Supporting Information

for

Tuning Reductive Species Formation of Perylene-Bisimide Derivatives in DMF via Aggregation Matter

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Contents

1. Titration NMR spectra

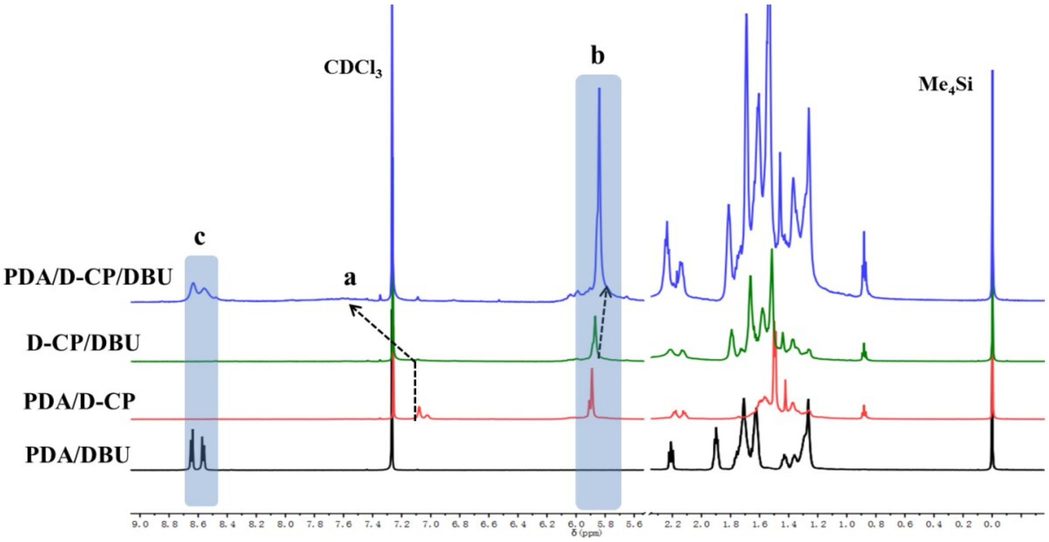


Fig. S1 ^{1}H NMR spectrum of the respective CDCl$_3$ solution of PDA/DBU, PDA/ D-CP, D-CP/DBU and D-CP/PDA/DBU (the molar ratio is 1:1 or 1:1:1; 1 mM each). Highlights are the signals for (a) pyrrole NH protons, (b) pyrrole methylene protons, (c) perylene aromatic protons.

2. Absorption spectra of 4Br-PDA

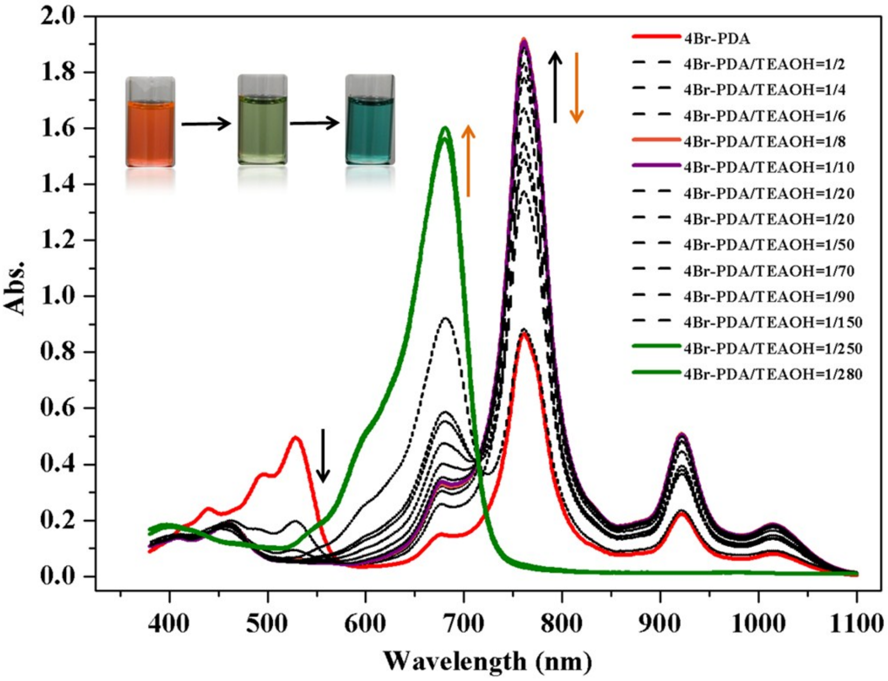


Fig. S2 Absorption spectra showing the titration of a 4Br-PDA solution (5×10^{-5} mol/L) in DMF with TEAOH. The pictures depicted in the inset are the systems of 4Br-PDA, 4Br-PDA/TEAOH (1:10), and 4Br-PDA/TEAOH (1:280).

Note: 4Br-PDA displayed significant radical anion absorption in DMF in the absence of a base.

3. EPR spectroscopy of TPE

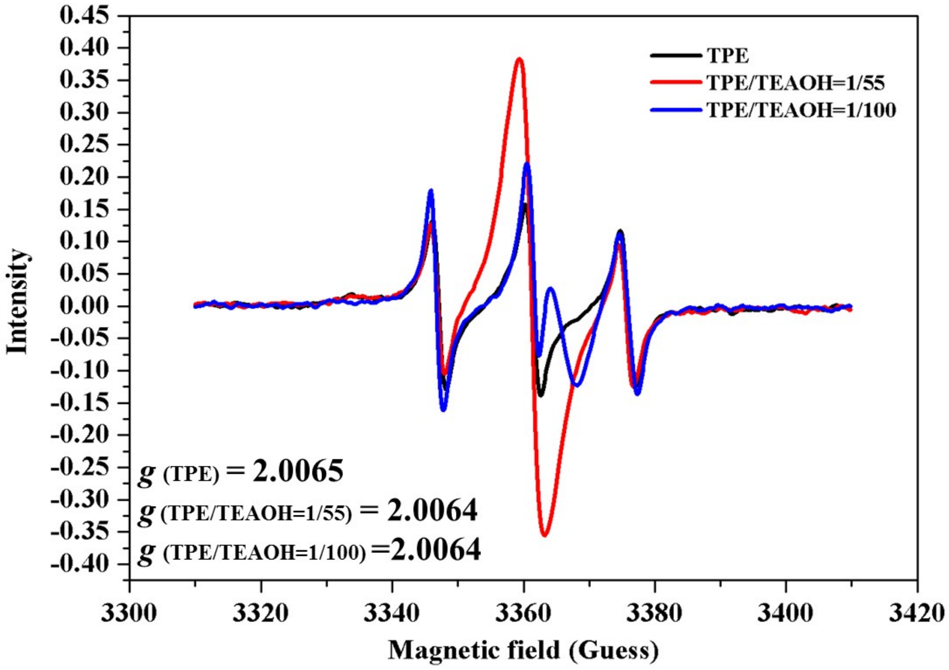


Fig. S3 EPR spectra of the radical anion generated from the DMF solutions of TPE (1×10^{-5} mol/L), TPE/TEAOH=1/55 and TPE/TEAOH=1/100, respectively.

In order to provide a direct and strong evidence for the formation of radical anion, electron paramagnetic resonance (EPR) spectroscopy measurements were performed with TPE as an example sample. As shown in Fig. S3, a solution of TPE in absence of TEAOH shows a significant EPR signal (blank line). As expected, increasing TEAOH concentration resulted in enhanced EPR signal. However, the EPR signal decreased with further addition of the base, a result of formation of the dianion of TPE as revealed by the UV-vis measurements (Fig. S7).

Quantitative analysis of the EPR data shown in the figure revealed the *g*-factors of the three TPE related solutions (TPE, TPE/TEAOH=1/55, TPE/TEAOH=1/100), which are 2.0065, 2.0064, and 2.0064, respectively. The positive EPR signals as observed and the reasonable *g*-factors of the systems further confirm formation of the TPE radical anion.[1,2] As for why there appears a group of EPR signals, it should be a result of complicated environment experienced by the radical anions as formed.

4. Light scattering and UV-vis tests

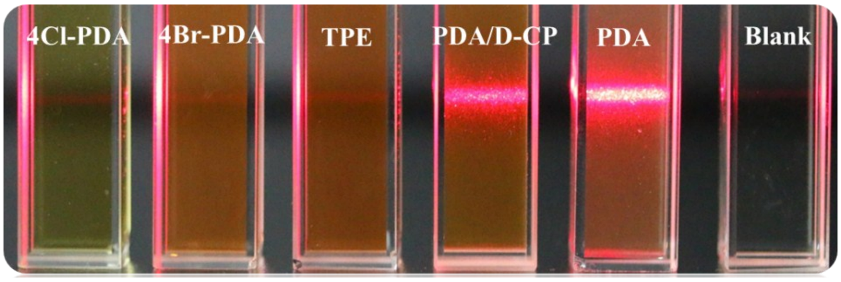


Fig. S4 Tyndall scattering results of the DMF solutions of 4Cl-PDA, 4Br-PDA, TPE, PDA/D-CP, and PDA (from left to right, 5×10^{-5} mol/L) and pure solvent.

Note: 4Cl-PDA, 4Br-PDA and TPE show negligible scattering if compared to PDA. As for the host-guest system, scattering observed should originate from the aggregation of the host-guest complex rather than PBI core. This statement was further confirmed by the results from UV-vis measurement (Fig. S5).

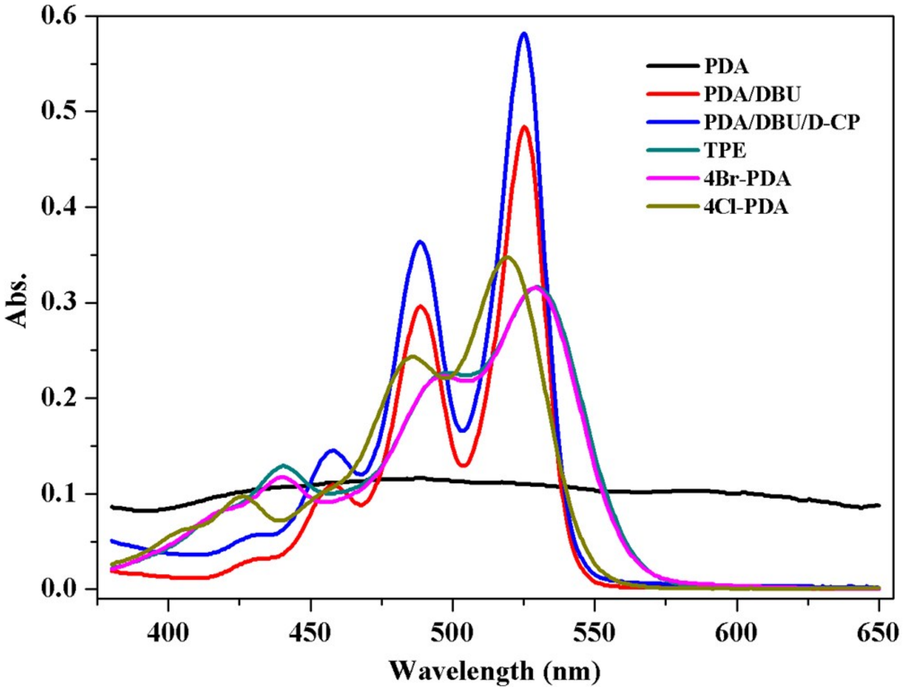


Fig. S5 UV-vis absorption spectra of the $CHCl_3$ solutions of PDA, PDA/DBU, PDA/DBU/D-CP, TPE, 4Br-PDA and 4Cl-PDA (1×10^{-5} mol/L).

Note: Typical PBI monomer absorption was observed in the host-guest solution under examination. For other systems under study, with exception of PDA, they all showed PBI monomer absorption. The absorption of the PDA solution is weak and lacks fine structures, demonstrating its poor solubility and strong aggregation in the solvent.

5. Cyclic voltammetry measurements

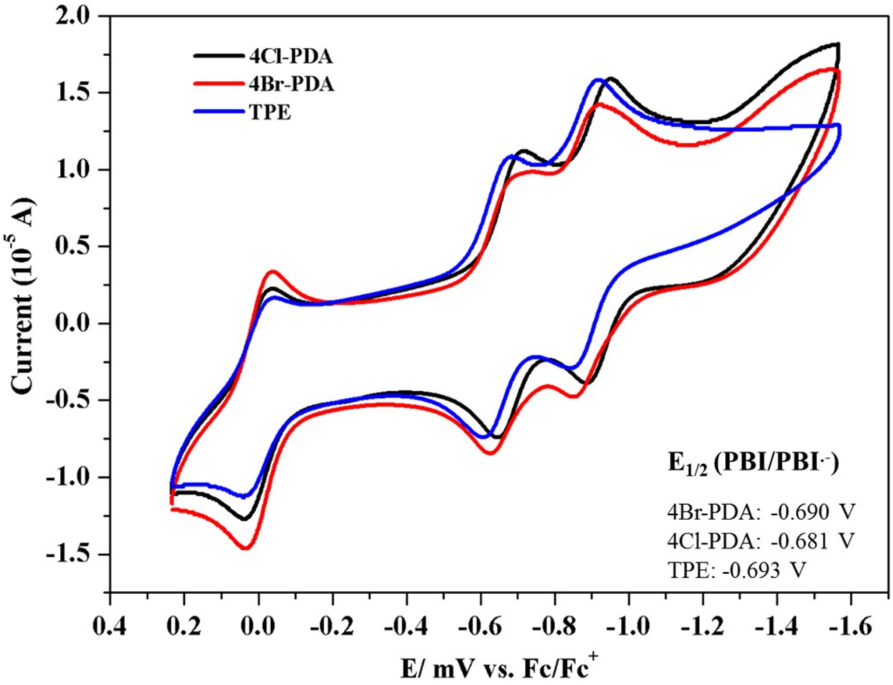


Fig. S6 Cyclic voltammograms of 4Cl-PDA (blank line), 4Br-PDA (red line) and TPE (blue line) in DMF (2×10^{-4} mol/L). Reference electrode: Ag/Ag$^+$, working and auxiliary electrode: Pt. 0.1 M TBAHFP, Fc/Fc$^+$, 25 ℃.

6. Absorption spectra of TPE

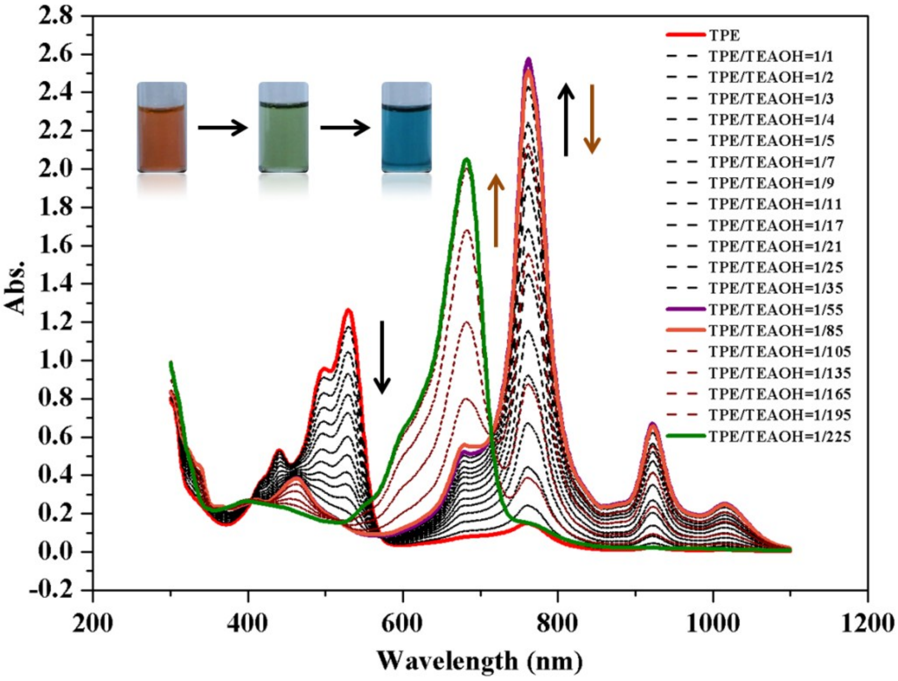


Fig. S7 UV-vis absorption spectra showing the titration of a DMF solution of TPE (5×10^{-5} mol/L) in DMF with TEAOH as a base. The pictures depicted in the inset are the systems of TPE, TPE/TEAOH (1:85), and TPE/TEAOH (1:225).

7. Calculated HOMO and LUMO

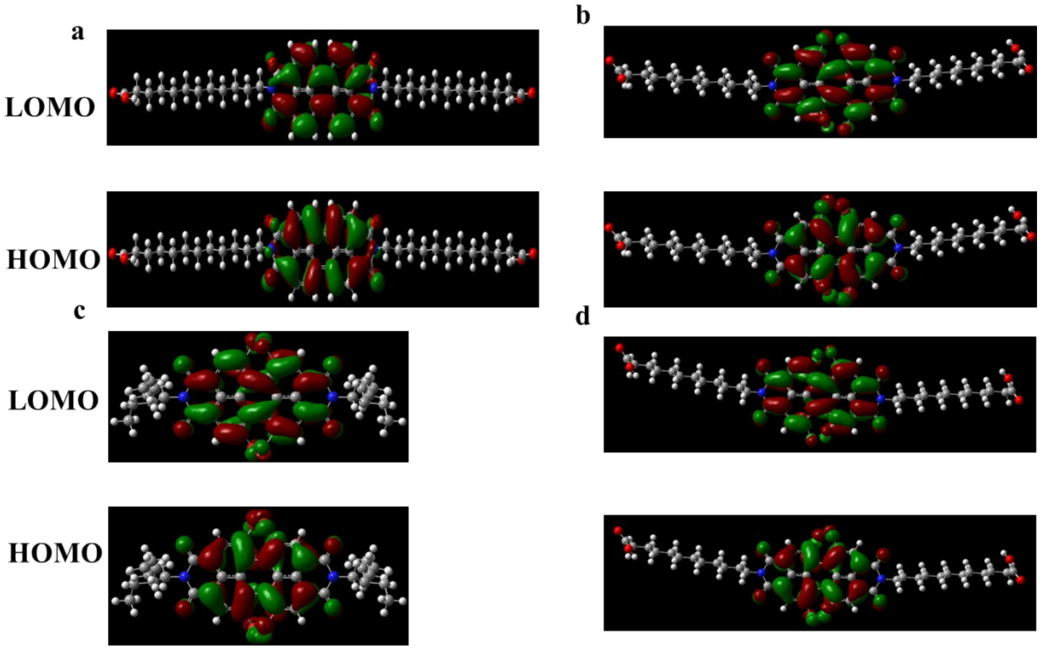
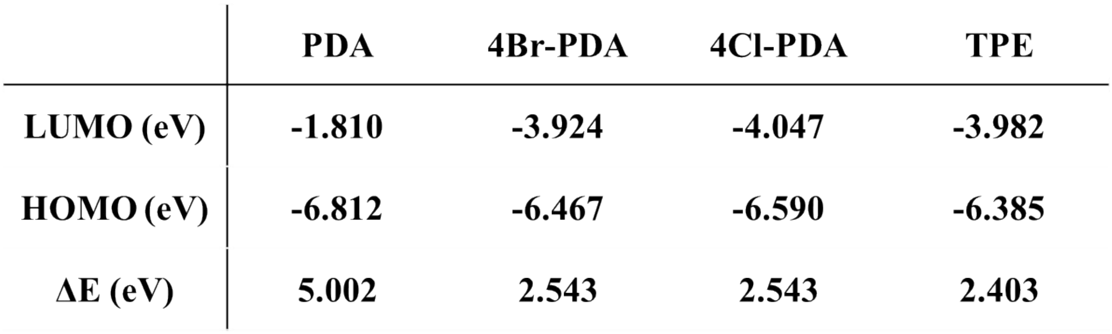


Fig. S8 Computed orbitals for compounds of (a) PDA, (b) 4Br-PDA, (c) TPE, (d) 4Cl-PDA.



	PDA	4Br-PDA	4Cl-PDA	TPE
LUMO (eV)	**-1.810**	**-3.924**	**-4.047**	**-3.982**
HOMO (eV)	**-6.812**	**-6.467**	**-6.590**	**-6.385**
ΔE (eV)	**5.002**	**2.543**	**2.543**	**2.403**

Table S1. Calculated HOMO and LUMO energies of PDA, 4Br-PDA, 4Cl-PDA and TPE.

8. Synthesis and characterization

8.1 Materials and reagents

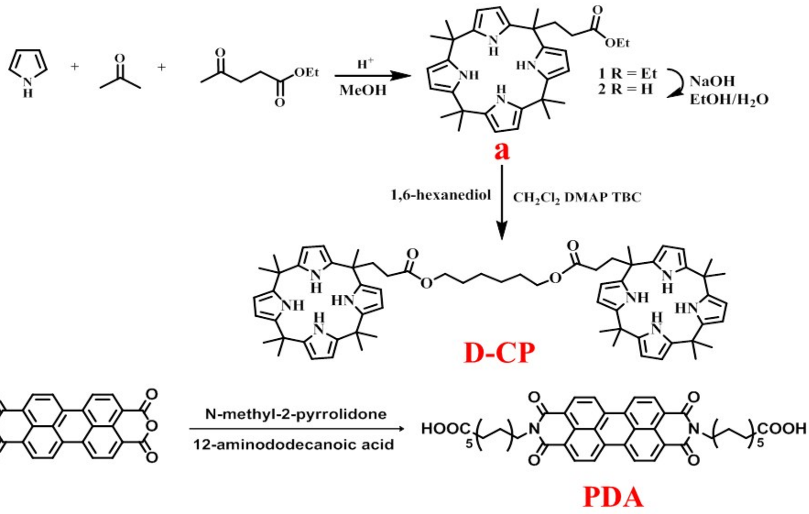
Pyrrole (J&K, 99.7%), ethyl levulinate (J&K, 98.0%), 1,6-hexanediol (J&K，97.0%), 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride (HWRK Chem, 97.0%), dibromoiso-cyanuric acid (DBI) (Energy Chemical, 97%), 4-dimethylaminopyridine (DMAP) (Aladdin, 99.0%), 2,4,6-trichlorobenzoyl chloride (TBC) (J&K, 98.0%), 3,4,9,10-perylene tetracarboxylic dianhydride (TCI, 98.0%), N-methyl-2-pyrrolidone (Aladdin, 99.0%), 12-aminododecanoic acid, (Alfa aesar, 98.0%), tetraethyl- ammonium hydroxide (TEAOH) (J&K, 25 wt% solution in H_2O), tetrabutyl- ammonium hexafluorophosphate (TBAHFP) (J&K, 98.0%), and 1,8-diazabicyclo- [5,4,0]undec-7-ene (DBU) (Aladdin, 99.7%) were used directly without further purification. Dichloromethane and triethylamine were distilled from calcium hydride under nitrogen before use. All other reagents were of analytical grade and used without further purification or treatment. Water used in this work was acquired from a Milli-Q reference system throughout.

8.2 Instrumentation and characterization

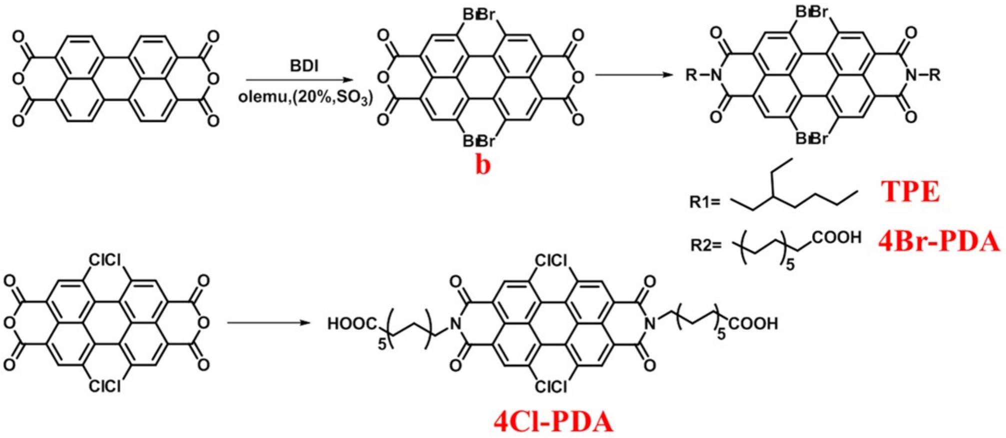
NMR measurements were conducted on Bruker AV 600 NMR spectrometer at room temperature. The MS data were collected on a Bruker maxis UHR-TOF mass spectrometer in ESI positive mode. UV-vis absorption spectra were recorded on a spectrophotometer (Lambda 950, Perkin-Elmer, USA) at room temperature. For cyclic voltammetry, a standard a CH Instruments (model CHI 660E Electrochemical Analyzer) with a three electrode single compartment cell was used. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAHFP). Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMXPLUS6/1 spectrometer under the settings of center field, 3360.00G, microwave freguency, 9.43GHz, power, 0.63 mW. The measurements were carried out using ferrocene/ferrocenium (Fc/Fc^+) as an internal standard for the calibration of the potential. Ag/Ag^+ reference electrode was used. Working and auxiliary electrode was Pt.

8.3 Synthesis

The structure and synthesis route of compounds in this article are shown in **Scheme 1** and **Scheme S1**. Compounds **PDA** and **a** were respectively synthesized by adopting a literature method.[3]



Scheme S1. Schematic representation of the synthesis routes of **D-CP** and **PDA**.



Scheme S2. Schematic representation of the synthesis routes of **TPE**, **4Br-PDA** and **4Cl-PDA**.

Synthesis of compound D-CP

D-CP was synthesized in the following way. Before the synthesis, all instruments used in the synthesis need to be strictly dried. Firstly, compound **a** (400 mg, 0.8 mmol) was dissolved in a mixture solution of dry dichloromethane (25 mL), dry triethylamine (280 μL, 2 mmol) and 2,4,6-trichlorobenzoyl chloride (390 mg, 1.6 mmol). The reaction mixture was stirred at room temperature under argon atmosphere for two hours. Then, 1,6-hexanediol (47 mg, 0.4 mmol) and DMAP (240 mg, 2 mmol) were added into the mixture. One hour later, the solvent was evaporated under reduced pressure.[4] The solid as resulted was purified by column chromatography on silica gel with a mixture liquid of dichloromethane and ethyl acetate (5:1, *v/v*) as eluent. The final product is a light yellow solid. ^{1}H NMR ($CDCl_3$ /Me_4Si, 600 MHz; **Fig. S9**): δ (ppm), 7.07-7.08 (4H, d, NH), 5.89-5.92 (8H, m, pyrrole-CH), 4.00-4.02 (2H, t, -CH_2-), 3.59-3.61 (2H, t, -CH_2-), 2.10-2.20 (4H, m, -CH_2). MS (ESI, m/z): Calcd for [(M+H^+)]: 1055.6845, Found: 1055.6836.

Synthesis of compound b

A mixture of 1,4,5,8- Perylene tetracarboxylic dianhydride (2.00 g, 5.08 mmol) and oleum (20% SO_2, 30 mL) was stirred at room temperature for 2 hours. Then the solution of dibromoisocyanuric acid (3.19 g, 11.1 mmol) in oleum (40 mL) was added dropwise in a course of 30 minutes. The mixture was heated to 90 °C and maintained at this temperature for 48 hours. After that upon cooling to room temperature, the solution was poured into crushed ice (500 g) and stirred at room temperature for about 1 hour. The generated precipitate was vacuum filtered and washed with deionized water, and dried in a vacuum oven. Finally, a dark red solid was obtained. This compound can be used for next step without further purification.

Synthesis of compound TPE

Compound **b** (2 g, 2.83 mmol) was dissolved in propionic acid (30 mL), then 2-ethylhexylamine (1.5 mL, 9.16 mmol) was injected into the solution. The mixture was refluxed at 130 ℃ under argon for 12 h. After cooling to room temperature, the solution was suspended in water (500 mL), and the precipitation was filtered and washed several times with water. The residue as obtained was purified by column chromatography on silica gel column with petroleum ether/ethyl acetate (v/v, 20:1) to yield compound **TPE** as a red solid. ^{1}H NMR ($CDCl_3$ /Me_4Si, 600 MHz; **Fig. S10**): δ (ppm), 8.83 (4H, s, perylene), 4.11-4.19 (4H, m, -CH_2-), 1.93-1.95 (2H, t, -CH-).

Synthesis of compound 4Br-PDA

Compound **b** (0.5 g, 0.71 mmol), 12-aminododecanoic acid (0.34g, 1.54 mmol) and 10 mL N-methyl-2-pyrrolidone were added to a flask, the mixture was stirred at room temperature for 30 minutes, and then stirred vigorously at 60-65°C for another 60 minutes. After that, 5 mL xylene was added to the mixture. After 3 h the mixture cooled down to room temperature and filtered. The dark red solid was washed thoroughly with methanol, acetic acid, methanol and diethyl ether. The collected solid was purified by column chromatography on silica gel column with dichloromethane/ acetic acid (v/v, 200:1) to yield compound 4Br-PDA as a red solid. ^{1}H NMR ($CDCl_3$ /Me_4Si, 600 MHz; **Fig. S11**): δ (ppm), 8.83 (4H, s, perylene), 4.22-4.24 (4H, t, -CH_2-), 2.30-2.32 (4H, t, -CH_2-), 1.73-1.76 (4H, m, -CH_2-), 1.57-1.61 (4H, m, -CH_2-).

Synthesis of compound 4Cl-PDA

Compared with the synthesis method of 4Br-PDA, the only difference is that the compound **b** is replaced by 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride. ^{1}H NMR ($CDCl_3$ /Me_4Si, 600 MHz; **Fig. S12**): δ (ppm), 8.69 (4H, s, perylene), 4.24-4.26 (4H, m, -CH_2-), 2.28-2.31 (4H, t, -CH_2-), 1.74-1.77 (4H, m, -CH_2-), 1.57-1.59 (4H, m, -CH_2-).

9. ^{1}H NMR spectra

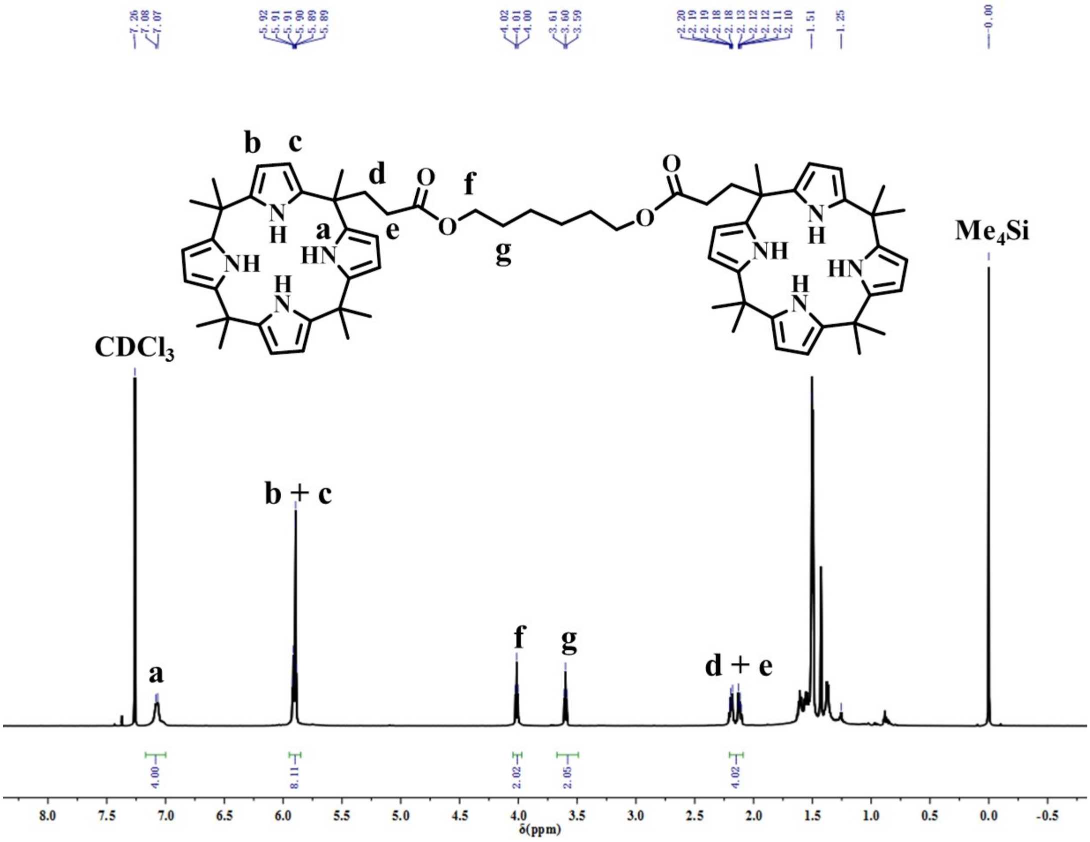


Fig. S9 ^{1}H NMR spectrum of **D-CP**.

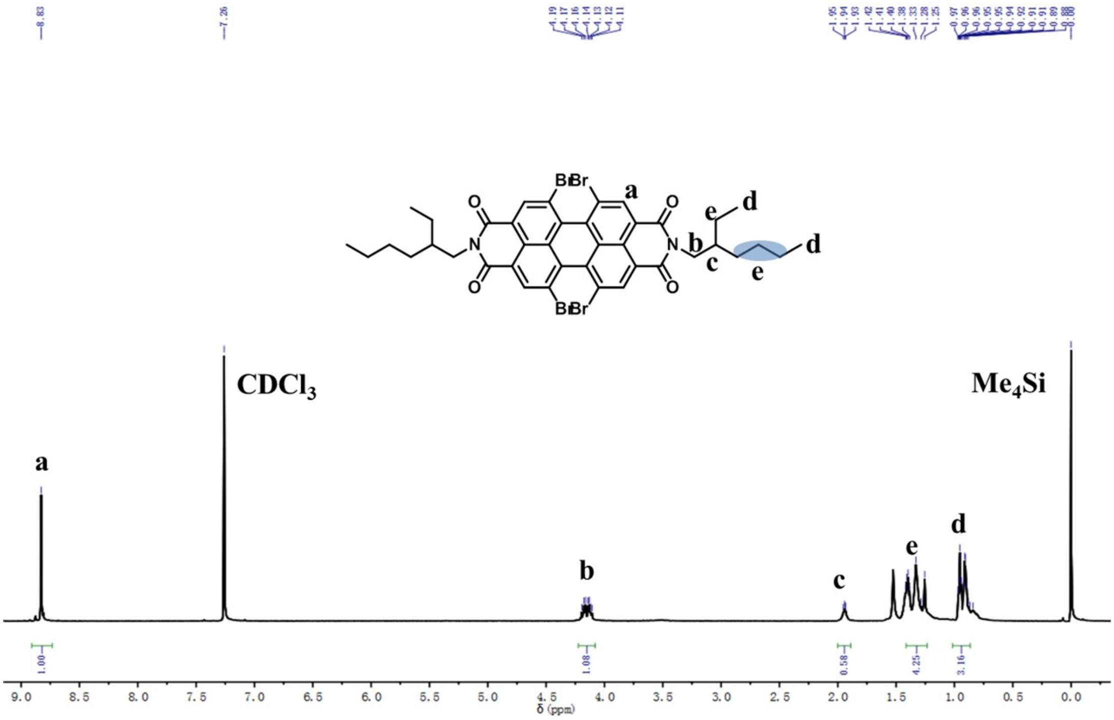


Fig. S10 ^{1}H NMR spectrum of compound **TPE**.

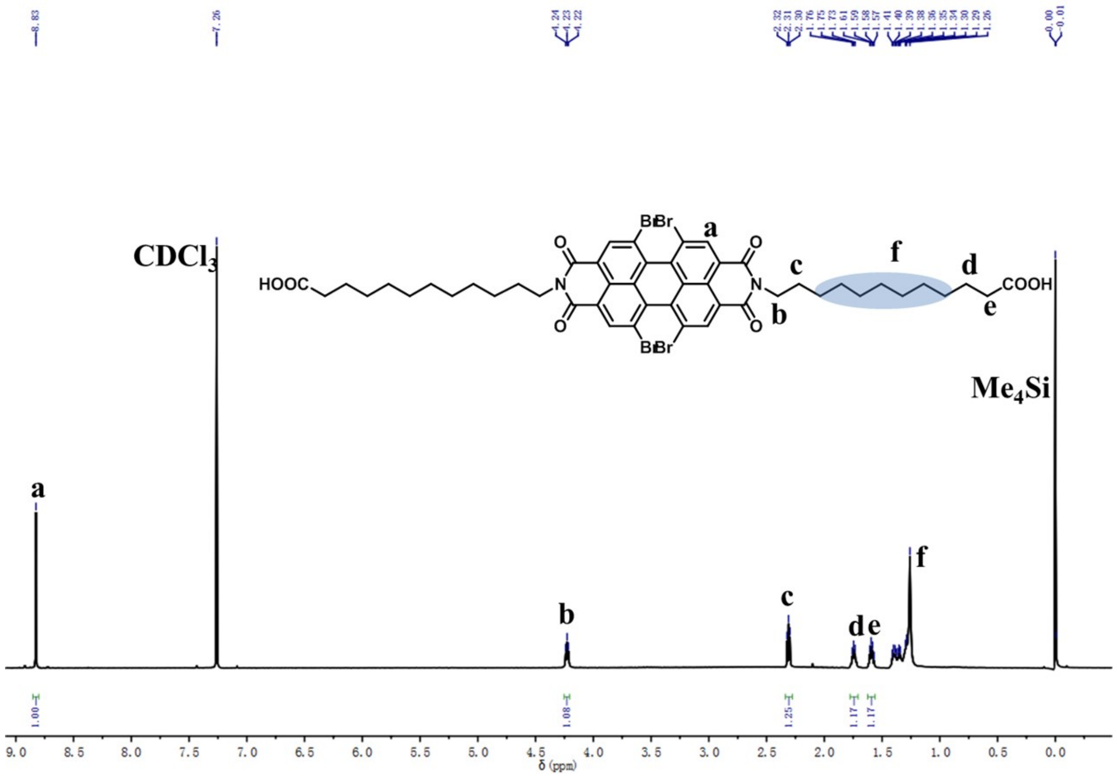


Fig. S11 ^{1}H NMR spectrum of compound 4Br-PDA.

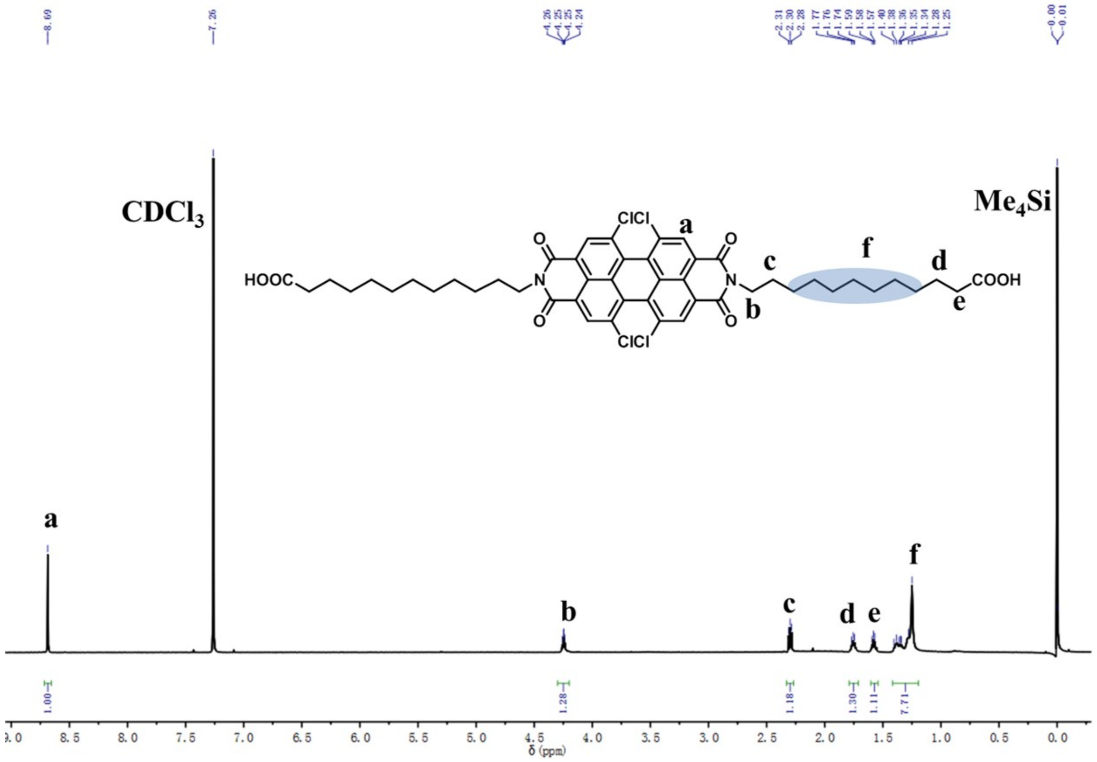


Fig. S12 ^{1}H NMR spectrum of compound 4Cl-PDA.

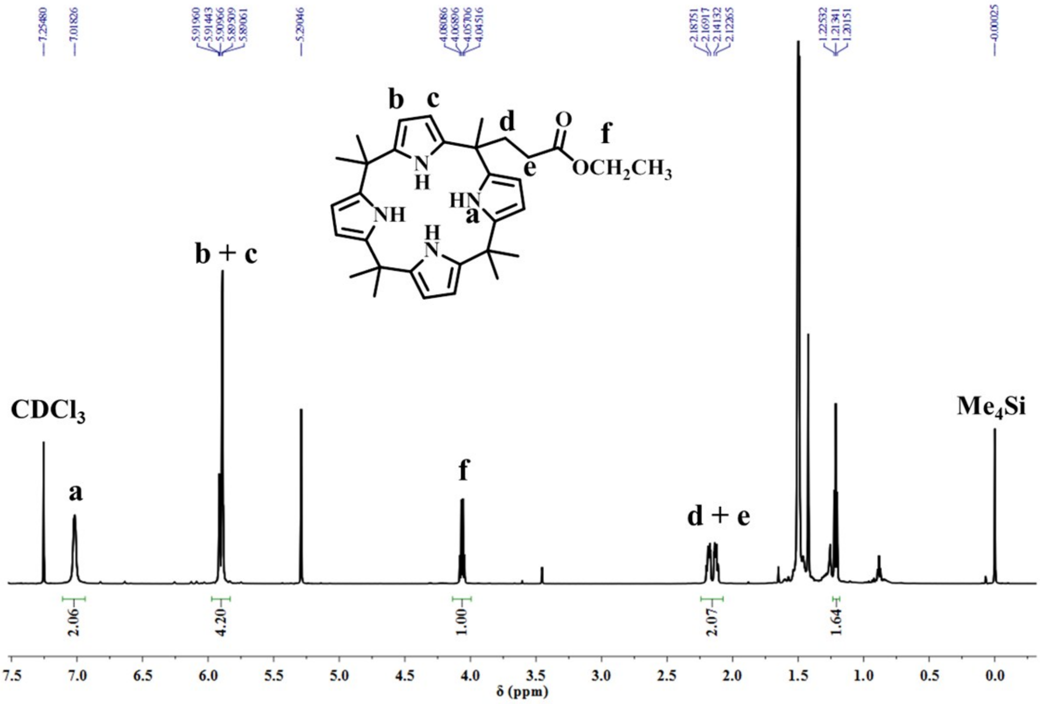


Fig. S13 ^{1}H NMR spectrum of compound **a**.

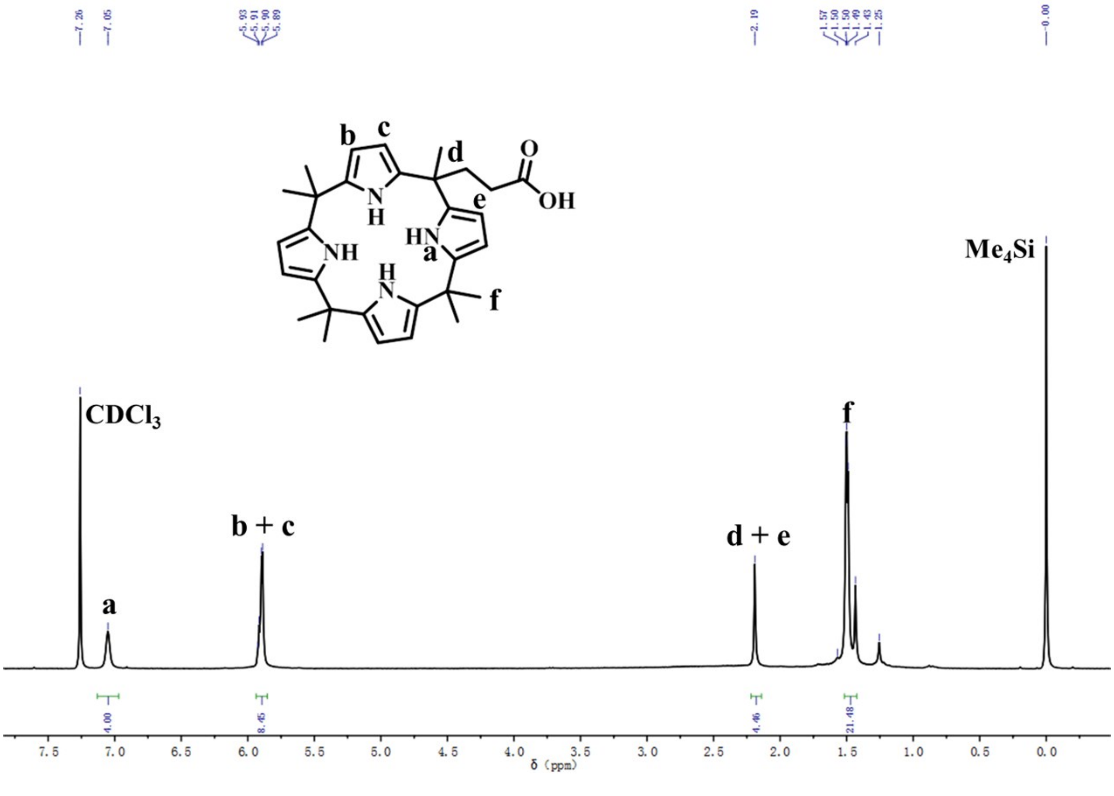


Fig. S14 ^{1}H NMR spectrum of compound **a-1**.

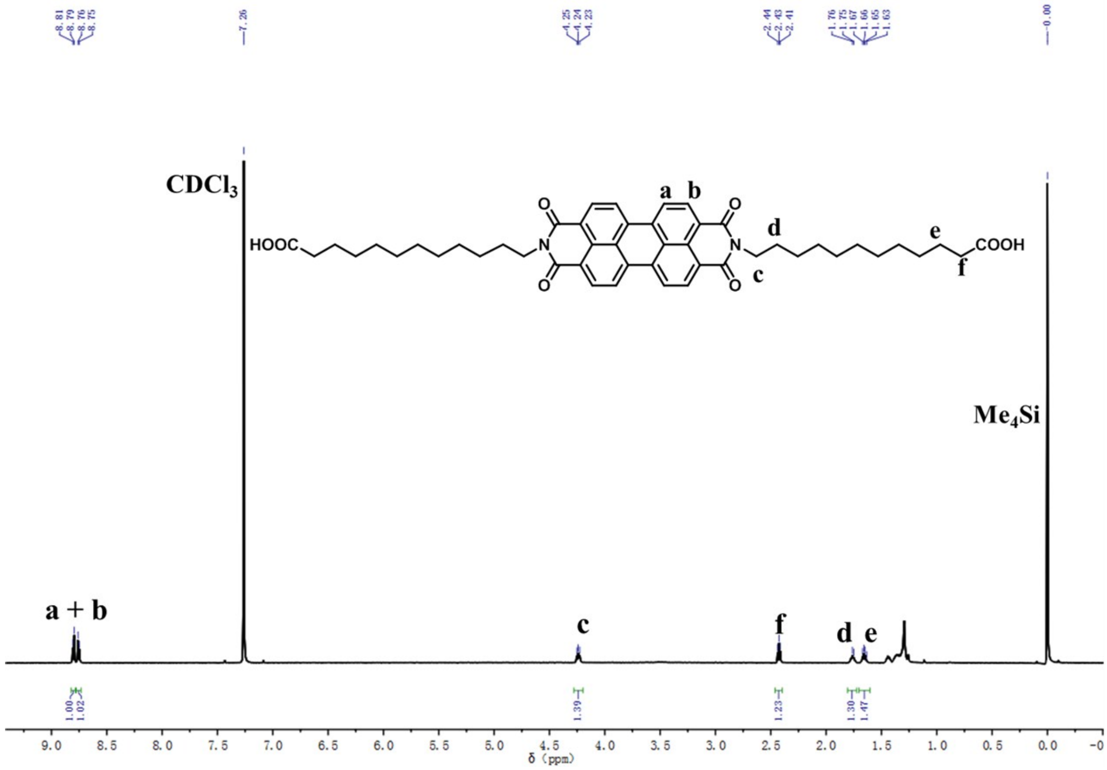


Fig. S15 ^{1}H NMR spectrum of compound PDA.

References

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