Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information:

Fusing Three Perylenebisimide Branches and A Truxene Core into A Star-Shaped Chromophore with Strong Two-Photon Excited Fluorescence and High photostability

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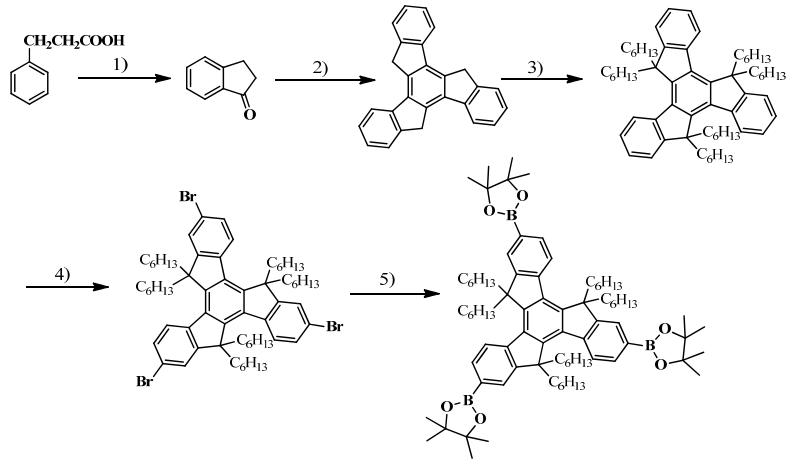
1. Materials and methods

Compound **1**[S1], **2**[S2], **PBI1**[S3], **6**[S3] were synthesized according to literature methods. Compound **3** was synthesized on the basis of Scheme S1 according to literature methods.[S4] All other reactants were purchased from commercial sources. NMR spectra were measured with a 400MHz Bruker spectrometer using TMS as reference for ^{1}H and ^{13}C NMR. Accurate mass correction is measured with MALDI Tof Mass Spectrometer (MALDI micro MX). Cyclic voltammetry (CV) was performed in 0.05M solution in CH_2Cl_2 with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon with a scan rate of 100 mV/s. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; internal standard: ferrocene (Fc). The energy of Fc/Fc^{+} is 5.08 eV relative to vacuum.[S5] UV-vis absorption spectrum is measured with UV-Vis Spectrophotometer (HP 8453). Fluorescence spectrum is measured with Fluorescence Lifetime Spectrometer (PTI-700). The fluorescence quantum yields were determined with Rhodamine 6G in ethanol as the reference.[S6]

Compound **4** and **Tr-PBI** were synthesized by employing sunlight as the catalyst and our group has reported the similar conversion.[S7] The apparatus are very common and not tailor-made. Generally, the mixture of all reactant is added into a conical flask and a economical allihn condenser is connected to the flask. Then the flask is heated in a oil bath, and the whole apparatus is exposed to sunlight in sunny days. The needed sunlight is natural daylight without being filtered.



Scheme S1 Synthetic routes of Compound **3**

1) PPA(polyphosphoric acid), 60□, 0.5h; 2) acetic acid, concentrated hydrochloric acid, 100℃, 16h; 3) n-BuLi, n-$C_6H_{13}Br$, -78℃; 4) Br_2, K_2CO_3, rt, 3h; 5) Pd(dppf)Cl_2, bis(pinacolato)diboron, CH_3COOK, toluene, 100℃, 24h

2. Specific synthetic steps of intermediates and target compounds

Synthesis of 4

A mixture of compound **3** (400 mg, 0.326 mmol), KOH 820 mg, 25ml THF, 7.8ml H_2O was stirred at reflux for 4 h under an argon atmosphere. Then, compound **2** (832 mg, 1.13 mmol), $Pd(PPh_3)_4$ 30 mg, were added and reflux for 12 h. The mixture was extracted with dichloromethane, washed with water, dried with $MgSO_4$ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethly acetate as eluent. Compound **4** was obtained as red solid (590mg, 65%). M.p.: 290-292℃ ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66-0.71 (m, 30H), 0.93-1.26 (m, 72H), 1.39-1.69 (m, 24H), 1.79- 2.01 (m, 30H) ,2.98 (s, 6H), 4.23-4.38 (m, 24H), 7.48 -7.58 (m, 9H), 7.96 (m,3 H), 8.13 (m, 6H), 8.21 (m, 3H), 8.35(m, 6H) ,8.46 ppm(m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.0, 19.1, 22.0, 23.9, 30.6, 31.4, 36.7, 56.1, 65.4 121.3, 122.3, 122.6, 126.3, 127.1, 127.7, 128.5, 128.7, 129.3, 129.4, 129.7, 130.1, 130.2, 130.3, 130.6, 131.1, 133.1, 133.3, 133.5, 135.4, 138.1, 139.6, 139.9, 141.5 ppm.; MALDI-TOF-MS: Calcd for $C_{183}H_{216}O_{24}Na$ 2820.5579, found: 2820.5347 ($[M+Na]^+$).

Synthesis of 5

A mixture of compound **4** (630 mg, 0.225 mmol), 150 mL toluene and 20 mg I_2 was illuminated by sunlight under reflux for 6 h. Toluene was removed by reduced pressure distillation and the crude product was purified by silica gel column chromatography with dichloromethane and ethly acetate as eluent. Compound **5** was obtained as yellow green solid (596 mg, 95%). M.p.: 253-255℃ ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.38 (m, 18H), 0.87 (m, 36H), 1.08 (m, 39H), 1.24 (m, 9H) , 1.62 (m, 18H), 1.97-1.81 (m, 24H), 2.19 (m, 6H), 2.92 (m, 6H), 3.78 (m, 6 H), 4.52-4.58 (m, 18H), 4.71(m, 6H), 8.58 (d, 6H), 9.13(d, 6H) ,9.34 (s, 3H), 9.80 (s, 3H), 9.96(s, 3H), 10.38 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =13.8, 14.1, 14.3, 19.5, 19.8, 22.3, 22.5, 24.8, 29.7, 29.8, 30.9, 31.4, 31.6, 31.8, 38.6, 57.2, 65.8, 116.9, 122.1, 124.4, 127.0, 127.2, 127.7, 127.9, 128.7, 129.4, 129.6, 130.1, 130.5, 132.8, 133.0, 139.1, 141.1, 148.3, 154.5, 169.0,169.2 ppm; MALDI-TOF-MS: Calcd for $C_{183}H_{210}O_{24}Na$ 2814.5110, found: 2814.5339 ($[M+Na]^+$).

Synthesis of Tr-PBA

A mixture of compound **5** (300 mg, 0.107 mmol) and 4.8 g 4-methylbenzenesulfonic acid was heated to 110 □ for 3h. The mixture was washed with water to remove the 4-methylbenzene sulfonic acid and filtrate. The filter cake was dealed with Soxhlet extractor to remove the soluble impurity. Compound **Tr-PBA** was obtained as black solid (193mg, 90%). M.p. >300℃. Due to the extremely poor solubility, compound **Tr-PBA** was not characterized and it was directly used for next reaction.

Synthesis of Tr-PBI (Route 1)

A mixture of compound **Tr-PBA** (50mg, 0.025 mmol), 3-pentanamine 21.7 mg, and butanol 2 mL was heated to 85 □ for 10 h. The solvent was removed by reduced pressure distillation and the crude product was purified by silica gel column chromatography with dichloromethane and ethly acetate as eluent. **Tr-PBI** was obtained as red solid (30 mg, 50%). M.p.>300℃ ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37(m, 18H), 0.72-1.16 (m, 84H), 2.18 (m, 12 H), 2.54 (m, 12H), 3.15 (m, 6H), 3.82(m, 6H) ,5.38 (m, 6H), 9.12(d, 6H), 9.35(d, 6H), 9.67 (s, 3H), 10.62 ppm (d, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =11.7; 13.9; 22.4, 25.0, 25.4, 29.7, 31.6, 38.3; 57.6, 58.1, 117.7, 119.8, 123.3, 123.5, 125.0, 125.3, 125.4, 127.7, 128.7, 129.4, 129.8, 133.9, 134.2, 139.1, 141.8, 149.3, 155.5, 164.8 ppm; MALDI-TOF-MS: Calcd for

$C_{165}H_{168}N_6O_{12}$ 2425.2720, found: 2425.2527 (M^-).

Synthesis of 7

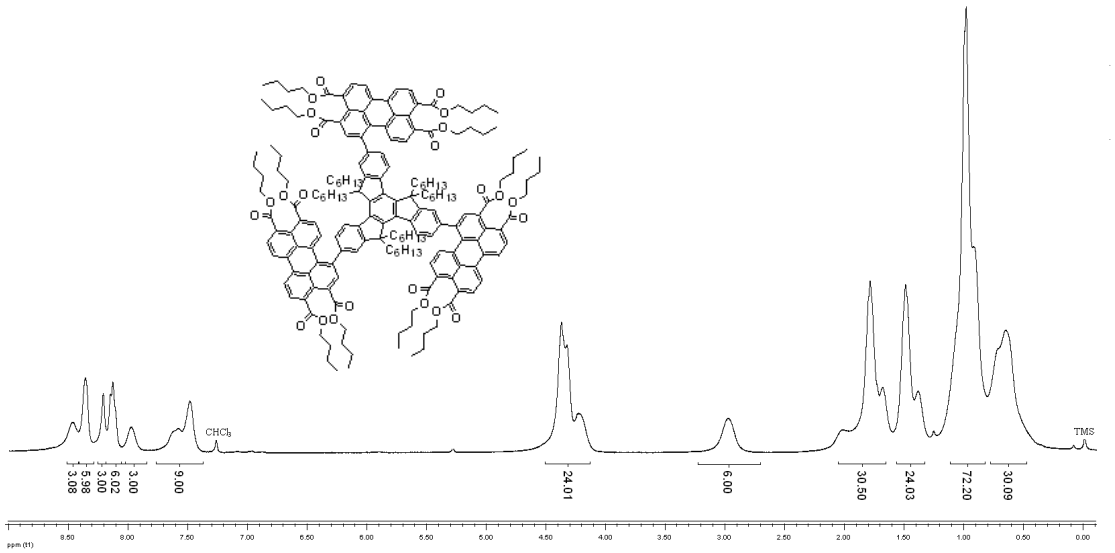
A mixture of compound **3** (57.5 mg, 0.047 mmol), KOH 118 mg, 5ml THF, 1ml H_2O was stirred at reflux for 4 h under an argon atmosphere. Then, compound **6** (100 mg, 0.164 mmol), $Pd(PPh_3)_4$ 6 mg, were added and reflux for 12 h. The mixture was extracted with dichloromethane, washed with water, dried with $MgSO_4$ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethly acetate as eluent. Compound **7** was obtained as red solid (62.8 mg, 55%). M.p. >300℃ ^{1}H NMR (400 MHz, CDCl3): δ = 0.57-1.06 (m, 96H), 1.57-2.31 (m, 30H), 3.03 (m, 6 H), 5.00-5.30(m, 6H), 7.54 (s, 3H), 7.66(s, 3H) ,8.06-8.19 (m, 6H), 8.56-8.73 ppm (m, 18H); ^{13}C NMR (100 MHz, CDCl3): δ =11.5, 14.2, 22.5, 24.2, 24.3, 25.0, 29.3, 29.5, 29.8, 31.6, 37.0, 56.4, 57.6, 57.9, 122.4, 122.8, 123.7, 126.9, 127.8, 128.3,128.8, 129.5 130.1, 131.2, 132.8,134.5, 134.9, 135.1, 136.7, 138.1, 140.6, 141.3, 142.1, 146.4, 155.8, 164.6 ppm; MALDI-TOF-MS: Calcd for $C_{165}H_{174}N_6O_{12}$ 2431.3190, found: 2431.3145 (M^-).

Synthesis of Tr-PBI (Route 2)

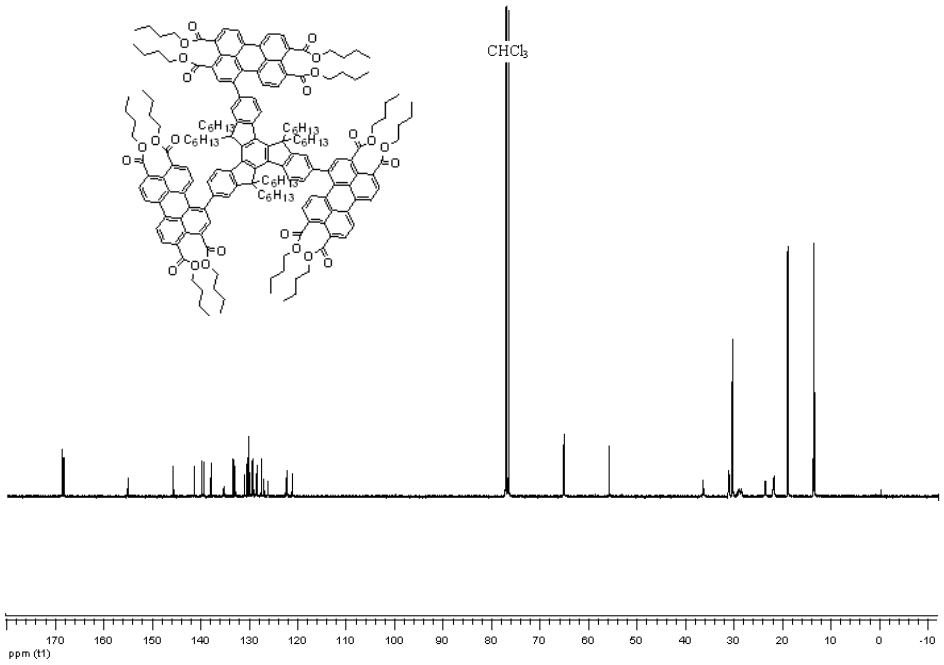
A mixture of compound **7** (400 mg, 0.165 mmol), 100 mL toluene and 15 mg I_2 was illuminated by sunlight under reflux for 6 h. Toluene was removed by reduced pressure distillation and the crude product was purified by silica gel column chromatography with dichloromethane and ethly acetate as eluent. **Tr-PBI** was obtained as red solid (380 mg, 95%).

3. Copy of NMR Spectrum

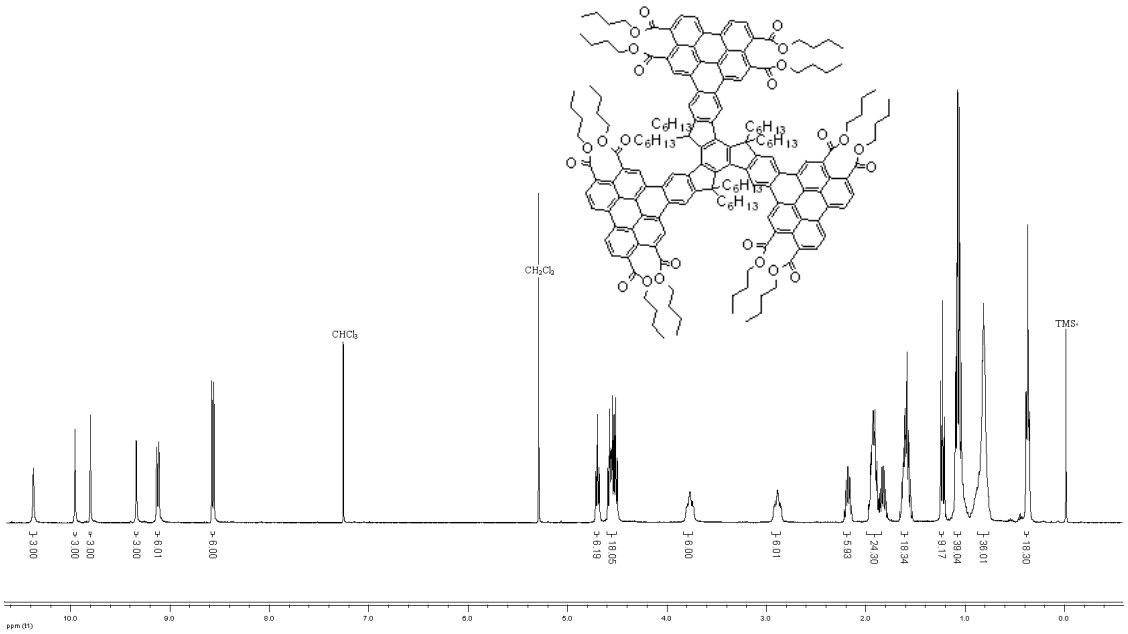
^{1}H NMR (400MHz) spectrum of **4** in $CDCl_3$



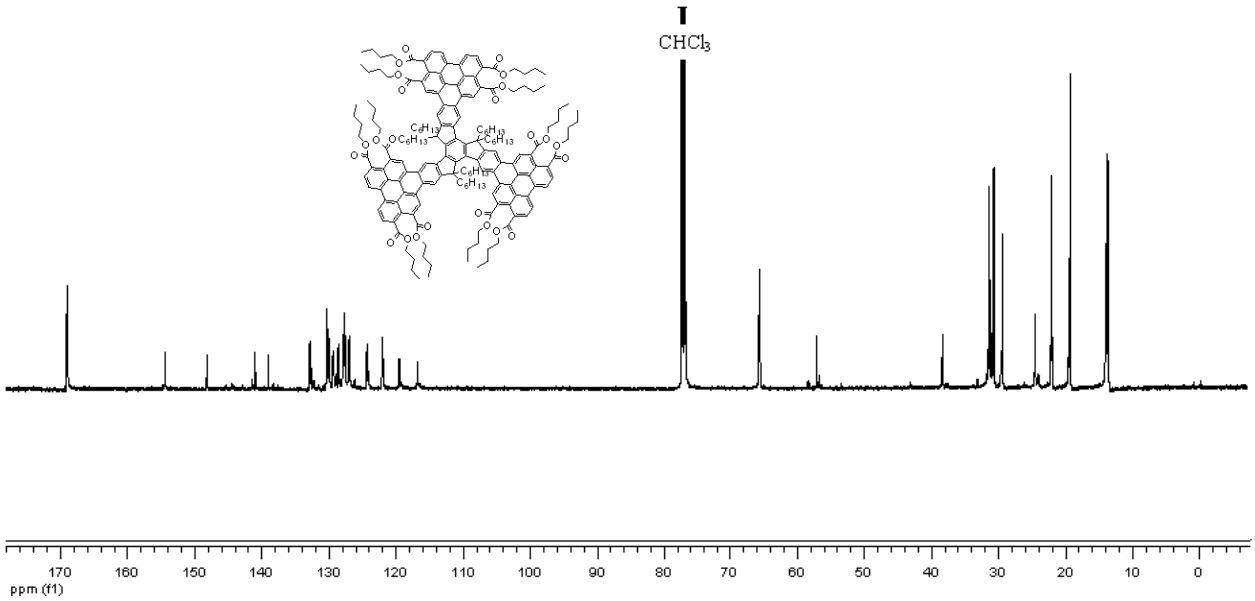
^{13}C NMR (100MHz) spectrum of **4** in $CDCl_3$



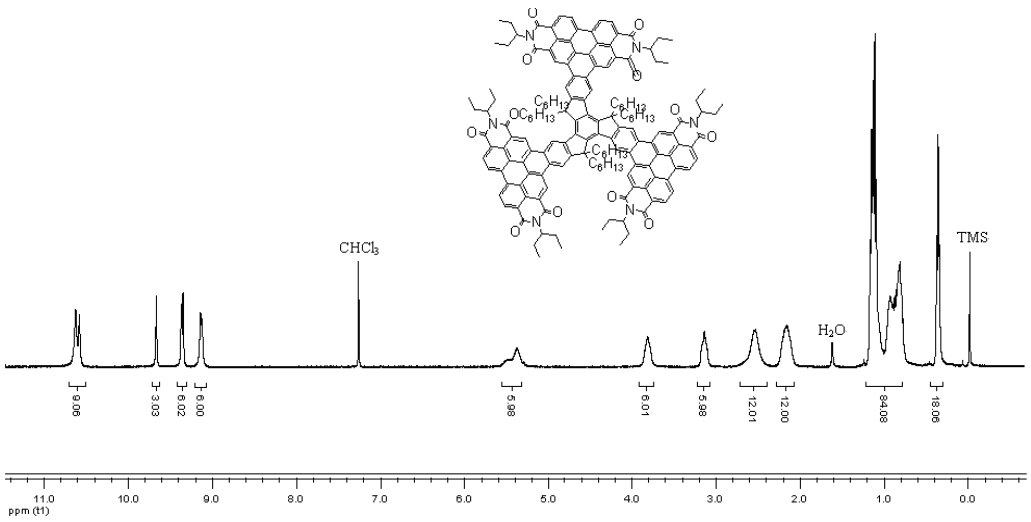
^{1}H NMR (400MHz) spectrum of **5** in $CDCl_3$



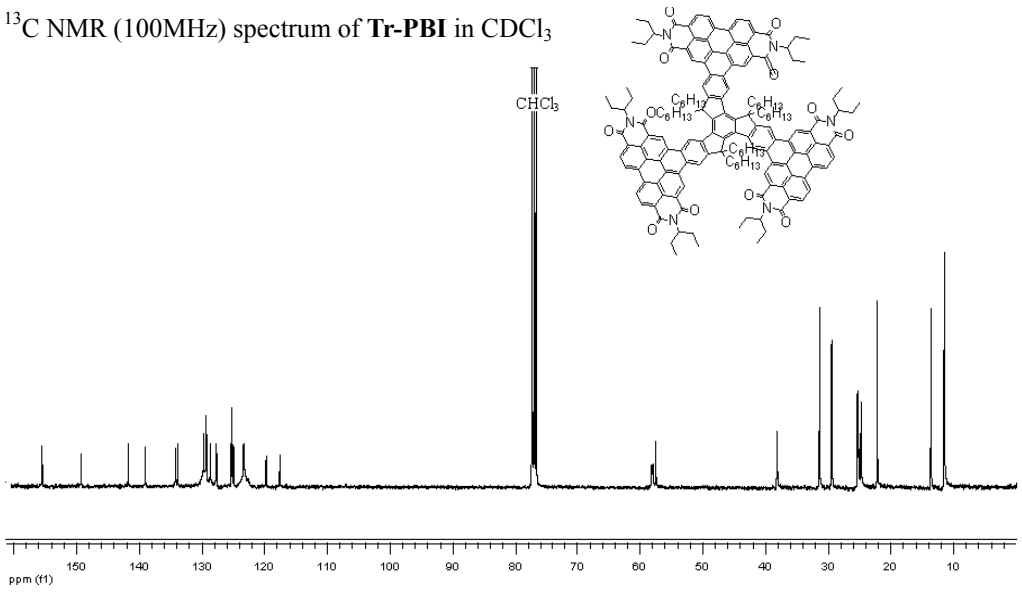
^{13}C NMR (100MHz) spectrum of **5** in $CDCl_3$



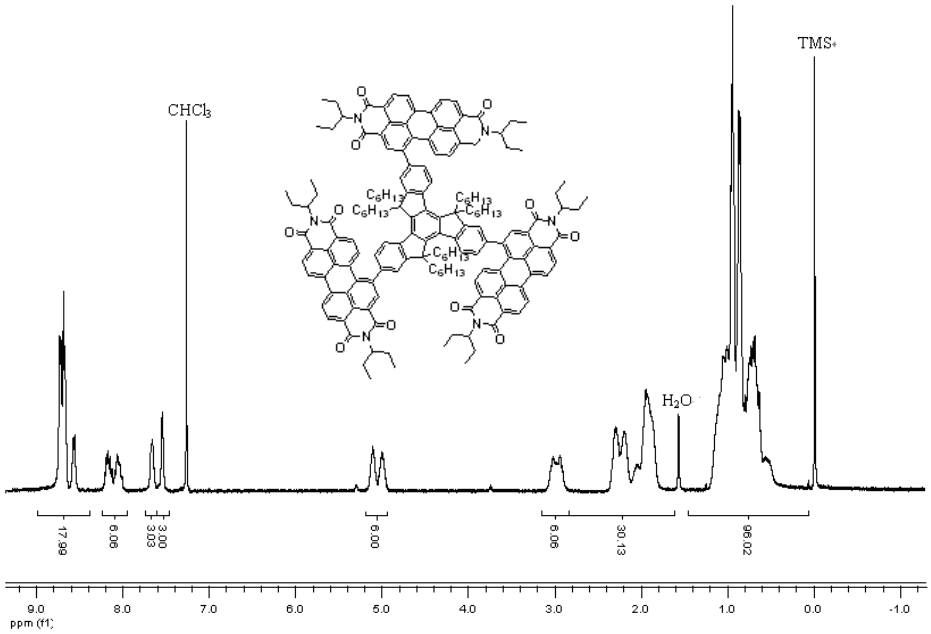
^{1}H NMR (400MHz) spectrum of **Tr-PBI** in $CDCl_3$



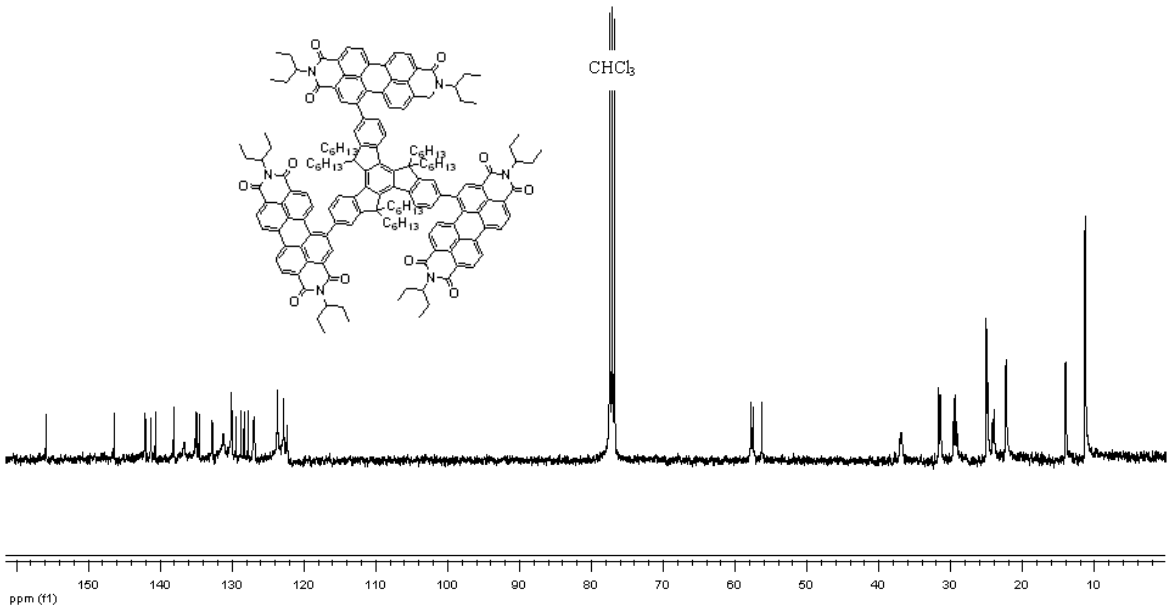
^{13}C NMR (100MHz) spectrum of **Tr-PBI** in $CDCl_3$



^{1}H NMR (400MHz) spectrum of **7** in $CDCl_3$



^{13}C NMR (100MHz) spectrum of **7** in $CDCl_3$



4. Electrochemical properties of PBI1 and Tr-PBI

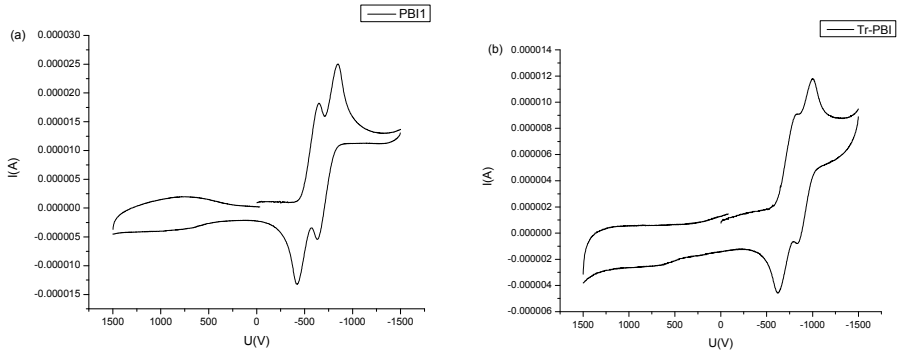


Figure S1. Cyclovoltammograms of **PBI1**(a) and **Tr-PBI**(b) in dichloromethane**.**

Table S1. HOMO and LUMO energy level of the studied compounds in dichloromethane (0.05 M)

	HOMO [a](eV)	LUMO(eV)
PBI1	**6.27**	**3.94**
Tr-PBI	**6.07**	**3.76**

[a] Calculated from the LUMO level and UV-vis absorption edge

5. Two-photon absorption cross-section (δ) measurement

Two-photon absorption spectrum and cross section of **PBI1** and **Tr-PBI** were measured with the two-photon-excited fluorescence (TPEF) method by using the femtosecond laser pulses.[S8] The TPEF technique is a common method for measurement of TPA except the *Z*-scan technique. The TPEF technique measures the fluorescence signal induced by two-photon absorption and can directly acquire the TPEF action cross section (δ×Φ) by comparison to a reference compound.[S9] Compared with the TPEF technique, the *Z*-scan technique has some drawbacks, e.g. laser intensities required by this method are higher than those used for the TPEF technique; it calls for more highly concentrated samples; its sensitivity is lower. What's more, the TPEF technique is quite suitable for compounds that have strong fluorescence. So in this work, the TPEF technique was used to measure the TPA property of PBI and the derivative.

Experiment was performed on a confocal microscopy system (TCS SP2, Leica) combined with fs-pulsed wavelength switchable laser source (Mai Tai Deepsee, 80MHz, Optical-physics). Laser beam was directed into the scan-module of microscopy system, and focused onto the sample (100*oil-immersion objective, numerical aperture(NA)1.4, Leica). The solution of sample was sealed in a microscope concave slide with cover slip. The fluorescence emission was collected by the same objective, projected onto PMT, then the fluorescence emission curve and intensity image were got. Fluorescence emission curve excited by different laser wavelength, from 700nm to 1000 nm (10nm per step) was detected. The intensities of the two-photon induced fluorescence spectra of the reference and sample emitted at the same excitation wavelength were recorded. Because of changes of power laser at different wavelength, in order to get reliably result, we keep other conditions stable, such as gain of PMT, detected area and concentration of sample, record laser power at every wavelength and use the power as normalized standard to obtain the corrected fluorescence intensity. Usually, the corrected fluorescence intensity is relative value and is the quotient of the original fluorescence intensity divided by laser power. That will not affect the accuracy because we use the TPEF technique. The TPA cross section (δ) of compounds in THF (1.0×10^{-4} M) were measured using fluorescein in water solution with pH=11 as the reference.[S10] The δ was calculated according to the following equation,[S11]

$$\delta_s = \frac{S_s \times \Phi_r \times \eta_r \times N_r}{S_r \times \Phi_s \times \eta_s \times N_s} \delta_r$$

where the subscripts s and r stand for the sample and reference molecule, S is the corrected intensity of two-photon-induced fluorescence, Φ is the fluorescence quantum yield, N is the concentration of the chromophore, and η is the collection efficiency of the experimental setup, δ_r is the TPA cross section of the reference molecule.

The two-photon excitation fluorescence emission spectras of **PBI1**(λ_{ex}= 770nm) and **Tr-PBI** (λ_{ex}= 990nm) are shown in Figure S2.

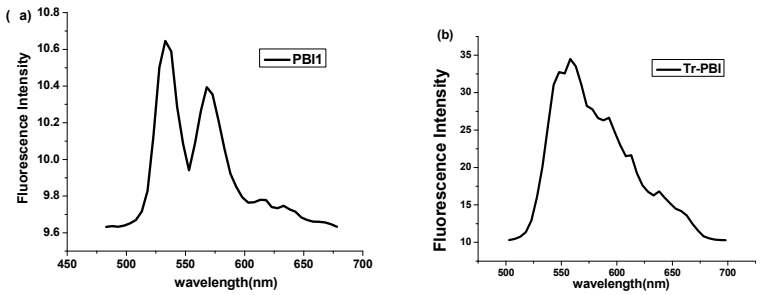
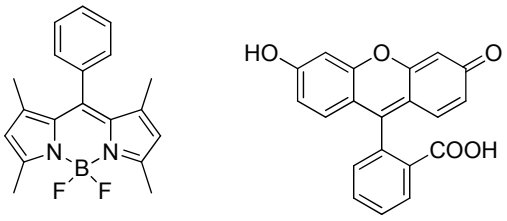


Figure S2. Two-photon excitation fluorescence emission spectras of **PBI1**(a) (λ_{ex}= 770 nm) and **Tr-PBI** (b) (λ_{ex}= 990 nm) in THF.

6. Photostability measurement

The photostability of these compounds was evaluated by using Nikon C1 confocal microscope. The structures of **BODIPY** and fluorescein are shown in Scheme S2. First, the solution of sample was sealed in a microscope concave slide with cover slip (the concentration of all the compounds is 10^{-5} M; **PBI1**, **Tr-PBI**, **BODIPY** were dissolved in THF; fluorescein was dissolved in an aqueous solution with pH=11; all solutions were air saturated). Then it was placed on the objective lens of the confocal microscope, and irradiated by the light in the range of 460-490 nm using a bandpass filters that transmits from 460 to 490 nm with the same light intensity. The fluorescent imagings were recorded with Nikon C1 confocal fluorescence microscope exciting at 488 nm (Ar Laser) at different lengths of time after exposure. The average fluorescent intensity was calculated from the software EZ-C1 3.90 Freeviewer. $\mathbf{I_0}$ is the fluorescent intensity of compounds without irradiation, **I** is the fluorescent intensity of compounds after a period of irradiation. The curves of **I** of these compounds dependent on irradiation time were shown in Figure S3.



BODIPY Fluorescein

Scheme S2. Structures of **BODIPY** and fluorescein

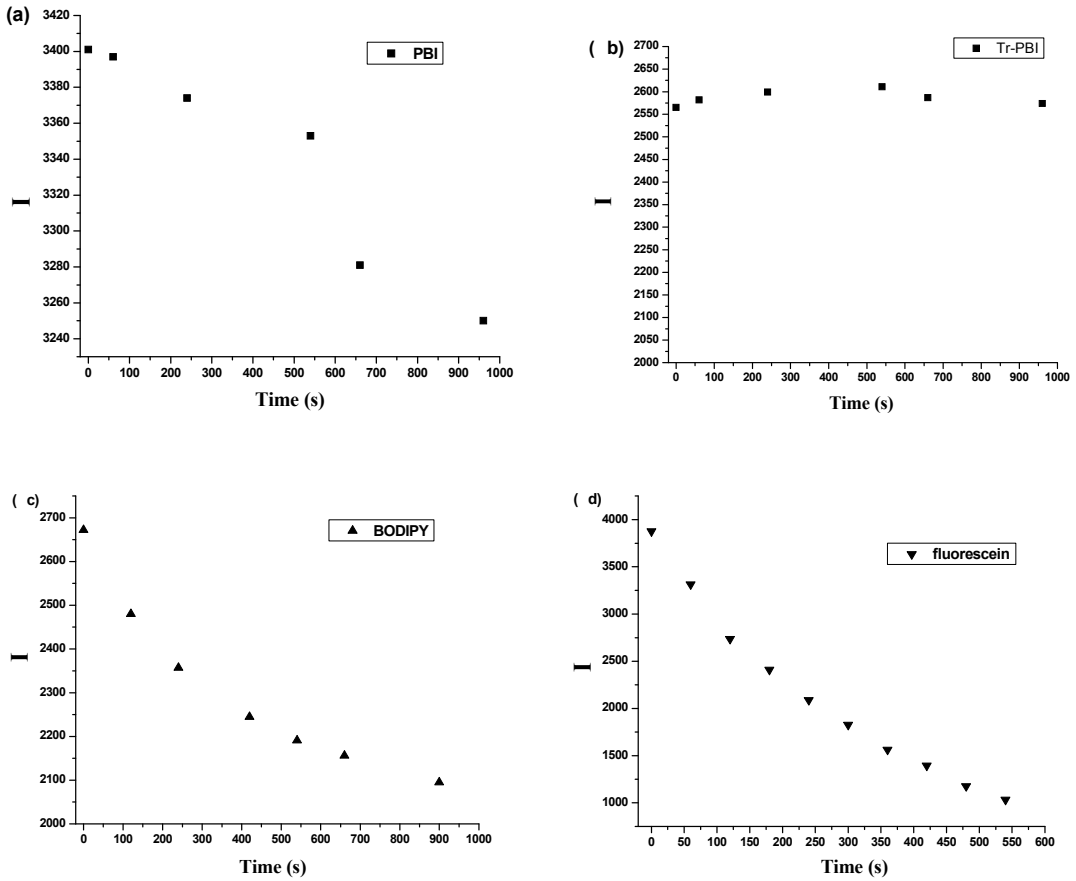


Figure S3. The changes of **I** of **PBI1** (a), **Tr-PBI** (b), **BODIPY** (c), and fluorescein (d) after certain periods of irradiation by the light in the range of 460-490nm.

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