivatives. Unlike common oligothiophenes, **nSTB**s feature a vibronic shoulder at longer wavelengths, implying they possess rigid frameworks. As shown in Figure 2b, the short oligomeric **nSTB**s showed a good linear relationship between the transition energy (E) and the inverse ring number ($1/n_{\mathrm{ring}}$), which was fitted by eq 1.

$$E(\mathrm{eV}) = 2.04 + 3.68/n_{\mathrm{ring}} \qquad (1)$$

The coefficient for the **STB** backbone appeared to be 3.68, which is close to that of a nonsubstituted oligothiophene (3.73) and much larger than that of oligo(3-alkylthiophenes) (3.15).[12] Fluorescence spectral measurement revealed that **PSTB** exhibits a very small Stokes shift and a better fluorescence quantum yield (790 cm^{-1} and 0.61, respectively) compared to those of **P3DDT**[13] (4970 cm^{-1} and 0.41, respectively) in DCM at rt. These results clearly indicate that the symmetrial double crossovers restrain the rotational motion of the bithiophene's dihedral angle, thereby enhancing the ECL. We expect that our molecular design concept can endow the IMWs with a similar effect that is generally realized by ladder-type conjugated systems (i.e., the planarization effect).[14]

It is well-known that most conjugated polymers show a significant red shift of absorption maxima (λ_{max}) in the solid state. The black lines in Figure 2d display a typical example established with **P3DDT**; a red shift of λ_{max} by 3200 cm^{-1} and an appearance of a shoulder at 2.0 eV were confirmed due to the strong $\pi-\pi$ stacking of polythiophene in the solid state.[15] In clear contrast, **PSTB** showed almost identical absorption spectra between the solution and solid state (Figure 2d, red lines, $\Delta\lambda_{\mathrm{max}} = 210$ cm^{-1}). This characteristic was also confirmed for oligomeric **nSTB**s. The plot between E at λ_{max} vs $1/n_{\mathrm{ring}}$ in the *film* state was fitted with an intercept of 2.01 and a coefficient of 3.68, which are similar to the values determined in solution (see Figures 2b and S9).[9] These results indicate that electronic cross-communication between the adjacent polythiophene backbones is indeed impeded by the "insulating" layer even in the solid state.

Although the semiconducting backbone is molecularly "insulated", the spin-coated film of **PSTB** is electrochemically active and exhibits a reversible redox peak at $E_{1/2} = 340$ mV versus Fc/Fc$^+$.[9] Thus, the film of **PSTB** can be doped with I_2 vapor. The absorption spectrum of the I_2-doped **PSTB** film is typical of the bipolaronic species. Exhalation of I_2 from the film (i.e., dedoping) was accompanied by UV/vis/NIR spectral changes, which matches well to the polaron−bipolaron model for charge delocalized π-platforms.[9] These doping/dedoping processes are completely reversible, demonstrating the chemical stability of **PSTB**. Using a four-probe method, the conductivity of the I_2-doped **PSTB** film was determined to be 2×10^{-3} S cm^{-1}. This value was poorer by 2 orders of magnitude than that of the I_2-doped **P3DDT** film measured under the same conditions. Considering the long ECL (i.e., delocalized π-conjugation) of **PSTB** demonstrated above, the low conductivity at the *bulk* state should originate from the limited interchain transfer integral of **PSTB**.[1,16] In fact, a time-resolved microwave conductivity (TRMC) method proved that **PSTB** intrinsically has an excellent *intrachain* hole mobility of 0.9 cm^2 V^{-1} s^{-1}.[9,17] We expect that **PSTB** shows a significant difference in the contributions between the interchain and intrachain charge carrier transports in its conduction mechanism.[18,19]

In conclusion, we have succeeded in the synthesis of a self-threading polythiophene (**PSTB**). The polyrotaxane-like three-dimensional architecture has led to a unique polythiophene backbone featuring extended π-electron delocalization sheathed within defect-free "insulating" layers. Studies on structure−property relationships of **PSTB**, e.g. effects of the "ring" size[10] and covering ratio, are now underway. We believe that our polythiophene could find use not only as molecular electric cords in nanointegrated circuits but also as anisotropic conducting materials when aligned.

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Supporting Information Available: Synthesis and characterization of **nSTB**s and **PSTB**, AFM image, spectral and electrochemical data, and TRMC profiles of **PSTB**. This material is available free of charge via the Internet at http://pubs.acs.org.

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