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Insulated Molecular Wire with Highly Conductive π-Conjugated Polymer Core

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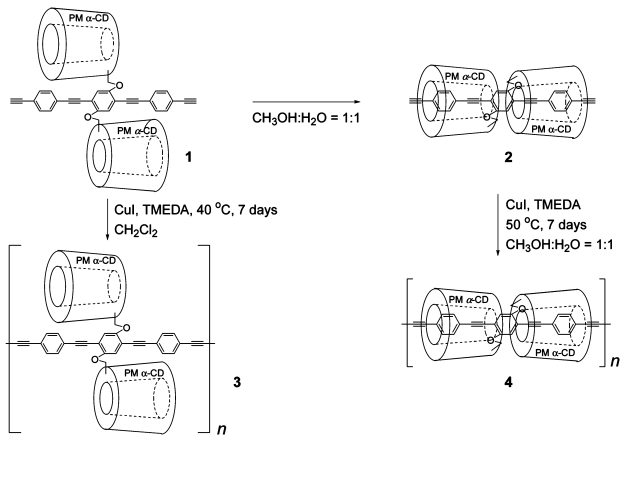
π-Conjugated polymers are often described as molecular wires because of their high charge mobility. The $\pi-\pi$ contacts between the chains can increase the conductivity of the material. However, encapsulation of the π-conjugated polymer increases the one-dimensionality of the conductance. This makes it interesting to study insulated molecular wires (IMWs), in which the conjugated polymer is encapsulated by a protective sheath that limits the $\pi-\pi$ interactions, thereby enhancing the conductivity relative to that of the corresponding uncovered π-conjugated polymers.[1] We have recently developed a new synthetic method for π-conjugated polyrotaxanes that involves the polymerization of permethylated α-cyclodextrin (PM α-CD)-based rotaxane monomers.[2] The IMWs are highly soluble in organic solvents and have a high covering ratio, rigidity, and photoluminescence efficiency. The rigid rodlike structure of the π-conjugated "core" polymers in these IMWs is thought to facilitate the effective transport of charge carriers. Herein, we report the morphology and charge mobility of PM CD-based polyrotaxanes as determined by atomic force microscopy (AFM) experiments and in situ time-resolved microwave conductivity (TRMC)[3] and transient absorption spectroscopy (TAS)[4] measurements, respectively.

Scheme 1. Syntheses of Fully Covered Polymer **4** and Uncovered Polymer **3** by Polymerization of **1** in Different Solvents



Highly insulated polyrotaxane **4** was synthesized by our previously reported method based on Glaser polymerization of **2** formed by the sequential intramolecular self-inclusion of **1** in a hydrophilic solution (1:1 CH_3OH/H_2O) (Scheme 1). As a reference, uncovered polymer **3** was synthesized by the polymerization of **1** in a lipophilic solution (CH_2Cl_2).

The morphology of **4** was investigated by performing AFM experiments using cleaved mica substrates. A highly dilute solution of high-molecular-weight polymer **4** ($M_w = 232$ kDa, $n = 84$, average length ≈ 200 nm) that was separated by gel-permeation chromatography (GPC) was used to prepare samples for the AFM experiments in order to avoid the aggregation of individual assemblies. From the AFM image and a section analysis (Figure 1), the expected average contour length and height of the polymer chains were determined to be ~200 nm and ~1.5 nm (equal to the outer diameter of the free PM α-CD calculated using the CPK model), respectively. In addition, the polymers had high linearity. A statistical analysis of the monomolecules of **4** yielded an average molecular length of 175 nm, which was close to the theoretical value calculated from the molecular weight, and the average molecular height was 1.4 nm (Figure S1 in the Supporting Information).

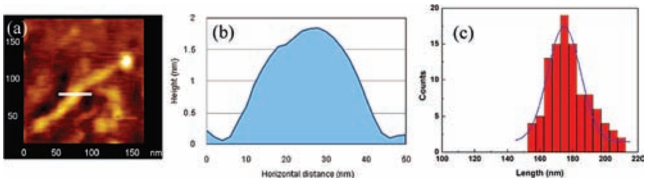


Figure 1. (a) Tapping-mode AFM image (175 nm × 175 nm) of **4** on a cleaved mica substrate. (b) Section analysis of the white line shown in (a). (c) Length histogram of **4** (for the height histogram, see Figure S1c).

The transparent nature of the solid phase of π-conjugated polymers enables both in situ flash-photolysis TRMC[4] and TAS measurements to be performed on the same solid film, and this makes it possible to carry out a thorough experimental and quantitative analysis of the intracore charge carrier mobility along the π-conjugated backbone. The polyrotaxane structure of **4** is expected to prevent π stacking of the conjugated main chains even in the solid phase, thereby increasing the lifetime of charged radicals in the conjugated backbone by preventing charge recombination processes. Direct UV (355 nm) excitation of **4** caused charge separation between polyrotaxane-conjugated core molecules and an oxygen residue with a low quantum yield, generating mobile holes on the conjugated cores (Figure S2). The observed conductivity transients were not single-exponential and were well-fitted with a double-exponential model. It should be noted that a low decay rate constant ($k \approx 4.2 \times 10^3$ s^{-1}) for **4** was estimated for the first component, resulting in an extremely long lifetime (τ) of ~200 μs, although rapid charge recombination ($\tau < 20$ μs) was observed in the case of **3**. This suggests that the insulating nature of the CD coating protects the holes in the core from being trapped by other molecules or fragments and/or recombination products. Next, the charge mobility of the polyrotaxanes in the solid state was examined by performing combined TRMC and TAS measurements. To increase the effective conjugation length in the core molecules, polyrotaxane **5**

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having only a poly(phenylene ethynylene) backbone, a diyne-free analogue of **4**, was synthesized by Sonogashira copolymerization of **2** with *p*-diiodobenzene rather than Glaser polymerization of **2** (eq 1). The formation of **5** was also confirmed by GPC, MALDI-TOF mass spectrometry (MS), and ^{1}H NMR spectroscopy. The obtained high-molecular-weight-polymer **5** (M_w = 321 kDa) was first fractionated by GPC and then analyzed by MALDI-TOF MS and NMR spectroscopy. From a CPK model of **5**, the covering ratio was estimated to be ~85%.

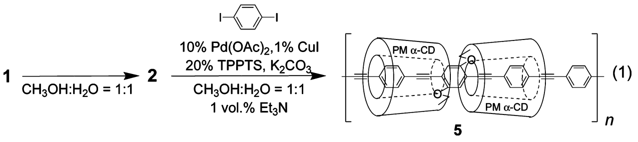

Figure 2 shows the observed kinetic traces of the transient conductivity and optical absorption of **5** upon irradiation by UV light (355 nm). For the quantitative analysis of photogenerated charge carriers, *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (PDCI) was used as an electron acceptor because of its high extinction coefficient ($\varepsilon_{\mathrm{PDCI}^{\bullet-}}$) of 7.4 × 10^4 cm^{-1} mol^{-1} dm^3 in the radical anion form.[6] The transient absorption spectrum showed a broad maximum at 600 nm, and the absorption was enhanced by the addition of PDCI to the film; this was confirmed from the distinct shoulder peak observed at 690 nm, which was attributed to the formation of PDCI radical anions (Figure S3). The absorption maximum was almost identical to that of PDCI$^{\bullet-}$ in solution, suggesting that the PDCI molecules were dispersed in the matrix of **5** without considerable aggregation. From the value of $\varepsilon_{\mathrm{PDCI}^{\bullet-}}$, the extinction coefficient of $\mathbf{5}^{\bullet+}$ ($\varepsilon_{\mathbf{5}^{\bullet+}}$) was estimated to be = 3.5 × 10^5 cm^{-1} mol^{-1} dm^3. The ratio of the oscillator strength of $\mathbf{5}^{\bullet+}$ to that of the singlet exciton transition of **5** at 375 nm was found to be ~3 by the numerical integration of the spectrum; this value was in good agreement with the ratio estimated by time-dependent density functional theory calculations (2.5) and that determined by singlet exciton bleaching at 410 nm (Figure S4). On the basis of the value of $\varepsilon_{\mathbf{5}^{\bullet+}}$, the concentration of [$\mathbf{5}^{\bullet+}$] was calculated at the pulse end from the TAS transient, and the photocarrier generation yield ϕ was found to be 3.4 × 10^{-4} immediately after pulse exposure. The value of ϕ for **5** was also confirmed to be 2 × 10^{-4} by photocurrent accumulation in a time-of-flight setup (Figure S5).[7]

Recently, it has been found that self-assembled discotic mesophases based on PDCI core molecules exhibit high charge carrier mobility of not only electrons but also holes, depending on the molecular packing.[8] However, PDCI$^{\bullet-}$ was observed as an isolated state in transient spectroscopy without a contribution from PDCI$^{\bullet+}$. The lifetime of the negative charge carriers on π-stacked PDCI (<10 μs) was also more than 10 times shorter than that of the conductivity transient shown in Figure 2. Thus, the excellent correlation between the two transients in Figure 2a clearly suggests that the positive charge on the π-conjugated core in the molecules of **5** contributed to the high conductivity of this compound over the entire time range. It is noteworthy that the minimum value of anisotropic hole mobility in the core estimated from the maximum value of ϕ (3.4 × 10^{-4}) was μ_+ = 0.5 cm^2 V^{-1} s^{-1}, which is 100 times that of **4** (μ_+ = 0.0045 cm^2 V^{-1} s^{-1}). From the anisotropic hole mobilities, the oscillating displacement of the charge carriers in an electric field (~10^2 V cm^{-1}) in a microwave cavity was estimated as ~5 nm with a turnover period of the microwave of 110 ps. This displacement is almost equivalent to the length of 5−10 repeating monomer units in **5** (1 unit = 0.68 nm from the optimized geometry of **5**); the number of repeating units in **4** was found to be <1. This is the first report of the formation of an almost perfectly insulated organic semiconductor wire in which the hole mobility along the π-conjugated polymer chain is extremely high and comparable to that in amorphous silicon.

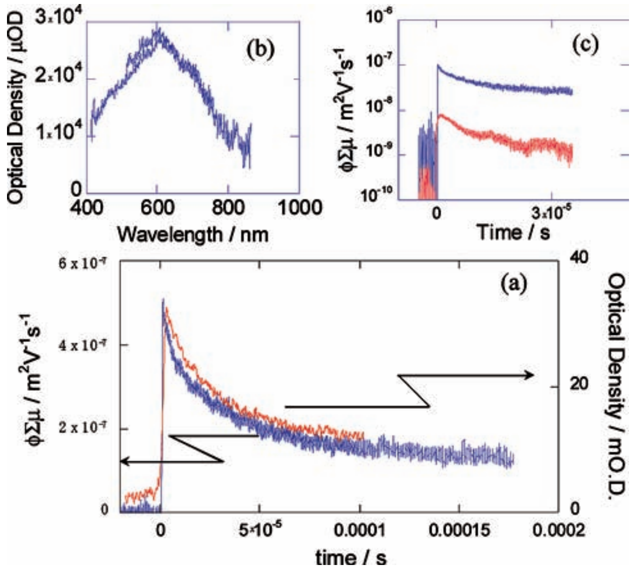

Figure 2. (a) Conductivity (blue) and optical absorption at 600 nm (red) transients of a thin film of **5** on a quartz substrate upon 355 nm excitation at 2.5 and 35 mJ cm^{-2}, respectively. (b) Transient absorption spectrum of **5** at 2 μs after pulse exposure. (c) Conductivity transients observed for **4** (red) and **5** (blue) upon 355 nm excitation at 4.6 × 10^{15} photons cm^{-1}.

In conclusion, we have synthesized a highly insulated molecular wire having a poly(phenylene ethynylene) backbone via Sonogashira copolymerization of a structurally defined rotaxane with a linker molecule. A combination of TRMC and TAS measurements revealed the formation of a highly insulating organic semiconductor wire in the solid state with extremely high hole mobility along the core π-conjugated polymer chain.

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Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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