Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information for:

Carbazole-Perylenebisimide Electron Donor/Acceptor Dyads Showing Efficient Spin Orbit Charge Transfer Intersystem Crossing (SOCT-ISC) and Photo-Driven Intermolecular Electron Transfer

Noreen Rehmat,[a] Antonio Toffoletti,[b] Zafar Mahmood,[c] Xue Zhang,[a] Jianzhang Zhao[a] and Antonio Barbon [b,]**

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling–Gong Road, Dalian 116024, P. R. China

E-mail: zhaojzh@dlut.edu.cn (J. Z.)

[b] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 34921 Padova, Italy. E-mail: antonio.barbon@unipd.it (A. B.)

[c] Light Industry and Chemical Engineering College, Guangdong University of Technology, Guangzhou 510006, P. R. China

Contents

1. General information

All the chemicals used in synthesis are analytically pure and were used as received. Solvents were dried and distilled before used for synthesis. ^{1}H chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. The mass spectra were measured by TOF MS MALDI spectrometer.

2. Synthesis of the Compounds

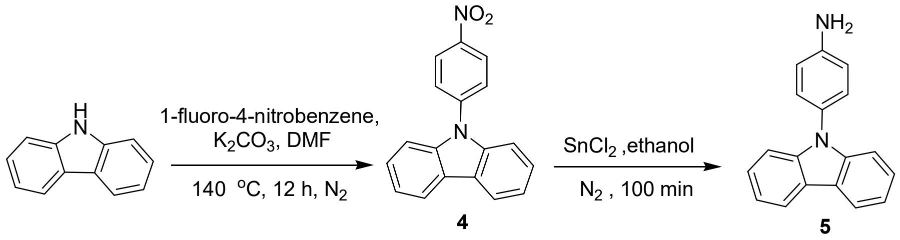


Chart 1: Synthesis routes to compounds 4 and 5.

Synthesis of Compound 1. Under N_2 atmosphere, the mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (2.0 g, 5.1 mmol), 3-aminopentane (0.6 mL, 5.1 mmol), 4-bromoanilines (875 mg, 5.1 mmol) and imidazole (20 g) was stirred at 140 °C for 4 h. After completion of reaction, the reaction mixture was cooled to 90 °C and then 50 mL water was added into reaction mixture and continued to stir for further 30 minutes. Then mixture was filtered using Büchner funnel and the residue solid was washed by 20 % KOH aqueous solution (3 × 50 mL). The crude product was dried in desiccator at 60 °C and purified with column chromatography (silica gel, CH_2Cl_2) to give a red solid (1.7 g, yield: 55 %). mp > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70–8.65 (m, 4H), 8.59 (d, 4H, *J* = 8.0 Hz), 7.71 (d, 2H, *J* = 8.0 Hz), 7.27 (s, 1H), 7.25 (s, 1H), 5.11–5.31 (m, 1H), 2.33–2.22 (m, 2H), 2.02–1.91 (m, 2H), 0.94 (t, 6H, *J* = 8.0 Hz).

Synthesis of Compound 2. Under N_2 atmosphere, the mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (2.0 g, 5.1 mmol), imidazole (20.0 g, 293.8 mmol) and 3-aminopentane (2.3 mL, 20.1 mmol) was stirred at 140 °C for 5 h. After completion of reaction, the reaction mixture was cooled to 90 °C and then 50 mL water was added into reaction mixture and continued to stir for further 30 minutes. Then mixture was filtered using vacuum crucible and residue solid was washed by 20 % KOH aqueous solution (3 × 50 mL). The crude product was dried in desiccator at 60 °C and purified with column chromatography (silica gel, CH_2Cl_2) to give a red solid (2.6 g, yield: 96%). mp > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70–8.63 (m, 8H), 5.11–5.04 (m, 2H), 2.33–2.21 (m, 4H), 2.00–1.89 (m, 4H), 0.93 (t, 12H, J = 8.0 Hz). TOF MALDI–HRMS ($[C_{34}H_{30}N_2O_4]^-$) Calcd: m/z = 530.2206. Found: m/z = 530.2220.

Synthesis of Compound 3. A mixture of Compound **2** (2.65 g, 5 mmol) and KOH (0.91 g, 0.016 mmol) in *tert*-butyl alcohol (100 mL) were heated at 100 °C for 1 h. The mixture was cooled to room temperature and poured into 10 % HCl (200 mL), and the precipitate was filtered. The residue was stirred into warm solution of potassium chloride (16 g, 0.21 mmol) and potassium hydroxide (20 g, 0.36 mmol) in 200 mL water. The solid was filtered and washed with aqueous solution. The solid was then stirred with water and filtered. Then HCl was added into dark red filtrate, resulting precipitate was filtered and dried at 90 under vacuum to afford black solid. The crude product was used in next step without further purification. TOF MALDI–HRMS ($[C_{29}H_{19}NO_5]^-$) Calcd: m/z = 461.1263. Found: m/z = 461.1256.

Synthesis of Compound 4. Under N_2 atmosphere, a mixture of carbazole (2.56 g, 15 mmol), 4-fluoronitrobenzene (6.50 mL, 21 mmol) and K_2CO_3 (10.56 g, 76 mmol) in 80 mL of *N,N*-dimethylformamide (DMF) was stirred at 140 °C for 12 h. After completion of reaction, reaction mixture was poured into distilled water, resulting yellow precipitates were collected by filtration and recrystallized from ethyl acetate to afford pure product as yellow solid (3.20 g, yield: 74%) mp > 250 °C. ^{1}H NMR (400 MHz; CDCl$_3$) δ 8.50 (d, 2H, J = 8.0 Hz), 8.16 (d, 2H, J = 8.0 Hz), 7.81 (d, 2H, J = 8.0 Hz), 7.52–7.44 (m, 4H), 7.36 (t, 2H, J = 8.0 Hz).

Synthesis of Compound 5. Under a N$_2$ atmosphere, mixture of compound 4 (3.00 g, 11 mmol) and stannous chloride dihydrate (15.20 g, 67 mmol) in EtOH (35 mL) was stirred at 70 °C for 100 min. After completion of reaction, the solvent was removed under reduced pressure and excessive NaOH solution was added slowly to the residue under vigorous stir. The mixture was extracted with ether when it became oyster white. The organic extracts were dried over anhydrous MgSO$_4$ and concentrated under reduced pressure to afford compound **2** as brown viscous liquid (2.56 g, 90%). ^{1}HNMR (DMSO, 400 MHz): δ 8.20 (d, 2H, J = 8.0 Hz), 7.42–7.38 (m, 2H), 7.27–7.22 (m, 4H), 7.19 (d, 2H, J = 8.0 Hz), 6.81 (d, 2H, J = 8.0 Hz), 5.44 (s, 2H).

Synthesis of PBI-Ph. Under N$_2$ atmosphere, the mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (1.0 g, 2.5 mmol), 3-aminopentane (0.3 mL, 2.5 mmol), aniline (237 mg, 2.5 mmol) and imidazole (20 g) was stirred at 140 °C for 4 h. After completion of reaction, the reaction mixture was cooled to 90 °C and then 50 mL water was added into reaction mixture and continued to stir for further 30 minutes. Then mixture was filtered using vacuum crucible and residue solid was washed by 20 % KOH aqueous solution (3 × 50 mL). The crude product was dried in desiccator at 60 °C and purified with column chromatography (silica gel, CH$_2$Cl$_2$) to give a red solid (600 mg, yield: 45 %). mp > 250 °C . ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.70–8.65 (m, 4H), 8.59–d, 4H, J =8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz), 7.27 (s, 1H), 7.25 (s, 1H), 5.11–5.31 (m, 1H), 2.33–2.22 (m, 2H), 2.02–1.91 (m, 2H), 0.94 (t, 6H, J = 8.0 Hz). TOF MALDI–HRMS ([C_{35}-$H_{24}N_2O_4$]$^-$) Calcd: m/z = 536.1736. Found: m/z = 536.1760.

3. Singlet Oxygen Photosensitizing Measurement

The $^1O_2$ quantum yields (Φ_Δ) of the photosensitizers (PBI-Cz dyads) were measured with 2,6-diiodobodipy as standard ($\Phi_\Delta = 0.83$ in DCM). The absorbance of the $^1O_2$ scavenger 1,3-diphenylisobenzofuran (DPBF) was adjusted around 1.0 in air saturated dichloromethane. Then, the photosensitizer was added to the solution of DPBF, and the photosensitizer's absorbance was adjusted around 0.2−0.3. The solution in the cuvette was irradiated with monochromatic light at the peak absorption wavelength for 10 s. Then the absorbance at 414 nm was measured after each irradiation. The slope of plots of absorbance of DPBF at 414 nm vs irradiation time for each photosensitizer was calculated. Singlet oxygen quantum yields (Φ_Δ) were calculated according to the following equation:

$$\phi_{\Delta,\mathrm{sam}} = \phi_{\Delta,\mathrm{s}td}\left(\frac{1-10^{A_{std}}}{1-10^{A_{sam}}}\right)\left(\frac{m_{sam}}{m_{std}}\right)\left(\frac{\eta_{sam}}{\eta_{std}}\right)^2$$

Where '*sam*' and '*std*' designate the photosensitizers and 2,6-diiodobodipy, respectively, A stands for absorbance, m is the slope of the curves of absorbance of DPBF (414 nm) vs the irradiation time, η is refractive index of the solvent.

4. Molecular structure characterization data

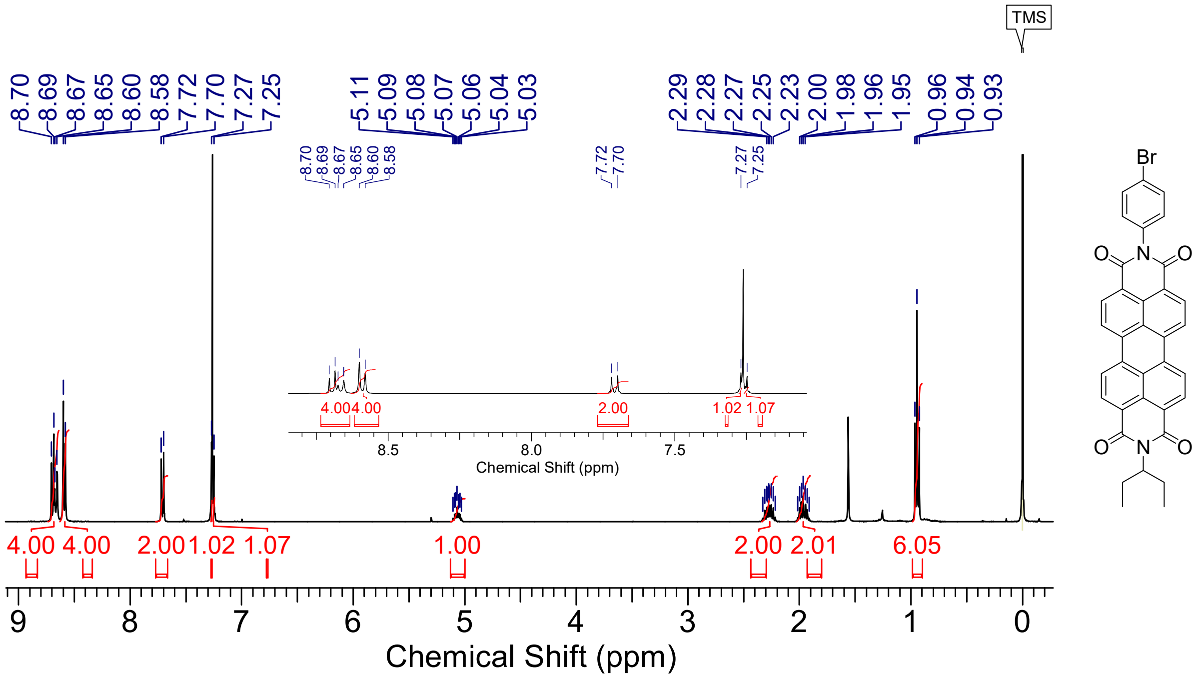


Figure S1. ^{1}H NMR spectrum of compound **1** (400 MHz, $CDCl_3$), 25°C.

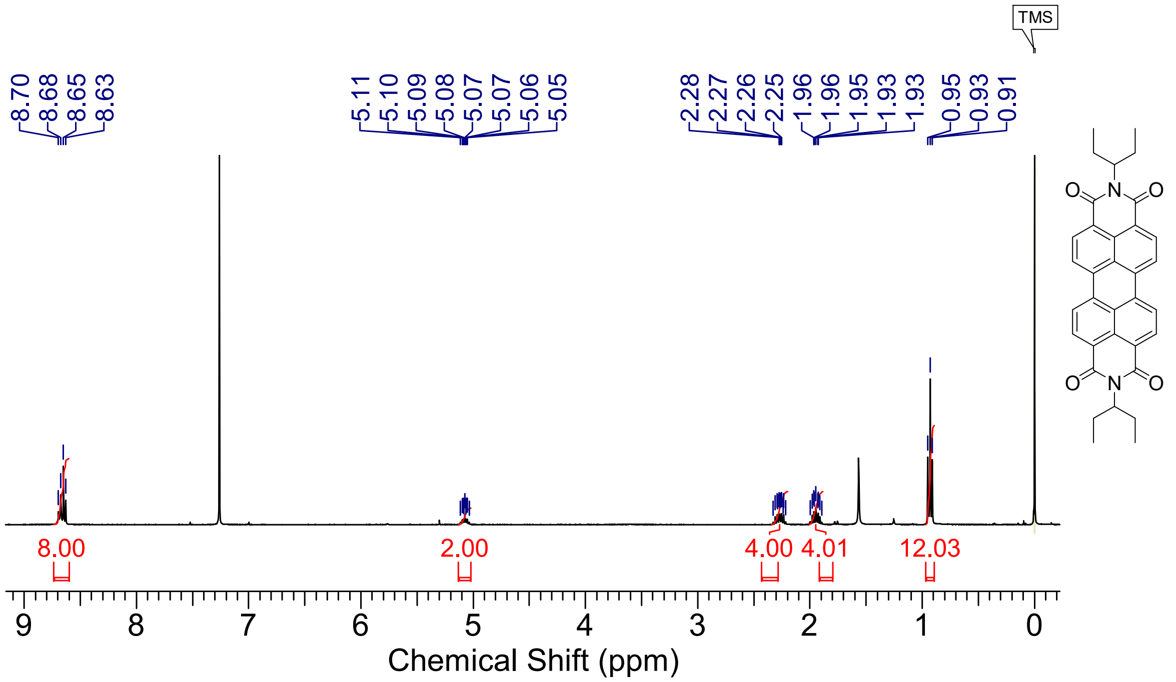


Figure S2. ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$), 25°C.

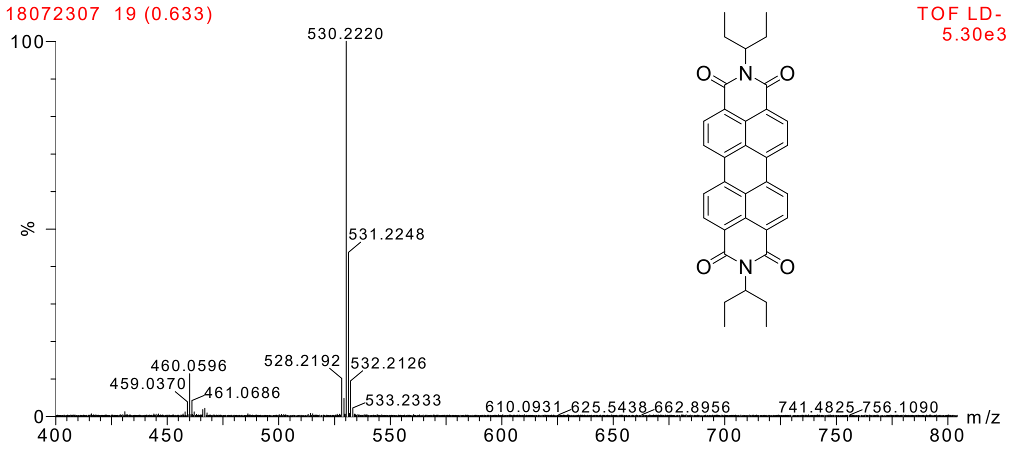


Figure S3. MALDI HR mass spectrum of compound **2**.

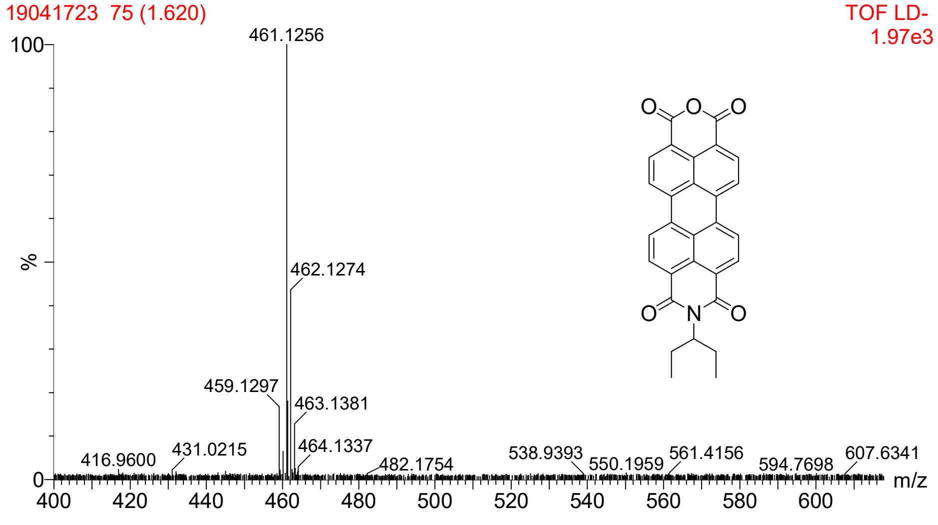


Figure S4. MALDI HR mass spectrum of compound **3**.

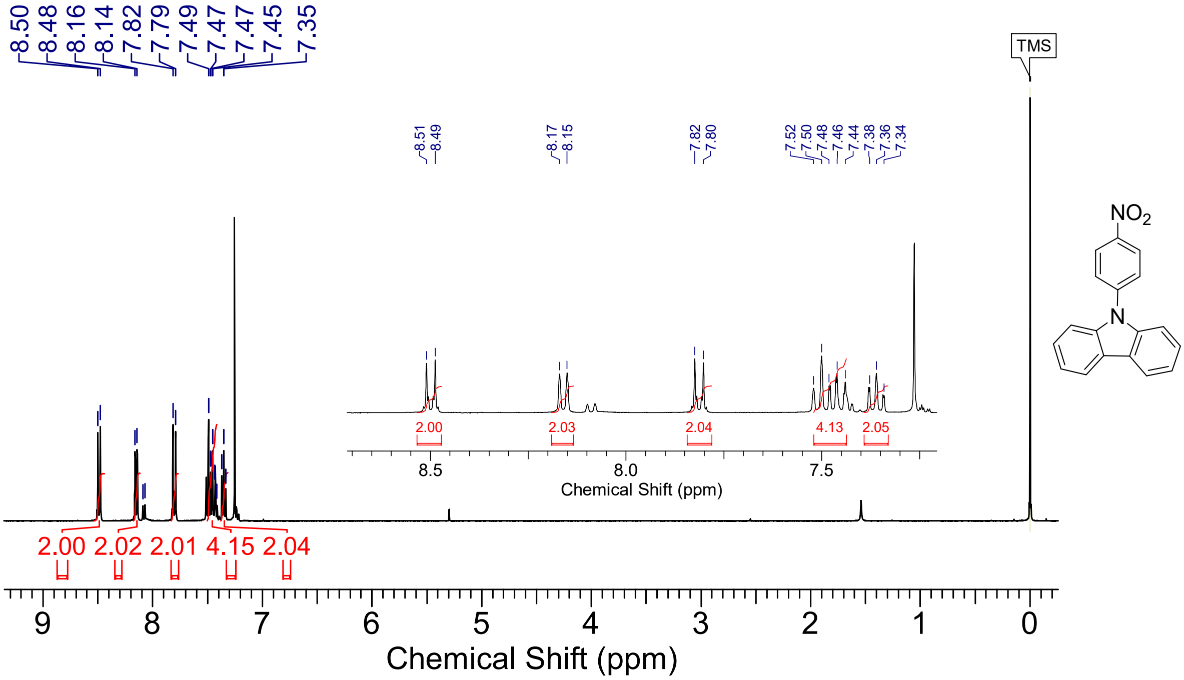


Figure S5. ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$), 25°C.

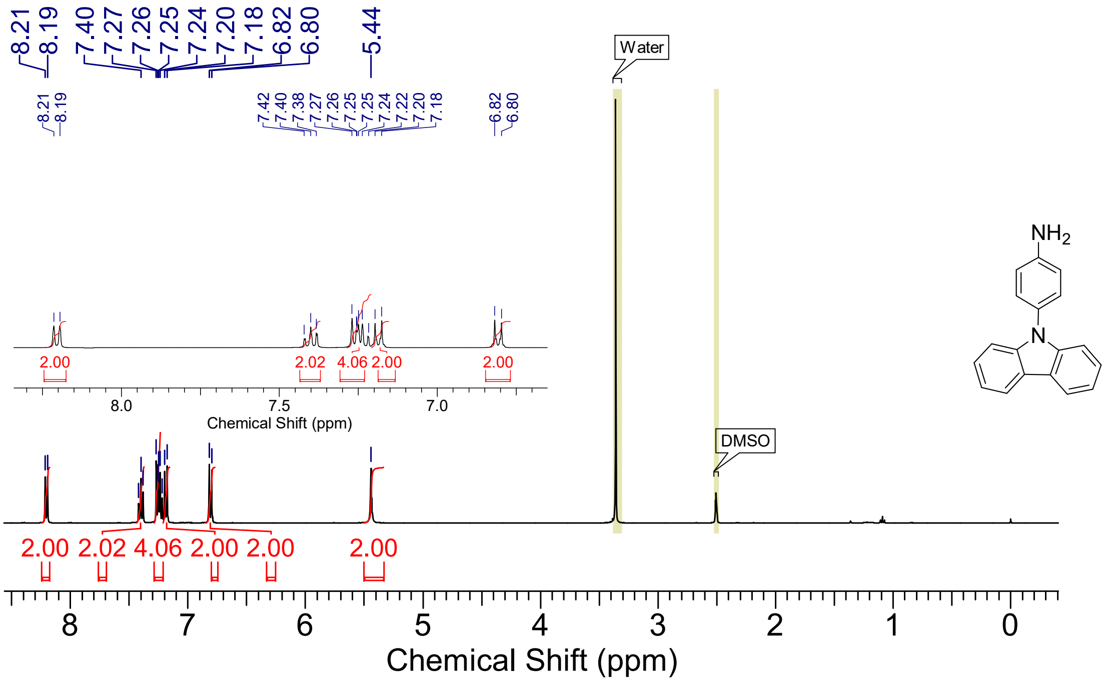


Figure S6. ^{1}H NMR spectrum of compound **5** (400 MHz, DMSO-d_6), 25°C.

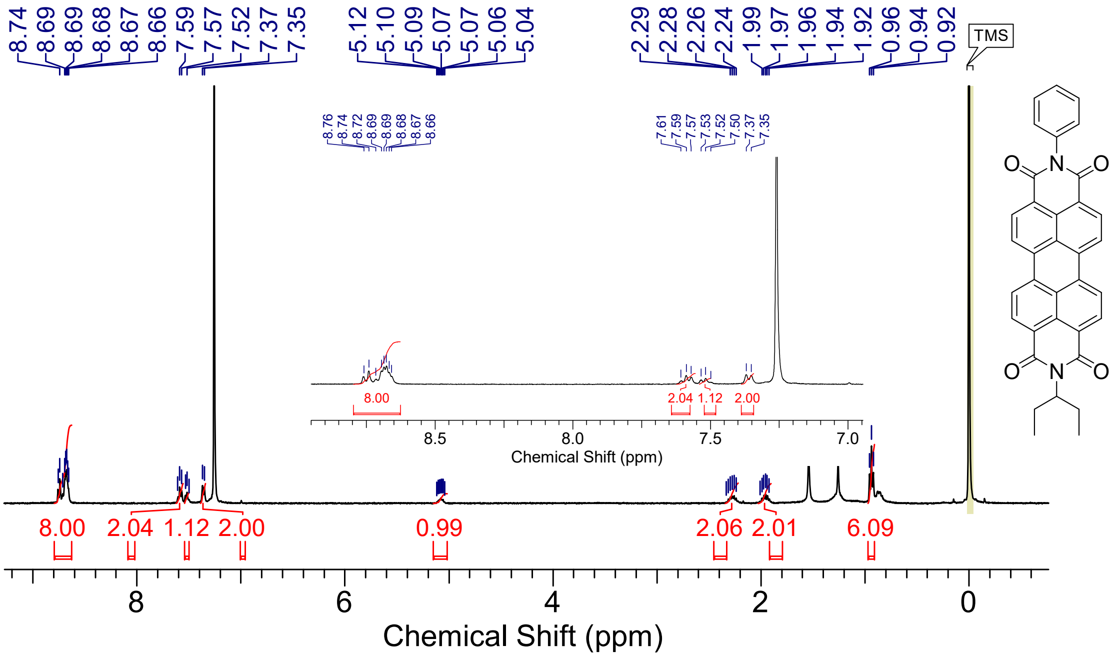


Figure S7. ^{1}H NMR spectrum of **PBI-Ph** in $CDCl_3$ (400 MHz), 25°C.

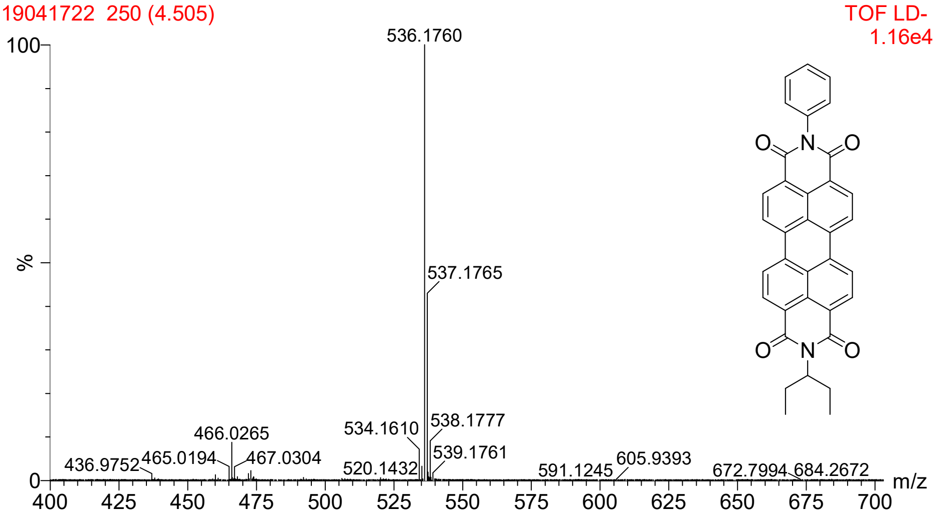


Figure S8. MALDI HR mass spectrum of **PBI-Ph**.

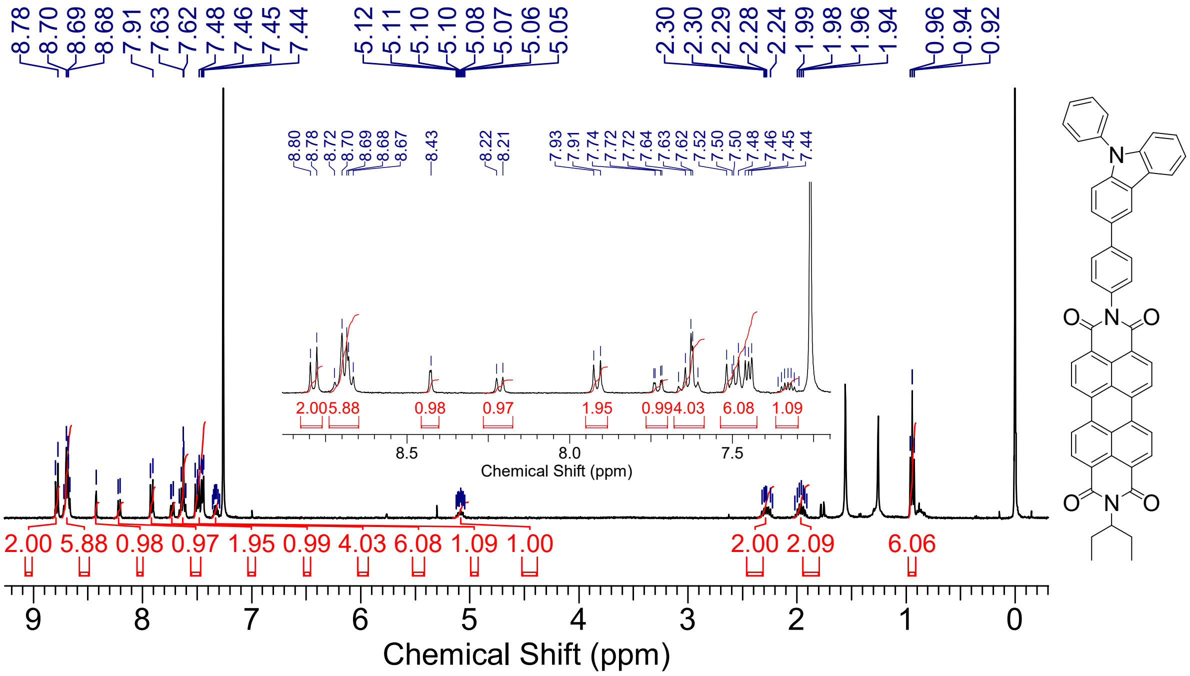


Figure S9. ^{1}H NMR spectrum of compound **PBI-Cz-1** in $CDCl_3$ (400 MHz), 25°C.

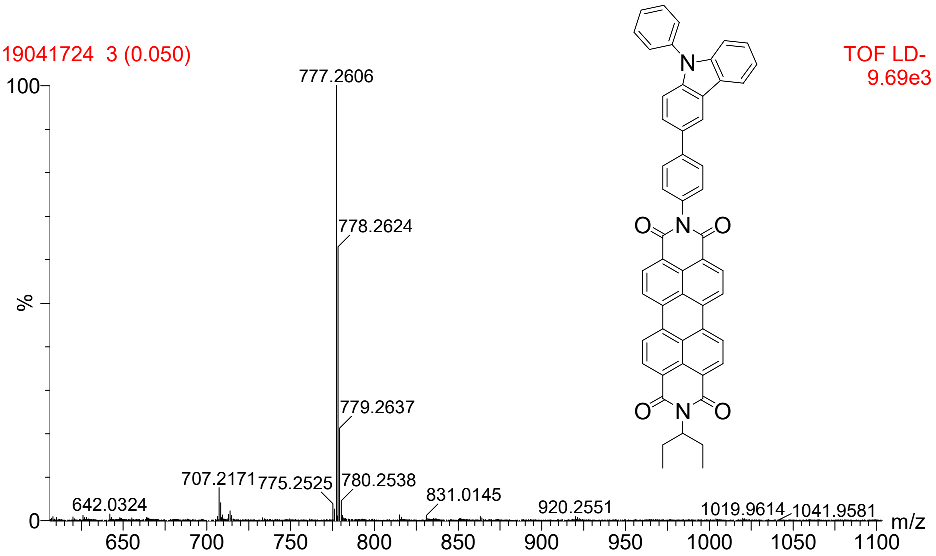


Figure S10. MALDI HR mass spectrum of **PBI-Cz-1**.

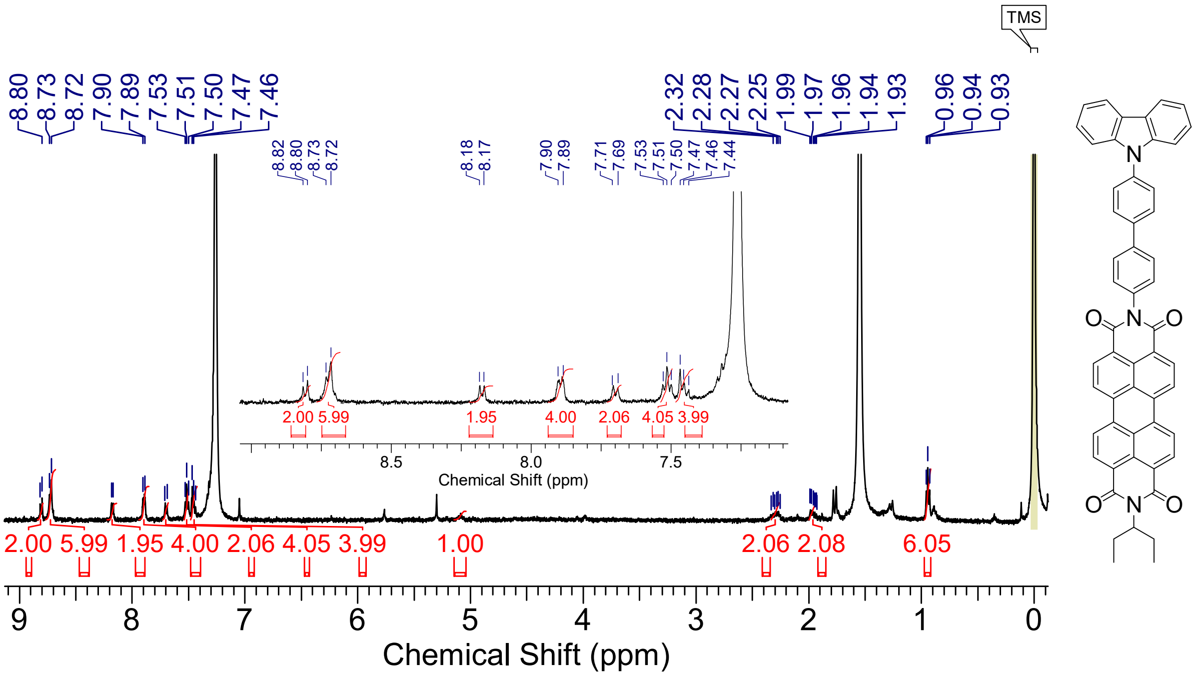


Figure S11. ^{1}H NMR spectrum of compound **PBI-Cz-2** (500 MHz, in $CDCl_3$), 25°C.

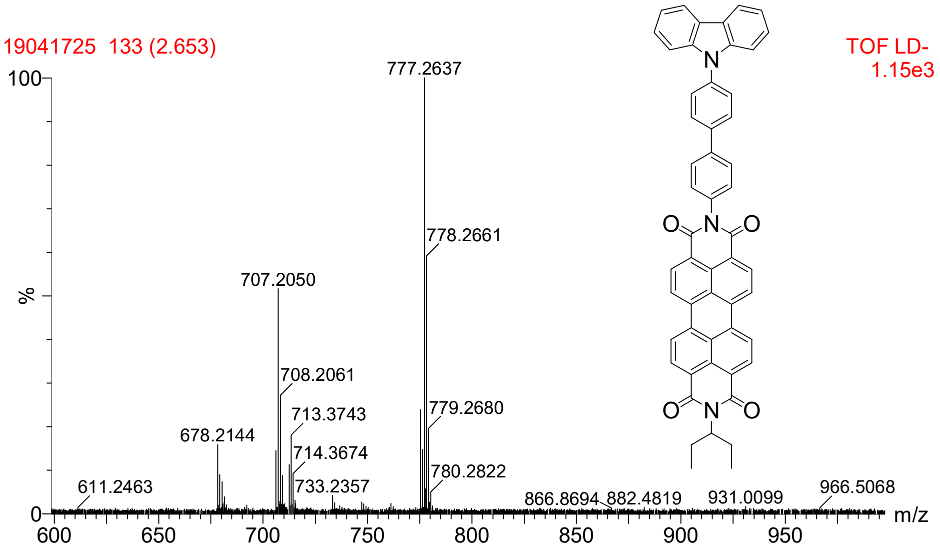


Figure S12. MALDI HR mass spectrum of **PBI-Cz-2**.

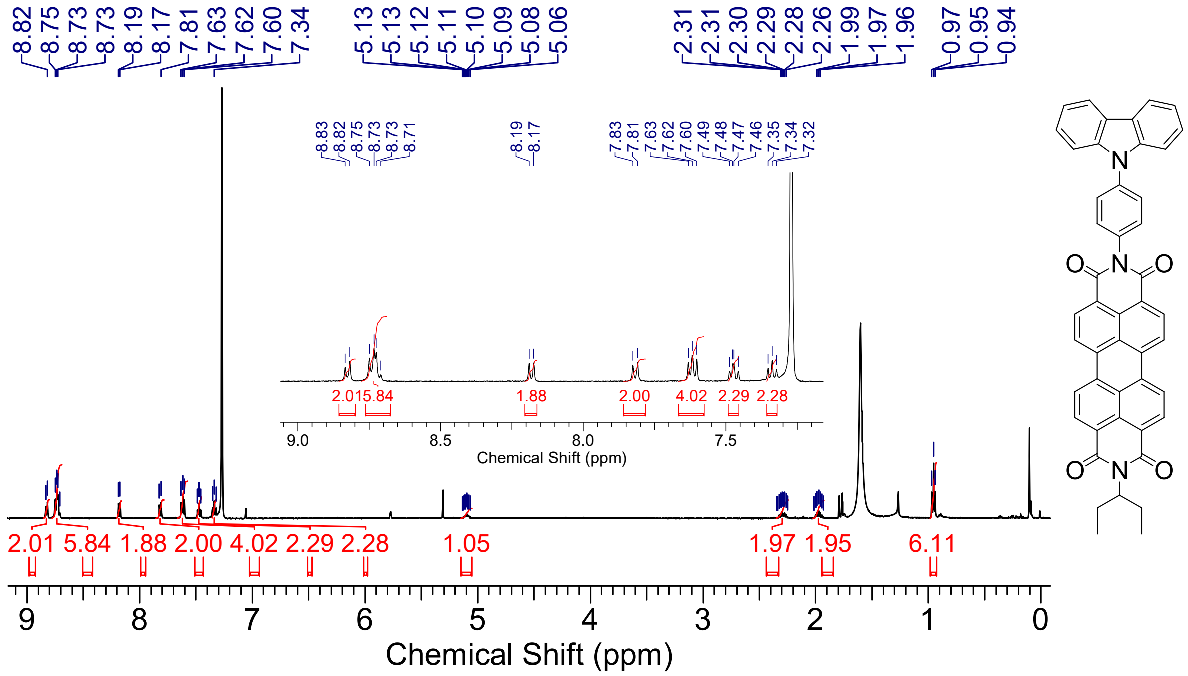


Figure S13. ^{1}H NMR spectrum of compound **PBI-Cz-3** (500 MHz, in $CDCl_3$), 25°C.

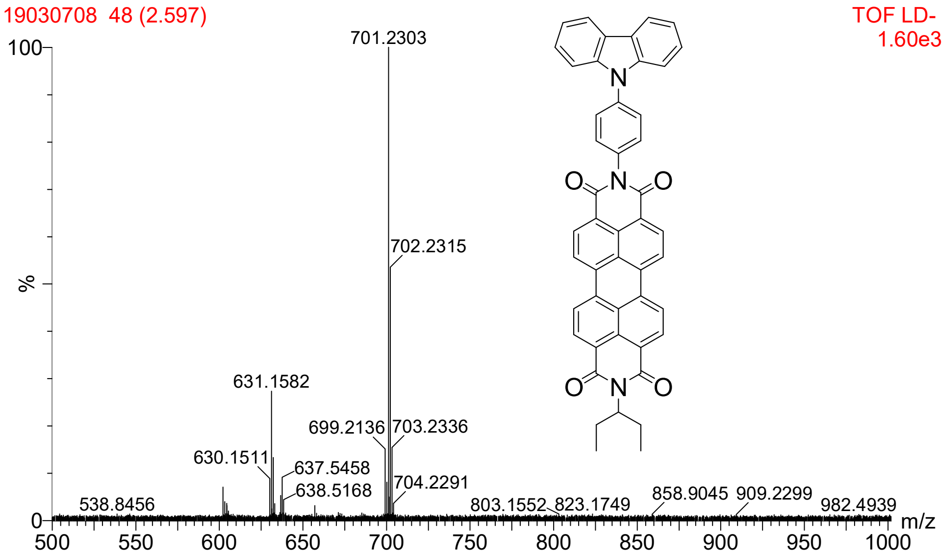


Figure S14. MALDI HR MS of **PBI-Cz-3**(CH_2Cl_2).

5. UV/Vis absorption spectra

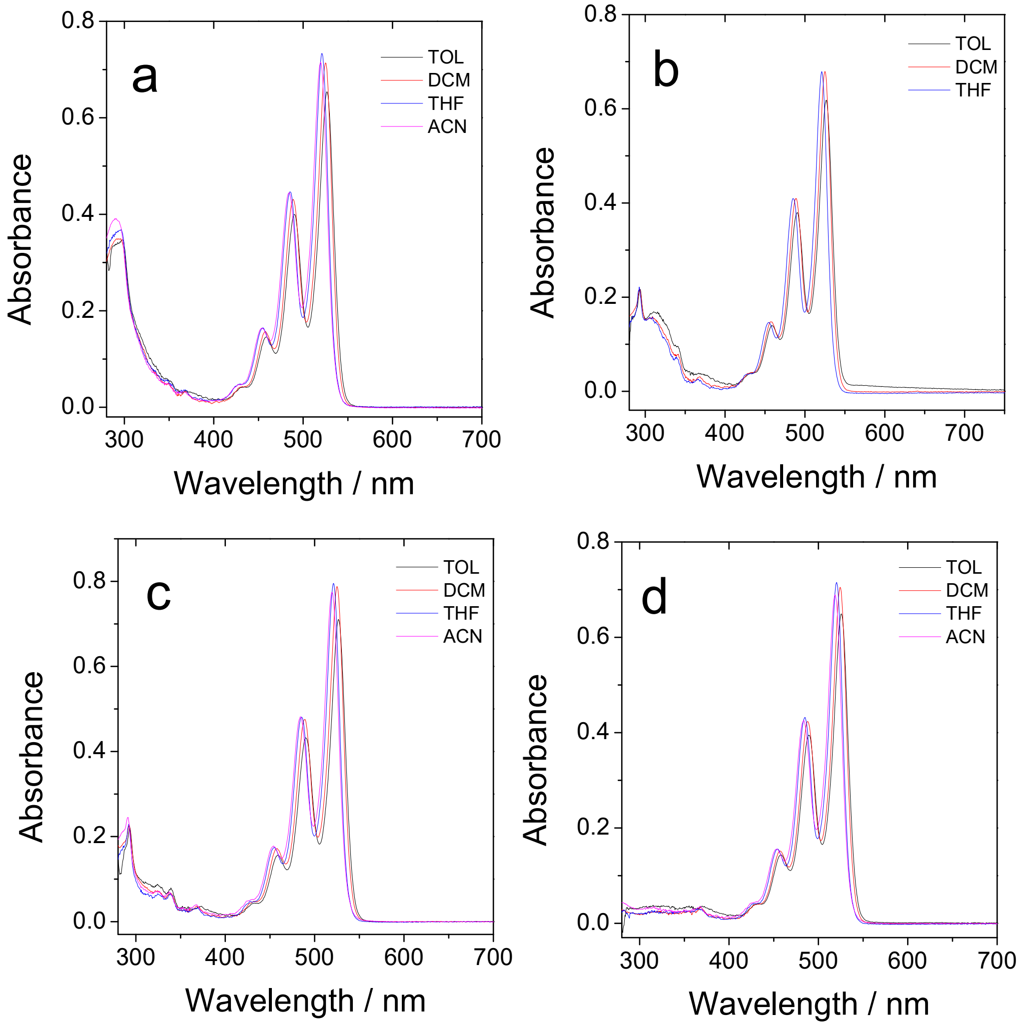


Figure S15. (a) UV–vis absorption spectra of (a) **PBI-Cz-1**; (b) **PBI-Cz-2**; (c) **PBI-Cz-3** and (d) **PBI-Ph** in different solvents, *c* = 1.0 × 10^{-5} M, 20 °C.

6. Fluorescence emission spectra

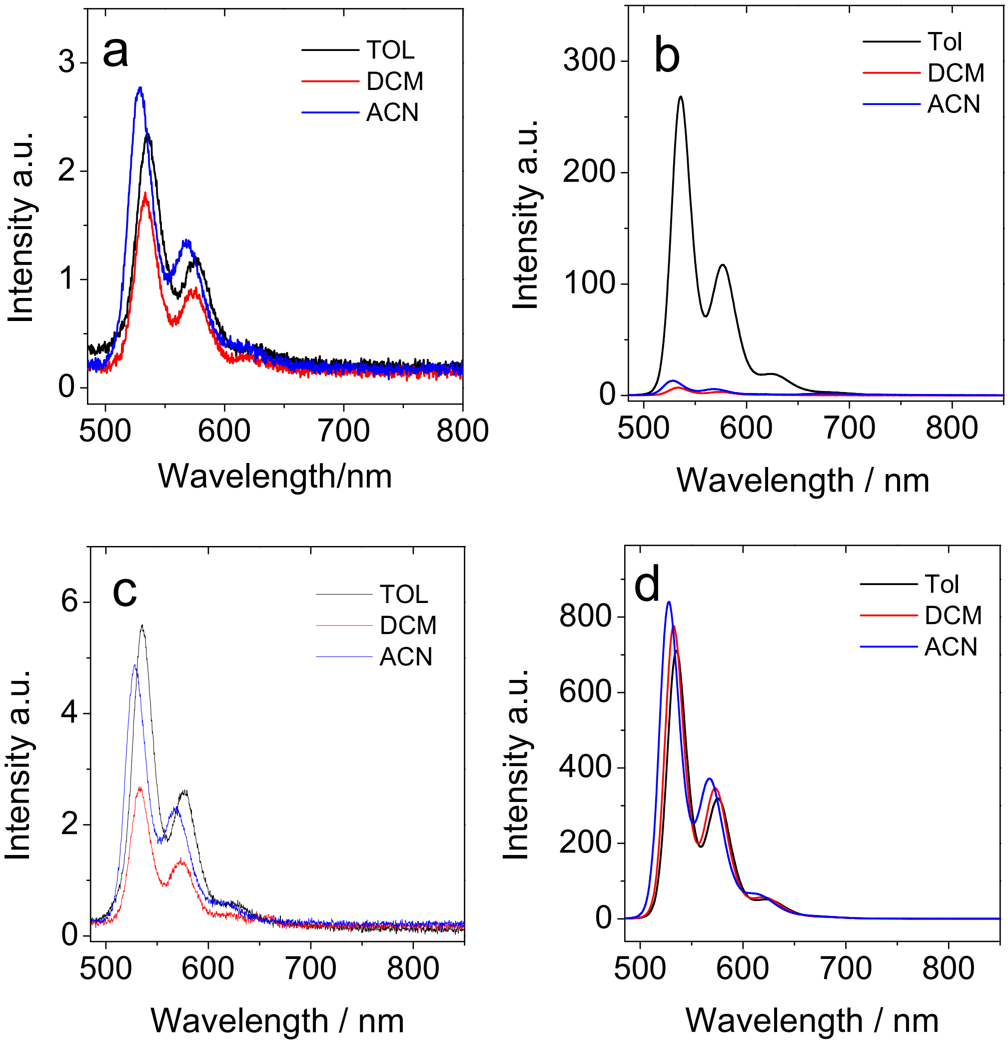


Figure S16. Fluorescence emission spectra of (a) **PBI-Cz-1**; (b) **PBI-Cz-2**; (c) **PBI-Cz-3** and (d) **PBI-Ph,** λ_{ex} = 475 nm. Optically matched solutions were used. All the compounds have the same absorbance at the excitation wavelength (A = 0.23), 20 °C.

7. Fluorescence emission decay curves.

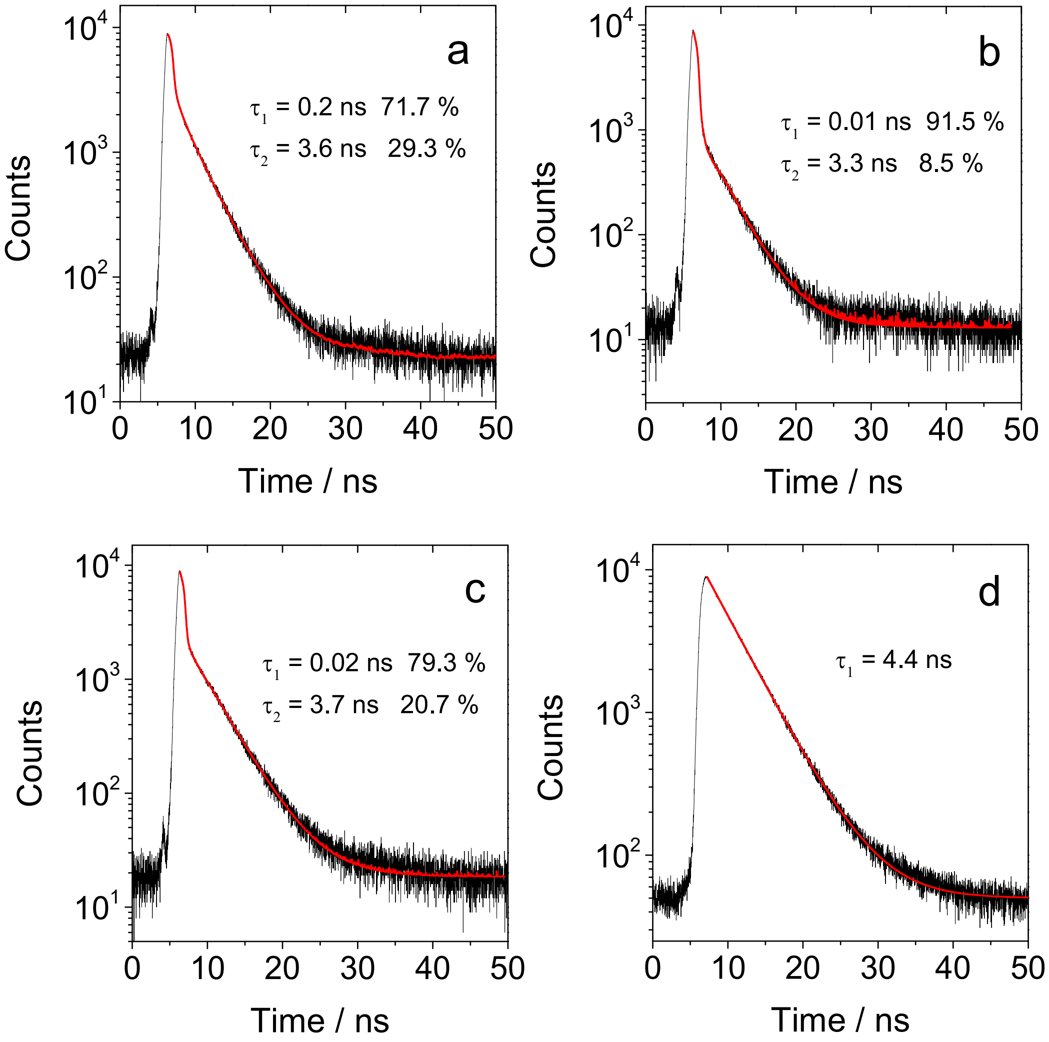


Figure S17. Fluorescence emission decay curves of; (a) **PBI-Cz-1**; (b) **PBI-Cz-2**; (c) **PBI-Cz-3** and (d) **PBI-Ph** (λ_{em} = 535 nm), λ_{ex} = 510 nm. $c = 1.0 \times 10^{-5}$ M in dichloromethane, 20 °C.

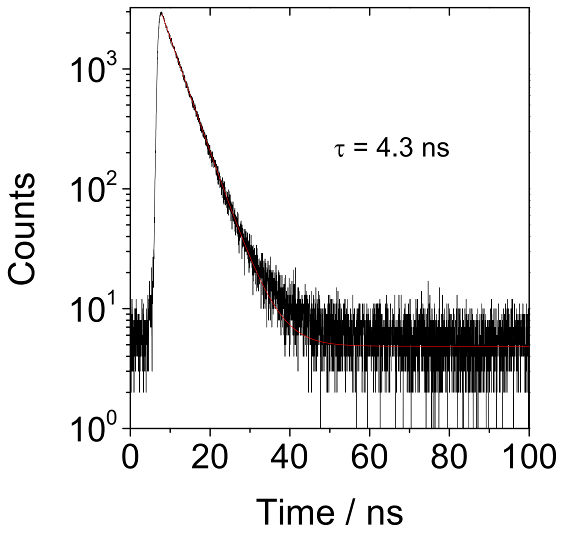


Figure S18. Fluorescence emission decay curve of **PBI**, (λ_{em} = 520 nm), λ_{ex} = 510 nm. $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.

8. Photoreduction

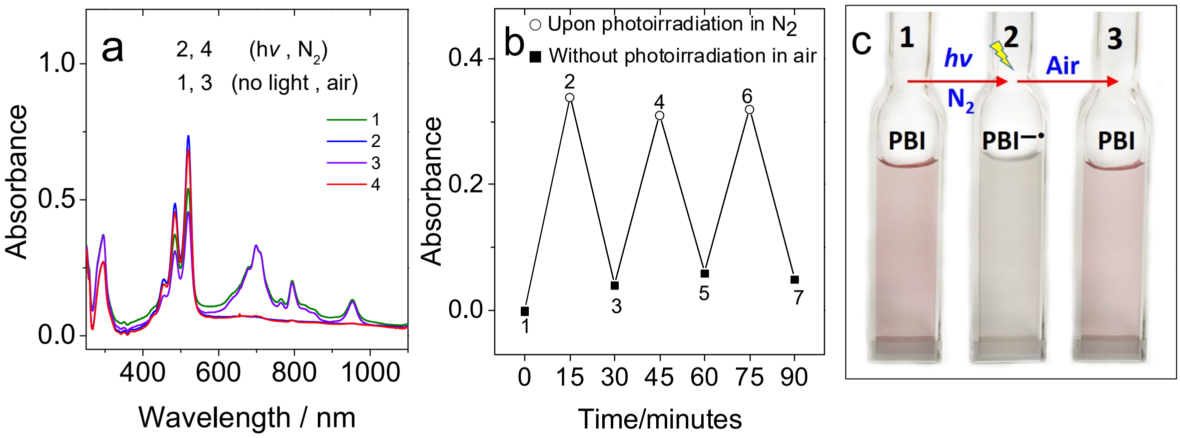


Figure S19. (a) UV−Vis absorption spectra changes of **PBI-Cz-1** upon continuous photo-irradiation in the presence of TEOA in the deaerated ACN and reversibility of the formation of PBI$^{-•}$ radical anion upon photo-irradiation; (b) **PBI-Cz-1,** Reversibility of the formation of PBI$^{-•}$ monitored at the 698 nm absorption band (after generation of the radical anion, re-exposure to air will oxidize the radical anion to the neutral form); (c) Photos showing the reversible color change of the **PBI-Cz-1**/TEOA mixed solution upon photo-irradiation and re-exposure to air: *c* [**PBI-Cz-1**] = 1.0 × 10^{-5} M, *c* [TEOA] = 1.0 × 10^{-4} M. The light source is a xenon lamp, power density is 180 mW/cm^2, photo-irradiation time: 15 min, 20 °C.

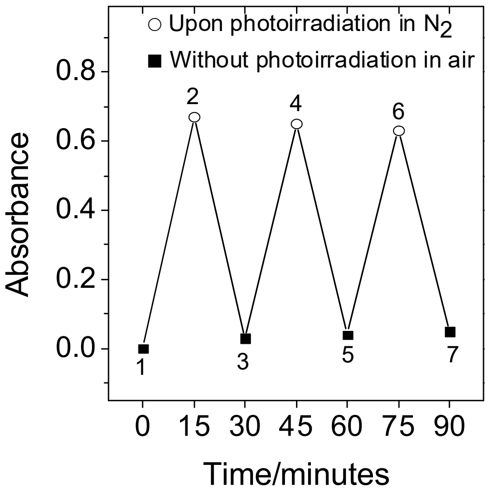


Figure S20. Reversibility of the formation of PBI$^{-\bullet}$ with **PBI-Cz-2**, monitored at the 698 nm absorption band (after generation of the radical anion, re-exposure to air will oxidize the radical anion to the neutral form).

9. Optimized Ground State Conformations and the Dihedral Angle.

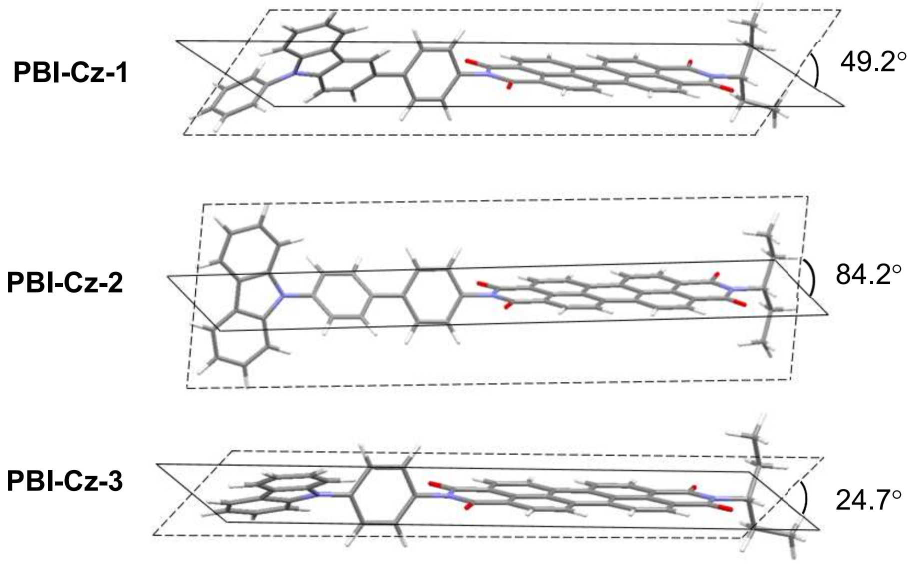
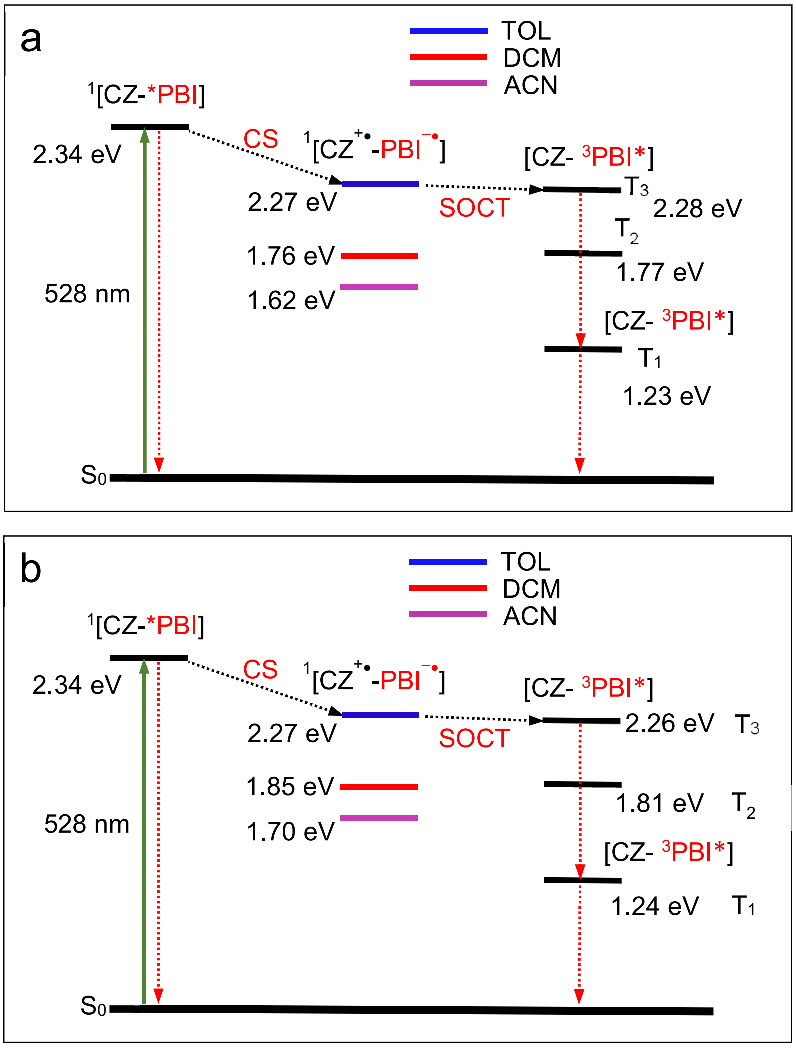


Figure S21. Optimized conformations and the dihedral angles (degree) of the PBI and Cz units in the dyads calculated by DFT (CAM-B3LYP/6-31G (d)) with Gaussian 09W. Solid lines indicate PBI plane and dash lines indicate Cz plane.

10. Photophysical processes

Scheme S1. Jablonski Diagram Demonstrating the Photophysical Processes Involved in (a) PBI-Cz-1 and (b) PBI-Cz-2 Upon Photoexcitation[a]



[a] The energy levels of the excited state are derived from the spectroscopic and electrochemical data. The triplet energy levels are estimated by TD-DFT method. The numbers in superscripts indicates the spin multiplicity.