A Long \( \pi \)-Conjugated Poly-\( \text{para} \)-Phenylene-Based Polymeric Segment of Single-Walled Carbon Nanotubes

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Supporting Information Placeholder

**ABSTRACT:** Conjugated polymers have attracted much attention for many years and have applications in various organic devices. Carbon nanotubes can be considered as all-carbon tube-shaped conjugated polymers containing only \( sp^2 \)-bonded atoms, which play an important role in nanotechnology and nanoelectronics. So far, no study has reported the realization of long \( \pi \)-conjugated polymers as diameter-specified carbon nanotube segments. Herein, we report the first synthesis of a \( \pi \)-conjugated polymeric segment (PS1) of armchair single-walled carbon nanotubes. PS1 is achieved by a rationally designed synthesis of a bifunctionalized cyclo-\( \text{para} \)-phenylene monomer, followed by inserting these ring-shaped units into the conjugated poly-\( \text{para} \)-phenylene backbone. Our PS1 was fully characterized by gel permeation chromatography (GPC) combined with NMR, FTIR, and Raman spectra. Its photophysical and unique electronic properties were also investigated. Possessing unique structural and physical properties, this long \( \pi \)-extended polymer PS1 can provide new insight for the development of bottom-up syntheses of uniform carbon nanotube segments and potential applications in electron-transport devices.

As a well-known prototype conjugated polymer, poly-\( \text{para} \)-phenylene (PPP) polymers have been widely studied, resulting in various synthesis approaches and the fabrication of photovoltaic devices. However, almost all direct aryl-aryl coupling reactions from 1,4-dihalobenzenes in solution to produce unsubstituted PPP lead to only low molecular weight oligomers (< 8 units). PPP is an insulator in neutral form, but its conductivity can increase to > 100 S cm\(^{-1} \) after chemical doping. From the point of view of chemical synthesis, PPP contains only \( sp^2 \)-carbon atoms and can be considered as conjugated segments of many carbon allotropes such as graphene, graphene nanoribbons, and carbon nanotubes (CNTs). Recently, Basagni and coworkers used a stepwise on-surface polymerization reaction to synthesize oriented graphene nanoribbons via the key intermediate of a PPP polymer. On the other hand, PPP polymers can also form carbon nanotube structures if these PPP polymers can be connected into cyclic conjugated structures with a fixed orientation.

Although CNTs have attracted much attention due to their unique electronic, optical, thermal, mechanical, and chemical properties, the practical applications of CNTs are significantly limited. Several major problems still exist, such as having no reliable methods to control the alignment during nanotube growth, difficulty in growing nanotubes with a fixed diameter and chirality, and no efficient method to separate random nanotube mixtures. Hence, the chemical synthesis of structurally uniform CNTs and highly conjugated CNT segments, is still a great challenge in chemistry and material science. In the last few years, bottom-up synthesis has emerged as a promising strategy and attracted much attention in the quest to develop different curved and/or cyclic aromatic structures. However, almost all the reported small precursors are CNT segments possessing only very limited 1D \( \pi \)-conjugated systems at the molecular scale.

To obtain a real CNT, it is highly desirable to extend the \( \pi \) systems longitudinally. Scott and coworkers proposed a Diels-Alder cycloaddition/reakomatization strategy to grow uniform diametric, single-chirality carbon nanotubes from molecular hydrocarbon templates, and this strategy has been successful for \( \pi \)-extension of small polyaromatic hydrocarbons. In 2014, using a surface-catalyzed cyclohydrogenation reaction, Fasel and coworkers obtained ultrashort singly capped [6,6]armchair nanotube seeds on a Pt(111) surface based on a hemispherical end-cap molecular template. Later, Zhu and coworkers successfully achieved nearly pure single-walled carbon nanotube (SWCNT) semiconductors based on structurally well-defined molecular end-caps to initiate nanotube growth.

![Scheme 1. The design of a long \( \pi \)-extended poly-\( \text{para} \)-phenylene-based polymeric segment of armchair [8,8] single-walled carbon nanotube.](image)

Herein we report the synthesis of a novel \( \pi \)-extended polymer (PS1) containing a cyclic conjugated macrocycle and a PPP backbone, which is a polymer constructed entirely from \( sp^2 \)-hybridized carbon atoms and represents the first polymeric segment of armchair [8,8]SWCNT. Possessing both linear and cyclic \( \pi \)-extended system, this conjugated polymer segment closely resembles a CNT. In this study, we design a bifunctionalized cyclo-\( \text{para} \)-phenylene that mimics the curved cyclic polyphenylene part of a CNT and a...
linear PPP backbone that mimics the linear polyphenylene part along the 1D direction of the CNT, as shown in Scheme 1. Our PS1 was fully characterized by gel permeation chromatography (GPC), as well as 1H NMR, Fourier transform infrared (FTIR), and Raman spectroscopies. In addition, its photophysical and electronic properties were investigated by UV-vis spectroscopy, fluorescence spectroscopy, time-resolved fluorescence decay, and the space charge limited current methods.

The successful synthesis of polymer PS1 from monomer 8 was confirmed by the combination of GPC, 1H NMR, FTIR, and Raman spectroscopies. The weight-average molecular weight (M_w), relative number-average molecular weight (M_n), and weight distribution of PS1 were measured by GPC (Figure 1a). The molecular weight distribution of PS1 shows a single broad peak with a polydispersity index of 1.44 and the number-averaged molecular weight is 16900 using polystyrene as the standard. To fully assign the aromatic protons in 8, we recorded the 2D 1H-1H COSY NMR spectrum (Figure S9). The multiplet at 7.53-7.48 ppm is correlated with the proton signal at 7.33 ppm, suggesting that the signal at 7.53-7.48 can be assigned to the d site and the doublet at 7.33 ppm belongs to the e site. Moreover, this proton signal at 7.24-7.18 ppm is correlated with the proton signal at 7.05-6.99 ppm, confirming the latter can be ascribed to the a site. It is found that, in PS1, d site and e site contain most of the protons (Figure 1b) and there are almost no protons at a site in 8. This result indicates that polymer PS1 has been successfully formed without destroying the cyclic structure of the monomer 8 unit.

The challenge of achieving the designed PS1 is to synthesize bifunctionalized cyclo-para-phenylene precursors with suitable bifunctional groups for polymerization. Our synthesis strategy is to connect the curved component and the bifunctionalized component into a cyclic molecule by a Pd-catalyzed Suzuki coupling reaction. The synthesis procedure of the bifunctionalized component is summarized in Scheme 2. Initially, 1,4-dibromo-2,5-phenylenediboronic acid (2) was synthesized from 1,4-dibromobenzene (1) by an iridium-catalyzed borylation reaction. Then, Suzuki-Miyaura coupling between 2 and 1-chloro-4-iodobenzene (3) in the presence of [Pd(PPh_3)4] catalyst produced compound 4 with a yield of >60%. Next, the Miyaura borylation reaction between compounds 4 and bis(pinacolato)diboron was conducted in dioxane at 90 °C to produce the bifunctionalized component precursor 5 with a good yield of >85%.

With the bifunctionalized component 5 in hand, the subsequent synthesis is embeds 5 into the ring-shaped carbon macrocyclic structure to fabricate the molecular bifunctionalized precursor 7 (Scheme 2). Under the standard conditions of the Pd-catalyzed Suzuki-Miyaura coupling reaction, the bifunctionalized component 5 reacted with a curved precursor 6 to give the key macrocycle intermediate 7. The targeted macrocyclic monomer 8 was then successfully obtained as a yellow solid after a reductive aromatization reaction with H_2SnCl_2. All these small molecules were fully characterized by 1H NMR, 13C NMR, and mass spectrometry (Figures S1-S8). In the last step, a polymerization reaction using 8 was carried out in dry DMF/toluene (v/v, 1:1) by nickel-mediated Yamamoto homocoupling reaction (Scheme 3). Finally, the π-extended polymer PS1 was obtained as a yellow solid with an excellent yield of >75%.
similar peak was also observed in the FTIR spectrum of PPP polymers. These FTIR results demonstrate that monomer 8 has been transformed into polymer PS1.

Moreover, Figure 1d shows the Raman spectra of PS1 (red plot) and 8 (black plot). In previous studies, the Raman peaks of PPP were located at 1215, 1285 and 1602 cm$^{-1}$ and the peaks of [8]cyclo-para-phenylene at 1200, 1262, 1505, and 1582 cm$^{-1}$. For 8, the main peaks are the D-band (1202 cm$^{-1}$ and 1264 cm$^{-1}$) associated with carbon macrocycle breathing, the G-band (1582 cm$^{-1}$) associated with C-C stretching, and a small peak at 1503 cm$^{-1}$ which is a peak associated with the G-band for PS1. The main peaks of the Raman spectrum are located at 1202, 1264, 1280, 1505, 1582, and 1602 cm$^{-1}$. Four of these peaks in PS1 (1202, 1264, 1505 and 1582 cm$^{-1}$) are consistent with the peaks for 8. Interestingly, compared to the Raman peaks in PPP, the other two peaks in PS1, located at 1280 and 1602 cm$^{-1}$, are comparable to the signals in PPP at 1215, 1285, and 1602 cm$^{-1}$, indicating the presence of the one-dimensional PPP backbone. The Raman spectra of PS1 and 8 further provide clear evidence of the presence of both cyclo-para-phenylene and linear PPP structures.

The PS1 was further characterized by UV-vis, fluorescence spectra, and time-resolved fluorescence decay in solution (Figure 2a). The absorption spectrum of PS1 shows an absorption maximum at 331 nm and an optical bandgap of 3.75 eV, which is slightly blue-shifted compared with those of monomer 8 (maximized at 337 nm) and [8]cyclo-para-phenylene (maximized at 340 nm). The absorption coefficient ($\varepsilon$) of 8 is ~4.95 × 10$^4$ L mol$^{-1}$ cm$^{-1}$. Also, the absorption spectra of polymer PS1 and 8 display an interesting shoulder peak at ~340 nm due to the presence of linear benzene rings.

The fluorescence spectra of PS1 and 8 show nearly the same maximum peak at ~540 nm (Figure 2b). By using anthracene as the reference ($\Phi_F = 30\%$ in ethanol), the fluorescence quantum yield for the 8 and PS1 were determined to be $\Phi_F = 22\%$ and $\Phi_F = 42\%$, respectively, which are much higher than in [8]cyclo-para-phenylene ($\Phi_F = 10\%$). The enhanced fluorescence quantum yield of PS1 may indicate a much longer and more rigid structure. The fluorescence colors of PS1, 8, and [8]cyclo-para-phenylene are shown in Figure 2b (inset). Time-resolved fluorescence decay measurements were conducted using a nanosecond pulsed laser system in a degassed CH$_2$Cl$_2$ solution at room temperature (Figures 2c-2d). The fluorescence decay of 8 follows first-order kinetics with a lifetime ($\tau_F$) = 7.1 ns at 534 nm when excited at ~390 nm. PS1 shows a similar single-exponential decay with a slightly longer fluorescence lifetime $\tau_F = 7.4$ ns at 534 nm. The similarity of the absorption, fluorescence spectra, and time-resolved fluorescence decay of PS1 and 8 in solution indicates that these optical properties are primarily governed by the cyclo-para-phenylenes and are slightly affected by the linear PPP backbone.

Considering the remarkable electronic properties of carbon nanotubes and related structures$^{40-42}$ and the novel polymeric structure of PS1 as a long polymeric segment of carbon nanotubes, we examined the potential application of PS1 as an electron-transport layer for optoelectronic devices on the electron mobility ($\mu_e$), which is measured by the space charge limited current (SCLC) method.$^{43}$

Electro-only ITO/ZnO/PS1/Ca/Al device was fabricated, as shown in Figure 3 (inset). Then, the $\mu_e$ value was calculated using the Mott-Gurney equation, revealing that the electron mobility of PS1 is ~2.0 × 10$^{-3}$ cm$^2$ V$^{-1}$s$^{-1}$ in the SCLC region (Figure 3). The measured electron mobility value of the electro-only ITO/ZnO/PS1/Ca/Al device indicates that polymer PS1 is promising for application in the electron-transport layer.

**ASSOCIATED CONTENT**

**Supporting Information**

Additional experimental data include Synthesis details,$^{1}$ H NMR,$^{13}$ C NMR, HR-MS, 2D NMR. This material is available free of charge via the Internet.

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**Notes**

The authors declare no competing financial interests.

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