

Electronic Supporting Information for:

Fluorescence Property and Aggregation Behavior of Tetraphenylethene-
Perylenebisimide Dyads

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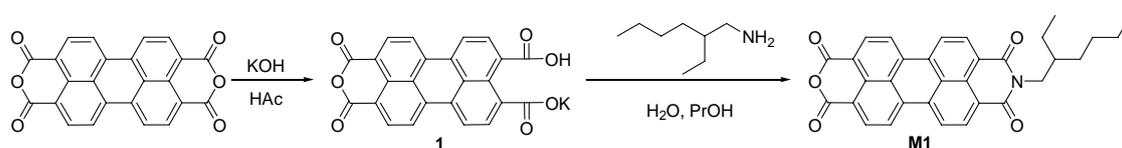
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Synthetic details.

1. Potassium 9-carboxy-1,3-dioxo-1,3-dihydrobenzo-[5,10]-anthrax-[2,1,9-def]isochromene-8-carboxylate (**1**).

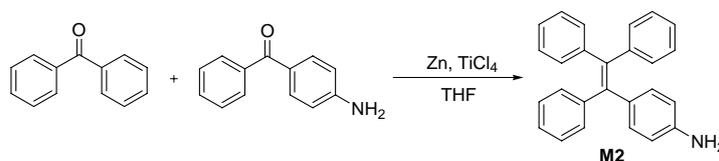
3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) (1.96 g, 5 mM) was dissolved in a 5% potassium hydroxide (22.4 g, 20 mM) solution at 90 °C under nitrogen. Then 14.0 g of 10% acetic acid was added dropwise into the flask over 30 min. The suspension was stirred for another 1 h at the same temperature. The precipitated product **1** was filtered at room temperature, washed with water, and dried at 130 °C. Yield: 67%. The product was used for further reaction without purification.



Scheme S1 Synthetic route to precursor compound **M1**.

2. 9-(2-Ethylhexyl)-1H-isochromeno[6',5',4':10,5,6]anthrax-[2,1,9-def]isoquinoline-1,3,8,10-(9H)-tetraone (**M1**):

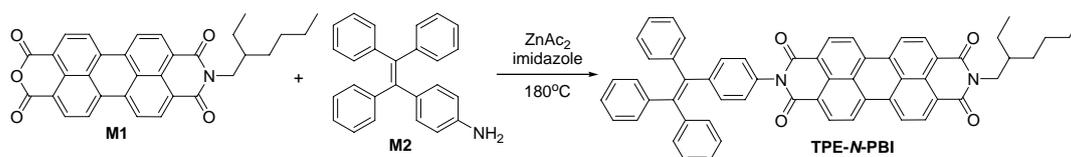
The synthetic route is shown in Scheme 1 and the experiment procedures are described as following. A mixture of compound **1** (1.25 g, 2.79 mM) and a 4.4 molar ratio of 2-ethylhexylamine (1.59 g, 12.3 mM) and 12 mL of H₂O-PrOH (v/v = 1:1) mixture as solvent was stirred at room temperature for 4 h and heated at 90 °C for another 2 h with stirring. The reaction mixture was then acidified with 10% hydrochloric acid, and the resulting precipitate was filtered and washed with water to remove residual amine. After which, the residue was stirred into hot 10% potassium hydroxide solution, and to the mixture was added 8% potassium chloride to separate the precipitated potassium salt of **M1** and the symmetrically substituted diimide from the soluble, unreacted compound **1**. The solid was then added into water and the insoluble, symmetrically substituted diimide was removed. The filtrate was acidified with 20% hydrochloric acid. The precipitate was filtered, washed with water, and dried to yield **M1** in 10% yield. FT-IR (KBr): $\nu = 769, 1732, 1698, 1656, 1594, 1404, 1321, 1245, 1022, 810, 739 \text{ cm}^{-1}$. ¹H NMR (400 MHz, *d*-DMSO, δ): 8.90-8.32 (m, 8H), 4.12-3.94 (m, 2H), 2.00-1.82 (m, 1H), 1.48-1.18 (m, 8H), 0.99-0.74 (m, 6H). HRMS (MALDI-TOF, *m/z*): [M]⁺ calcd. for C₃₂H₂₅NO₅: 503.1733, found: 503.1737 (see Fig. S1, S2 and S7).



Scheme S2. Synthetic route to amino-functionalized tetraphenylethene **M2**.

3. 4-(1,2,2-Triphenylvinyl)aniline (TPE-NH₂, M2):

The synthetic route is shown in Scheme 2 and the experiment details are described below. Zinc dust (1.2 g, 18 mmol) was added into a 250 mL two-necked round-bottomed flask. The flask was degassed and flushed with dry nitrogen three times, after which THF (60 mL) was injected. The mixture was cooled to -5 to 0 °C by an ice-salt bath, then titanium tetrachloride (1 mL, 9 mmol) was added slowly. The mixture was allowed to warm to 25 °C and kept for 0.5 h and then refluxed at 74 °C for 2 h. The mixture was cooled to -5 to 0 °C again, treated with 0.5 mL of pyridine, and stirred for 10 min. Then a THF solution (10 mL) of benzophenone (0.58 g, 3.2 mmol) and 4-aminobenzophenone (0.51 g, 2.6 mmol) was added slowly. After refluxing overnight, the reaction was quenched with a 10% potassium carbonate aqueous solution and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography, using petroleum ether/DCM (5:1 by volume) as eluent. The target compound (0.47 g) was obtained as a light yellow solid in 51.6% yield. ¹H NMR (400 MHz, CDCl₃, δ): 7.23-6.94 (m, 15H), 6.90-6.75 (d, J = 9.6 Hz, 2H), 6.50-6.40 (d, J = 9.6 Hz, 2H), 4.00-3.50 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 144.48, 144.38, 144.32, 141.04, 139.80, 132.75, 131.70, 131.62, 131.59, 127.95, 127.79, 127.78, 126.55, 126.39, 126.35, 115.24 (see Fig. S3).

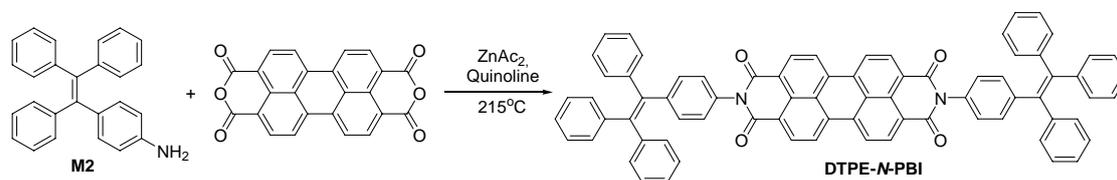


Scheme S3. Synthetic route to mono-TPE modified PBI (TPE-N-PBI).

4. 2-(2-Ethylhexyl)-9-(4-(1,2,2-triphenylvinyl)phenyl)anthrax-[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (TPE-N-PBI):

The typical synthetic procedures are described as below and the synthetic route is shown in Scheme 3. M1 (0.5 g, 1 mmol), M2 (0.7 g, 2 mmol), zinc acetate (0.1 g) and imidazole (10 g) were added into a 100 mL two-necked round-bottomed flask. The flask was degassed and flushed with dry nitrogen three times. And then the mixture was heated to 180 °C and stirred for 24h and then cooled to room temperature. The mixture was poured into 100 mL of ice water and the precipitate was filtered and washed with water. After drying, the residue was purified by silica gel column chromatography, using petroleum ether/DCM (1:1 by volume) as eluent. The target compound (0.20 g) was obtained as a dark red solid in 24.1% yield. FTIR (KBr): ν = 1697, 1657, 1595, 1440, 1403, 1354, 1256, 1179, 1125, 1075, 852, 810, 747, 700, 625, 584 cm^{-1} . ¹H NMR (400 MHz, CDCl₃, δ): 8.69-8.31 (m, 8H), 7.25-7.03 (m, 19H), 4.20-4.04 (m, 2H), 1.99-1.83 (m, 1H), 1.47-1.20 (m, 8H), 1.00-0.81 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 167.97, 163.62, 163.42, 144.37, 143.90, 143.62, 143.58, 142.02, 140.37, 134.65, 134.18, 133.32, 132.69, 132.39, 131.74, 131.63, 131.58, 131.24, 131.07, 129.70, 129.20, 129.01, 128.15, 128.06, 127.96, 127.89, 126.32,

126.16, 123.58, 123.39, 38.99, 38.21, 32.14, 30.60, 29.90, 29.55, 29.16, 23.99, 23.30, 23.20, 22.90, 14.32, 14.25, 11.19, 10.85. HRMS (MALDI-TOF, m/z): $[M]^+$ calcd. for $C_{58}H_{44}N_2O_4$: 832.3301, found: 832.3318 (see Fig. S4, S5 and S8).



Scheme S4. Synthetic route to dual-TPE modified PBI (DTPE-N-PBI).

5. 2,9-Bis(4-(1,2,2-triphenylvinyl)phenyl)anthra[2,1,9-def:6,-5,10-d'e'f']diisoquinoline-1,3,8,10-(2H,9H)-tetraone (DTPE-N-PBI):

PTCDA (0.5 g, 1 mmol), M2 (0.7 g, 2 mmol) and zinc acetate (0.1 g) was added into a 100 mL two-necked round-bottomed flask. The flask was degassed and flushed with dry nitrogen three times, after which quinoline (20 mL) was injected. The mixture was stirred at 215 °C for 36 h and then cooled to room temperature. The mixture was poured into 100 mL of ice water and the precipitate was filtered. The residue was stirred into 10% hydrochloric acid, and the resulting precipitate was filtered and washed with water. After that, the residue was added into hot 10% potassium hydroxide and was stirring at 90 °C for 0.5 h. The precipitate was filtered, washed with DCM, THF and methanol and dried to yield **DTPE-N-PBI** in 44.2% yield. FT-IR (KBr): $\nu = 1709, 1670, 1594, 1506, 1404, 1346, 1253, 1174, 810, 748, 700 \text{ cm}^{-1}$. HRMS (MALDI-TOF, m/z): $[M]^+$ calcd. for $C_{76}H_{46}N_2O_4$: 1050.3458, found: 1050.3488 (see Fig. S6 and S9).

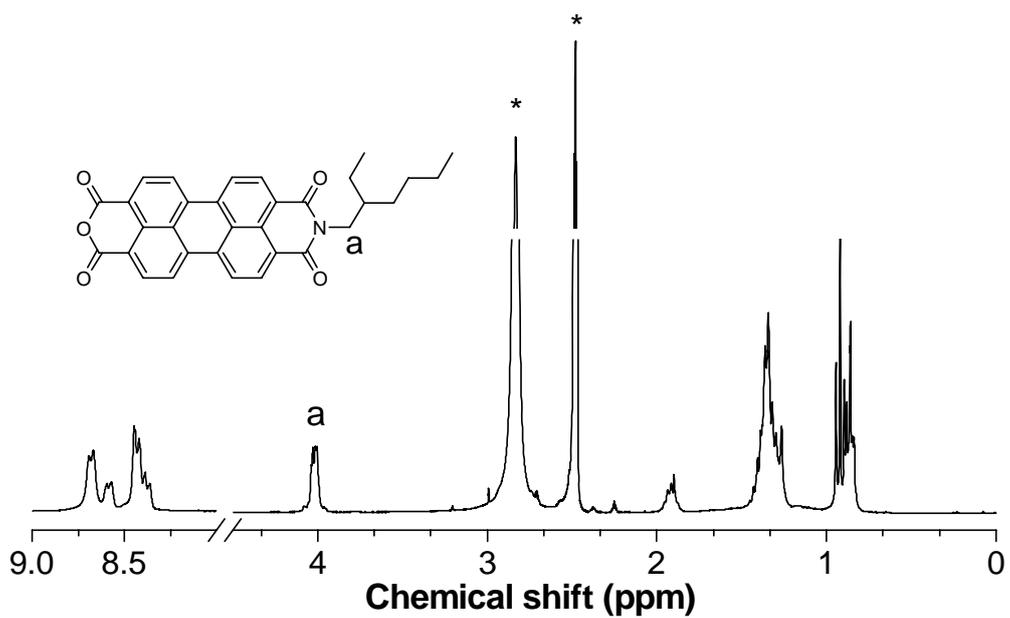


Fig.S1 ^1H NMR spectra of M1 in *d*-DMSO. The solvent peak is marked with asterisk.

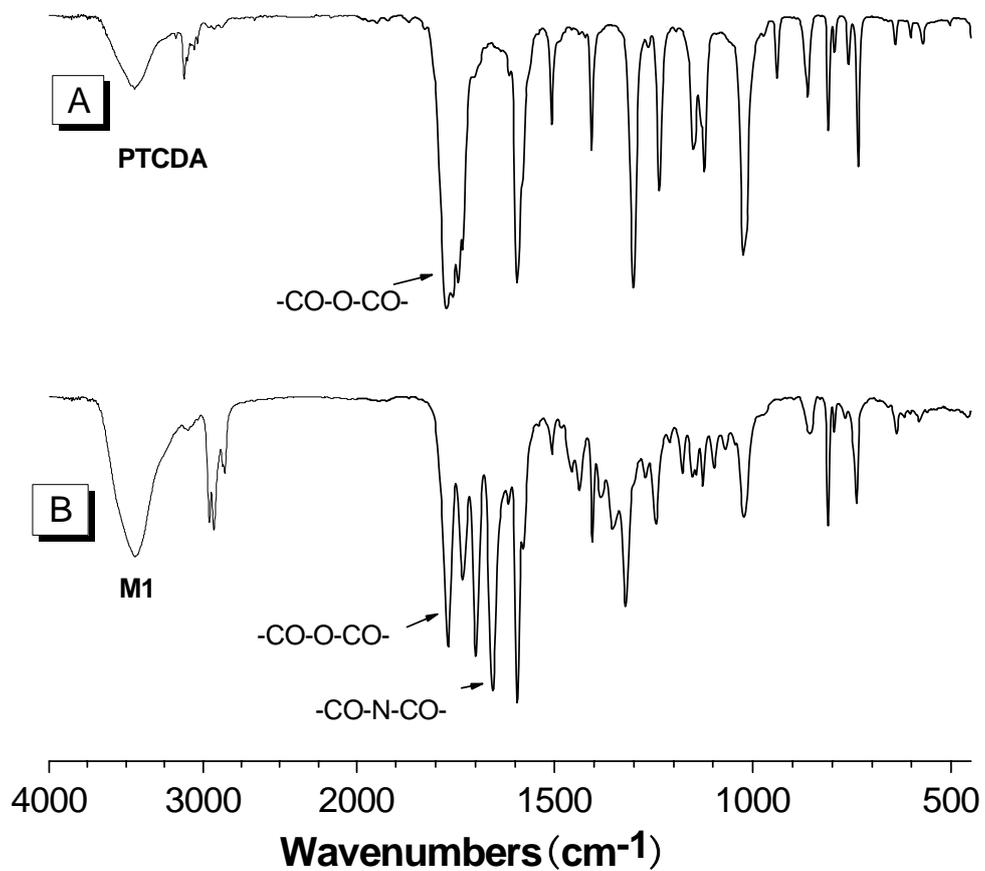


Fig.S2 FT-IR spectra of (A) PTCDA and (B) M1.

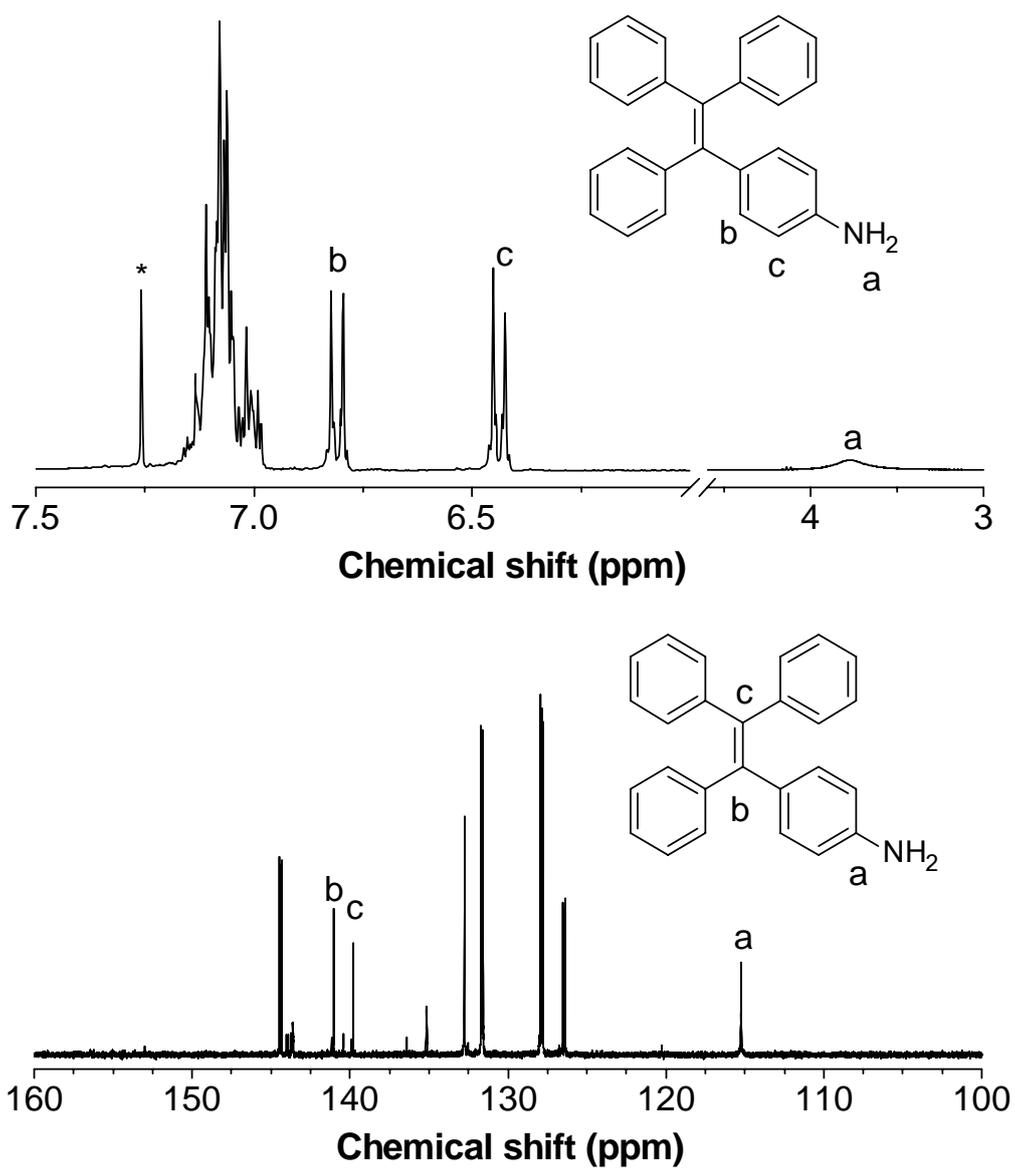


Fig.S3 ¹H NMR and ¹³C NMR spectrum of TPE-NH₂ in CDCl₃. The solvent peak is marked with asterisk.

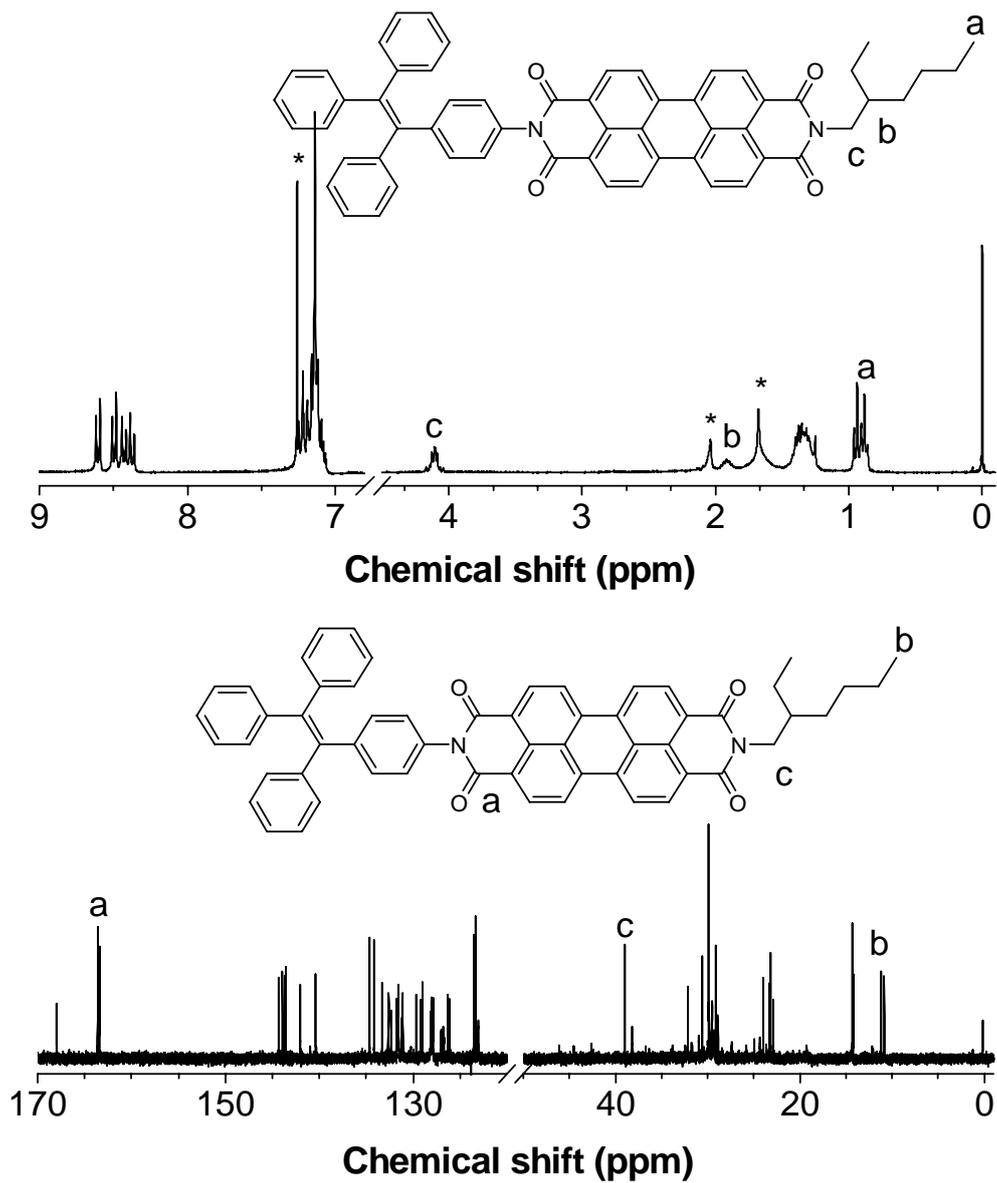


Fig.S4 ¹H NMR and ¹³C NMR spectrum of TPE-N-PBI in CDCl₃. The solvent peaks are marked with asterisks.

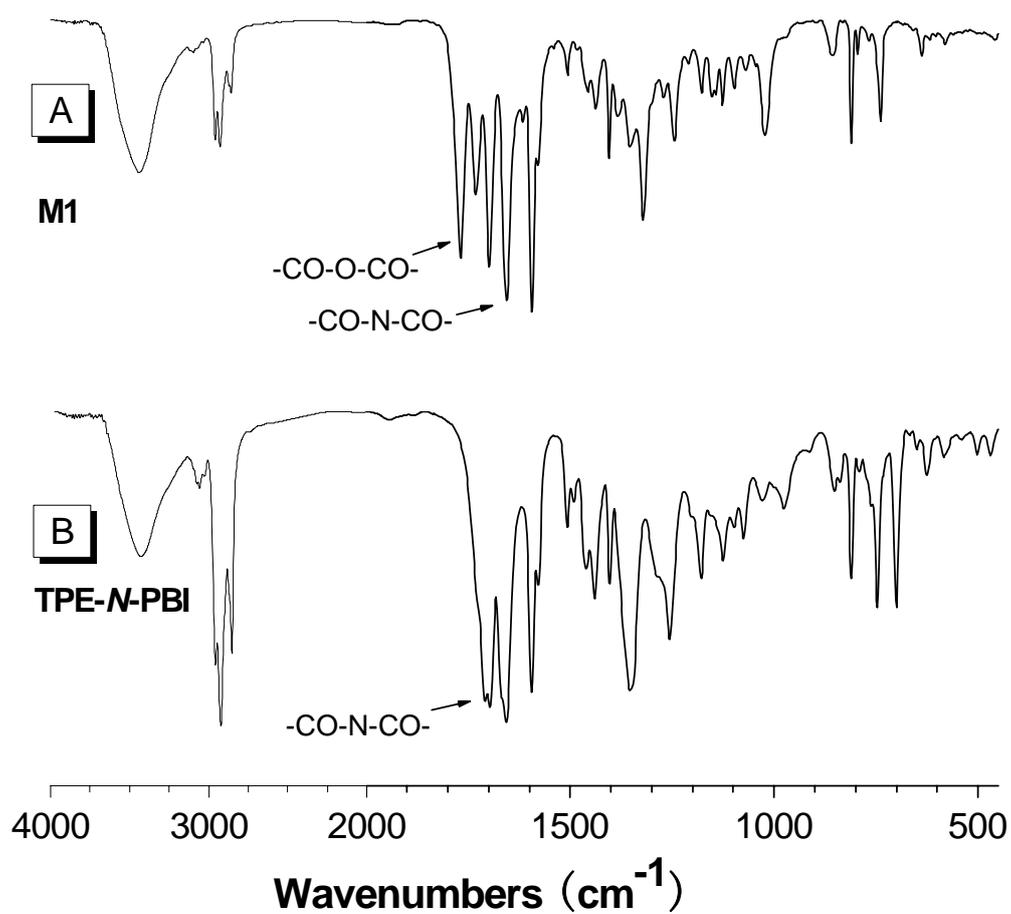


Fig.S5 FT-IR spectra of (A) M1 and (B) TPE-N-PBI.

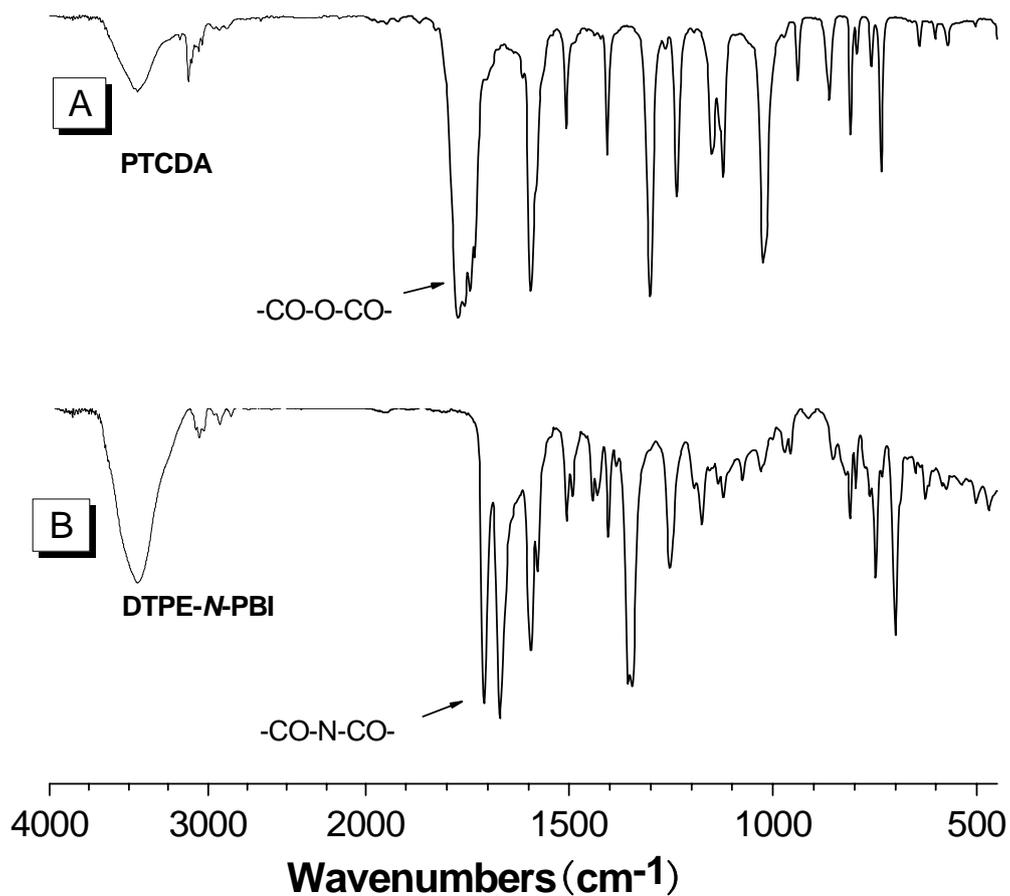


Fig.S6 FT-IR spectra of (A) PTCDA and (B) DTPE-N-PBI.

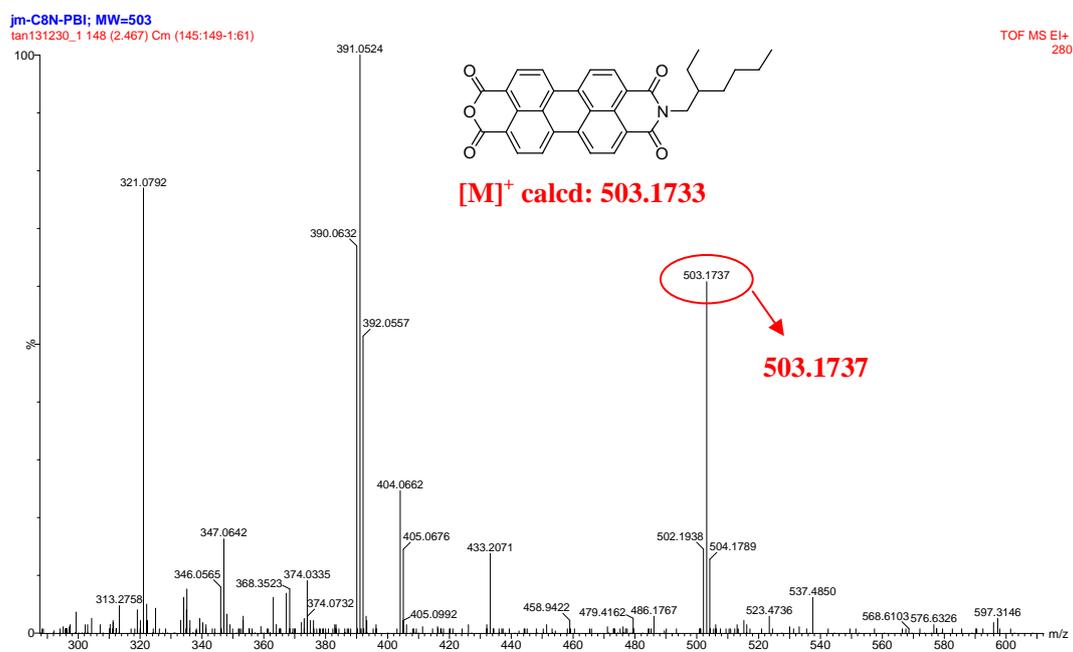


Fig.S7 MALDI-TOF mass spectra of M1.

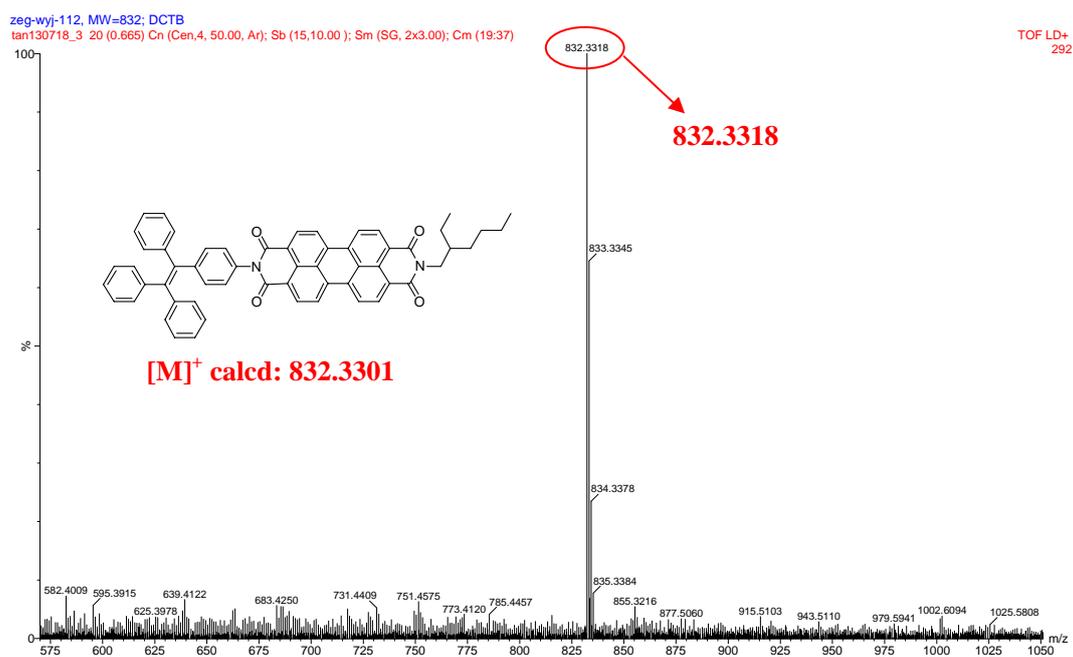


Fig.S8 MALDI-TOF mass spectra of TPE-*N*-PBI.

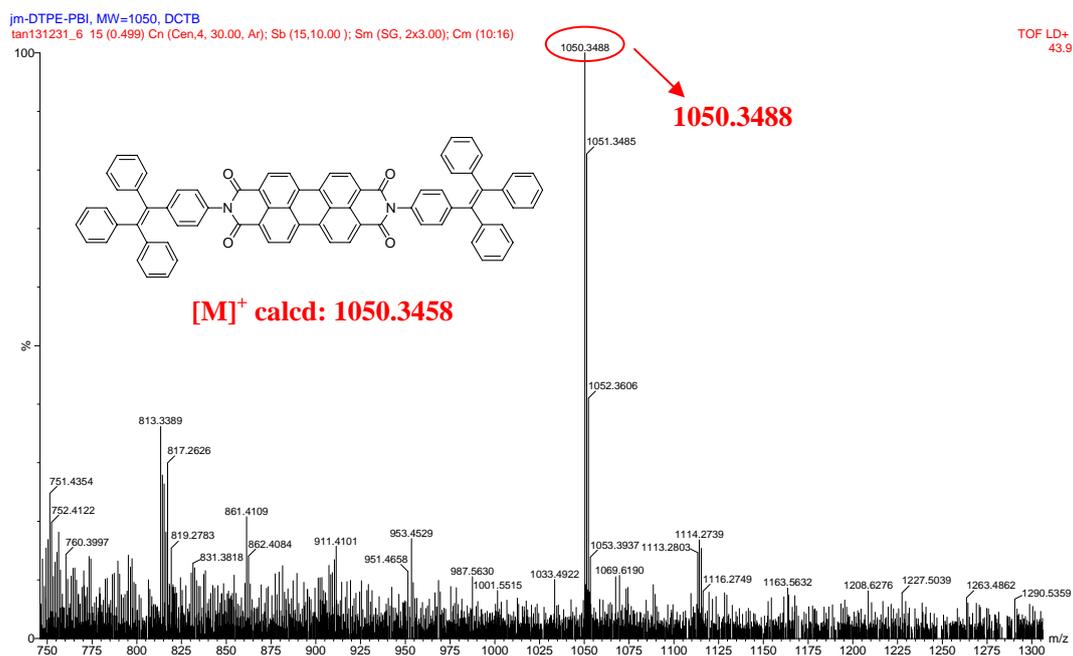


Fig.S9 MALDI-TOF mass spectra of DTPE-*N*-PBI.

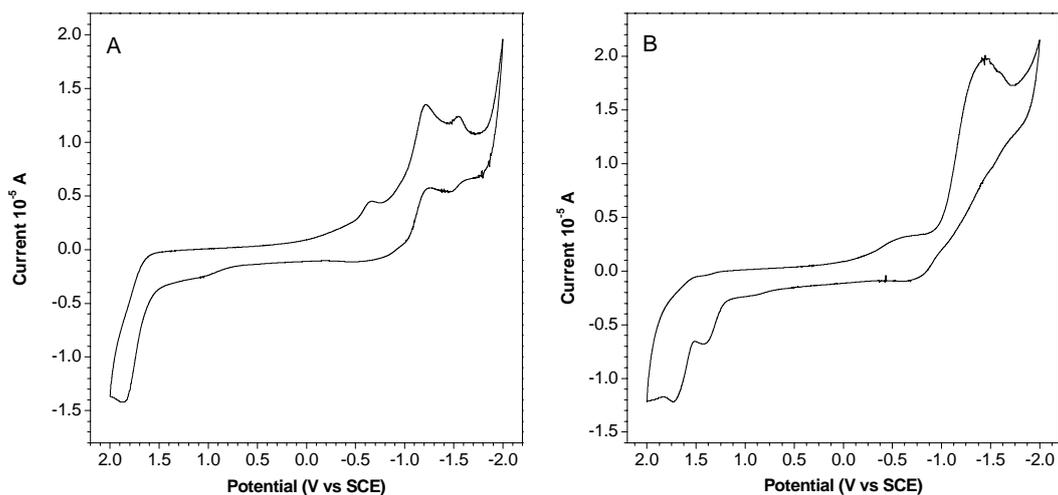


Fig. S10 The cyclic voltammograms of (A) M1 and (B) DTPE-N-PBI measured in DCM containing 0.1M $[nBu_4N]^+[PF_6]^-$ at a scan rate of 50 mV/s. AgCl was used as reference electrode and ferrocene as a calibration. To obtain well-resolved CV signal, the concentration of TPE-N-PBI and M1 in DCM was 1.0×10^{-4} M, which was higher than that used in the optical spectrum measurements.

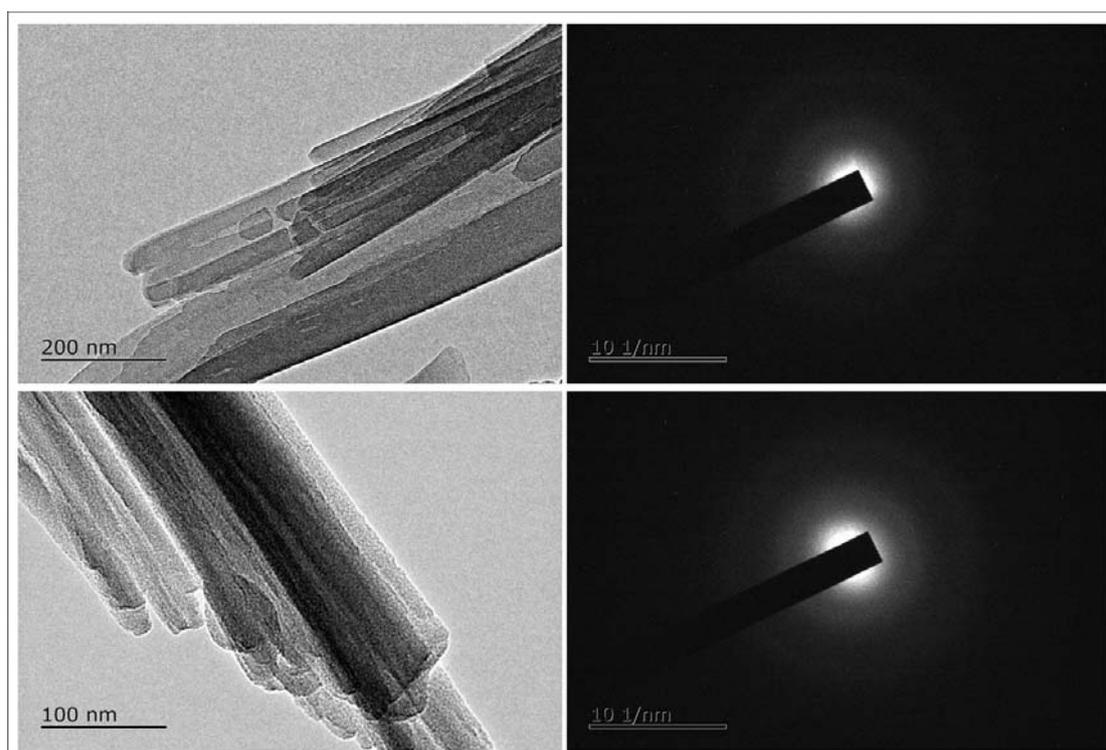


Fig. S11 Typical X-ray diffraction patterns of DTPE-N-PBI aggregates at different areas. Only dispersive halos can be observed on the patterns. The images were recorded on a high resolution transmittance electron microscope (HRTEM) instrument.

Table S1 Data Summary of the Optical and Electromnic Properties of M1, TPE-*N*-PBI and DTPE-*N*-PBI

	M1	TPE- <i>N</i> -PBI	DTPE- <i>N</i> -PBI
$\lambda_{\text{abs,sol}} / \text{nm}$	521	527	527
$\lambda_{\text{em,sol}} / \text{nm}$	535	539	539
$\lambda_{\text{em,agg}} / \text{nm}$	524	529	523
$\Phi_{\text{F, sol}} / \%$	57.86	0.32	0.39
$\Phi_{\text{F, agg}} / \%$	36.91	0.55	1.48
$\Phi_{\text{F, film}} / \%$	0.9	0.5	0.5
HOMO _{cal} / eV	-6.21	-5.34	-5.34
LUMO _{cal} / eV	-3.67	-3.43	-3.41
$\Delta E_{\text{cal}} / \text{eV}$	2.54	1.91	1.93
HOMO _{meas} / eV	-6.20	-6.40	
LUMO _{meas} / eV	-3.88	-4.12	
$\Delta E_{\text{meas}} / \text{eV}$	2.32	2.28	