

# Fusion at the Non-K-Region of Pyrene: An Alternative Strategy To Extend the $\pi$ -Conjugated Plane of Pyrene

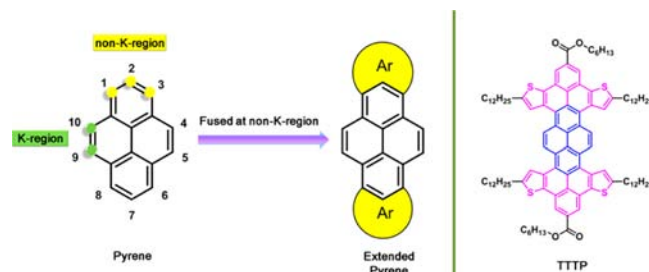
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## ABSTRACT



A large fused pyrene derivative TTTP was facily developed through fusion at the non-K-region of pyrene, which represents the first example of extending such a  $\pi$ -conjugated plane at its non-K-region. The investigation of its photophysical properties and other characterizations indicated that TTTP exhibited strong aggregation behaviors and self-assembled into highly ordered one-dimensional nanowires due to its large  $\pi$ -conjugated plane.

Developing fused polycyclic aromatics with large  $\pi$ -conjugated plane has been of great research interest due to their strong intermolecular  $\pi$ – $\pi$  stacking, which is beneficial to charge carrier transport in optoelectronic applications.<sup>1</sup> These  $\pi$ -extended molecules usually exhibit significant self-assembly properties, such as forming one-dimensional (1D) micro- and nanowires,<sup>2</sup> which show

great potential in electronic devices, such as organic field-effect transistors,<sup>3</sup> photodetectors,<sup>4</sup> and gas sensors.<sup>5</sup>

Pyrene, which has been widely investigated for its unique properties,<sup>6</sup> is a promising building block to develop new extended  $\pi$ -systems for organic optoelectronics. Among the reported pyrene derivatives, most of them were developed through connecting pyrene with other aromatic units (as shown in Figure 1b).<sup>7</sup> Recently, a few pyrene derivatives fused at the K-region were developed (as shown in Figure 1c), and they exhibited interesting properties.<sup>8</sup> However, extending the  $\pi$ -conjugated plane of pyrene by fusing at the non-K-region (as shown in Figure 1d) is still an

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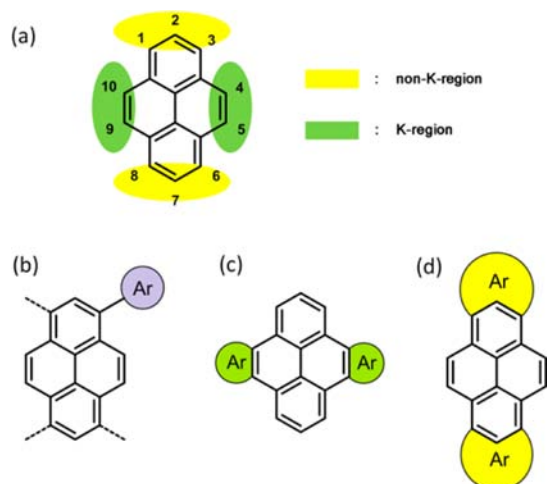
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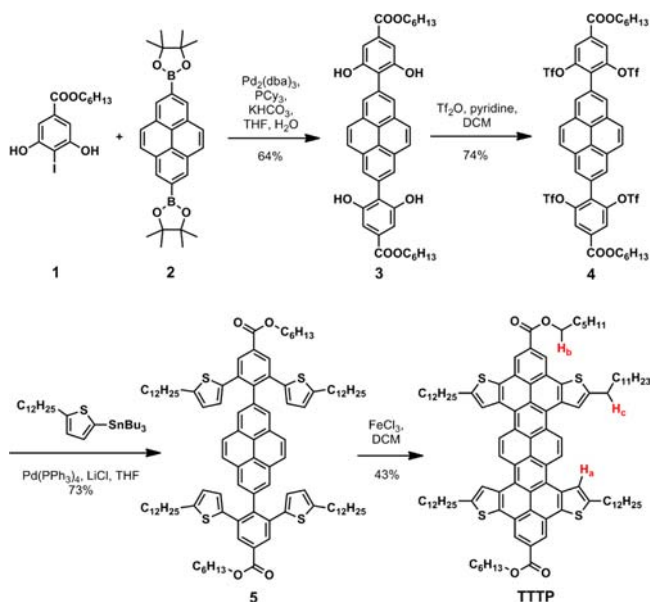
**Figure 1.** (a) K-region and non-K-region of pyrene; (b) functionalized at the active positions (1, 3, 6, 8-positions) by single bond connection; (c) fused at the K-region; (d) fused at the non-K-region, our work.

unexplored area, which is a challenge for developing new types of functional materials with unique properties due to the different conjugation modes.

Herein, we develop a new strategy to expand the  $\pi$ -conjugated plane of pyrene through fusion at the non-K-region, and a thiophene-fused “superpyrene” tetrathienopyrene (**TTTP**) has been achieved in high yield. **TTTP** represents the first example of non-K-region fused pyrene derivatives. Thiophene units are incorporated to further extend the  $\pi$ -conjugated plane and facilitate the final cyclization reaction. In addition, the incorporation of thiophenes is expected to improve the stability of the desired compound and provide intermolecular S–S interactions to promote ordered organization of molecules.<sup>9</sup> **TTTP** exhibits a strong self-assembly trend due to the enlarged  $\pi$ -conjugated plane, and highly ordered 1D nano-wires are obtained through the solution process.

The synthetic route to **TTTP** is shown in Scheme 1. Compound **1** was obtained by an iodination of 3,5-dihydroxybenzoic acid,<sup>10</sup> followed by alkylation with bromohexane. A palladium-catalyzed Suzuki coupling reaction between **1** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene

**Scheme 1.** Synthetic Approach to **TTTP**



(**2**)<sup>11</sup> gave compound **3** in 64% yield. The reaction between compound **3** and trifluoromethanesulfonic anhydride in the presence of pyridine gave compound **4** in 74% yield. A palladium-catalyzed Stille cross-coupling reaction of **4** with tributyl(5-dodecylthiophene-2-yl)stannane provided compound **5** in 73% isolated yield. A cyclo-dehydrogenation of compound **5** was performed by oxidative cyclization with  $\text{FeCl}_3$  to afford the target compound **TTTP**, constructing four C–C single bonds in one step. After purification by column chromatography and recrystallized from methanol, **TTTP** was obtained in 43% isolated yield as a dark-red powder. The overall yield of **TTTP** from compound **1** is around 15%. The six peripheral alkyl chains in **TTTP** guarantee the solubility of the large  $\pi$ -plane in common organic solvents, such as  $\text{CHCl}_3$  and chlorobenzene, and facilitate the solution processability. The structure and the purity of **TTTP** were fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and high resolution mass spectrometry (see the Supporting Information). To our knowledge, this is the first work to extend the  $\pi$ -conjugated plane of pyrene by fusing at the non-K-region.

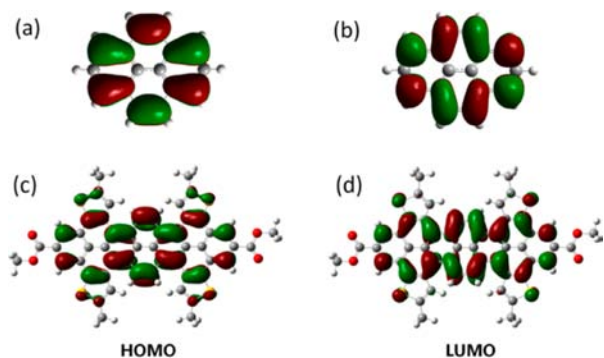
The thermal properties of **TTTP** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). **TTTP** shows good thermal stability with a high decomposition temperature of 375 °C under nitrogen atmosphere. Only a pair of phase transitions ascribed to the disturbance of alkyl chains (21 °C for cooling and 80 °C for heating) was observed before the decomposition temperature in DSC trace. The electrochemical property of **TTTP** in solution was investigated by cyclic voltammetry (CV) in acetonitrile containing 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte (see the Supporting Information). The HOMO and LUMO energy levels of **TTTP** are estimated from the onset of the oxidative peak and the optical energy gap ( $E_g^{\text{opt}}$ ) to be  $-5.21$  and  $-3.25$  eV, respectively.

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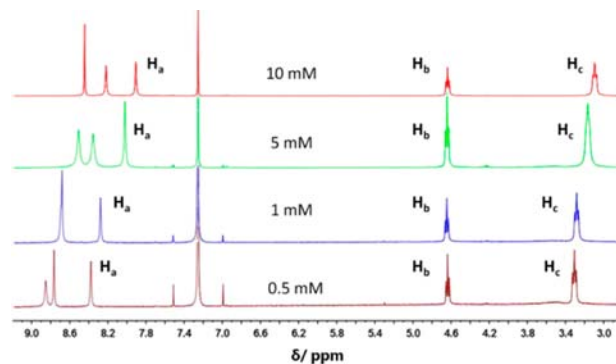
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**Figure 2.** HOMO and LUMO distributions of pyrene (a, b) and **TTTP** (c, d) calculated at the B3LYP/6-311G(d,p) level. The alkyl chains were replaced by methyl groups for computational simplicity.

To deeply understand the influence of the  $\pi$ -extension at the non-K-region on the geometry and electronic structure of pyrene, density functional theory (DFT) calculations were carried out at the B3LYP/6-311G(d,p) level. The long alkyl chains were replaced by methyl groups for simplicity. As shown in Figure 2, the optimized geometry of **TTTP** displays an almost planar  $\pi$ -skeleton, and both the HOMO and LUMO of **TTTP** are mainly delocalized over the entire backbone. Interestingly, nodal planes were observed in the HOMO and LUMO of **TTTP** as shown in Figure 2. The electron density distributes symmetrically at the two sides of the nodal plane both in HOMO and LUMO, which is quite similar to that in the molecular orbitals of pyrene. The nodal planes of pyrene's HOMO and LUMO lie perpendicular to the molecule skeleton and pass through the 2- and 7-positions.<sup>11b</sup> Therefore, the non-K-region fused pyrene derivative **TTTP** shows a similar electronic structure to the parent pyrene molecule and can be regarded as a thiophene-fused "superpyrene". The electron density distribution of **TTTP** is quite different from the ones extended at the K-region of pyrene,<sup>8</sup> in which no such a nodal plane exists, and this brings **TTTP** with new photophysical and electronic properties.

The self-assembly behaviors of **TTTP** with an extended  $\pi$ -plane were first examined by concentration-dependent  $^1\text{H}$  NMR characterization in  $\text{CDCl}_3$ . All three signals of the aromatic protons shifted upfield, and the distribution of resonances became wider as the concentration increased from 0.5 to 10 mM at room temperature, as shown in Figure 3. For instance, the signal at chemical shift  $\delta = 8.39$  ppm, which is assigned to  $\text{H}_a$ , shifted upfield to  $\delta = 7.91$  ppm as the concentration increased from 0.5 to 10 mM. Moreover, the signal at chemical shift  $\delta = 3.30$  ppm, which corresponds to the methylene group of dodecyl ( $\text{H}_c$ ), moves to  $\delta = 3.09$  ppm as the concentration increased. Interestingly, no shift was observed for the signal at chemical shift  $\delta = 4.63$  ppm when the concentration varied, which is assigned to a methylene group ( $\text{H}_b$ ) of hexyl chain connected with the ester group. The upfield shifts of the



**Figure 3.** Concentration-dependent  $^1\text{H}$  NMR spectra of **TTTP** (400 MHz, 298 K,  $\text{CDCl}_3$ ).

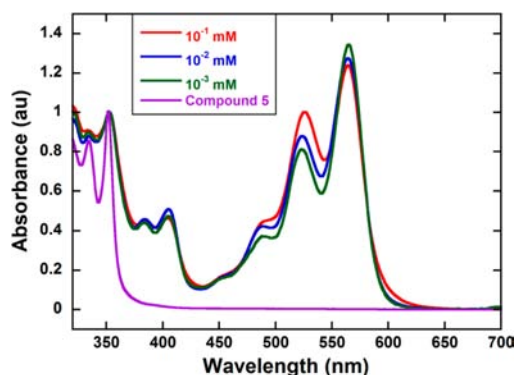
signals are a result of shielding from the ring current of neighboring aromatic molecules by cofacial stacking.<sup>3b,12</sup> Thus, we suppose that the molecules may stack along its short axis of the conjugated plane, so that the methylene protons of dodecyl locate above or below the conjugation plane, while the methylene protons of ester hexyl leave away from the large  $\pi$ -system. The overall results from the concentration-dependent  $^1\text{H}$  NMR behaviors indicate that the extended conjugated **TTTP** has a strong aggregation tendency.

Concentration-dependent absorption and photoluminescence spectra of **TTTP** were measured in  $\text{CHCl}_3$  to further investigate the intermolecular  $\pi$ - $\pi$  interaction. As shown in Figure 4, two absorption bands with well-resolved vibronic structures are observed in solution at different concentrations. The absorption maximum  $\lambda_{\text{max}}$  peaked at 565, 523, and 488 nm, which are attributed to the 0-0, 0-1, and 0-2 transitions, respectively. As the concentration increased from  $10^{-3}$  to  $10^{-1}$  mmol/L, the intensity of 0-0 vibrational absorption at 565 nm decreased and those of 0-1 and 0-2 vibrational absorptions at 523 and 488 nm increased. No shift of the absorption maximum  $\lambda_{\text{max}}$  was observed, which indicates an *H*-aggregation of **TTTP** in the high concentrated solution.<sup>13</sup> The photoluminescence features of **TTTP** in dilute solution ( $10^{-3}$  mmol/L) behave as a mirror-structure to its absorption spectrum, with two major vibrational emission located at 580 and 622 nm. As the concentration increased, significant redshift was observed (see the Supporting Information), also indicating an aggregation trend of **TTTP** in solution. As a comparison, the precursor **5** shows absorption features similar to those of 2-substituted pyrene derivatives<sup>11b</sup> in  $\text{CHCl}_3$ , peaking at 351 and 332 nm and without concentration-dependent phenomenon. After cyclization, the maximum absorption of the fused **TTTP** with a larger conjugated plane red-shifts to 565 nm. The redshift is much larger than those of similar pyrene

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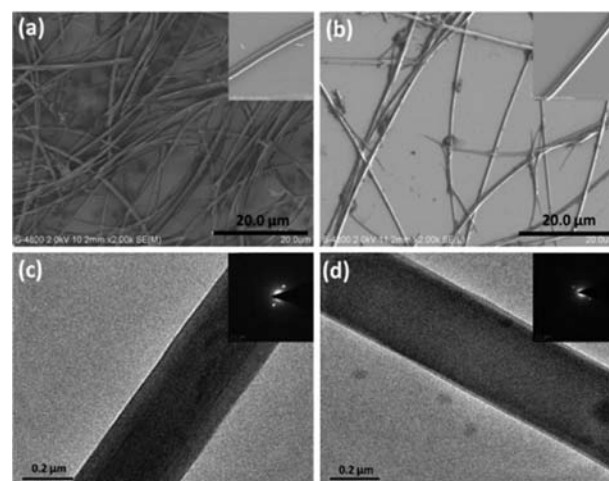
derivatives extended at the K-region.<sup>8b,c</sup> Potentially, extension of the  $\pi$ -plane at the non-K-region of pyrene is more efficient to tune the bandgap of fused pyrene derivatives.



**Figure 4.** Concentration-dependent UV-vis absorption spectra of **TTTP** in  $\text{CHCl}_3$  and UV-vis absorption spectrum of compound **5** in  $10^{-2}$  mmol/L (normalized at 350 nm).

1D nanowires were obtained through the self-assembly of **TTTP** in solution as shown in Figure 5a,b. First, a suspension of **TTTP** in 1,4-dioxane or cyclohexane was heated to form a homogeneous solution. Second, the solution was kept at a certain temperature and then cooled to room temperature slowly, allowing the molecules to self-assemble through  $\pi$ - $\pi$  interaction. Thus, 1D nanowires precipitate gradually in the solution. The nanowires obtained in 1,4-dioxane are about 500–800 nm in width and hundreds of micrometers in length, whereas those obtained in cyclohexane are much thinner and shorter, with a width around 300–400 nm. Deep analyses of these nanowires were performed by transmission electron microscope (TEM) and selected-area electron diffraction (SAED) as shown in Figure 5c,d. Both two kinds of nanowires exhibit the same diffraction patterns as analyzed by SAED, indicating the same ordered packing mode within the nanowires.

In summary, we have developed a facile strategy to extend the conjugated plane of pyrene by fusing at its non-K-region, which provides a new type of extended pyrene derivatives with unique properties. The cyclodehydrogenation reaction



**Figure 5.** SEM (a, b, scale bar: 20  $\mu\text{m}$ ), TEM (c, d, scale bar: 0.2  $\mu\text{m}$ ), and SAED (insets in c and d) analysis of the nanowires grown from 1,4-dioxane (a, c) and cyclohexane (b, d).

through oxidation with  $\text{FeCl}_3$  was performed successfully on a pyrene backbone to construct four C–C single bonds in one step, leading to the large conjugated molecule **TTTP**. **TTTP** exhibits electronic structures similar to the parent pyrene molecule, thus can be regarded as a thiophene-fused “superpyrene”. **TTTP** prefers *H*-aggregation in concentrated solution, which is beneficial to charge transport. Ordered 1D nanowires with high aspect ratios are also obtained, which are promising for the application in organic nanoelectronic devices.

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**Supporting Information Available.** Experimental details and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.