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Soluble Ladder Conjugated Polymer Composed of Perylenediimides and Thieno[3,2-*b*]thiophene (LCPT): A Highly Efficient Synthesis via Photocyclization with the Sunlight

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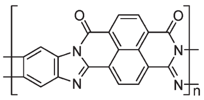
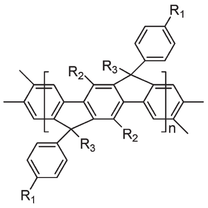
Supporting Information

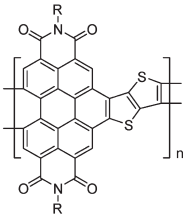
Organic semiconductors are an important class of electronic materials that offer intriguing prospects for high throughput, low-cost electronic circuitry on flexible substrates. Design and synthesis of novel organic semiconductors is essential work. Ladder conjugated polymers have rigid and planar frameworks, which enhance electron delocalization, conductivity, and thermal stability, and some of them have proved to be excellent organic semiconductors. For example, BBL with ladder planar conjugated system shows high performance in air-stable organic field-effect transistors and solar cells,[1,2] and LPPP and its derivatives with ladder conjugated systems have been utilized in efficient solution processable blue-light-emitting diodes.[3,4] At present, limited ladder conjugated polymers were reported, and some of them such as BBL,[5] polyquinoxalines,[6] and their derivatives were insoluble in organic solvent, which cause processing difficulties. Only limited methods[7−13] are feasible to obtain soluble ladder conjugated polymers due to challenges such as synthetic inaccessibility, poor solubility, and chemical instability, and thus the soluble ladder conjugated polymers are scarce. Considering their intriguing photoelectric properties and promising applications, intensive efforts should be directed toward novel design and highly efficient synthesis of those polymers.



BBL



LPPP



LCPT

Perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs) with planar and large aromatic core, high extinction coefficients, and near unity fluorescence quantum yield have showed wide range applications in solar cells[14,15] and field-effect transistors.[16−18] Thiophene oligomers,[19] fused thiophene-based polymers,[20] and especially thiophene-based polymer P3HT[21] were extensively investigated as excellent organic semiconductors.[22] Optical and electronic properties of donor−acceptor (D−A) conjugated polymers could be tunable through the intramolecular charge transfer from donor to acceptor, so design and synthesis of D−A type conjugated polymers is an effective way to obtain potential semiconductor polymers.[23,24] Many D−A type perylene−thiophene systems have been constructed for photovoltaic applications.[25−27] As a D−A type polymer, single-stranded copolymers of PDIs and thiophene derivatives show good performance in n-channel OFETs and solar cells.[28,29] However, there is still no report on ladder type perylene−thiophene systems.

Photocyclization is an efficient way to get ring-expanded compounds and has also been used in the cyclization of phenyl-substituted perylene diimides.[30] Recently, we first reported ladder conjugated perylene−ester-based oligomers which are synthesized by photocyclization under the sun.[31] However, the yields of several photocyclization reactions in our previous work are not quantitative, which will be a big obstacle in the synthesis of perfect polymers. Now, we found that photocyclization of **3** under sunlight in the presence of catalytic amount I_2 leads to quantitative cyclized product **4**, which opens a window to the synthesis of ladder type polymers by photocyclization, as shown in Scheme 1. On the basis of above highly efficient model reaction, we designed soluble polymer LCPT, which is a ladder conjugated copolymer of PDIs and thieno[3,2-*b*]thiophene. By photocyclization of single-stranded copolymer of PDIs and thieno[3,2-*b*]thiophene (SCPT) under the sun, LCPT was quantitative obtained (Scheme 1).

Because the extremely poor solubility of common PDIs and most ladder type molecules in organic solvents often hampers synthesis, characterizations, and further processing, we introduced bulky 12-tricosanyl groups to the imide sites. *N,N*′-Bis(12-tricosanyl)perylene diimides exhibit excellent solubility in dichloromethane, THF, toluene, hexane, etc., which makes further polymerization possible.

Photocyclization is the key in the synthesis of LCPT. As shown in Scheme 1, to check the feasibility of synthetic route for LCPT, reference compound **4** with planar aromatic core was synthesized by photocyclization first. Compound **4** was quickly obtained in quantitative yield just by illumination of **3** with the sunlight in the presence of catalytic amount I_2 in boiling toluene.

Precursor polymer SCPT was obtained by Stille coupling reaction of 1,7-dibromo-*N,N*′-bis(12-tricosanyl)perylene diimides (**5**) with **2** in 86% yield (Scheme 1), and the number-average

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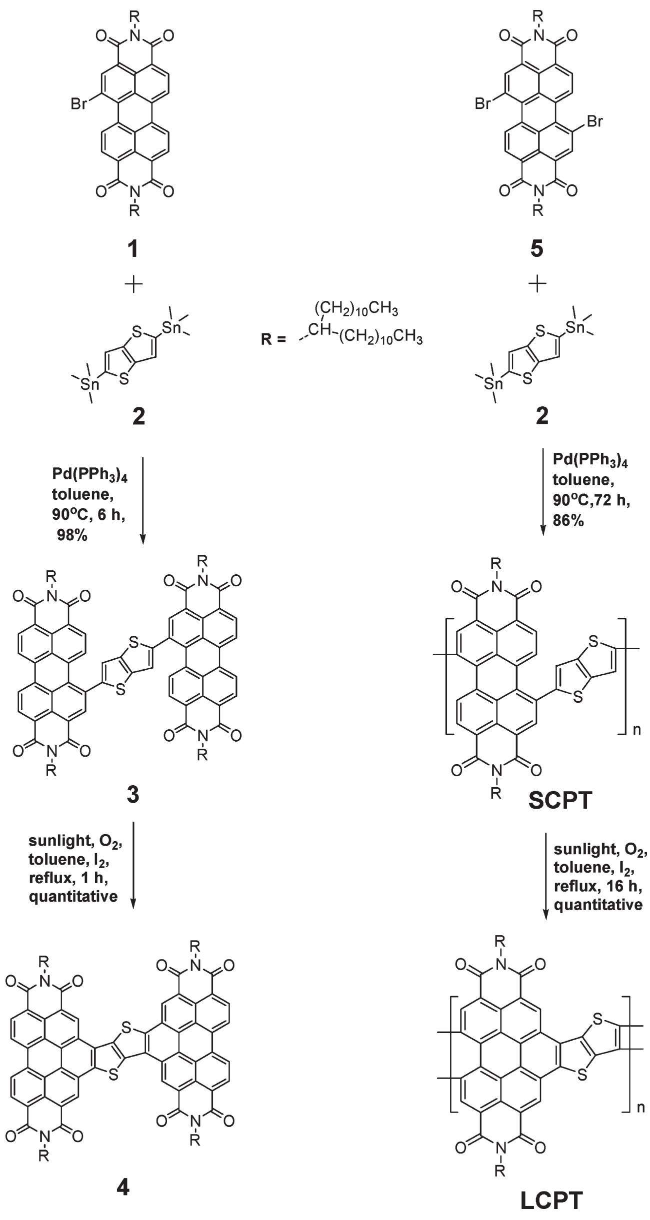
Scheme 1. Synthesis of 3, 4, SCPT, and LCPT



molecular weight and polydispersity index were estimated as 18 500 and 1.27, respectively, using GPC with polystyrene standards (see Supporting Information).

Target polymer LCPT was quantitatively obtained by illumination of SCPT with the sunlight in the presence of catalytic amount I_2 in boiling toluene; the color of above reaction mixture changed gradually from black to red, and meanwhile the fluorescence was from nothing to strong red emission; though the color unchanged 6 h later, another 10 h was taken to guarantee the thorough photocyclization of SCPT. Though SCPT shows excellent solubility in common organic solvent, higher than 30 mg/mL in chloroform or toluene, LCPT exhibits moderate solubility, about 7 mg/mL in chloroform or toluene at room temperature which is too low to be characterized by NMR, and LCPT shows poor solubility in solvents such as THF, hexane and CH_2Cl_2. To increase its solubility, H^1 NMR of LCPT was done in $Cl_2C_6D_4$ at 120 °C. In the low-field section of H^1 NMR spectra of LCPT, all the peaks for SCPT disappeared, and a broad peak (see Supporting Information) located at 10.0 ppm appeared; it was unable to get satisfactorily resolved ^1H NMR spectra of LCPT due to its poor solubility, which also existed in previous ladder conjugated porphyrin-based polymers.[8]

The electrochemical properties of SCPT, LCPT, **3**, and **4** were investigated by cyclovoltammetry (Figure 1). The two polymers and the two compounds all show two reduction peaks, indicating they can accept at least two electrons, while within the accessible scanning range in DMF or dichloromethane no oxidation waves could be detected. Both the first and the second reduction waves of LCPT are at 0.13 and 0.16 V lower potentials than those of SCPT, indicating a bit higher LUMO energy of LCPT relative to SCPT. The LUMO energy of LCPT is 3.98 eV (based on the assumption that the energy of Fc/Fc^+ is 5.08 eV relative to vacuum),[32] which indicates strong electron-accepting ability of LCPT. Compound **3** and **4** have the similar trend, and both the first and the second reduction waves of **4** are at 0.15 and 0.16 V lower potentials than those of uncyclized **3**.

To well explain different electrochemical and optical properties of LCPT, SCPT, **3**, and **4**, aromatic core structures of **3** and **4** were optimized, and their frontier molecular orbitals were calculated by the Gaussian 03 program, DFT-B3LYP/6-31G method, and the results are given in Figure 1. As shown in Figure 1, aromatic core of **4** was planar, while that of **3** was seriously twisted, and a 62° dihedral angle between perylene core and thieno[3,2-*b*]thiophene core exists. Serious twist of **3** may make electronic communication between perylene core and thieno[3,2-*b*]thiophene core more difficult than that in **4** and lead to different frontier molecular orbitals. For the aromatic core of **4**, electron density of HOMO and LUMO spreads over the whole core. While for aromatic core of **3**, electron density of LUMO is mostly localized on the perylene core. The calculated LUMO of **4** is 0.082 eV higher than that of **3**, and the HOMO of **4** is 0.218 eV lower than that of **3**. Consequently, the calculated band gap of **4** is 0.300 eV wider than that of **3**, and it is very near to experimental value (optical band gap of **4** is 0.31 eV wider than that of **3**). In a word, cyclized **4** with planar aromatic core shows a little higher LUMO energy, lower HOMO energy, and wider band gap relative to uncyclized **3**. And the above result offers an explanation for a bit higher LUMO energy of LCPT relative to that of SCPT. The planar structure of large conjugated system in LCPT increases electron communication between different conjugated units. Strong electron-accepting ability and good intramolecular electron communication make LCPT promising electron-accepting material.

Figure 2 shows the absorption spectrum of **3** and SCPT and absorption and emission spectrum of **4** and LCPT in $CHCl_3$. Though it displays a broad absorption across the range of 300−650 nm, LCPT exhibits a little blue shift absorption relative to SCPT, and it is consistent with wider band gap results from planar aromatic system. SCPT exhibits no fluorescence, and it may come from the following two reasons: (1) Because of incompletely conjugated aromatic system, electron transfer from thieno[3,2-*b*]thiophene core to perylene core may quench the fluorescence of the molecule. (2) Strong molecular vibration of SCPT may consume the most energy and make it nonfluorescent. While LCPT is a strong fluorescent material with a fluorescence quantum yield of 0.20, and it is may be derived from the rigid conjugated core of LCPT. Broad absorption and strong fluorescence make LCPT potential light harvesting or photoelectric materials. Time-dependent UV−vis absorption changes for compound **3** and SCPT during

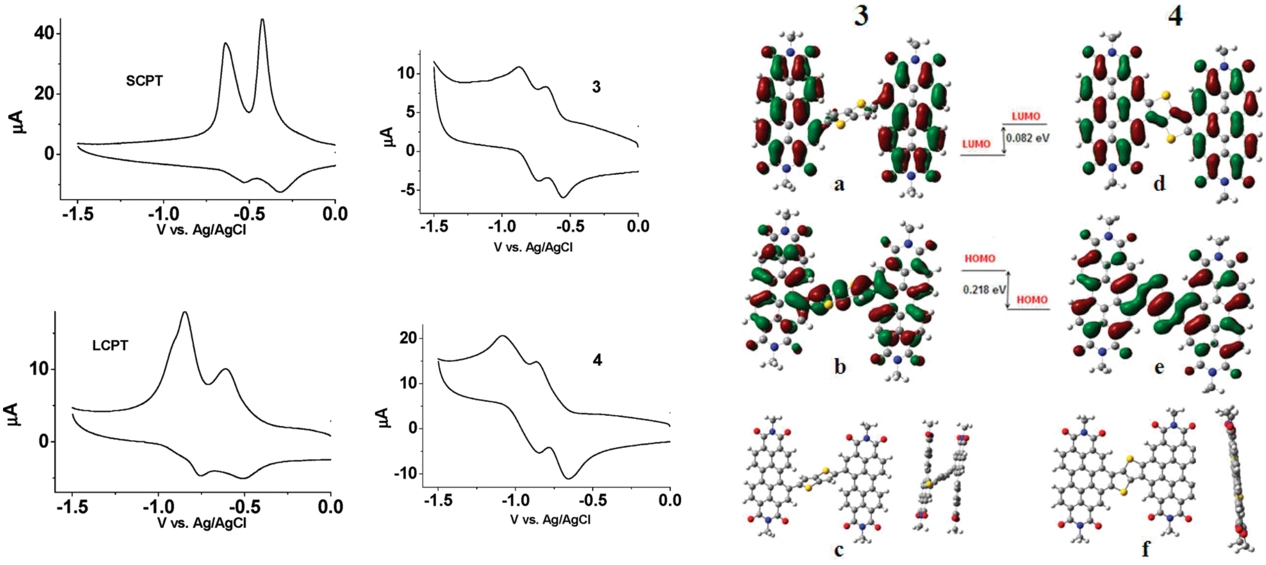


Figure 1. Reductive cyclic voltammograms of SCPT, LCPT, **3**, and **4** (left, vs Ag/AgCl). Optimized structures (c, f), HOMO (b, e), and LUMO (a, d) of aromatic core for **3** and **4** (right, a, b, c for **3**, and d, e, f for **4**).

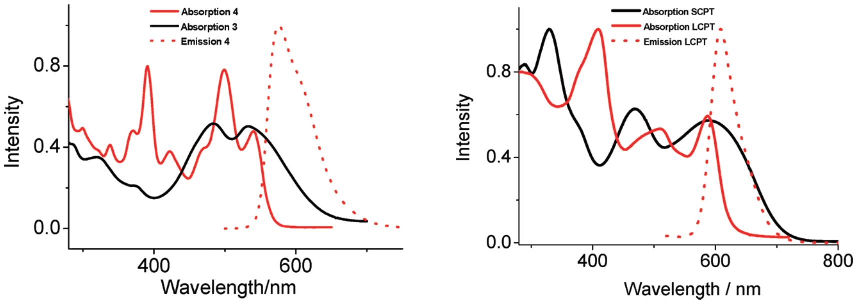


Figure 2. Absorption of **3** and SCPT and absorption and emission of **4** and LCPT in $CHCl_3$.

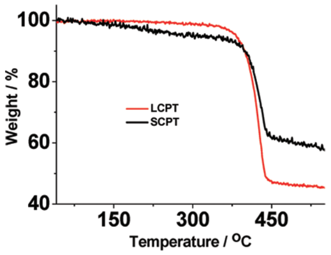


Figure 3. TGA curves of SCPT and LCPT at a heating rate of 10 °C/min under ambient conditions.

photocyclization were also investigated in toluene. It is clear that both of them underwent a gradual absorption change during photocyclization (see Figure S1 in Supporting Information).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of SCPT and LCPT were performed at the scanning rate of 10 °C/min under ambient conditions. As shown in Figure 3, LCPT shows much better thermal stability than SCPT, and the 5% weight loss temperature of LCPT (380 °C) is 60 °C higher than that of SCPT (320 °C). DSC measurement of the two polymers did not show any transitions in the range from room temperature to 350 °C (see Supporting Information).

In summary, for the first time, photocyclization with the sunlight was employed as a highly efficient and easy accessible method to obtain soluble ladder conjugated polymer. With this method, soluble ladder conjugated polymer composed of perylenediimides and thieno[3,2-*b*]thiophene (LCPT) was obtained in quantitative yield by photocyclization of SCPT. LCPT, with a planar large conjugated system, exhibits strong electron accepting ability, broad absorption, strong fluorescence, and excellent thermal stability, which make it not only an interesting object of fundamental importance but also a potential photoelectric material. Investigations on their performances in devices are in progress.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** All the characterization data and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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