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Controllable and Stepwise Synthesis of Soluble Ladder-Conjugated Bis(Perylene Imide) Fluorenebisimidazole as a Multifunctional Optoelectronic Material

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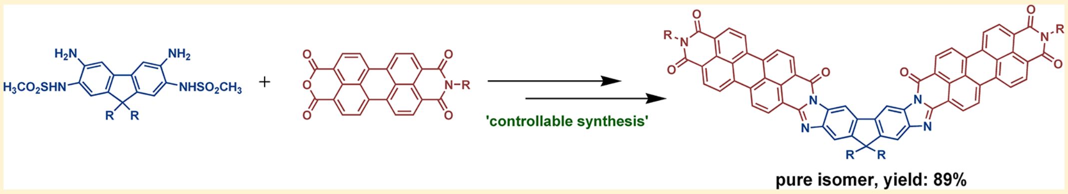
Supporting Information



ABSTRACT: By a controllable and stepwise strategy, a soluble ladder-conjugated perylene derivative **BPI-FBI** as the only product has been synthesized, which avoids the tough work to isolate regioisomers generated by a conventional one-step condensation method. **BPI-FBI** exhibits broad absorption spectra covering the whole visible region from 300 to 700 nm because of the large π-conjugation skeleton and has a low LUMO level inheriting the prototype PDI. In the steady-state space-charge-limited current (SCLC) devices, **BPI-FBI** exhibits an intrinsic electron mobility of 1.01×10^{-5} cm^2 V^{-1} s^{-1}. With a high two photon absorbing activity in the near-infrared region from 1200 to 1400 nm, **BPI-FBI** also exhibits good optical limiting performance, which will be useful for sensor or human eye protection and stabilization of light sources for optical communications.

INTRODUCTION

Organic ladder-conjugated molecules, in which the conjugated monomers are fused simultaneously with two single/double bonds to form ladderlike frameworks, have attracted much attention because of the advantages of high resistance to mechanical, thermal, and chemical degradation.[1−11] Ladder-conjugated perylene/naphthalene carboxylic benzimidazoles, always synthesized by the condensation of aryl-ortho-dianhydride and aryl-ortho-diamine,[12−15] have been demonstrated with high electron-transporting mobility, superior light absorption in the wavelength range of visible light and large two-photon absorption (2PA), which endow them with extensive applications in organic electronic devices and nonlinear optical devices.[16−22] As a representative and extensively studied ladder-conjugated polymer, **BBL** (Figure 1a) exhibited high conductivities and had successfully been used in bilayer organic solar cells.[23,24] Furthermore, in the optical nonlinearities, the ladder-conjugated molecules bis(benzimidazo)perylene (**BBIP**) (Figure 1b) possess exceptionally high 2PA cross sections in the wavelength range from 700 to 1000 nm and realizes an application in optical power limiting.[22] However, there remain two intertwined issues to be addressed for the widespread applications of these promising ladder conjugated materials. On the one hand, the materials' impurity cannot be ignored to impact the device performances, which is caused by the fact that most ladder molecules are the mixture of a lot of regioisomers rather than the single ones. On the other hand, the poor solubility resulted from their rigid and planar frameworks makes it infeasible to fabricate the organic electronic devices by the solution-processed way. While the improvement of solubility is indeed a helpful factor for the purification, this cannot always guarantee the successful isolation of pure regioisomers. Klaus Müllen et al. reported a series of soluble ladder-conjugated perylenebisamidine derivatives via a convenient one-step synthetic scheme. Although these chromophores exhibit good solubility by introducing four aryloxy groups in the bay regions of the perylene core, the final products are the mixture of syn/anticonfigurations (Figure 1c).[25] Therefore, developing the soluble ladder-conjugated perylene/naphthalene derivatives for solution-processed devices and how to obtain the pure isomers are the challenging projects for organic electronics.

In the past years, we have been engaged in the development of soluble n-type ladder-conjugated molecules based on perylene/naphthalene diimides (PDI/NDI).[26−29] Compared with the benzene-based ladder-conjugated PDI/NDI derivatives, the fluorene-based ones are easier to realize high

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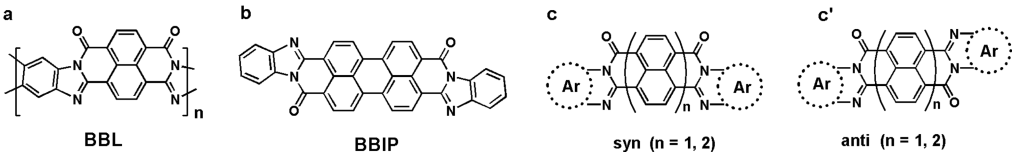
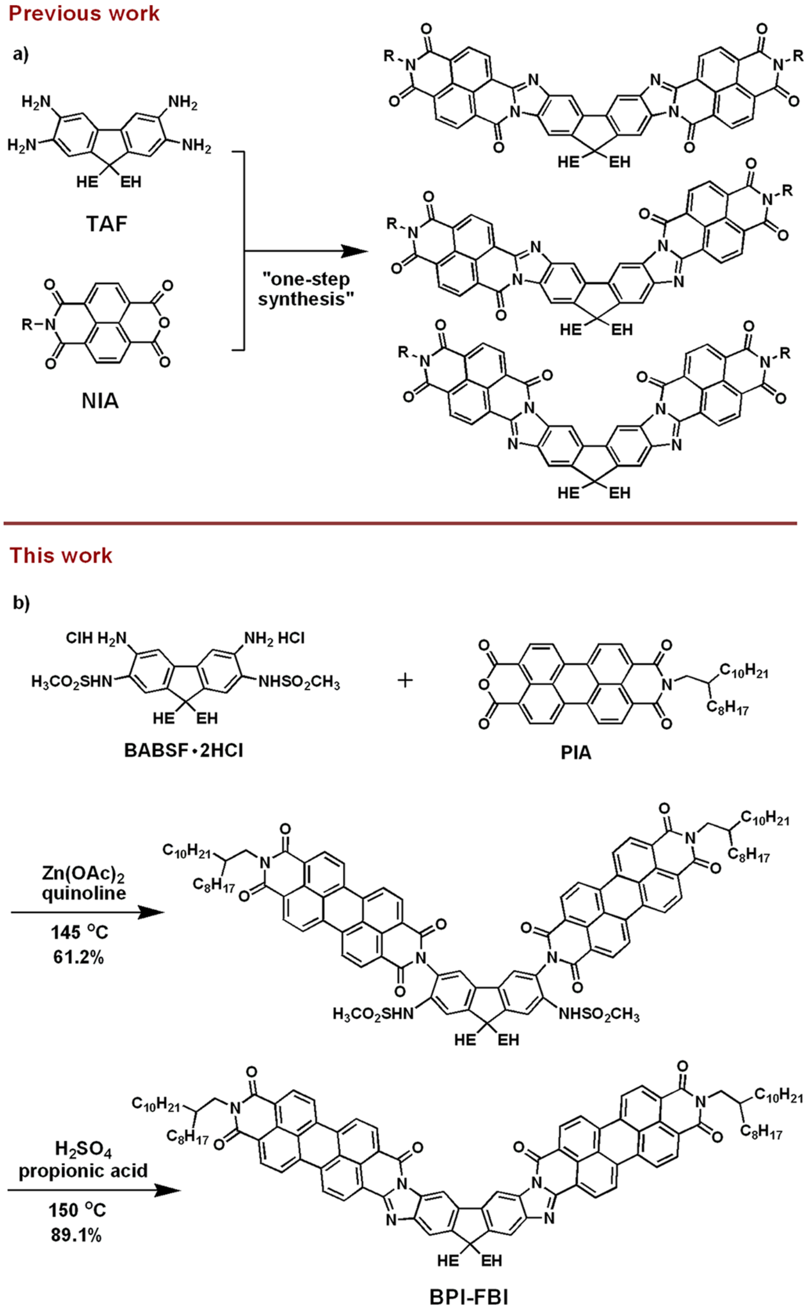


Figure 1. Structures of the ladder-conjugated perylene/naphthalene benzimidazoles.

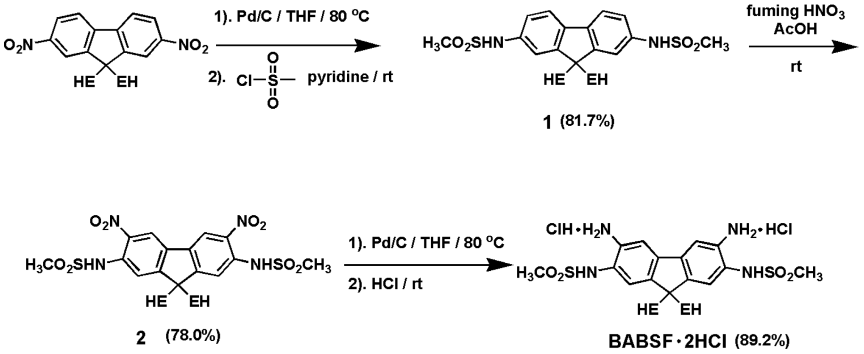
Scheme 1. Synthesis of the Perylene/Naphthalene Benzimidazoles: (a) One-Step Condensation Synthesis and (b) Controllable and Stepwise Synthesis



solubility, since the 9,9-bis-substituted fluorene core could slightly distort the whole conjugated structures, therefore inhibiting the aggregation and further enhancing the solubility.[26,29] However, such condensation productions are also including many regioisomers (Scheme 1a). Although every pure isomers were successfully isolated by column chromatography, it should be noted, it is still a tough project to separate them because of their extremely similar polarity.

As we know, every isomer exhibits special intrinsic properties, and the different configurations would affect aggregation morphologies and quality of the thin film. We have also proved that the related photophysical properties of every pure isomer were significantly varied.[26,27] However, due

Scheme 2. Synthesis of the Intermediate BABSF·2HCl



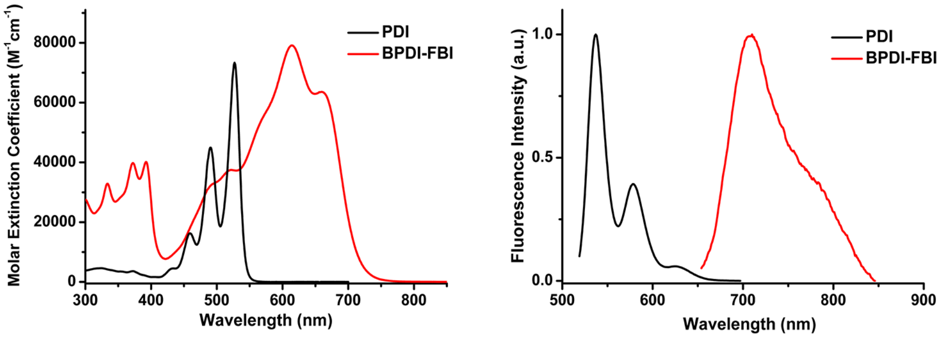


Figure 2. UV−vis absorption and fluorescence spectra in toluene (10^{-6} M).

to the difficulty of obtaining a pure isomer, the relationship between the organic electronic device performances and the accurate molecular structures is rarely reported about. Therefore, exploiting the pure isomers is significant to further investigate their device properties.

Herein, for the first time, we have successfully synthesized the bis(perylene imides) fluorenebisimidazole (**BPI-FBI**) through a controllable synthesis with high yields (Scheme 1). As we expected, the synthetic strategy produces **BPI-FBI** as the only product, without any need to isolate a series of regioisomers generated by the conventional condensation of perylene/naphthalene anhydrides with *ortho*-diaminebenzenes. We want to avoid such tough isolations because we had previously experienced the challenging purifications of three regioisomeric products by the reaction between 2, 3, 6, 7-tetraamino-fluorene (**TAF**) and naphthaleneimide anhydride (Scheme 1a). Also, in this investigation, **BPI-FBI** has been qualified as a multifunctional material with a moderate electron mobility and good optical limiting performance. We believe that this new strategy would be a universal approach to synthesize the pure isomers of this type of the ladder-conjugated molecules with a large scale preparation.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. Scheme 1b shows the synthesis of the target molecule BPI-FBI. From the viewpoint of synthetic chemistry, it is much better to take the advantage of controllable synthesis to produce the desirable ladder-conjugated molecule as the only product, rather than to separate it from the mixture of several regioisomers. To avoid isomers generating, we propose an effective strategy to synthesize this type of ladder-conjugated PDI derivatives. First, two amino groups of the TAF are selectively protected, while the other two would react with PIA (perylene imide anhydride) to give the intermediate with a single bond connected. Second, the intermediate would be intramolecular cyclized to the object ladder-conjugated molecules in strong acid condition. And in this strategy, it is crucial to choose the protecting group. Although acetyl is always used for protecting the amino group, it is easily intramolecularly condensed by itself under the heating condition to form the byproduct, therefore not obtaining the target molecule. In this reaction process, methanesulfonyl is chosen to protect the amino group because the starting material is commercially available and, more importantly, stable to common conditions except for strong acid.

BABSF·2HCl, as a key intermediate, was efficiently synthesized with high yields involving nitration, hydrogenation, and protection reactions (Scheme 2). The ethylhexyl (EH) substituents at C-9 position of fluorene ensure good solubility of the corresponding ladder-conjugated molecules. The protecting 2,7-diamido-9,9-bisalkylfluorene is prepared by methanesulfonyl chloride under room temperature previously with a high yield. In the next step, the key intermediate was obtained by hydrogenized nitration with Pd/C as the catalyst, and in order to avoid oxidation, the production was immediately converted to the air-stable bishydrochloride (BABSF·2HCl) by bubbling HCl gas into the reaction solution for 45 min. Then through the controllable synthesis, the pure isomer BPI-FBI is successfully synthesized in a high yield of 89.1%.

Photophysical Properties. The absorption and fluorescence spectra of the compounds in toluene (10^{-6} M) are shown in Figure 2. For comparison, the compound PDI was characterized (Figure S1 of the Supporting Information). Due to the increase of the π-conjugation skeleton, the absorption spectra of **BPI-FBI** cover a broad wavelength range from 300 to 700 nm. The absorption peaks are red-shifted from 527 nm of

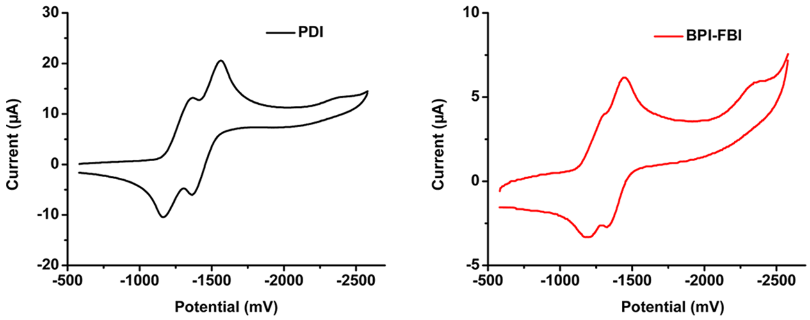


Figure 3. Cyclic voltammograms in DCM solution of 0.1 M Bu_4NPF_6 with scan rate of 100 mV/s.

PDI to 614 nm of **BPI-FBI**, simultaneously retaining high extinction coefficients over 70000 M^{-1} cm^{-1}. The optical band gaps, calculated from the absorption onsets, are 2.24 and 1.66 eV for PDI and **BPI-FBI**, respectively. In thin films, as shown in Figure S2 of the Supporting Information, the spectra of **BPI-FBI** show a broader absorption to 800 nm with the peak value of 633 nm, which has a red shift of 19 nm relative to that in solution because of the intermolecular interactions. The emission spectra of PDI have a peak at 537 nm in toluene, while the emission maxima of **BPI-FBI** of 708 nm is observed, which has a remarkable red shift of 171 nm relative to PDI. Also, we have measured a monomeric model perylene imide benzimidazole (**PIBI**) (Figure S1 of the Supporting Information). Compared with those of PDI, as shown in Figure S3 of the Supporting Information, the absorption and fluorescence spectra of **PIBI** and **BPI-FBI** become gradually red shifts. All these results indicate that the large red shifts are mainly contributed to the efficiently extended ladder-conjugated structure of **BPI-FBI**.

Electrochemical Properties. The electrochemical properties of the compounds were studied by cyclic voltammetry (CV) in a three-electrode electrochemical cell with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the electrolyte and Ag/AgCl as a reference electrode. Both the compounds displayed two reversible and one irreversible reduction waves in dichloromethane (Figure 3). The lowest unoccupied molecular orbital (LUMO) levels are estimated from the onset reduction potential relative to the reference energy level of Fc/Fc^+ (5.08 eV below vacuum).[30] They exhibit similar onset reduction potentials of about −1.15 V, and their LUMO energy levels are calculated to be −3.91 and −3.94 eV for PDI and **BPI-FBI**, respectively, which indicate that the ladder-conjugated PDI derivative does not influence the LUMO level of the prototype material. Their highest occupied molecular orbital (HOMO) energy levels are calculated from the corresponding LUMO energy levels and the optical band gap, and the HOMO levels are −6.20 and −5.63 eV for PDI and **BPI-FBI**, respectively.

Furthermore, the HOMO and LUMO molecular orbitals were calculated by density functional theory calculations at the B3LYP/6-31G(d) level. As shown in Figure 4, the HOMO orbital is delocalized throughout the whole conjugated molecule, while their LUMO orbital is majorly localized on the electron-deficient PDI units, which clearly indicate the reason for the classical n-type performance of the molecule. The theoretical results not only are in good agreement with the experimental data that the LUMO level of **BPI-FBI** is similar to that of PDI while the HOMO level is increasing largely but also indicate efficient charge migration may occur from the unit of fluorene to its bilateral moieties upon electronic excitation and are therefore benefiting for the nonlinear absorption.

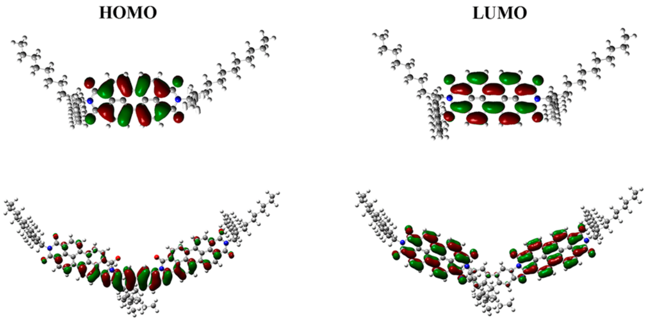


Figure 4. Theoretical calculated HOMO and LUMO molecular orbitals of PDI (top) and **BPI-FBI** (bottom).

Electron Mobility. The low LUMO level of **BPI-FBI** endows it with the potential application in n-type organic semiconductor devices. Then we have evaluated the electron-transporting mobility by the steady-state space-charge-limited current (SCLC) model. Using the solution-processed way, the electron-only device structure is ITO/ZnO (10 nm)/**BPI-FBI**/BCP (10 nm)/LiF (1.5 nm)/Al (100 nm) (ITO = indium tin oxide, BCP = 2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline). *J*−*V* curves of the SCLC device with spin-coated **BPI-FBI** as the active layer were recorded (Figure 5). The SCLC in this case of mobility, depending on the field, can be approximated by the following formula,[31,32]

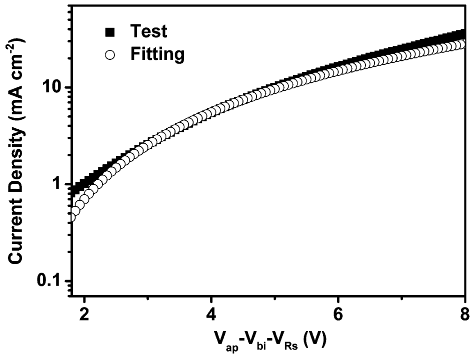


Figure 5. Current density versus voltage (*J*−*V*) characteristics of the electron-only device.

$$J = \frac{9}{8}\varepsilon\varepsilon_0\frac{E^2}{L}\mu_0\,\exp(0.89\gamma\sqrt{E})$$

where E is the electric field across the sample; ε and ε_0 are the relative dielectric constant and permittivity of the free space, respectively; and L is the thickness of the organic layer, with μ_0 the zero-field mobility and γ describing the field activation of the mobility. At a typical electric field of 10^5 V cm^{-1} (corresponding to an applied voltage of 1 V across a 100 nm thick device), the apparent electron mobility calculated from the currents in the square law region of 1.01×10^{-5} cm^2 V^{-1} s^{-1} has been determined for the device, which indicates the ladder-conjugated molecule exhibits good electron-transporting performance.

Two-Photon Absorption. The two-photon absorption spectra were determined by using laser pulses (<120 fs) tunable from 1200 to 1400 nm generated by a mode-locked Ti—sapphire laser. The data were obtained by a two-photon excited fluorescence method with Coumarin 307 (100 mM solution in methanol) as a reference, as well as by the nonlinear transmission method.[33] Figure 6 shows the 2PA spectra of **BPI-FBI**, which shows the large cross section over 600 GM from 1200 to 1400 nm, and the maximum value is 1110 GM at 1220 nm. The high and broad 2PA spectra indicate that the ladder-conjugated molecule **BPI-FBI** has the capability to be efficiently excited at many different wavelengths in the near-infrared region and has a potential application in the optical communication wavelengths.

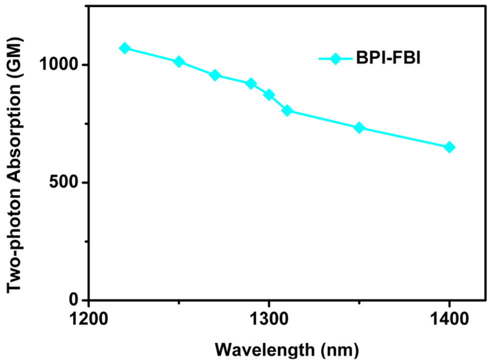


Figure 6. Two-photon absorption spectra of **BPI-FBI** in toluene.

Optical Power Limiting. Since in this molecule's 2PA wavelength range, 1310 nm is one of the optical communication wavelengths, we investigated the optical limiting behaviors at this particular wavelength. The concentration of the molecule was fixed at 2.5 mM in toluene. The output—input intensity curves can be theoretically fitted by the following equation based on the 2PA mechanism,[34]

$$T(I_0) = \frac{1}{1 + \beta(\lambda) I_0 l_0}$$

where $T(I_0)$ is the measured value of the nonlinear transmission, I_0 is the initial intensity of the incident light beam, $\beta(\lambda)$ is the 2PA coefficient, and l_0 is the optical path length (thickness) of the sample. From the characteristic curves in Figure 7a, when the input energy increased from 3.5 to 41.0 μJ (~12 times increase), the transmitted energy changed from 0.27 to 3.41 μJ (~5.5 times increase). When **BPI-FBI** is used as a two-photon absorbing medium to stabilize the input laser, a more than 2-fold reduction in laser fluctuation may be achieved. And as shown in Figure 7b, the device exhibits high transmittance for low intensity inputs, and has less than 50% transmittance for a high input intensity of 210 GW cm^{-2}, which is a desirable property for the optical-limiter. Because for an ideal optical-limiter, it is expected to have high transmittance for low intensity inputs, while blocking the transmittance for high intensity inputs, such as laser beams. These results demonstrate that the ladder-conjugated PDI molecule **BPI-FBI** promises a good potential as an optical limiter.

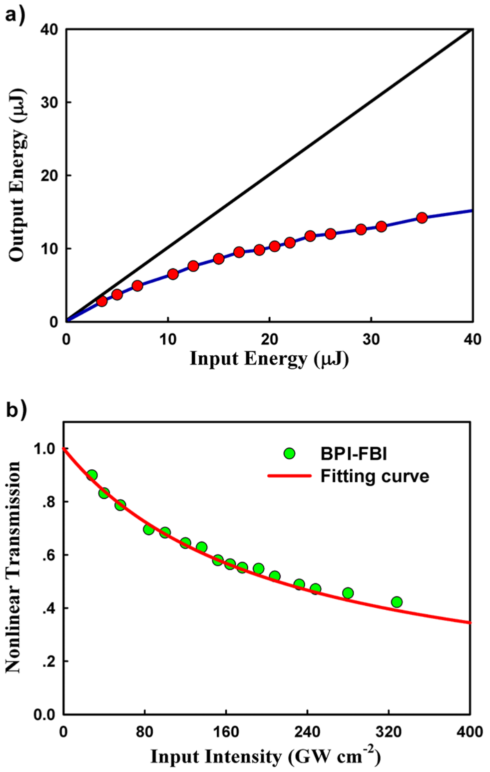


Figure 7. (a) Measured output pulse energy and (b) nonlinear transmission data versus input energy (or intensity) of **BPI-FBI**.

■ CONCLUSION

In summary, through protecting the two amino groups of 2, 3, 6, 7-tetraamino-fluorene and stepwise synthetic strategy, we overcome a challenge in conventional one-step condensations to synthesize the ladder-conjugated materials from perylene/naphthalene anhydrides/bisanhdrides and have successfully synthesized a soluble ladder-conjugated PDI derivative, **BPI-FBI**, as the only product in a high yield. This strategy, avoiding the difficult or even impossible purifications of the mixed regioisomers, would be a universal approach to easily obtain the pure isomers of this type of the ladder-conjugated molecules with a large scale preparation. As an n-type organic semiconductor with the electron mobility of 1.01×10^{-5} cm^2 V^{-1} s^{-1}, **BPI-FBI** exhibits a broad absorption spectra covering the whole visible region from 300 to 700 nm and the low LUMO level inheriting the prototype PDI. With a high two photon absorbing activity in the near-infrared region, **BPI-FBI** also exhibits good optical limiting performance, which will be useful for sensor or human eye protection, and stabilization of light sources for optical communications.

■ EXPERIMENTAL SECTION

Measurement and Characterization. ^{1}H NMR and ^{13}C NMR spectra were measured at room temperature on a 400 NMR spectrometer using perdeuterated solvents as internal standards. Molecular weights are determined by using matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-HRMS). Melting points were obtained with a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification is conducted with silica gel. All solvent mixtures are given as volume/volume ratios. Cyclic voltammetry were recorded on a three-electrode system. UV spectra and fluorescence spectra are recorded on a corrected spectrometer. The current-density–voltage curves of the SCLC devices were measured using a corrected system. For the nonlinear optical experiments, the excitation pulse (1 kHz, 240–2600 nm, pulse-width <120 fs) was generated from an optical parametric amplifier pumped by a regenerative amplified femtosecond Ti–sapphire laser system (800 nm, 1 kHz, pulse energy 4 mJ, pulse-width <120 fs), which was seeded by a femtosecond Ti-sapphire oscillator (80 MHz, pulse width, 70 fs, 710–920 nm).

Synthesis. Compound 2,7-dinitro-9,9-bis(2-ethylhexyl)fluorene and **PIA** were synthesized according to the previous reports.[26,35] All chemicals were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures, and the solvents for spectra studies are of spectroscopic grade without further purification.

*2,7-Dimethanesulfonylamido-9,9-bis(2-ethylhexyl)fluorene (**1**).* A mixture of 2,7-dinitro-9,9-bis(2-ethylhexyl)fluorene (5.0 g, 10.4 mmol), 250 mg Pd/C, 80 mL dry THF, and 2 MPa H_2 was heated to 80 °C for 8 h. Pd/C was filtered, and the filtrate was added to the solvent of pyridine 12 mL, and then 20 mL methanesulfonyl chloride was added dropwise slowly at room temperature. After that, the reaction mixture was stirred for 1 h. Then the mixture was extracted with dichloromethane. The organic extracts were washed with dilute hydrochloric acid, water, saturated $NaHCO_3$ (aq), and saturated NaCl (aq). Then the organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the final crude product was purified by column chromatography with dichloromethane to obtain the pure product **1** (4.90 g, 81.7%) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65–7.63(d, J = 8 Hz, 2H), 7.36(s, 2H), 7.27–7.23(m, 4H), 3.01(s, 6H), 2.06–1.95(m, 4H), 0.92–0.46(m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.5, 138.4, 135.5, 120.7, 120.5, 117.4, 55.6, 44.7, 39.0, 34.8, 33.9, 28.1, 26.9, 22.9, 14.2, 10.5. MALDI-TOF-HRMS: calcd for $C_{31}H_{48}N_2O_4S_2$, 576.3056 [M^+]; found, 576.3024.

*2,7-Dimethanesulfonylamido-3,6-dinitro-9,9-bis(2-ethylhexyl)-fluorene (**2**).* To a solution of compound **1** (4.8 g, 8.32 mmol) in 80 mL glacial acetic acid, 48 mL fuming nitric acid was added dropwise at −10 °C. The reaction solution was stirred for 10 min at −10 °C. The resulting mixture was poured into ice water and then filtered. The crude solid was purified by column chromatography with dichloromethane as the eluent to obtain the pure product **2** (4.33 g, 78.0%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.94(s, 2H), 8.63(s, 2H), 7.98(s, 2H), 3.17(s, 6H), 2.15–2.12(m, 4H), 0.95–0.48(m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.6, 136.7, 134.5, 134.2, 118.2, 115.7, 57.5, 45.0, 41.1, 34.9, 33.8, 28.1, 26.8, 22.9, 14.0, 10.3. MALDI-TOF-HRMS: calcd for $C_{31}H_{45}N_4O_8S_2$, 665.2679 [$M - H^-$]; found, 665.2667.

*2,7-Dimethanesulfonylamido-3,6-diamino-9,9-bis(2-ethylhexyl)-fluorene tetrahydrochloride (**BABSF·2HCl**).* To a suspension of compound **2** (0.5 g, 0.75 mmol), 25 mg Pd/C and 20 mL dry THF, 2 MPa H_2 was filled. The reaction mixture was stirred at 80 °C for 9 h, after which the reaction mixture was filtered under reduced pressure. Dry hydrogen chloride was bubbled into the filtrate until the solution turned to light yellow. The resulting solution was evaporated to about 1 mL, and a little ethyl ether was added. The product **BABSF·2HCl** (455 mg, 89.2%) was obtained after precipitating as a light yellow solid. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.01(s, 2H), 7.62(s, 2H), 3.07(s, 6H), 2.24–2.11(m, 4H), 0.89–0.43(m, 30H). ^{13}C NMR(100 MHz, CD_3OD, 25 °C): δ= 153.8, 141.2, 131.4, 130.6, 125.4, 117.5, 57.2, 45.7, 39.2, 36.3, 34.9, 29.5, 27.7, 23.7, 14.3, 10.6. MALDI-TOF-HRMS: calcd for $C_{31}H_{52}Cl_2N_4O_4S_2$, 678.2807 [$M^-$]; found, 678.2820.

Compound BPI-FBI. A mixture of **BABSF·2HCl** (0.4 g, 0.588 mmol), **PIA** (1.03 g, 1.53 mmol), 648 mg zinc(II) acetate (anhydrous) and 12 mL quinoline was heated to 145 °C for 14 h. The mixture was extracted with dichloromethane, washed with dilute hydrochloric acid, water, saturated $NaHCO_3$ (aq), and saturated NaCl (aq). Then the organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the final crude product was purified by column chromatography with dichloromethane: ethyl acetate = 20:1 to obtain the pure product (0.69 g, 61.2%) as a red solid (poor solubility). MALDI-TOF-HRMS: calcd for $C_{119}H_{144}N_6O_{12}S_2$, 1913.0284 [$M^-$]; found, 1913.0343.

Then a mixture of the above-obtained intermediate (0.5 g, 0.261 mmol), 8 mL concentrated sulfuric acid and 8 mL propionic acid was heated to 150 °C for 5 h. The mixture was extracted with dichloromethane, washed with water, saturated $NaHCO_3$ (aq), and saturated NaCl (aq). Then the organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the final crude product was purified by column chromatography with toluene:ethyl acetate = 12:1 to obtain the pure product **BPI-FBI** (0.40 g, 89.1%) as a blue black solid. Mp: 266.7–268.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.57–8.52(m, 6H), 8.25(s, 2H), 8.05–7.93(m, 12H), 3.91(m, 4H), 2.36(m, 4H), 1.92(m, 2H), 1.25–0.78(m, 106H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.6, 162.9, 158.7, 150.5, 148.3, 144.3, 140.1, 134.1, 133.9, 132.1, 131.4, 129.0, 126.2, 125.5, 123.2, 122.8, 115.5, 107.5, 54.5, 45.9, 44.6, 35.1, 32.1, 31.9, 30.3, 29.9, 29.6, 28.4, 26.7, 23.3, 22.9, 14.3, 10.6. MALDI-TOF-HRMS: calcd for $C_{117}H_{136}N_6O_6$, 1721.0521 [M^-]; found, 1721.0496.

ASSOCIATED CONTENT

Supporting Information

PDI and PIBI structures, absorption and fluorescence spectra, computational details, and ^{1}H and ^{13}C spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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