

Supporting Information

Near-Unity Quantum Yields for Singlet Oxygen Generation in Heterofluorene Perylenediimides

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Experimental Section

1. Synthesis and Compound Data

***N,N'*-Bis(1-ethylpropyl)-2,5,8,11-tetrakis(9-phenyl-9H-carbazol-3-yl)perylene-**

3,4:9,10-tetracarboxylic acid (1): A mixture of *N,N'*-Bis(1-ethylpropyl) perylene-3, 4, 9, 10-tetracarboxylic acid (106.0 mg, 0.20 mmol), 9-phenyl-9H-carbazol-3-yl boronic acid neopentyl glycol ester (568mg, 1.6 mmol), and [RuH₂(CO)(PPh₃)₃] (45.8 mg, 0.05 mmol) in 1.5 ml of mesitylene and 1.5 ml of pinacolone was stirred under argon at 160 °C (bath temp) for 48h. The reaction mixture was purified by Petroleum ether/CH₂Cl₂ 1:2. After recrystallization from CH₂Cl₂/Methanol, compound was obtained in 50% yield (150 mg). ¹H NMR (CD₂Cl₂): δ 0.85 (t, J = 7.4, 12H), 1.60-1.66 (m, 4H), 2.00-2.03 (m, 4H), 4.69-4.77 (m, 2H), 7.17-7.19 (m, 4H), 7.32-7.37 (m, 8H), 7.40-7.47 (m, 12H) 7.53-7.60 (m, 16H) 8.01-8.03 (d, 4H) 8.22 (s, 4H) 8.60 (s, 4H); ¹³C NMR (CD₂Cl₂): δ 11.18, 25.19, 57.52, 57.97, 109.47, 109.91, 120.06, 121.51, 123.28, 124.96, 126.11, 126.93, 127.02, 127.57, 127.94, 129.92, 131.52, 132.70, 134.37, 137.49, 140.36, 141.32, 148.33; λ_{max} (ε[M⁻¹cm⁻¹]) = 468 (1.8×10⁴), 500 (4.3×10⁴), 534 (6.4×10⁴) nm; Fluorescence (CH₂Cl₂, λ_{ex} = 490 nm) λ_{em} = 540, 582 nm; HR-MS (MALDI-MS): m/z = 1495.7.

***N,N'*-Bis(1-ethylpropyl)-2,5,8,11-tetrakis(9,9-dimethyl-9H-fluorene-2-yl)perylene-**

3,4:9,10-tetracarboxylic acid (2): A mixture of *N,N'*-Bis(1-ethylpropyl) perylene-3, 4, 9, 10-tetracarboxylic acid (106.0 mg, 0.20 mmol), RuH₂(CO)(PPh₃)₃ (45.8 mg, 0.05 mmol), and 9,9-dimethyl-9H-fluorene-2-ylboronic acid neopentyl ester (306 mg, 1.00 mmol) in 3.0 ml of mesitylene and pinacolone (1:1) was stirred under argon at 160 °C (bath temp) for 40 h. The reaction mixture was purified by CH₂Cl₂/Petroleum ether 1:1. After recrystallization from CH₂Cl₂/Ethanol, compound was obtained in 60% yield (156 mg). ¹H NMR (CD₂Cl₂): δ 0.87 (t, J = 7.4, 12H), 1.46 (s, 24H), 1.58–1.68 (m, 4H), 1.98–2.09 (m, 4H), 3.84 (s, 12H), 4.71-4.78 (m, 2H), 7.28-7.34 (m, 8H), 7.42-7.46 (m, 2H), 7.74-7.76 (d, 4H), 7.80-7.82 (d, 4H), 8.55 (s, 4H); ¹³C NMR (CD₂Cl₂): δ 11.22, 24.90, 25.94, 46.96, 57.74, 67.43, 99.71, 119.90, 120.19, 121.72, 122.54, 123.04, 125.23, 127.17, 127.49, 131.41, 132.77, 138.71, 141.46, 148.09, 153.66, 163.68; UV/Vis (CH₂Cl₂): λ_{max} (ε[M⁻¹cm⁻¹]) = 467 (23000), 498 (38000), and 536 (49000) nm;

HR-MS (MALDI-MS): $m/z = 1299.64$. Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 490 \text{ nm}$) $\lambda_{\text{em}} = 555, 609 \text{ nm}$;

N,N'-Bis(1-ethylpropyl)-2,5,8,11-tetrakis(dibenzothiophene-1-yl)perylene-3,4:9,10-tetracarboxylic acid (3): A mixture of N, N'- Bis (1-ethylpropyl) perylene-3, 4, 9, 10-tetracarboxylic acid (106.0 mg, 0.20 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (45.8 mg, 0.05 mmol), and p- dibenzothiophene-1-yl-boronic acid neopentyl ester (296.2 mg, 1.00 mmol) in 3.0 ml of mesitylene and pinacolone (1:1) was stirred under argon at 160 °C (bath temp) for 40 h. The reaction mixture was purified by Petroleum ether/ CH_2Cl_2 1:2. After recrystallization from CH_2Cl_2 /Ethanol, compound was obtained in 70% yield (176.3 mg). ^1H NMR (CD_2Cl_2): δ 0.69 (t, $J = 7.4$, 12H), 1.32–1.52 (m, 4H), 1.61–1.89 (m, 4H), 4.46–4.55 (m, 2H), 7.31-7.47(m, 12H), 7.48-7.58(m, 4H), 7.61-7.78(m, 4H) 8.14-8.17(m, 8H), 8.53 (m, 4H); ^{13}C NMR (CD_2Cl_2): δ 11.07, 21.45, 24.71, 57.68, 120.66, 121.85, 122.55, 124.52, 125.03, 126.38, 126.87, 127.72, 131.19, 133.53, 135.68, 137.61, 138.46, 139.14, 145.22, 156.22, 162.01; UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon[\text{M}^{-1}\text{cm}^{-1}]$) = 464 (20000), 495 (33000), and 532 (41000) nm; HR-MS (MALDI-MS): $m/z = 1259.58$. Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 490 \text{ nm}$) $\lambda_{\text{em}} = 542, 578 \text{ nm}$;

2. Spectral Characterization and Photophysical Parameters

Steady-State Spectroscopic Measurements. The UV-visible absorption spectra were measured on a Shimadzu UV-3600 spectrometer with a slit width of 1 nm. The fluorescence emission spectroscopy was measured on a Hitachi F-4500 spectrophotometer. The fluorescence quantum yield was obtained by the comparative method using Rhodamine 6G as a standard ($\Phi_{\text{F}} = 0.95$) in case of a dilute solution ($A < 0.10$). Near-infrared luminescence spectroscopy were performed with Edinburgh FLS-920 apparatus at 77 K, The excitation wavelength at 490 nm were produced by a xenon lamp. The solvents used were chromatographic grade and purchased.

Quantum Chemical Calculations. We performed theoretical calculations by the DFTB3LYP/6-31G(d) method with the GAUSSIAN-03 software package. (Frisch M. J. et al. Gaussian03, RevisionB.1, Gaussian, Inc., Pittsburgh, PA, 2003.) The optimized

configurations were generated using the GaussView software.

Fluorescence Lifetime Measurements. The home-built ps time-resolved fluorescence apparatus is described as below: The excitation laser pulses (480 nm) were generated by an optical parametric amplifier (OPA-800CF, Spectra Physics), and pumped by a regenerative amplifier (Spitfire, Spectra Physics). The excitation energy at the sample was ~ 100 nJ/pulse. Fluorescence collected with the 90°-geometry was dispersed by a polychromator (250is, Chromex) and detected with a streak camera (C5680, Hamamatsu Photonics). The spectral resolution was 0.2 nm, and the temporal resolution was about 100 ps on the measured delay-time-range setting.

Femtosecond Transient Absorption Spectroscopy. The laser pulses of the femtosecond transient absorption was generated by A Ti:sapphire femtosecond laser system. The a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) delivered laser pulses at 800 nm (120 fs, 1 kHz) as a seed to aregenerative amplifier (Spitfire, Spectra Physics), and were then divided into two components. The major one was used to generate the pump pulses (480 nm, 130 fs, 1 kHz), and the minor to generate the probe pulses. The probe wavelength was selected by a band-pass filter. Using a computer-controlled motorized translation stage, the time delay between the probe and pump beams were regulated. The temporal resolution was determined about 150 fs and the transmitted light was detected by a linear image sensor (S8377-512Q, Hamamatsu). The 1 mm rotating sample cell was excited by 0.1 μ J/pulse. A typical absorbance at the excitation wavelength was 0.4–0.6.

Nanosecond flash photolysis. The SHG output (532 nm) and the THF output (355 nm) of the Nd:YAG laser (Continuum Surelite II, 7 ns fwhm) were used for direct excitation and for anthracene-sensitization excitation, respectively. A pulsed xenon arc lamp was used to provide the analyzing light. The configuration of the monitoring light with respect to the excitation laser pulse is a perpendicular geometry. The liquid samples (1.0 cm quartz cell) were settled on the platform at the intersection of the monitoring light and the excitation pulse. All the samples are optically dilute at the laser excitation wavelength. The signals were detected by the Edinburgh LP920

and recorded on the Tektronix TDS 3012B oscilloscope and computer. The triplet lifetimes were obtained by kinetic analysis of the transient absorption. The dissolved oxygen was removed, through bubbling with high purity N₂ for ~30 min. All the spectra were measured at room temperature if no further notification.

Measurement of singlet oxygen yield. Through continuous photolysis procedure, the quantum yield for generation of singlet oxygen has been described as below. (Diwu Z, et al. *J. Photochem. Photobiol. A: Chem.* **1992**, *64*, 273.) Briefly, 9,10-diphenylanthracene (DPA) was used as a substrate to intercept singlet oxygen because of its nonradiative deactivation. The consumption of singlet oxygen in air-saturated CH₂Cl₂ solution was measured under 532 nm continuous laser irradiation. The concentration of DPA was prepared at ~ 8 × 10⁻⁴ M. To ensure that an equal number of photons were absorbed at the same irradiation time in all experiments, the absorption of each photosensitizer was adjusted to 0.50 in a 1 cm cell at the wavelength of 532 nm. Therefore, the DPA can efficiently intercept the singlet oxygen. hypocrellin A (HA) (Φ_Δ= 0.84 in CH₂Cl₂) was used as the reference. The singlet oxygen quantum yield was calculated using the equation on:

$$\Phi_{\Delta}^S = \Phi_{\Delta}^R \times \frac{k^S / A^S}{k^R / A^R}$$

The *k* is the slope of singlet oxygen consumption, the *A* is the absorbance at 532nm and the suffixes “S” and “R” refer to the sample and the reference, respectively.

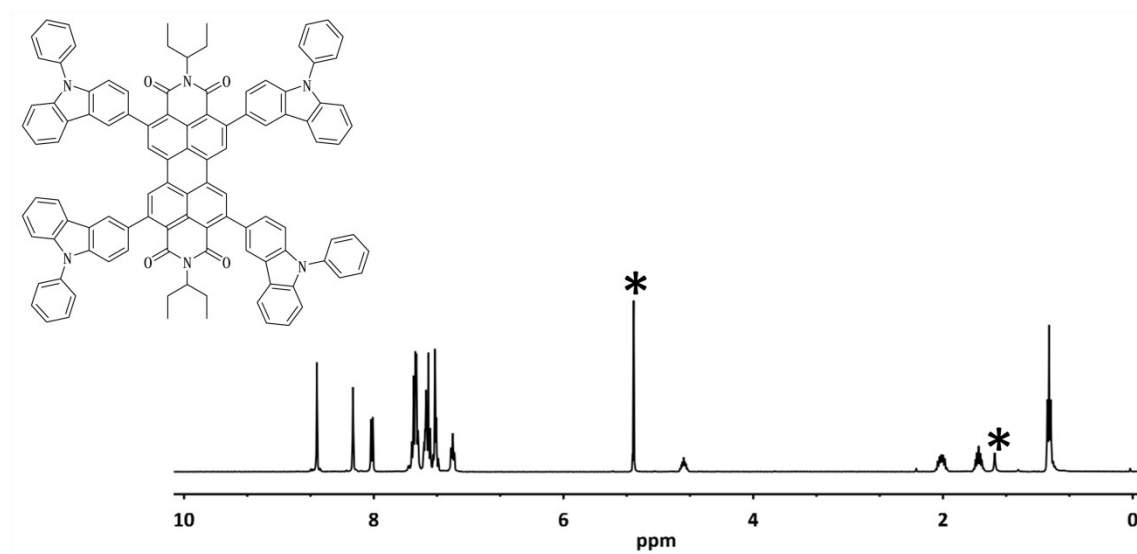


Figure S1. ^1H NMR spectrum of *compound 1* in CD_2Cl_2

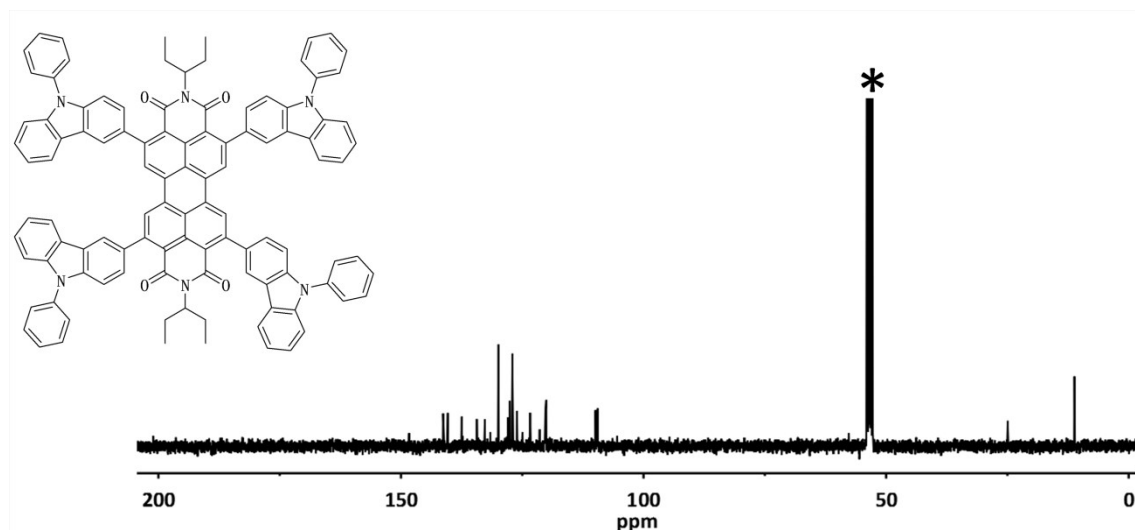


Figure S2. ^{13}C NMR spectrum of *compound 1* in CD_2Cl_2

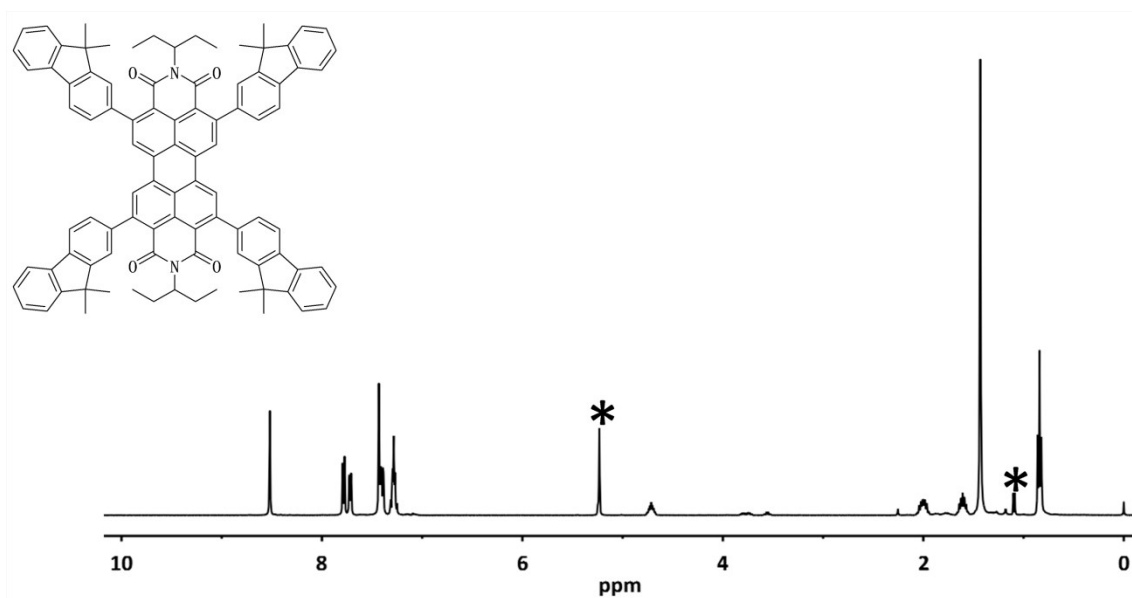


Figure S3. ¹H NMR spectrum of *compound 2* in CD₂Cl₂

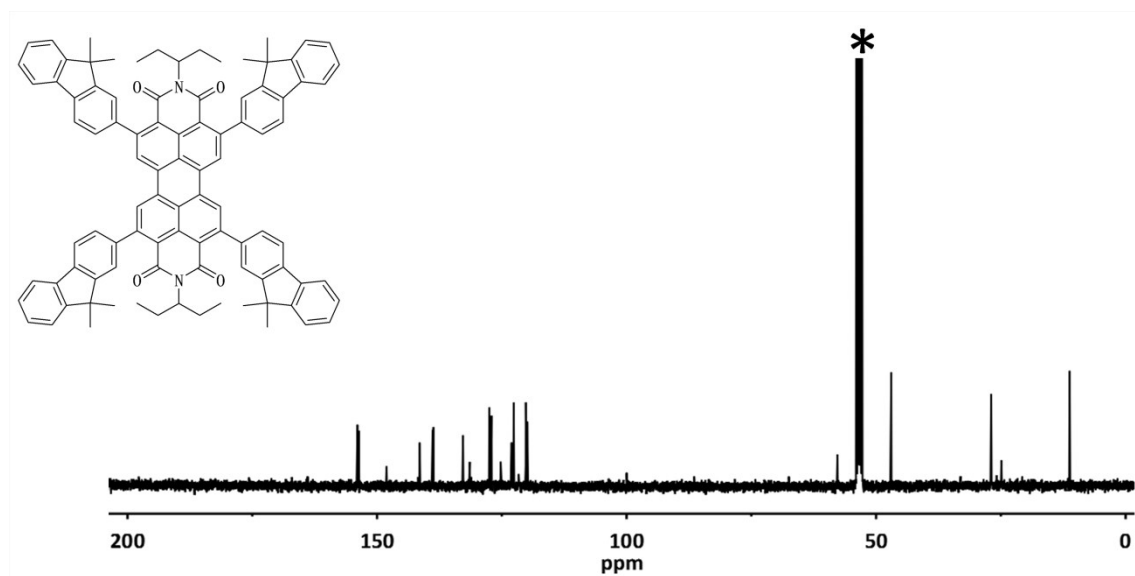


Figure S4. ^{13}C NMR spectrum of *compound 2* in CD_2Cl_2

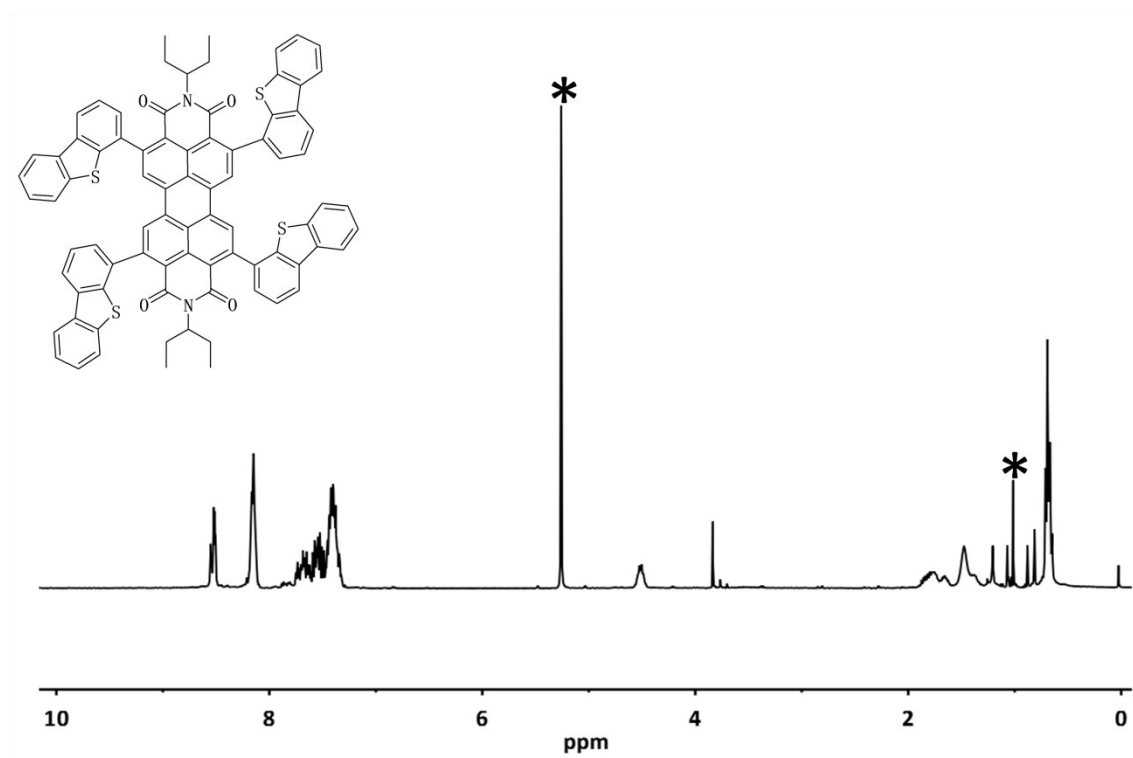


Figure S5. ¹H NMR spectrum of *compound 3* in CD₂Cl₂

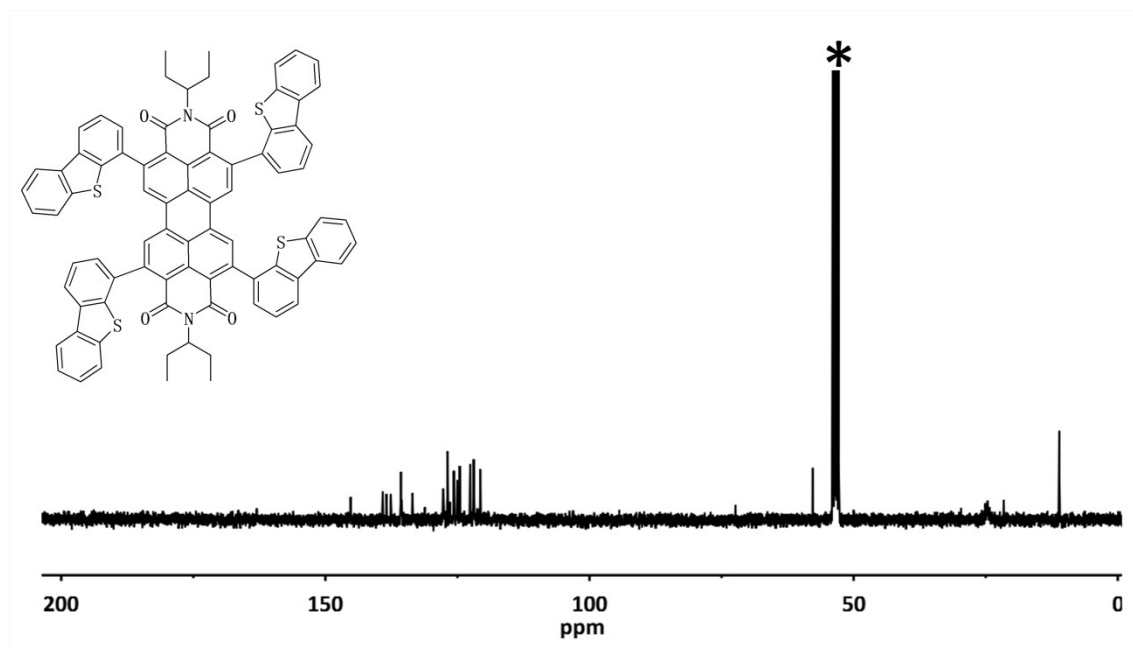


Figure S6. ^{13}C NMR spectrum of *compound 3* in CD_2Cl_2

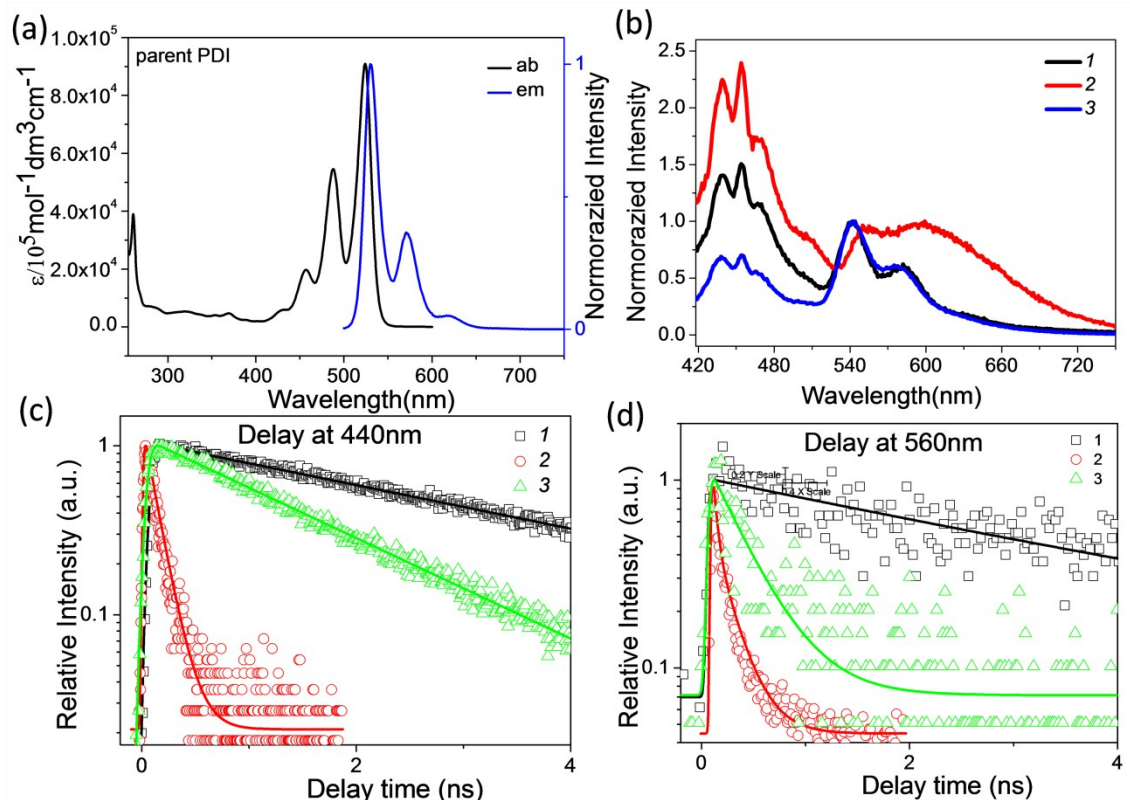


Figure S7. Steady-state absorption spectra (black) and fluorescence spectra (blue) of parent PDI in CH_2Cl_2 solutions. (b) fluorescence spectra of 1-3 at $1 \times 10^{-5} \text{ M}$ in CH_2Cl_2 solutions (c) (d) decay and fitting curves of monomeric CH_2Cl_2 at 440nm and 560nm.

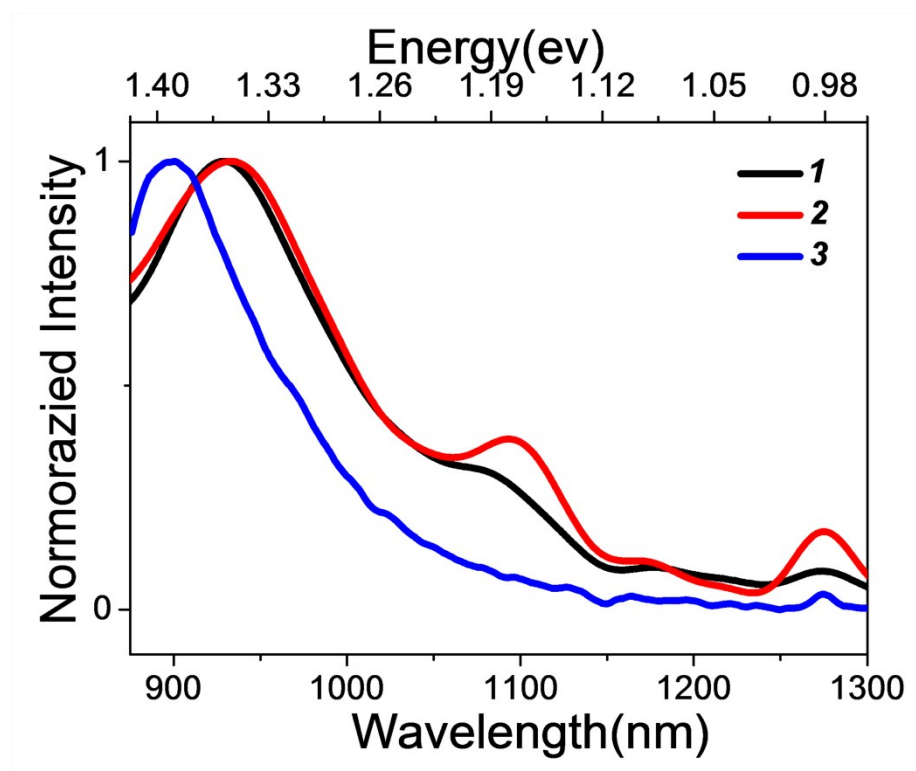


Figure S8. Near-infrared phosphorescence spectra in N_2 -saturated CH_2Cl_2 at 77 K.

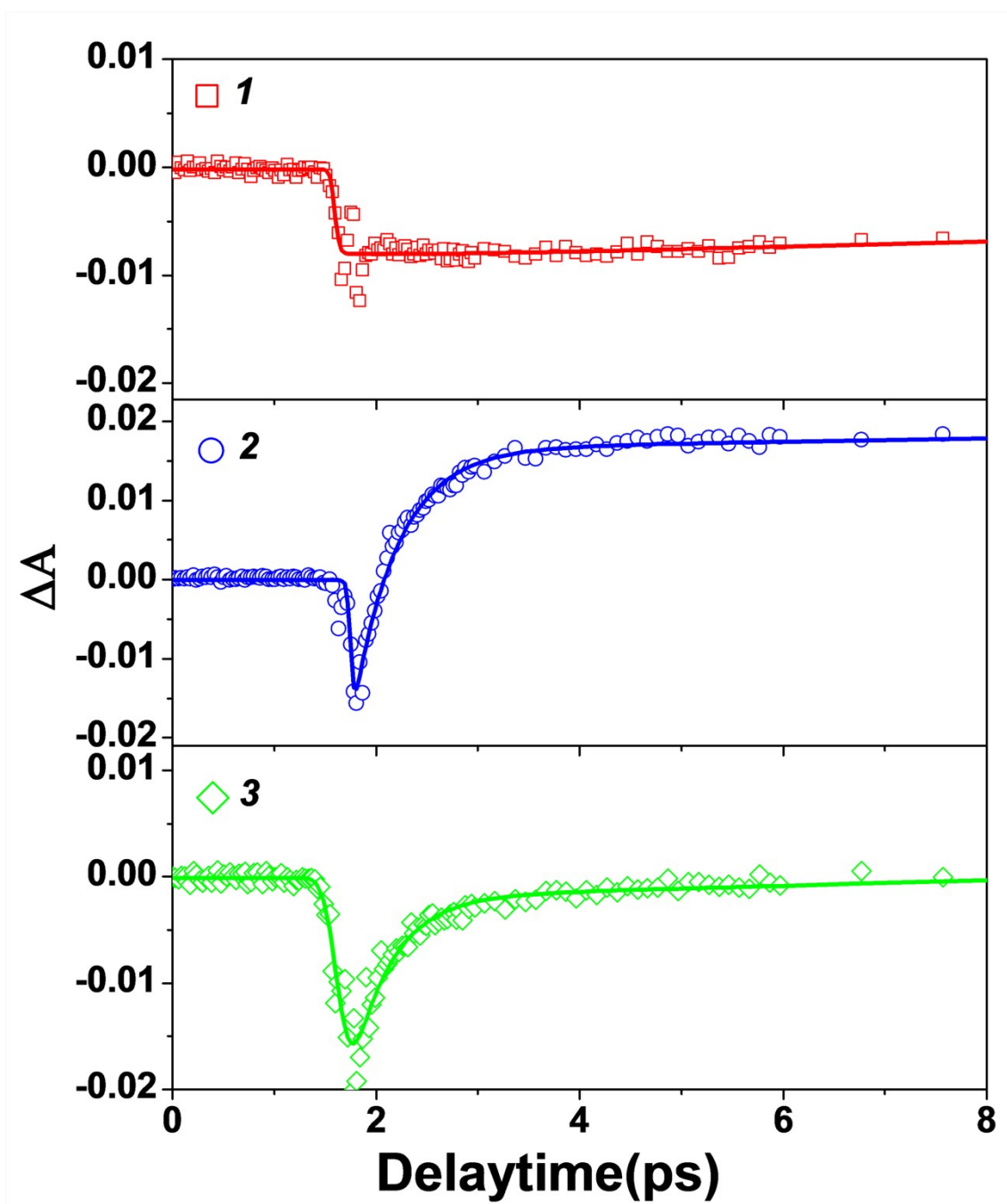


Figure S9. The linear fitting results are also shown. The corresponding time-absorption profiles at 555nm for 1-3.

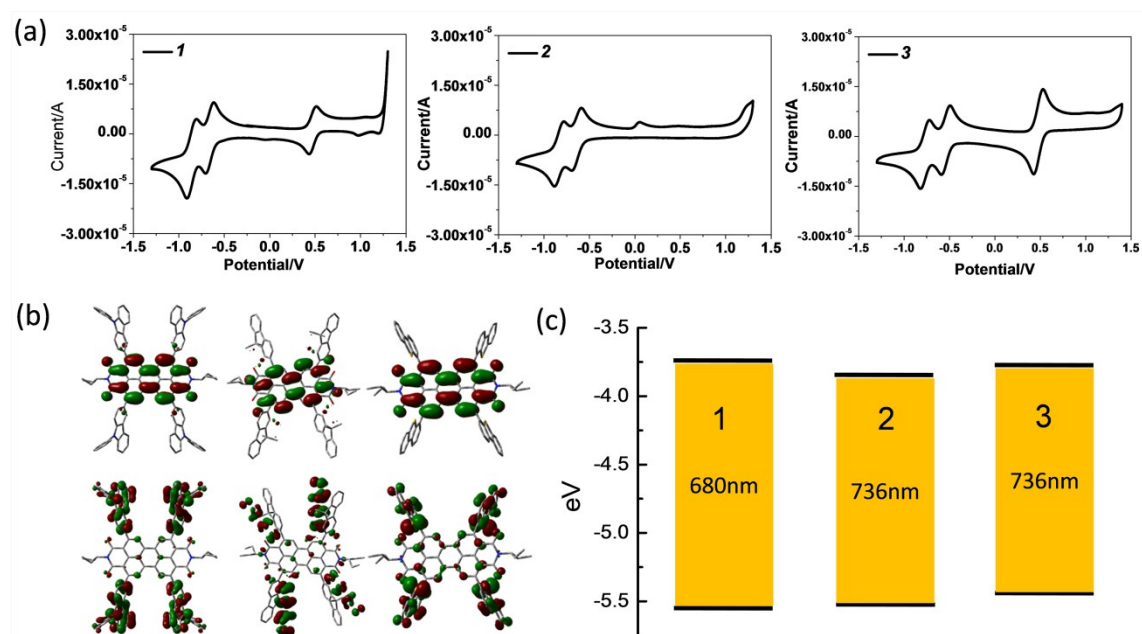
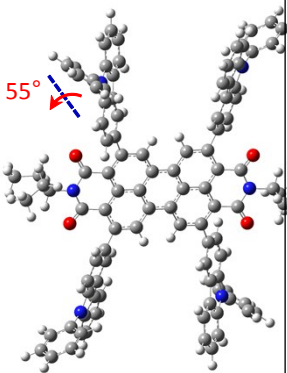
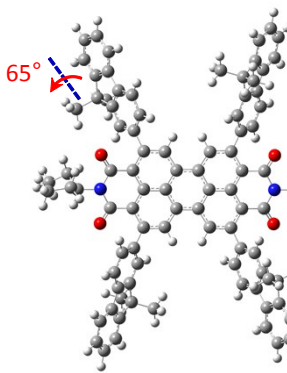
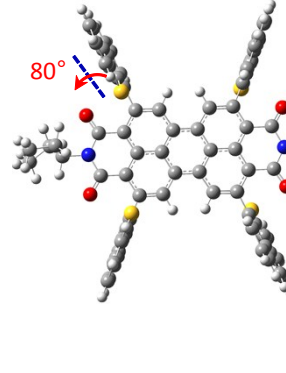


Figure S10. (a) cyclic voltammograms of 1-3 in dichloromethane containing 0.1 M *t*-Bu4NPF6 at the scan rate of 100 mV/s. (b) The HOMO and LUMO obtained by density functional method at the B3LYP/6-31G level. (c) Impact of various core substituents on the redox potentials (black lines; vs ferrocene/ferrocenium redox couple) and the optical properties (colored boxes) of PBI dyes. There is a good match between the energy of the optical gap ($\Delta E = h \times \nu$) and the electrochemical gap ($\Delta E = E_{ox} - E_{red}$)

Table S1. The calculated excitation energies (eV) of the Low-lying excited singlet and triplet states for the three compounds by B3LYP/6-31G(d).

Excited States	1	2	3
S1	1.7468	1.9138	1.9098
S2	1.7704	1.9415	1.9116
S3	1.7772	2.0205	1.9473
S4	1.7789	2.0291	1.9557
T1	0.8426	1.2807	0.7931
T2	1.4146	1.8280	1.6464
T3	1.4293	1.8511	1.6596
T4	1.4511	1.8915	1.6719

1	2	3
		

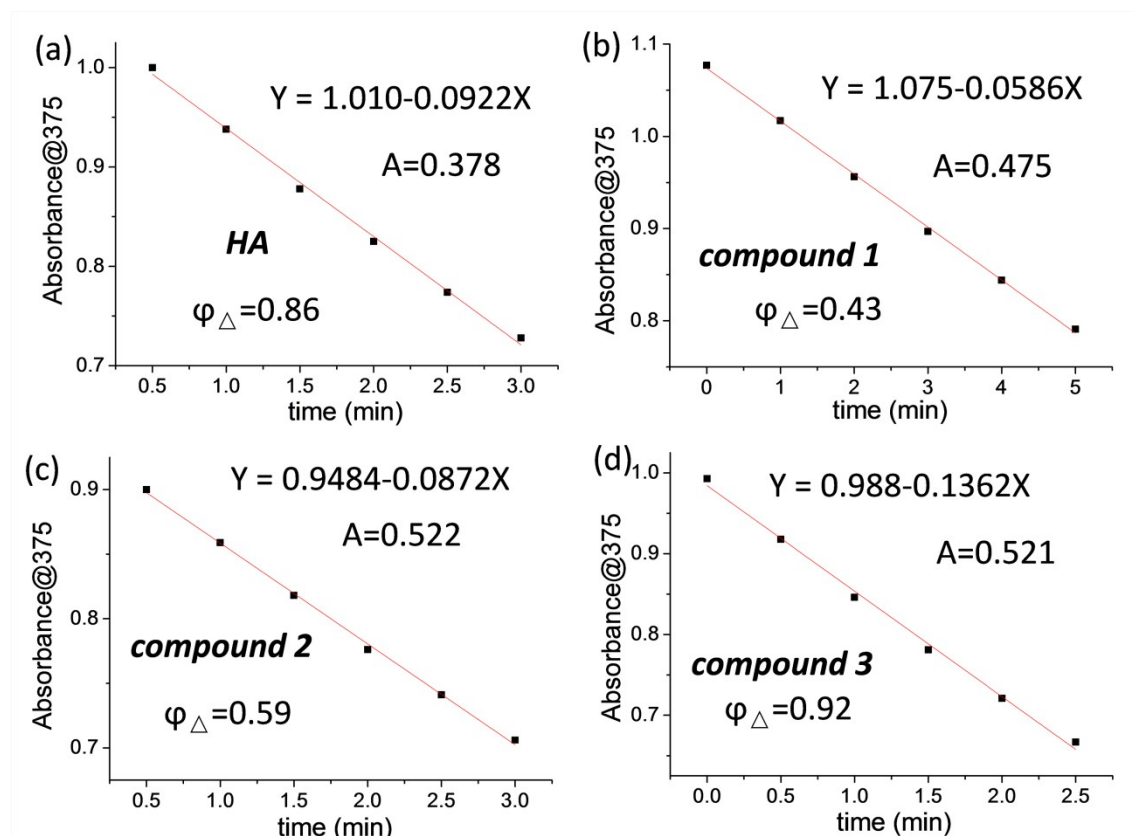


Figure S11. The decrease of the absorbance at 375 nm of DPA as a function of irradiation time for (a) hypocrellin A, (b) (c) (d) for 1-3. The linear fitting results are also shown.