Electronic Supplementary Information for:

Spin-Orbit Charge Transfer Intersystem Crossing in the Perylenemonoimide-Phenothiazine Compact Electron Donor-Acceptor Dyads

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Contents

1. General Information

All the chemicals used in synthesis are analytically pure and were used as received. Solvents were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on the Bruker Avance spectrometers (400 MHz or 500 MHz). ^{1}H and ^{13}C 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 HRMS (MALDI-TOF) and HRMS (EI).

The fluorescence spectra of compounds were recorded on a RF-5301PC spectrofluorometer (Shimadzu, Japan) at room temperature. In the comparison of the fluorescence intensity of different solutions, optically matched solution of compounds were sued, i.e. the absorbance of compounds at the excitation wavelength were adjusted to be the same, in order to eliminate the effect of fluorescence intensity caused by the difference in the absorbance of compounds. The fluorescence quantum yields were measured with the relative method, i.e. **BDP-1** was used as standard (molecular structure was shown in Scheme S1. Φ_F = 4.4% in toluene). In some cases **BDP** was used as standard for the fluorescence quantum yield measurement (Φ_F = 72% in THF). Luminescence lifetimes were measured on an OB920 luminescence lifetime instrument (Edinburgh Instruments, U.K.), equipped with EPL picosecond pulsed laser and TCSPC detection modules.

The radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) of compounds were calculated using the following equation S1 and S2, based on the *fluorescence* of the charge transfer state (CT emission):

$$k_r = \Phi_F / \tau \qquad \text{(S1)}$$

$$k_{nr} = (1 - \Phi_F)/\tau \qquad \text{(S2)}$$

In the above equations, Φ_F is the fluorescence quantum yield and τ is the fluorescence lifetime of the compound.

Singlet oxygen quantum yields (Φ_Δ) of compounds were measured with 1,3-diphenylisobenzofuran (DPBF) as singlet oxygen scavenger. By following the absorption (λ_{max} = 414 nm) of DPBF, the $^{1}O_2$ production was monitored. For calculation of singlet oxygen quantum yield (Φ_Δ), the following equation S3 was used:

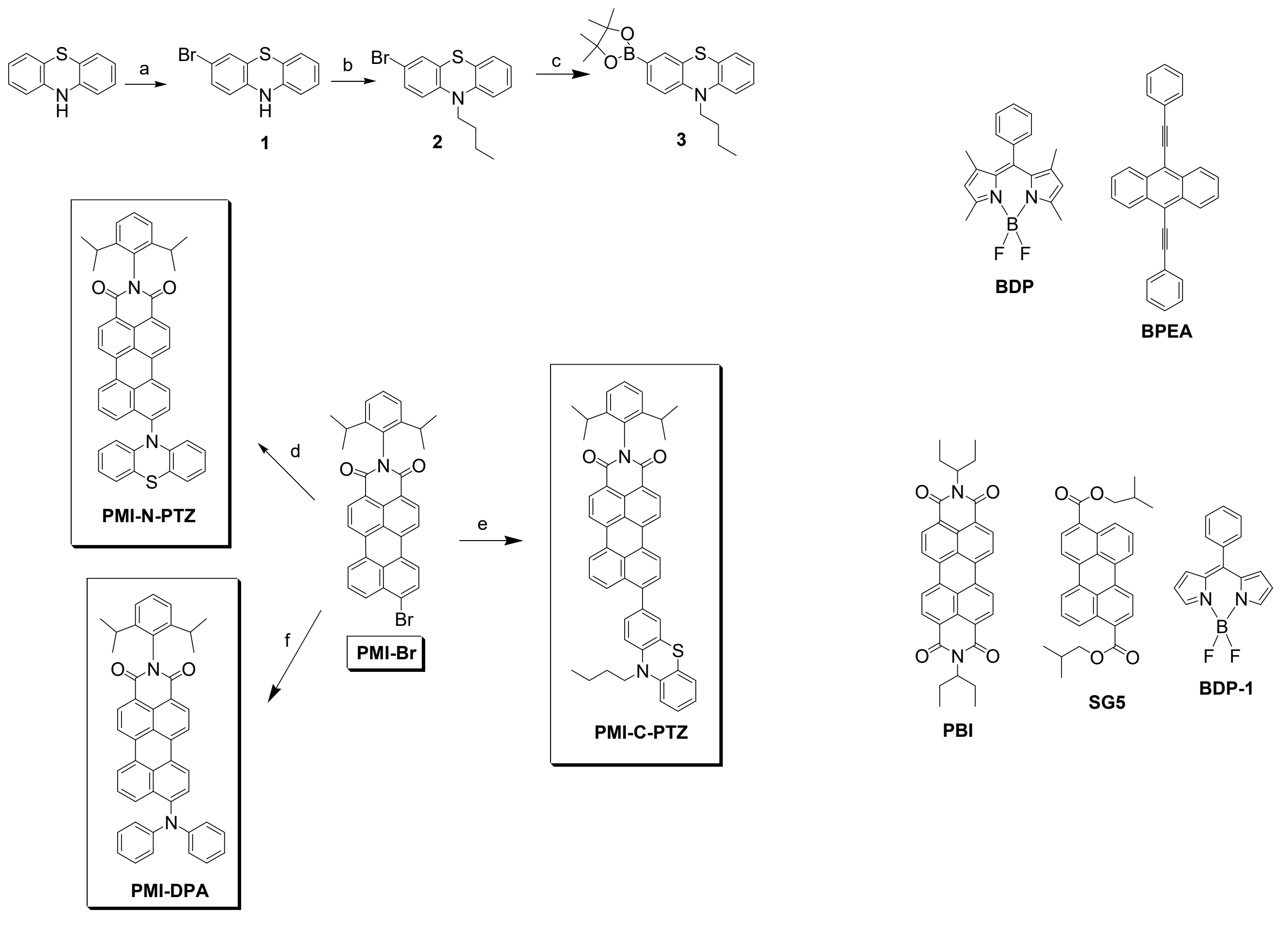
$$\Phi_{sam} = \Phi_{std}\left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right)\left(\frac{m_{sam}}{m_{std}}\right)\left(\frac{\eta_{sam}}{\eta_{std}}\right)^2 \qquad \text{(S3)}$$

In the above equation, "std" and "sam" stands for standard and sample. η, A, Φ and m stands for refractive index of the solvent, absorbance at excitation wavelength, singlet oxygen quantum yield and slope of the absorbance of DPBF changing with time, respectively. For measurement, optically matched solutions of sample and standard were used. DiiodoBodipy was used as standard (Φ_Δ = 85% in toluene) for the measurement of the singlet oxygen quantum yield.

The nanosecond transient absorption spectra were measured on an LP980 laser flash photolysis spectrometer (Edinburgh Instruments, UK). The samples were excited with a nanosecond pulsed laser (Opolette 355II+UV nanosecond pulsed laser, the wavelength is tunable in the range of 200−2200 nm, OPOTEK, USA) and the signal was digitized with a Tektronix TDS 3012B oscilloscope. Each sample was purged with N_2 in 15min before measurement.

2. Syntheses of the Compounds

Scheme S1. Synthesis of PMI Derivatives[a]



[a] Key: (a) NBS, THF, ice bath, 1 h, under N_2, yield: 20%; (b) *n*-C_4H_9Br, KOH, dry DMF, RT, overnight, under N_2, yield: 88%; (c) bis(pinacolato)diboron, AcOK, Pd(dppf)Cl_2.CH_2Cl_2, 1,4-dioxane, 80 °C, 18 h, yield: 45%; (d) phenothiazine, tri-*tert*-butylphosphine, sodium *tert*-butoxide, $Pd_2(dba)_3$, dry toluene, 80 °C, 8 h, under N_2, yield: 61%; (e) compound **3**, K_2CO_3, $Pd(PPh_3)_4$, DMF/H_2O, 80 °C, 3 h, under N_2, yield: 42%; (f) diphenylamine, similar to step (d), yield: 55%.

Compound PMI-N-PTZ. Compound **PMI-Br** (100 mg, 0.18 mmol), phenothiazine (42.6 mg, 0.21 mmol) and sodium *tert*-butoxide (51.3 mg, 0.53 mmol) were mixed together with dry toluene (5 mL) in a 25 mL two-necked round bottom flask under N_2 atmosphere. Then $Pd_2(dba)_3$ (8.1 mg, 0.01 mmol) and tri-*tert*-butyl phosphine (4.4 mg, 0.02 mmol) were added and the reaction mixture was stirred at 80 °C under N_2 for 9 h. Water (5 mL) and CH_2Cl_2 (25 mL) were added after the reaction mixture was cooled down to room temperature. The organic layer was washed with saturated NaCl solution (3 × 30 mL) and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified with column chromatography (silica gel, petroleum ether/CH_2Cl_2 = 2:3, v/v) to give a dark brown solid (74.2 mg, yield: 61%). Mp: > 250 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.74 (t, 3H, J = 8.0 Hz), 8.58 (m, 3H), 8.27 (d, 1H, J = 8.0 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.67 (t, 1H, J = 8.0 Hz), 7.51 (t, 1H, J = 8.0 Hz), 7.35 (d, 2H, J = 4.0 Hz), 7.09 (d, 2H, J = 8.0 Hz), 6.83 (t, 4H, J = 8.0 Hz), 6.20 (d, 2H, J = 4.0 Hz), 2.82–2.75 (m, 2H), 1.20 (d, 12H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 163.91, 163.90, 145.73, 143.55, 137.13, 136.71, 132.21, 132.08, 130.10, 130.94, 130.50, 130.26, 130.11, 130.07, 129.51, 128.43, 127.09, 126.96, 126.85, 126.59, 124.56, 124.34, 124.05, 122.94, 121.68, 121.45, 121.00, 120.75, 120.19, 115.79, 31.59, 29.17, 24.04, 22.66, 14.11. HRMS (MALDI-TOF): Calcd ($[C_{46}H_{34}N_2O_2S]^+$), m/z = 678.2341; found, m/z = 678.2353.

Compound PMI-C-PTZ. Compound **PMI-Br** (100 mg, 0.18 mmol), 10-butyl-3-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (81.5 mg, 0.22 mmol), K_2CO_3 (89.0 mg, 0.64 mmol), DMF (5 mL) and water (0.5 mL) were mixed together in a 25 mL two-necked round bottom flask under N_2 atmosphere. After bubbling, the $Pd(PPh_3)_4$ (10.3 mg, 0.01 mmol) was added and the reaction mixture was stirred at 80 °C under N_2 for 3 h. Water (30 mL) was added after the reaction mixture was cooled down to room temperature. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified with column chromatography (silica gel, petroleum ether/CH_2Cl_2 = 1:10, v/v) to give a dark red solid (55.1 mg, yield: 42%). Mp: 241–243.3 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.66

(d, 2H, *J* = 8.0 Hz), 8.48–8.44 (m, 4H), 8.07 (d, 1H, *J* = 4.0 Hz), 7.61 (t, 1H, *J* = 8.0 Hz), 7.55 (d, 1H, *J* = 4.0 Hz), 7.49 (t, 1H, *J* = 4.0 Hz), 7.35–7.30 (m, 4H), 7.19 (d, 2H, *J* = 4.0 Hz), 6.99 (d, 3H, *J* = 32.0 Hz), 4.08 (s, 2H), 2.81–2.76 (m, 2H), 1.87 (s, 2H), 1.55–1.52 (m, 2H), 1.20 (d, 12H, *J* = 8.0 Hz), 1.02 (t, 3H, *J* = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 163.98, 145.73, 137.71, 137.48, 132.00, 131.11, 130.53, 129.48, 129.41, 128.96, 127.37, 127.07, 126.96, 124.00, 123.94, 123.54, 120.97, 120.30, 120.06, 115.75, 29.76, 29.14, 24.03, 20.27, 13.93. HRMS (MALDI-TOF): Calcd ($[C_{50}H_{42}N_2O_2S]^-$), *m*/*z* = 734.2967; found, *m*/*z* = 734.2964.

Compound PMI-DPA. Compound **PMI-Br** (100 mg, 0.18 mmol), diphenylamine (36.2 mg, 0.21 mmol) and sodium *tert*-butoxide (51.3 mg, 0.53 mmol) were mixed together with dry toluene (5 mL) in a 25 mL two-necked round bottom flask under N_2 atmosphere. Then $Pd_2(dba)_3$ (8.1 mg, 0.01 mmol) and tri-*tert*-butyl phosphine (4.4 mg, 0.02 mmol) was added and the reaction mixture was stirred at 80 °C under N_2 for 9 h. Water (4 mL) and CH_2Cl_2 (25 mL) were added after the reaction mixture was cooled down to room temperature. The organic layer was washed with saturated NaCl solution (3 × 30 mL) and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified with column chromatography (silica gel, petroleum ether/CH_2Cl_2 = 1:3) to give a dark purple solid (64.0 mg, yield: 55%). Mp: > 250 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.66 (s, 2H), 8.55 (d, 4H, *J* = 8.0 Hz), 8.13 (d, 1H, *J* = 8.0 Hz), 7.58–7.52 (m, 2H), 7.47 (s, 1H), 7.40 (d, 2H, *J* = 8.0 Hz), 7.33 (t, 4H, *J* = 8.0 Hz), 7.14–7.06 (m, 6H), 2.83–2.77 (m, 2H), 1.19 (d, 12H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 164.01, 148.37, 147.07, 145.74, 137.62, 137.44, 132.13, 132.04, 131.39, 131.10, 130.62, 129.82, 129.43, 127.64, 127.40, 127.13, 126.79, 126.65, 124.73, 124.16, 123.99, 122.95, 122.83, 121.04, 120.53, 120.22, 119.89, 31.59, 29.12, 24.03, 22.65, 14.11. HRMS (MALDI-TOF): Calcd ($[C_{46}H_{36}N_2O_2]^+$), *m*/*z* = 648.2777; found, *m*/*z* = 648.2759.

Compound 1. Under N_2 atmosphere, the phenothiazine (2.0 g, 10.0 mmol) was dissolved in dry THF (20 mL) in a double-necked round-bottomed flask. Then NBS (1.8 g, 10.0 mmol) was also dissolved in dry THF (20 mL) and added dropwise over 1 h with an additional funnel. The reaction mixture was stirred under the ice bath and quenched by water (40 mL) after the addition of NBS was completed. The aqueous layer was extracted by DCM (3 × 50 mL). The organic layer was combined and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 8:1) to give a light green solid (555 mg, yield 19.9%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.71 (s, 1H), 7.15–7.11 (m, 2H), 7.02–6.98 (m, 1H), 6.92 (d, 1H, J = 8.0 Hz), 6.78–6.75 (m, 1H), 6.68 (d, 1H, J = 8.0 Hz), 6.61 (d, 1H, J = 8.0 Hz). HRMS (ESI): Calcd ($[C_{12}H_8BrNS - H]^-$), *m/z* = 276.9561; found, *m/z* = 275.9483.

Compound 2. Under N_2 atmosphere, the mixture of **1** (1.0 g, 3.6 mmol), anhydrous potassium hydroxide (303 mg, 5.4 mmol) and dry DMF (5 mL) were added and stirred at 0 °C for 10 min. Then 1-bromobutane (0.47 mL, 4.3 mmol) was added dropwise to the reaction mixture and stirred at room temperature for 13 h. After the reaction was finished (monitored via TLC), the mixture was poured to the ice water (30 mL) and extracted with DCM (3 × 30 mL). Organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, petroleum ether) to give a yellow oil (1.06 g, yield 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23–7.20 (m, 2H), 7.16–7.09 (m, 2H), 6.93 (t, 1H, J = 8.0 Hz), 6.85 (d, 1H, J = 8.0 Hz), 6.69 (d, 1H, J = 8.0 Hz), 3.80 (s, 2H), 1.79–1.71 (m, 2H), 1.48–1.39 (m, 2H), 0.94 (t, 3H, J = 8.0 Hz). HRMS (EI): Calcd ($[C_{16}H_{16}BrNS]^+$), *m/z* = 333.0187; found, *m/z* = 333.0191.

Compound 3. Under N_2 atmosphere, the mixture of **2** (333 mg, 1 mmol), bis(pinacolato)diboron (381 mg, 1.5 mmol), potassium acetate (245 mg, 2.5 mmol), $Pd(dppf)Cl_2.CH_2Cl_2$ (24.5 mg, 0.03 mmol) and dry 1,4-dioxane (10 mL) were added and stirred at 80 °C for 18 h. Then the reaction mixture was cooled to the room temperature, poured to the ice water (20 mL) and extracted with DCM (3 × 30 mL). Organic layer was washed with water (2 × 100 mL) and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel, petroleum ether: DCM = 3:2) to give a yellow oil (170 mg, yield 45%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.49–7.47 (m, 1H), 7.33 (d, 1H, J = 4.0 Hz), 7.22–7.18 (m, 1H), 7.15–7.12 (m, 1H), 7.04 (t, 2H, J = 8.0

Hz), 6.97 (t, 1H, *J* = 8.0 Hz), 3.90 (t, 2H, *J* = 8.0 Hz), 1.69−1.62 (m, 2H), 1.43−1.34 (m, 2H), 1.27 (s, 12H), 0.88 (t, 3H, *J* = 8.0 Hz). HRMS (EI): Calcd ($[C_{22}H_{28}BNO_2S]^+$), *m/z* = 381.1934; found, *m/z* = 381.1940.

3. Molecular Structure Characterization Data

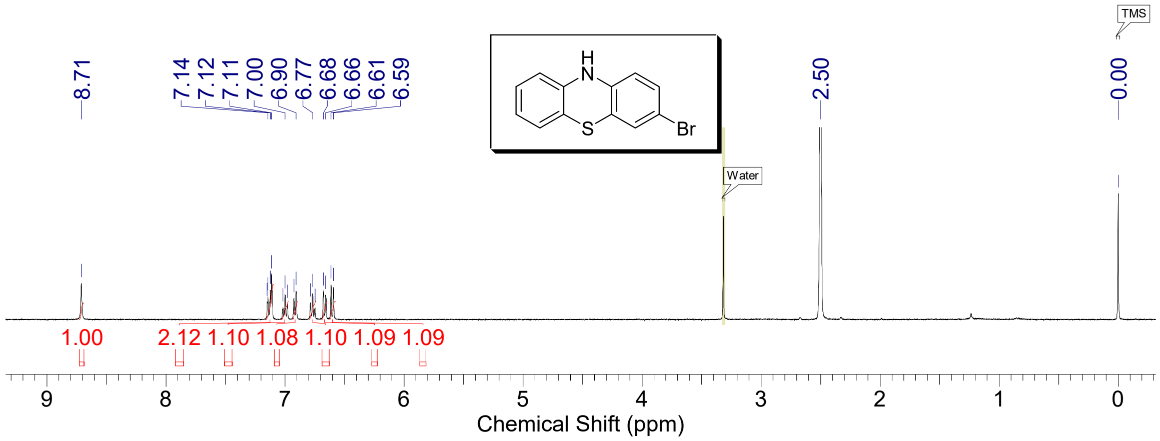


Figure S1. ^{1}H NMR spectrum of compound **1** (DMSO-d_6, 400 MHz).

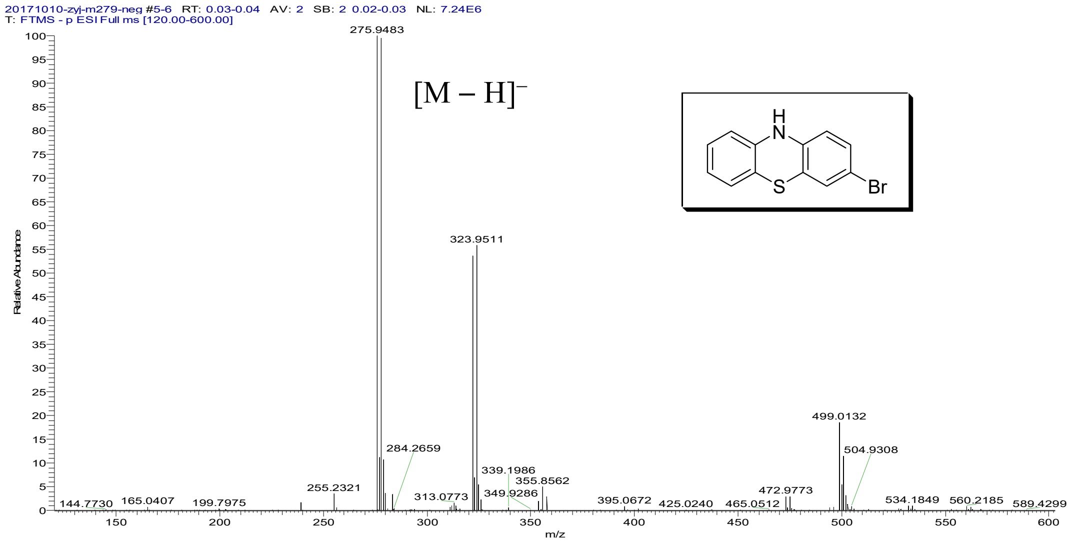


Figure S2. ESI-HRMS spectrum of compound **1**.

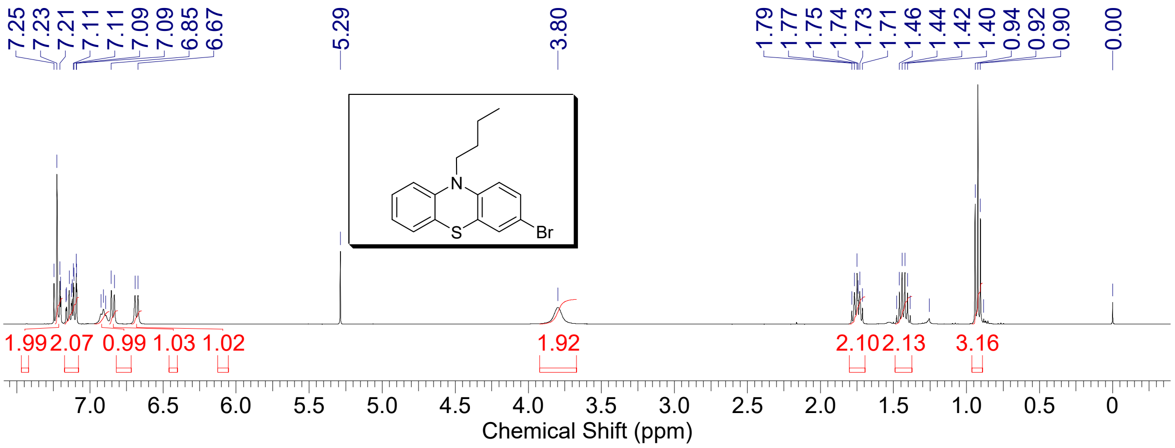
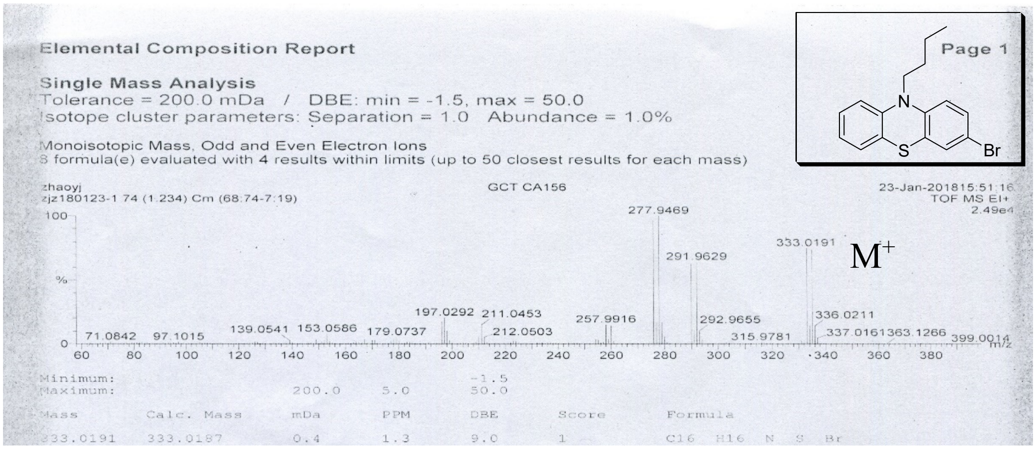


Figure S3. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 400 MHz).



Elemental Composition Report

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
8 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

zhaoyj
zjz180123-1 74 (1.234) Cm (68:74-7:19)
GCT CA156
23-Jan-201815:51:16
TOF MS EI+
2.49e4

```
Minimum:                                  -1.5
Maximum:                  200.0    5.0    50.0

Mass       Calc. Mass     mDa      PPM    DBE     Score    Formula

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```

Figure S4. TOF-HRMS spectrum of compound **2**.

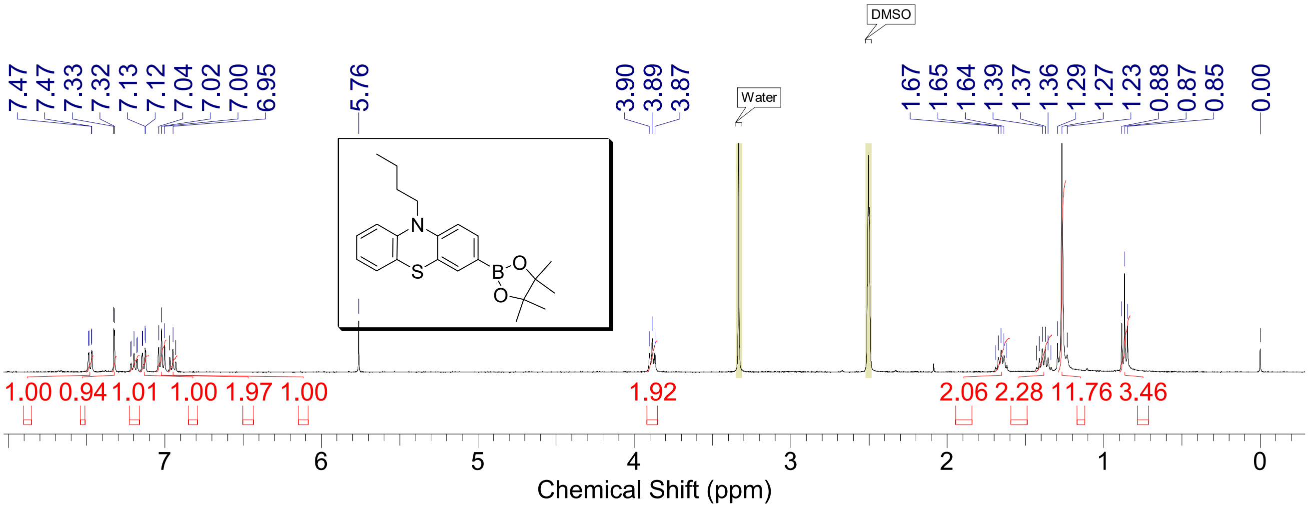
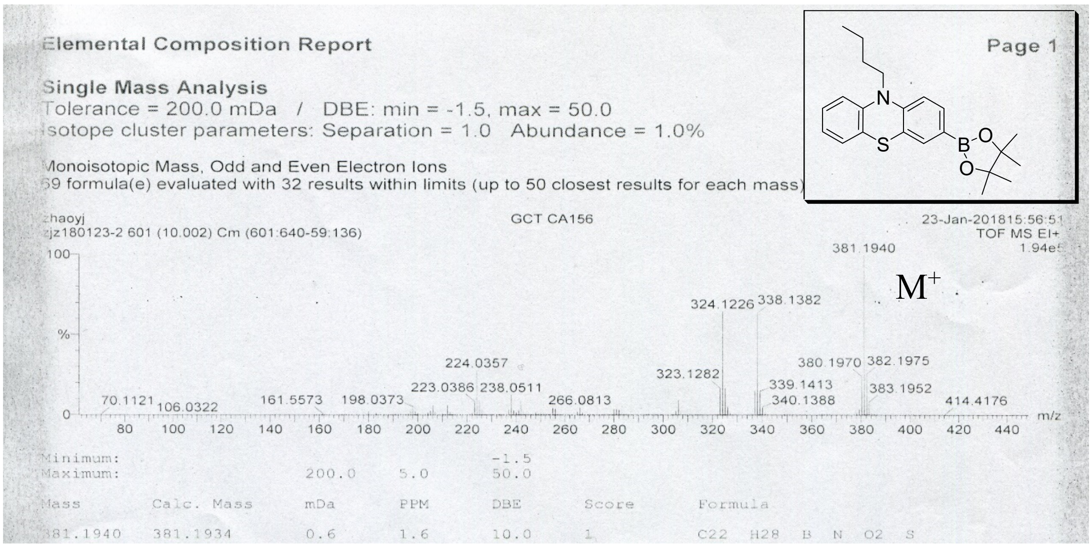


Figure S5. ^{1}H NMR spectrum of compound **3**. (DMSO-d_6, 400 MHz).



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 32 results within limits (up to 50 closest results for each mass)

zhaoyj
zjz180123-2 601 (10.002) Cm (601:640-59:136)

GCT CA156

23-Jan-201815:56:51
TOF MS EI+
1.94e5

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Minimum:                              -1.5
Maximum:             200.0     5.0    50.0

Mass      Calc. Mass    mDa     PPM    DBE     Score    Formula

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Figure S6. TOF-HRMS spectrum of compound **3**.

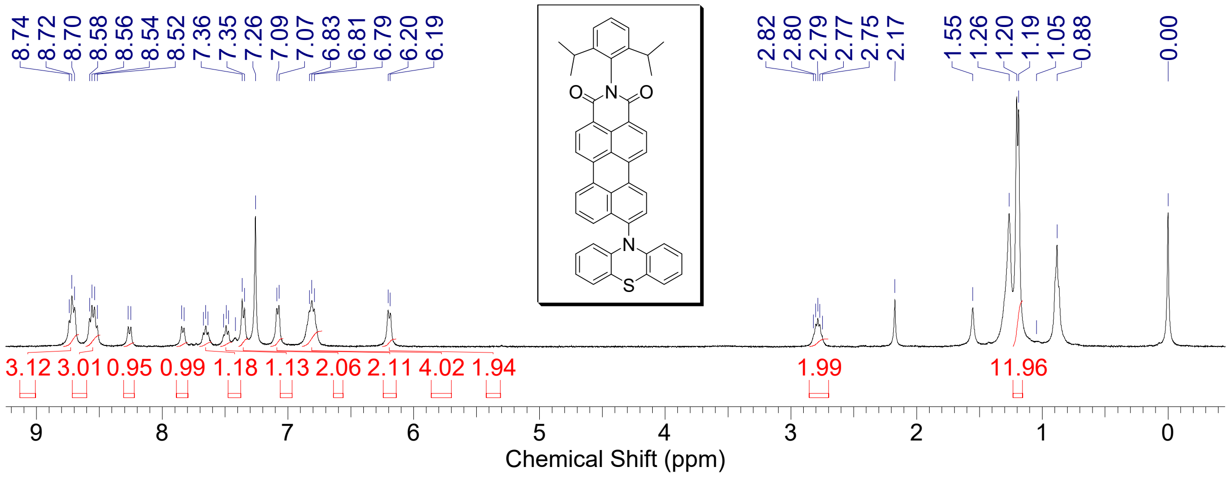


Figure S7. ^{1}H NMR spectrum of compound **PMI-N-PTZ** ($CDCl_3$, 400 MHz).

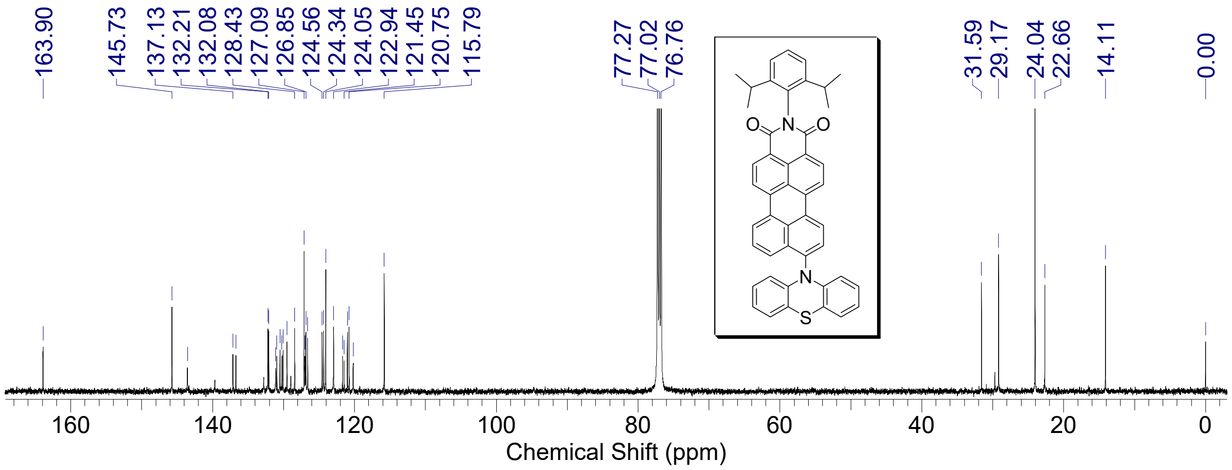


Figure S8. ^{13}C NMR spectrum of **PMI-N-PTZ** ($CDCl_3$, 126 MHz).

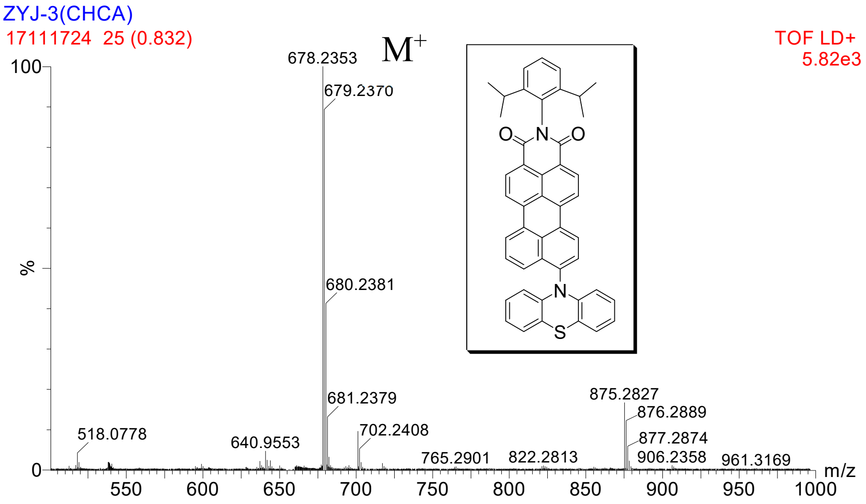


Figure S9. MALDI-HRMS spectrum of **PMI-N-PTZ**.

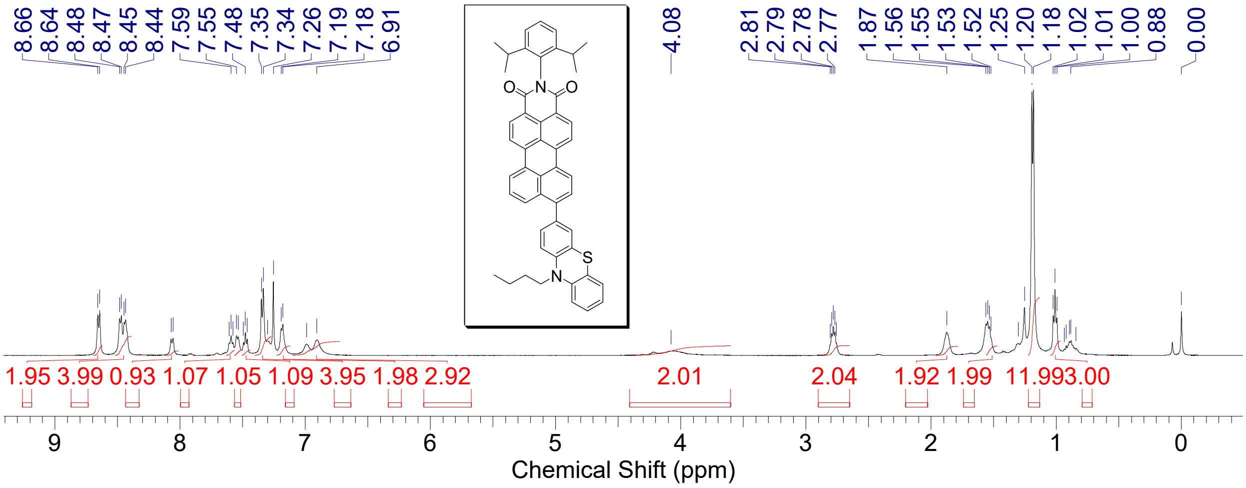


Figure S10. ^{1}H NMR spectrum of **PMI-C-PTZ** ($CDCl_3$, 400 MHz).

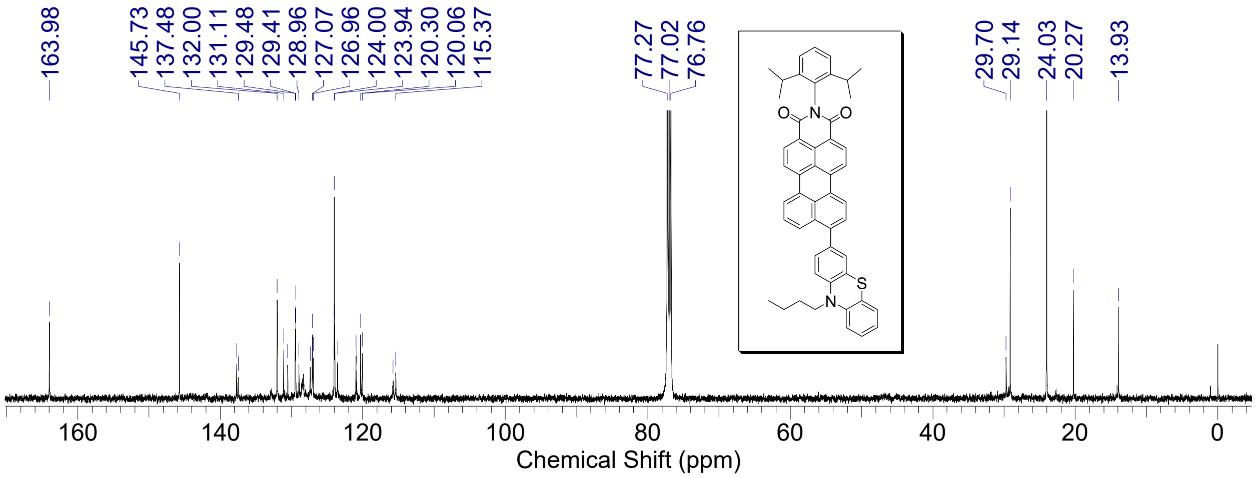


Figure S11. ^{13}C NMR spectrum of **PMI-C-PTZ** ($CDCl_3$, 126 MHz).

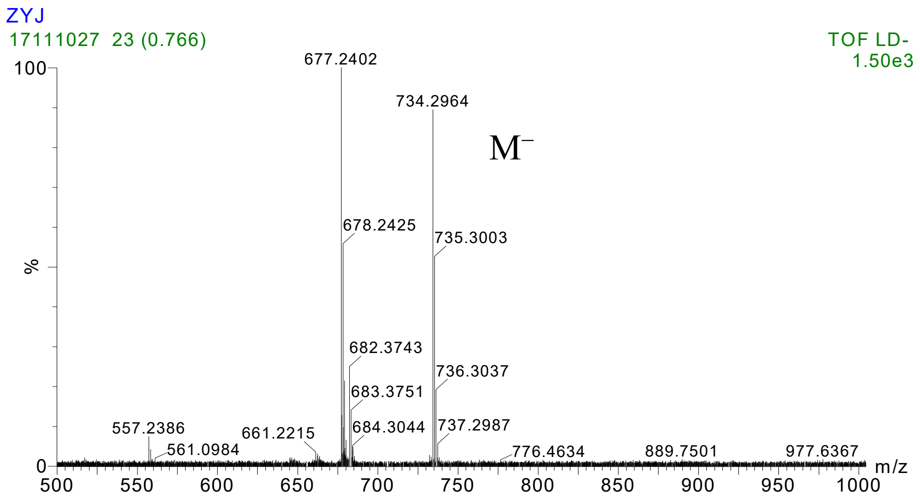


Figure S12. MALDI-HRMS spectrum of **PMI-C-PTZ**.

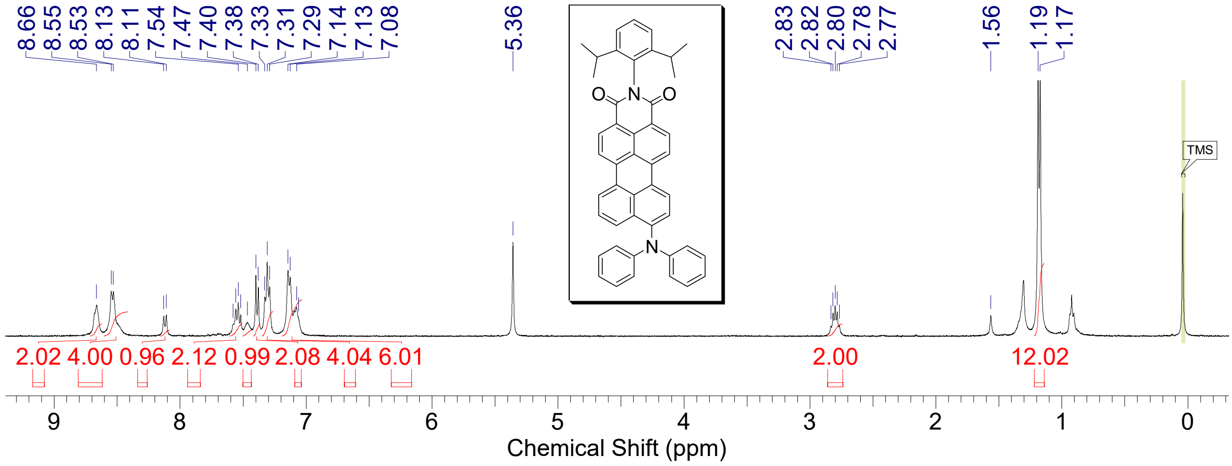


Figure S13. ^{1}H NMR spectrum of **PMI-DPA** (CD_2Cl_2, 400 MHz).

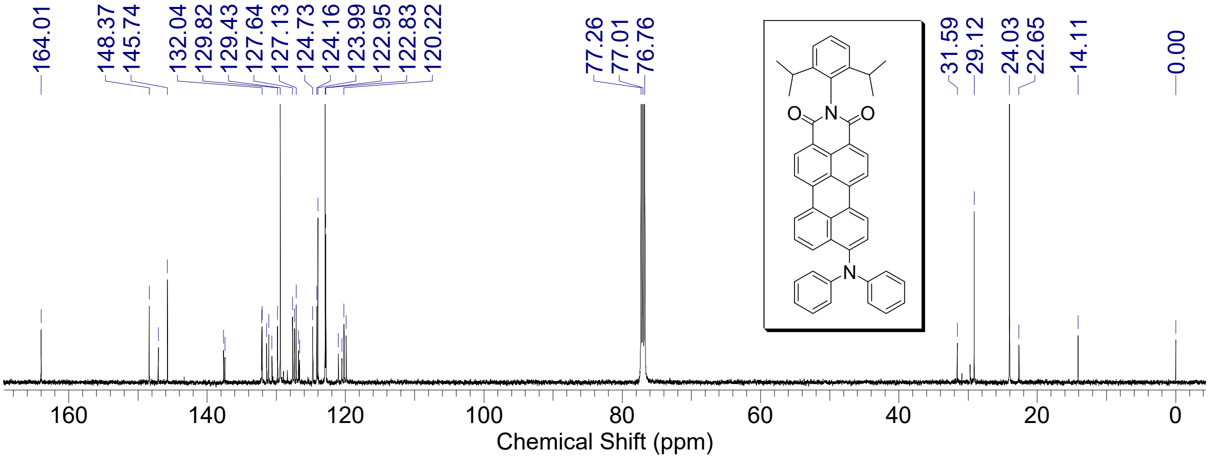


Figure S14. ^{13}C NMR spectrum of **PMI-DPA** ($CDCl_3$, 126 MHz).

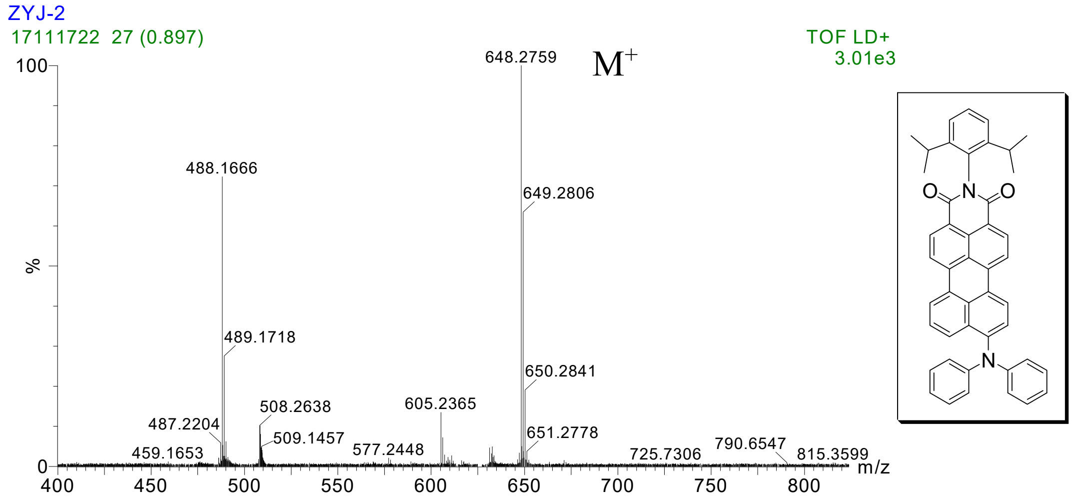


Figure S15. MALDI-HRMS spectrum of **PMI-DPA**.

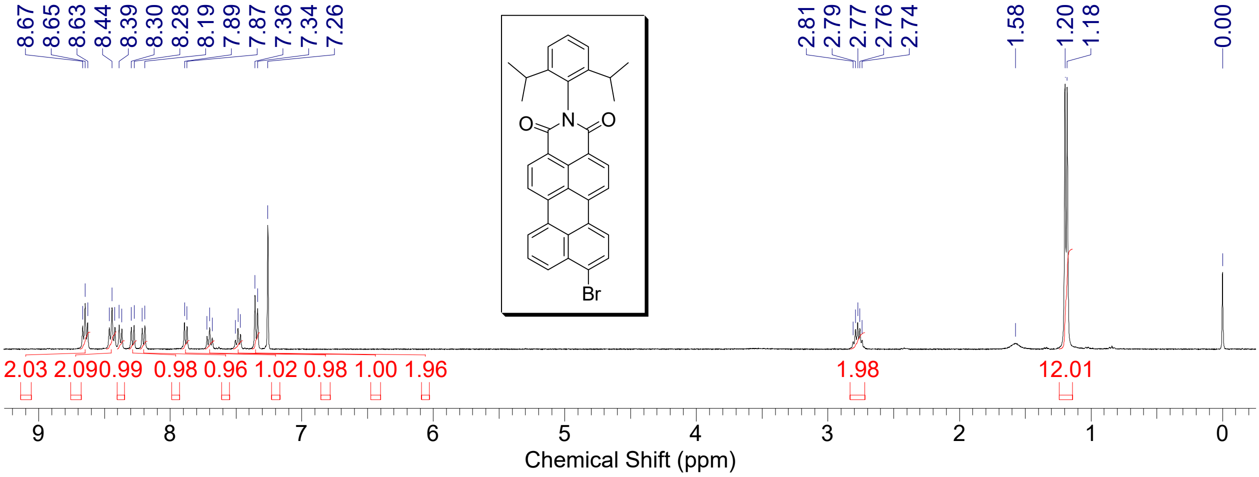


Figure S16. ^{1}H NMR spectrum of **PMI-Br** ($CDCl_3$, 400 MHz).

4. UV−Vis Absorption Spectra

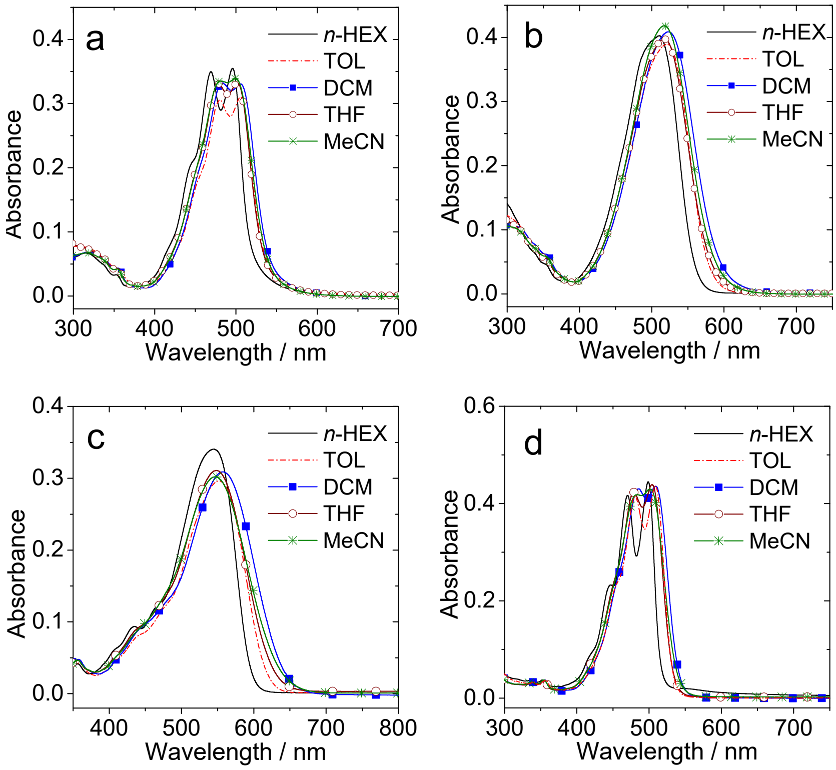


Figure S17. UV−Vis absorption spectra of (a) **PMI-N-PTZ**; (b) **PMI-C-PTZ**; (c) **PMI-DPA** and (d) **PMI-Br** in different solvents. *c* = 1.0 × 10^{-5} M, 20 °C.

5. Fluorescence Spectra

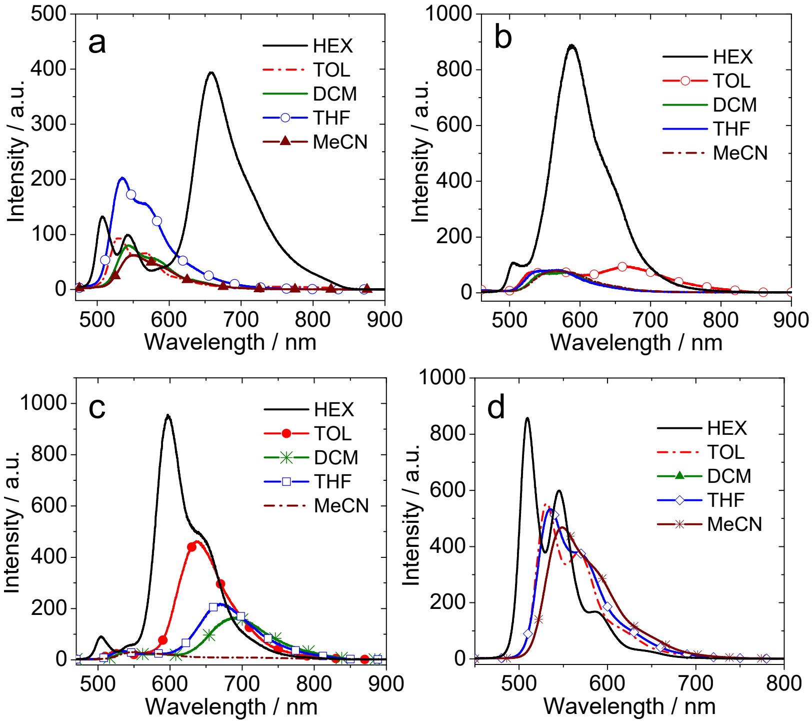


Figure S18. Fluorescence emission spectra of (a) **PMI-N-PTZ** (λ_{ex} = 465 nm, A = 0.302); (b) **PMI-C-PTZ** (λ_{ex} = 450 nm, A = 0.104); (c) **PMI-DPA** (λ_{ex} = 460 nm, A = 0.101) and (d) **PMI-Br** (λ_{ex} = 440 nm, A = 0.160) in different solvents. Optically matched solutions were used (the concentration is varied slightly for the compounds). 20 °C.

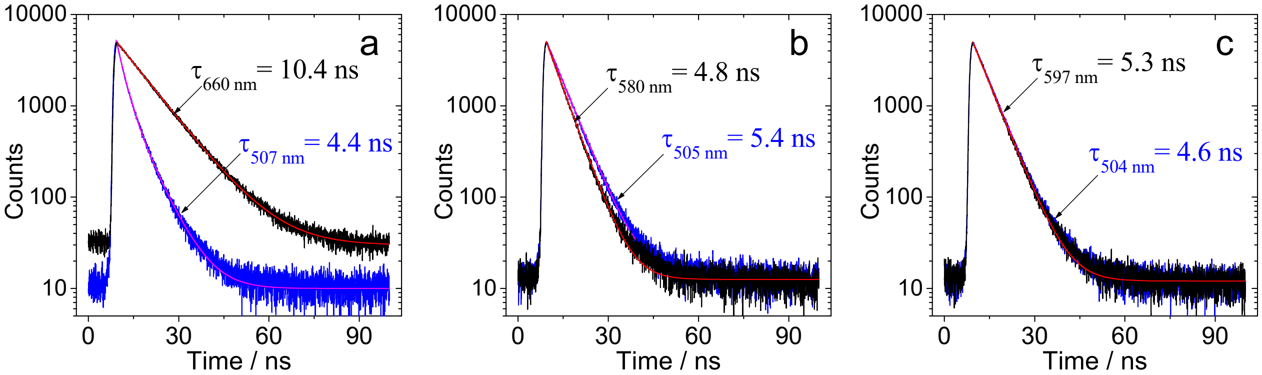


Figure S19. The fluorescence decays of (a) **PMI-N-PTZ**; (b) **PMI-C-PTZ**; (c) **PMI-DPA**. λ_{ex} = 445 nm. $c = 1.0 \times 10^{-5}$ M for **PMI-N-PTZ** and **PMI-C-PTZ**, and $c = 1.5 \times 10^{-5}$ M for **PMI-DPA** in deaerated *n*-hexane. 20 °C.

6. Singlet Oxygen Quantum Yield

Table S1. Singlet Oxygen Quantum Yields of PMI Derivatives in Different Solvents [a]

	n-Hexane	Toluene	DCM	THF	MeCN
PMI-N-PTZ	57.3	14.0	–[b]	–[b]	–[b]
PMI-C-PTZ	6.5	13.6	–[b]	< 1.0	1.0
PMI-DPA	–[b]	< 1.0	< 1.0	–[b]	1.2
PMI-Br	14.8	21.9	11.5	17.3	23.0

[a] In percentage, λ_{ex} = 500 nm. DiiodoBodipy was used as standard compound, Φ_{Δ} = 85% in toluene. [b] Not observed.

7. Nanosecond Time-resolved Transient Absorption Spectra

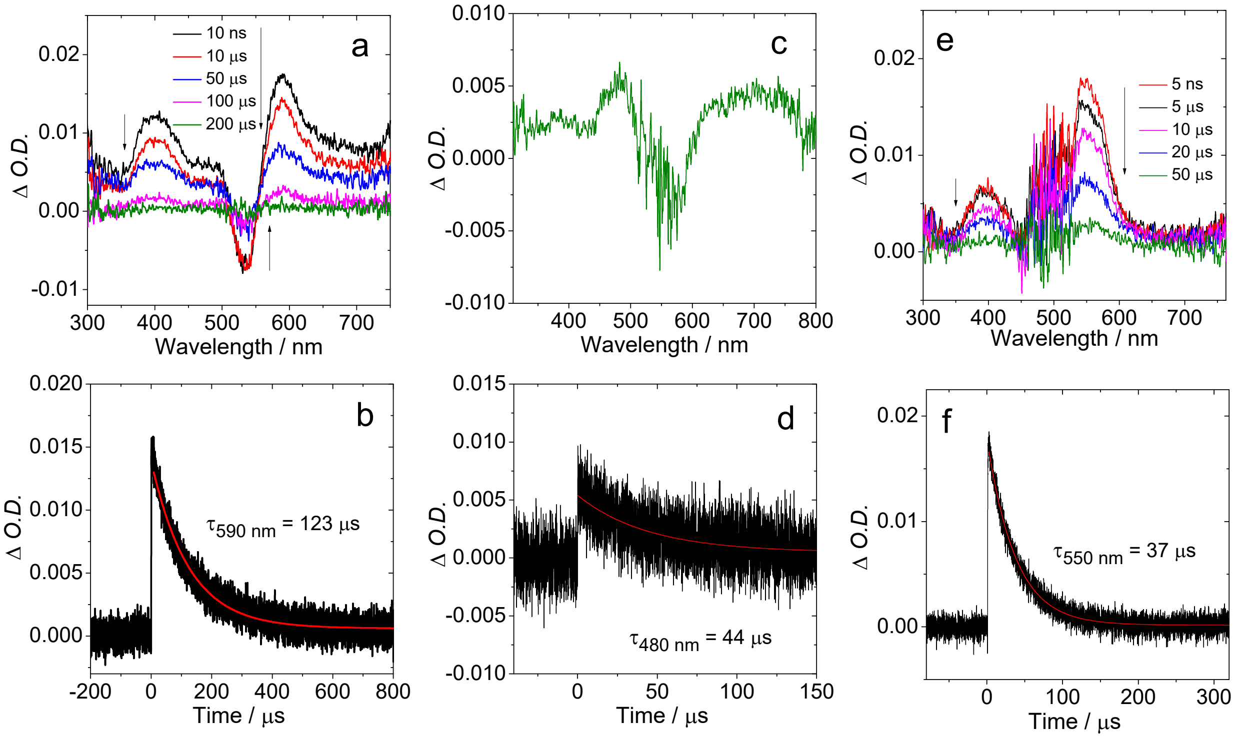


Figure S20. Nanosecond transient absorption spectra of (a) **PMI-C-PTZ** (λ_{ex} = 532 nm, $c = 2.0 \times 10^{-5}$ M in deaerated toluene) and (b) the related decay trace at 590 nm; (c) **PMI-DPA** (λ_{ex} = 532 nm, $c = 6.0 \times 10^{-5}$ M in deaerated *n*-hexane) and (d) the related decay trace at 480 nm. (e) **PMI-Br** (λ_{ex} = 532 nm, $c = 1.0 \times 10^{-4}$ M in deaerated acetonitrile) and (f) the related decay trace at 550 nm. 20 °C.

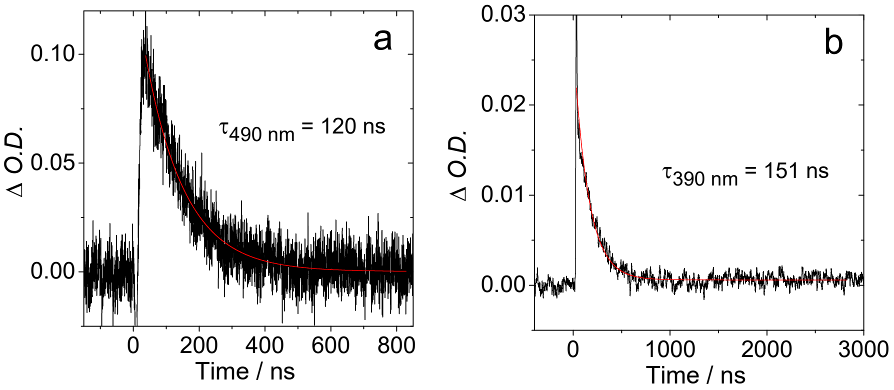


Figure S21. The decay trace of triplet state of (a) **PMI-N-PTZ** (λ_{ex} = 500 nm, c = 5.0 ×10^{-6} M in aerated *n*-hexane); (b) **PMI-C-PTZ** (λ_{ex} = 532 nm, c = 2.0 ×10^{-5} M in aerated toluene). 20 °C.

8. Delayed Fluorescence Spectra

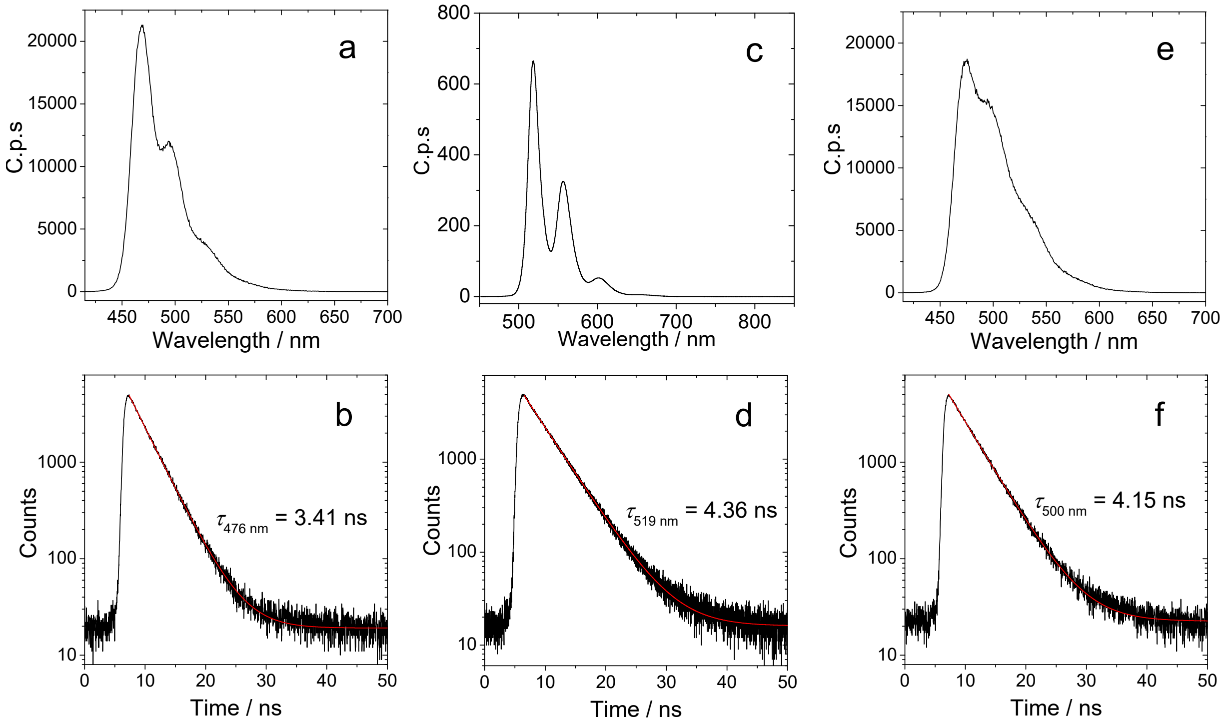


Figure S22. The fluorescence emission spectra of (a) BPEA and (b) the related decay at 476 nm; (c) PBI and (d) the related decay trace at 519 nm; (e) SG5 and (f) the related decay trace at 500 nm. $c = 1.0 \times 10^{-5}$ M in *n*-hexane. 20 °C.

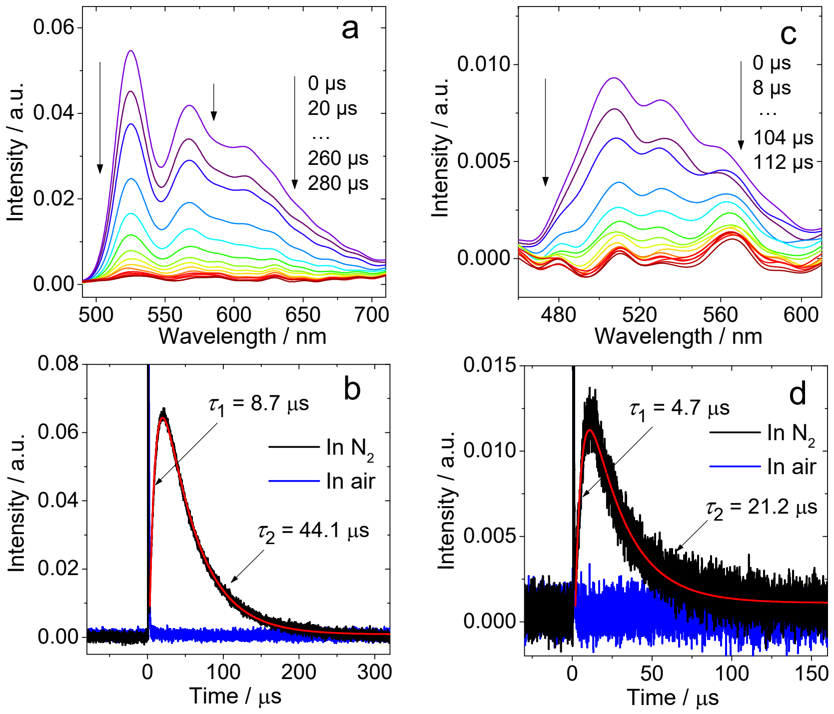


Figure S23. Delayed fluorescence spectra of the mixture of **PMI-N-PTZ** with (a) PBI ($c = 5.0 \times 10^{-6}$ M) and (b) the related decay trace at 520 nm; (c) SG5 ($c = 1.0 \times 10^{-4}$ M) and (d) the related decay trace at 510 nm. **PMI-N-PTZ** was used as photosensitizer ($c = 2.0 \times 10^{-5}$ M, λ_{ex} = 500 nm). The spike in the delayed fluorescence traces is the scattered laser. 20 °C.

9. Discussion on the Decay of the Charge Separated States (CSS) of the Dyads

The decay of the CSS of the dyads include a few processes (please refer to the Scheme 2 in the main text), i. e. the ISC process giving the localized triplet state; the radiative decay to the ground state (S_0), and the non-radiative to the ground state. All these processes for the decay of the CSS of the dyads are actually charge recombination, i.e. the electron transfer. The Marcus theory for the electron transfer kinetics predicts that there is no simple exponential relationship between the energy gap of the states (herein it is the energy gap between the CSS and the ground state).

Moreover, it is inappropriate to compare the non-radiative decay rate constants of the different compounds, based on the different energy gaps. The reason is that other factors, such as the reorganization energy (λ) and the electronic coupling between the electron donor and acceptors (V_{DA}). These parameters all contribute to the electron transfer rate constants (related to the non-radiative decay of the dyads in this manuscript), and these parameters are different for the dyads. The relationship between the energy gap (can be approximated as the Gibbs free energy changes of the electron transfer) and the electron transfer rate constant is described by the Marcus equation S4:[1]

$$k_{\mathrm{et}} = \frac{2\pi^{3/2}V^2 \exp\left(- \frac{(\Delta G + \lambda)^2 / 4\lambda}{k_{\mathrm{B}}T} \right)}{h(\lambda k_{\mathrm{B}}T)^{1/2}} \tag{S4}$$

ΔG is the Gibbs free energy change between the equilibrium reactant and the product state; λ is the total reorganization energy; V is the electronic coupling matrix element. T is the temperature and the k_B is the Boltzmann constant.

10. DFT Optimized Ground State Geometry.

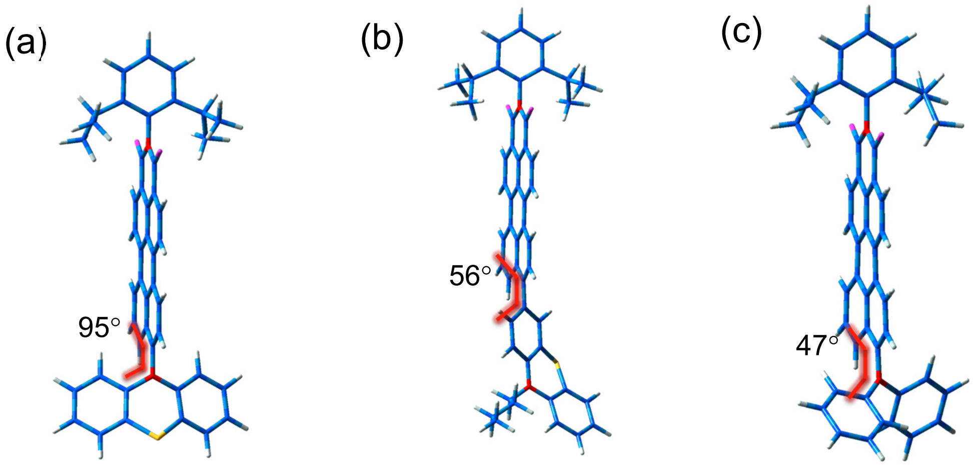


Figure S24. Optimized ground state conformations and the dihedral angles of (a) **PMI-N-PTZ**; (b) **PMI-C-PTZ** and (c) **PMI-DPA** calculated with DFT theory at B3LYP/6-31G (d) level with Gaussian 09W.

11. Fluorescence Excitation Spectra.

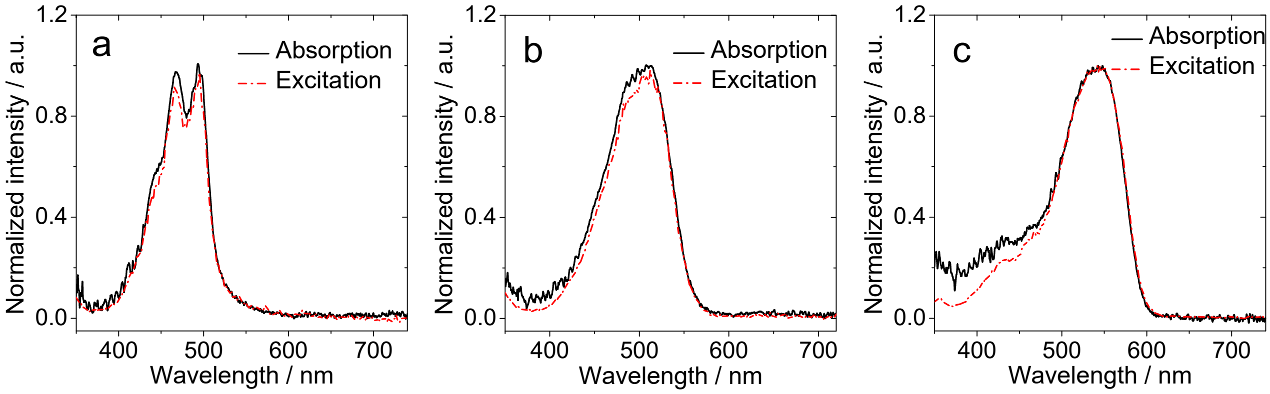
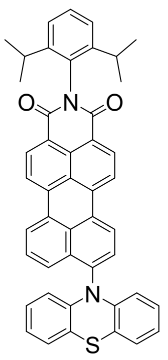


Figure S25. Normalized fluorescence excitation spectra and UV−Vis absorption spectra. (a) **PMI-N-PTZ** (λ_{em} = 750 nm); (b) **PMI-C-PTZ** (λ_{em} = 730 nm) and (c) **PMI-DPA** (λ_{em} = 750 nm) in *n*-hexane. $c = 1.0 \times 10^{-6}$ M, 20 °C.

12. x,y,z Coordinates of the Optimized Ground State Geometry of the Compounds

PMI-N-PTZ



PMI-N-PTZ

Charge = 0; Multiplicity = 1

Symbolic Z-Matrix:

C	0.22726	4.05931	-4.87702
C	-0.33492	2.76094	-4.81381
C	0.59123	4.69926	-3.71512
C	-0.58175	2.15731	-3.54343
C	-0.19529	2.83166	-2.33077
C	-1.08727	0.81789	-3.51933
C	-1.38195	0.18176	-4.72932
C	-1.16871	0.8001	-5.96252
H	-1.40712	0.29452	-6.89202
H	-1.80269	-0.81686	-4.72443
H	1.08468	5.66218	-3.78343
C	-0.35774	2.21408	-1.19175
C	-0.97623	0.92368	-1.08399
C	-1.4277	0.21596	-2.23832
C	-0.02884	2.87979	-0.00773
C	-1.2515	0.37794	0.20795
C	-0.92936	1.11145	1.37417
C	-0.36	2.36618	1.25094
C	-1.86177	-0.89316	0.33083
H	0.42861	3.85627	-0.05752
H	-0.15237	2.93531	2.15077
C	-2.13197	-1.48535	1.66363
C	-1.20882	0.56307	2.72087
O	-2.60974	-2.60731	1.78675

O	-0.92674	1.17101	3.74662
N	-1.81714	-0.70071	2.78368
C	-2.00706	-1.04535	-2.07448
C	-2.20954	-1.60154	-0.80815
H	-2.65865	-2.58241	-0.69508
H	-2.31111	-1.62127	-2.94082
C	0.36748	4.12173	-2.44493
H	0.7197	4.61988	-1.5659
C	-3.37815	-1.62109	5.98767
C	-3.16485	-1.03664	4.73892
C	-1.98914	-1.30096	4.03672
C	-1.02556	-2.14915	4.58379
C	-1.23867	-2.73305	5.83246
C	-2.41522	-2.46933	6.5343
H	-4.30536	-1.41292	6.54093
H	-0.47944	-3.40157	6.26388
H	-2.5831	-2.92991	7.51858
C	0.27255	-2.44073	3.80822
H	0.91737	-3.04866	4.40782
C	-4.22875	-0.10104	4.1353
H	-5.08098	-0.06624	4.78136
C	-0.06555	-3.18378	2.50239
H	-1.04542	-3.60717	2.57639
H	-0.03489	-2.49659	1.6828
H	0.64877	-3.96385	2.3407
C	0.98069	-1.1143	3.47548
H	0.75411	-0.83181	2.46863
H	0.6418	-0.35138	4.14482
H	2.03817	-1.23808	3.58182
C	-4.65365	-0.63095	2.75318
H	-4.13001	-0.09502	1.98931

H	-4.4189	-1.67252	2.68294
H	-5.70725	-0.4935	2.62697
C	-3.64118	1.3144	3.98395
H	-2.78631	1.41553	4.61945
H	-3.35006	1.47282	2.96658
H	-4.37895	2.0383	4.26067
C	-0.63749	2.07916	-6.01326
H	-0.46327	2.53427	-6.96585
C	4.1378	3.81726	-8.04356
C	3.20906	4.67052	-8.63734
C	2.00147	4.96748	-8.00168
C	1.67144	4.36184	-6.77329
C	2.61568	3.50404	-6.18907
C	3.83865	3.24797	-6.80867
C	-0.72461	5.05637	-6.8694
C	-0.60977	5.73808	-8.09499
C	-1.75282	6.11562	-8.80295
H	-1.63518	6.62734	-9.75413
C	-3.14892	5.20859	-7.06806
C	-2.01284	4.79214	-6.3755
H	5.08076	3.60824	-8.53945
H	3.42597	5.13827	-9.59371
H	2.40259	3.04006	-5.2351
H	4.54914	2.58706	-6.32057
H	-4.13005	5.00106	-6.65098
H	-2.12496	4.26329	-5.43547
S	0.98019	6.24291	-8.71006
N	0.4175	4.61182	-6.14924
C	-3.02532	5.86701	-8.28958
H	-3.90521	6.18364	-8.84125

Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6–31G(d)

Charge = 0

Spin = Singlet

E(RB3LYP) = –2431.61367173 a.u.

RMS Gradient Norm = 0.00000497 a.u.

Imaginary Freq = 0

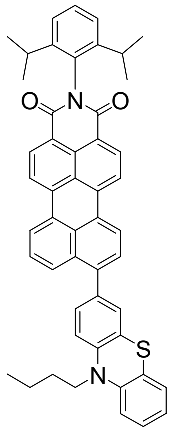
Dipole Moment = 3.6940 Debye

Point Group = C1

PMI-C-PTZ

Charge = 0; Multiplicity = 1

Symbolic Z-Matrix:



PMI-C-PTZ

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C	0.13092	2.71434	-4.84384
C	1.05708	4.65266	-3.74515
C	-0.11591	2.11071	-3.57346
C	0.27056	2.78507	-2.3608
C	-0.62142	0.7713	-3.54936
C	-0.91611	0.13516	-4.75935
C	-0.70286	0.75351	-5.99255
H	-0.94127	0.24792	-6.92205
H	-1.33684	-0.86345	-4.75446
H	1.55052	5.61559	-3.81346
C	0.10811	2.16748	-1.22178
C	-0.51039	0.87709	-1.11402

C	-0.96186	0.16936	-2.26835
C	0.437	2.83319	-0.03776
C	-0.78566	0.33134	0.17792
C	-0.46351	1.06485	1.34414
C	0.10584	2.31959	1.22091
C	-1.39593	-0.93976	0.3008
H	0.89445	3.80968	-0.08755
H	0.31347	2.88871	2.12074
C	-1.66612	-1.53195	1.6336
C	-0.74298	0.51648	2.69084
O	-2.1439	-2.65391	1.75672
O	-0.4609	1.12442	3.71659
N	-1.3513	-0.74731	2.75364
C	-1.54122	-1.09195	-2.10451
C	-1.74369	-1.64813	-0.83818
H	-2.1928	-2.62901	-0.72511
H	-1.84526	-1.66787	-2.97085
C	0.83333	4.07513	-2.47496
H	1.18554	4.57328	-1.59593
C	-2.90649	-1.64737	5.91523
C	-2.69318	-1.06292	4.66647
C	-1.51748	-1.32724	3.96427
C	-0.55389	-2.17543	4.51134
C	-0.767	-2.75933	5.76001
C	-1.94356	-2.49561	6.46186
H	-3.83369	-1.4392	6.46849
H	-0.00777	-3.42784	6.19144
H	-2.11143	-2.95619	7.44614

C	0.74421	-2.46701	3.73577
H	1.38903	-3.07494	4.33538
C	-3.75708	-0.12732	4.06285
H	-4.60931	-0.09252	4.70892
C	0.40612	-3.21006	2.42995
H	-0.57376	-3.63345	2.50395
H	0.43678	-2.52287	1.61036
H	1.12044	-3.99013	2.26826
C	1.45235	-1.14057	3.40304
H	1.22578	-0.85809	2.39618
H	1.11346	-0.37766	4.07238
H	2.50984	-1.26436	3.50938
C	-4.18198	-0.65723	2.68073
H	-3.65835	-0.1213	1.91687
H	-3.94723	-1.69879	2.6105
H	-5.23558	-0.51978	2.55453
C	-3.16952	1.28812	3.91151
H	-2.31464	1.38925	4.547
H	-2.87839	1.44654	2.89413
H	-3.90728	2.01202	4.18823
C	-0.17164	2.03257	-6.04329
H	0.00258	2.48767	-6.99588
C	-1.7248	11.31591	-5.35459
C	-1.93369	9.95273	-5.14512
C	-1.22478	9.00111	-5.87801
C	-0.23608	9.3872	-6.8071
C	-0.03526	10.76526	-6.99867
C	-0.77929	11.71337	-6.29451

C	0.75009	7.1338	-7.0127
C	-0.14156	6.52692	-6.10124
C	0.11661	5.26248	-5.57479
H	-0.58878	4.84092	-4.86363
C	1.22702	4.50888	-5.9835
C	2.09992	5.09678	-6.90699
C	1.87599	6.37916	-7.39693
H	-2.2954	12.04866	-4.79227
H	-2.67195	9.6145	-4.42329
H	0.70661	11.11591	-7.70345
H	-0.59826	12.76822	-6.48075
H	2.98251	4.55559	-7.2344
H	2.60051	6.79385	-8.08443
S	-1.69803	7.29367	-5.71879
N	0.51036	8.42191	-7.52812
C	1.23857	8.84833	-8.73019
H	1.30362	7.97841	-9.39265
H	0.60344	9.57498	-9.24784
C	2.64546	9.4475	-8.52856
H	3.29881	8.72391	-8.02704
H	2.59631	10.31195	-7.85648
C	3.27413	9.86705	-9.86444
H	3.31825	8.99733	-10.53558
H	2.62106	10.59912	-10.36078
C	4.6777	10.46061	-9.7065
H	5.09793	10.74862	-10.67639
H	4.66198	11.35436	-9.07115
H	5.36415	9.73964	-9.24641

Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6–31G(d)

Charge = 0

Spin = Singlet

E(RB3LYP) = –2588.87440520 a.u.

RMS Gradient Norm = 0.00000388 a.u.

Imaginary Freq = 0

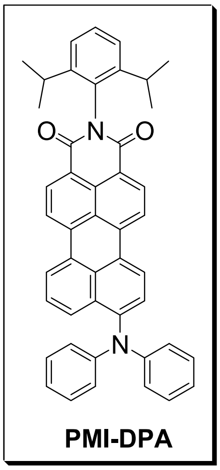
Dipole Moment = 9.3214 Debye

Point Group = C1

PMI-DPA

Charge = 0; Multiplicity = 1

Symbolic Z-Matrix:


PMI-DPA

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C	2.02544	-0.51103	0.59518
C	1.48396	0.4977	-0.26532
C	1.16253	-1.3696	1.35315
C	1.73146	-2.28037	2.23924
C	3.12105	-2.37952	2.40135
H	3.52678	-3.08531	3.12037
H	1.10035	-2.92484	2.83988
H	4.41185	1.79026	-1.45954
C	0.02902	0.65213	-0.3844

C	-0.82742	-0.24418	0.33128
C	-0.29621	-1.26166	1.18477
C	-0.55976	1.63948	-1.18121
C	-2.24552	-0.11931	0.18978
C	-2.79355	0.8887	-0.6395
C	-1.94557	1.75653	-1.30986
C	-3.11067	-1.00334	0.8781
H	0.0594	2.34309	-1.72495
H	-2.38229	2.52473	-1.93942
C	-4.5804	-0.88497	0.75626
C	-4.25562	1.02496	-0.81329
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N	-5.06824	0.12449	-0.09597
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H	-0.82028	-2.9154	2.46757
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C	6.98886	3.31368	1.21314
H	5.39817	1.97293	1.79155
C	8.0605	3.53792	0.3483
H	6.7507	4.04484	1.98117
H	8.65227	4.4453	0.4411

C	6.33385	-1.20247	-0.36999
C	5.73476	-2.03984	-1.32244
C	7.53924	-1.60479	0.23033
C	6.32501	-3.25879	-1.65599
H	4.80914	-1.73346	-1.79894
C	8.12965	-2.81534	-0.12365
H	8.00531	-0.9641	0.97237
C	7.52549	-3.65349	-1.06463
H	5.84536	-3.89595	-2.39431
H	9.06202	-3.11061	0.35047
H	7.98482	-4.60071	-1.33185
C	2.37309	1.31052	-0.96528
H	2.00127	2.08049	-1.63123
C	-8.55686	-0.4028	-1.33837
C	-7.1675	-0.54675	-1.21591
C	-6.51116	0.24494	-0.24751
C	-7.21516	1.14922	0.5781
C	-8.60417	1.23688	0.40827
C	-9.27588	0.47507	-0.5383
H	-9.07877	-1.00267	-2.0801
H	-9.16278	1.92639	1.03671
H	-10.35311	0.56472	-0.65167
C	-6.62698	2.10534	1.62731
H	-7.47166	2.31548	2.29682
C	-6.54028	-1.605	-2.13672
H	-7.25233	-1.68708	-2.96859
C	-5.51053	1.57268	2.54343
H	-5.72792	0.56198	2.90069

H	-4.5315	1.56288	2.0553
H	-5.42333	2.23111	3.41589
C	-6.23405	3.45899	0.99696
H	-5.41882	3.34832	0.27769
H	-7.08242	3.90278	0.46452
H	-5.91814	4.16046	1.7794
C	-6.51193	-2.99305	-1.46058
H	-5.85565	-3.0046	-0.58684
H	-7.51269	-3.28276	-1.1219
H	-6.16047	-3.75072	-2.17226
C	-5.18786	-1.27957	-2.79582
H	-5.16007	-0.25592	-3.1804
H	-4.34221	-1.41575	-2.11541
H	-5.03068	-1.9638	-3.63813
C	3.96782	-1.5882	1.65729
H	5.04002	-1.66785	1.78571
C	8.37986	2.59988	-0.64261
H	9.20623	2.76182	-1.30274

Calculation Type = FREQ

Calculation Method = RB3LYP

Basis Set = 6–31G(d)

Charge = 0

Spin = Singlet

E(RB3LYP) = –2034.62832480 a.u.

RMS Gradient Norm = 0.00000286 a.u.

Imaginary Freq = 0

Dipole Moment = 7.3687 Debye

Point Group = C1

13. Reference

[1] J. W. Verhoeven, *J. Photochem. Photobio C: Photochem Rev*., 2006, **7**, 40–60.