

Supporting information:

Highly Uniform Supramolecular Nano-Film Derived From Carbazole-containing Perylene Diimide Via Surface-supported Self-assembly and its Electrical Bistable Memory Behavior

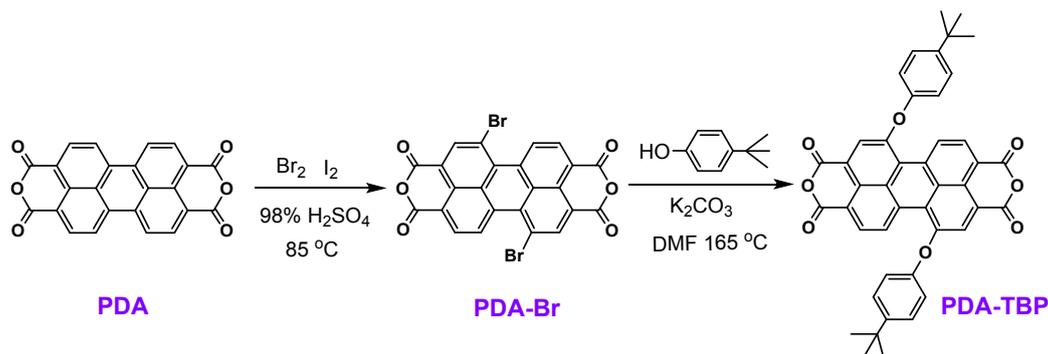
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1 Compound Synthesis.

1.1 Synthesis of PDA-TBP



Scheme S1. Synthetic route of PDA-TBP.

Synthesis of 1, 7-Dibromoperylene-3,4:9,10-tetracarboxylic dianhydride (PDA-Br)

In a 250 mL three necked flask, (7.272 g, 18.5 mmol) PDA was added to 113 mL 98% H₂SO₄. Then the mixture was stirred at 55 °C for 16 h. Iodine (0.519 g, 2 mmol) was added to the reaction mixture at 85 °C. Bromine (2.1 mL, 41mmol) was added dropwise into the reaction flask over 1 h and stirred for 27 h at 85 °C. The mixture was then poured very cautiously into 50 mL water, and washed by 70 mL 80% H₂SO₄, and then washed by water until the pH revealed 7. The mixture was drying on by acetone. Then, the solvent in the remaining mixture solution was removed to obtain a crimson solid.

FTIR (cm⁻¹): (C-H phenyl) 3058; (C=O anhydride) 1773, 1727; (C=C phenyl) 1592, 1501, and (C-Br) 804.

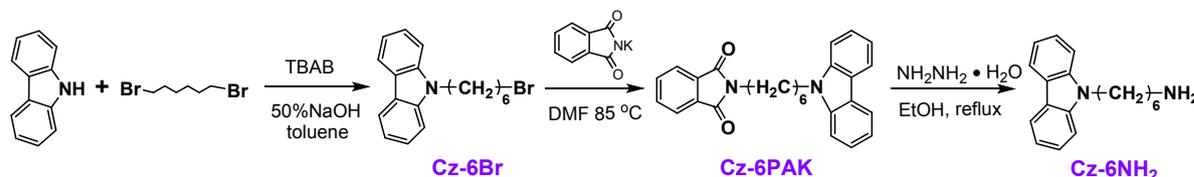
Synthesis of 1,7-(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic dianhydride (PDA-TBP)

A solution of PDA-Br (1.012g, 1.82mmol), 4-tert-butylphenol (0.915 g, 6mmol), and K₂CO₃(1.015 g, 7.24mmol) in 40 ml DMF were brought to reflux for 7 h under nitrogen atmosphere with stirring. The reaction mixture was then poured into 60 mL 25% cold acetic acid. The mixture was filtered, washed by water until the pH reaches 7. The residue was purified by column chromatography with dichloromethane as

eluent to afford PDA-TBP, and then dried in vacuum environment.

FTIR (cm⁻¹): (C-H phenyl) 3058; (C-H aliphatic) 2962; (C=O anhydride) 1767, 1737; (C=C phenyl) 1595, 1506.

1.2 Synthesis of Cz-6NH₂



Scheme S2. Synthetic route of Cz-6NH₂.

Synthesis of 1-bromo-6-carbazol-9-ylhexane (Cz-6Br)

In a 100 ml round bottom flask, carbazole (3.01 g, 18 mmol), 1,6-dibromohexane (10 mL), cetyl trimethyl ammonium bromide (CTAB, 0.4g, 1.098 mmol), 15mL toluene and 50% sodium hydroxide (14.8 mL) were added. The reaction mixture was stirred at room temperature for 5 days. The mixture was poured into water. The solution was extracted by 50 ml dichloromethane. The organic layer was washed with water and brine, and dried on anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography using Petroleum Ether/ CH₂Cl₂ (4:1) as the eluent to obtain a white solid.

FTIR (cm⁻¹): (C-H aliphatic) 2927, 2855; (C=C phenyl) 1593, 1458; (C-N-C) 755,727; (C-Br) 638. ¹H NMR (CDCl₃, 400 MHz), δ(ppm): 8.10 (d, 2H, J=7.7Hz), 7.49~7.39 (m, 4H), 7.23 (t, 2H, J =7.4 Hz), 4.32 (t, 2H, J=7.1Hz), 3.36 (t, 2H, J=6.7Hz), 1.94~1.87 (m, 2H), 1.85~1.78 (m, 2H), 1.51~1.34 (m, 4H). see **Figure S1**.

Synthesis of N-(6-carbazol-9-ylhexyl) phthalimide (Cz-6PAK)

A mixture of 3a (7.9 g, 24 mmol) and potassium phthalimide (8.86 g, 47.9 mmol) in DMF (150 mL) was stirred for 14h at 85 °C, then poured into saturated aqueous NH₄Cl and extracted with ethyl acetate. The organic layer was washed with water and brine followed by drying on anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by column

chromatography with chloroform/petroleum ether (5:1) as eluent to afford as a white solid.

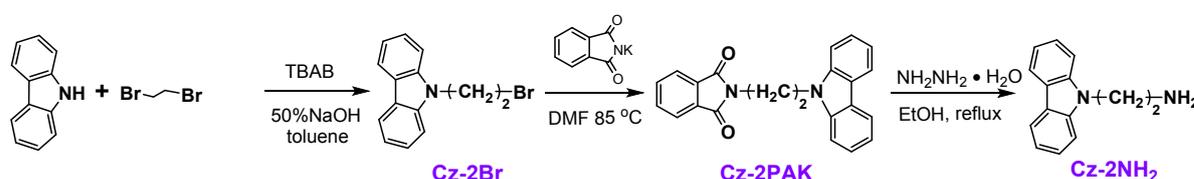
FTIR (cm⁻¹): (C-H aliphatic) 2933, 2861; (C=O imide) 1767, 1715; (C=C phenyl) 1598, 1487; (C-N-C) 722. ¹H NMR (CDCl₃, 400 MHz), δ(ppm): 8.08(d, 2H, J=7.7Hz), 7.84~7.81(m, 2H), 7.71~7.68(m, 2H), 7.47~7.37(m, 4H), 7.21(t, 2H, J=7.4Hz), 4.30(t, 2H, J=7.2Hz), 3.66(t, 2H, J=7.2Hz), 1.92~1.83(m, 2H), 1.69~1.61(m, 2H), 1.46~1.35(m, 4H). see **Figure S2**.

Synthesis of 6-carbazol-9-ylhexylamine (Cz-6NH₂)

To a solution of 4a (7.9g, 19.95 mmol) in ethanol (200 mL), hydrazine monohydrate (6 mL) was added. The reaction mixture was stirred for 2 h under reflux followed by the removal of the solvent under reduced pressure. The residue was dissolved in chloroform and 10% aqueous NaOH. The solution was extracted with chloroform. The organic layer was dried on anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure to afford as a yellowish solid.

FTIR (cm⁻¹): (N-H stretch) 3431; (C-H aliphatic) 2925, 2854; (N-H bend) 1627; (C=C phenyl) 1594, 1484; (C-N-C) 751, 724. ¹H NMR (CDCl₃, 400 MHz), δ(ppm): 8.09 (d, 2H, J=7.7Hz), 7.48~7.38 (m, 4H), 7.22 (t, 2H, J=7.4Hz), 4.30 (t, 2H, J=7.2Hz), 2.64(t, 2H, J=6.5Hz), 1.88(t, 2H, J=6.9Hz), 1.43~1.37(m, 8H). see **Figure S3**.

1.3 Synthesis of Cz-2NH₂



Scheme S3. Synthetic route of Cz-2NH₂.

The Cz-2NH₂ is synthesized following an exactly same procedure as described above for Cz-6NH₂ just by replacing the 1,6-dibromohexane with 1,2-dibromoethane. The synthetic protocol is illustrated in **Scheme S3**.

For 1-bromo-2-carbazol-9-ylhexane (Cz-2Br).

FTIR (cm⁻¹): (C-H aliphatic) 2912; (C=C phenyl) 1595, 1456; (C-N-C) 747,720; C-Br

526. ^1H NMR (CDCl_3 , 400 MHz), $\delta(\text{ppm})$: 8.12 (d, 2H, $J=7.8\text{Hz}$), 7.53~7.49 (m, 2H), 7.46 (d, 2H, $J=8.1\text{ Hz}$), 7.31~7.28 (m, 2H), 4.74 (t, 2H, $J=7.6\text{Hz}$), 3.71 (t, 2H, $J=7.6\text{Hz}$). see **Figure S4**.

For N-(2-carbazol-9-ylhexyl) phthalimide (Cz-2PAK).

FTIR (cm^{-1}): (C-H aliphatic) 2944; (C=O imide) 1771, 1715; (C=C phenyl) 1594, 1483; (C-N-C) 722,716. ^1H NMR (CDCl_3 , 400 MHz), $\delta(\text{ppm})$: 8.07(d, 2H, $J=7.7\text{Hz}$),7.82~7.79(m, 2H), 7.71~7.69(m, 2H), 7.52(d, 2H, $J=8.2\text{Hz}$), 7.43(t, 2H, $J=7.6\text{Hz}$), 7.22(t, 2H, $J=7.4\text{Hz}$), 4.59(t, 2H, $J=7.3\text{Hz}$), 4.12(t, 2H, $J=7.3\text{Hz}$). see **Figure S5**.

For 2-carbazol-9-ylhexylamine (Cz-2NH₂).

FTIR (cm^{-1}): (N-H stretch) 3348; (C-H aliphatic) 2926, 2863; (N-H bend) 1624; (C=C phenyl) 1594, 1485; (C-N-C) 751, 722. ^1H NMR (CDCl_3 , 400 MHz), $\delta(\text{ppm})$: 8.11 (d, 2H, $J=7.7\text{Hz}$), 7.47 (d, 4H, $J=3.87\text{Hz}$), 7.26~ 7.23(m, 2H), 4.41 (t, 2H, $J=6.18\text{Hz}$), 3.23(t, 2H, $J=6.18\text{Hz}$), 1.15(s, 2H). see **Figure S6**.

2 Instruments and measurements.

Fourier transform infrared (FT-IR) spectra were recorded under ambient conditions on a Bruker Tensor 27 infrared spectrophotometer. KBr was used as a nonabsorbent medium. Proton nuclear magnetic resonance (^1H NMR, 400/600 MHz) spectra were recorded on a Bruker AV400/600 spectrometer using CDCl_3 . Ultraviolet-visible (UV/vis) absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence emission spectra were measured using HITACHI F-4500 fluorescence spectrometer. Surface morphologies were recorded on a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM). The TEM studies were performed using a TECHNAI G2 20 S-TWIN microscope operating at an accelerating voltage of 120 kV. X-ray diffraction (XRD) measurements were carried out on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with

graphite monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The atomic force microscopy (AFM) images were obtained using a Digital Instrument Dimension Icon operating in ScanAsyst mode. Cyclic voltammetry (CV) measurement was performed on a CHI660D Electrochemical Workstation (Shanghai Chenhua Instruments Inc., China) using a three-electrode cell under a nitrogen environment. The perylene diimide film on ITO electrode (working electrode) were scanned anodically and cathodically (scan rate: 100 mV s^{-1}) in a solution of tetrabutylammonium tetrafluoroborate ($n\text{-Bu}_4\text{BF}_4$) in dry acetonitrile (0.1 M) with Ag/AgCl and a platinum net as the reference electrode and auxiliary electrode, respectively. Ferrocene was used as the external reference for calibration (0.38 V vs. Ag/AgCl). The current-voltage (I-V) characteristics of the sandwich devices were recorded using a Keithley 4200 SCS semiconductor parameter analyzer equipped with a Micromanipulator PW-600 probe station (Advanced Technology Co. Ltd, Hong Kong) in a clean and metallic shielding box in an ambient environment at room temperature.

3 Molecular simulation.

All calculations were carried out with the density functional theory (DFT) method at the B3LYP/6-31G (d) level. All of the calculations were performed using Gaussian 09 program on the cloud computing platform of Beijing University of Chemical Technology (CHEMCLOUDCOMPUTING@BUCT).

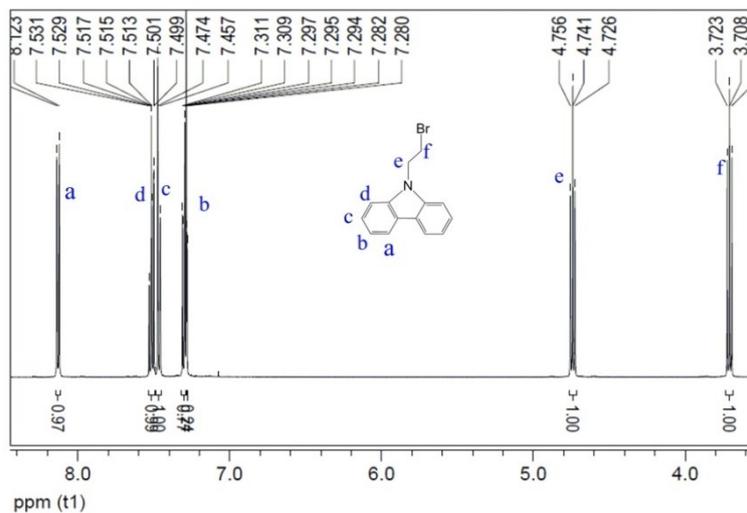


Fig. S4. ¹H NMR spectrum of 1-bromo-2-carbazol-9-ylethane (Cz-2Br) in CDCl₃.

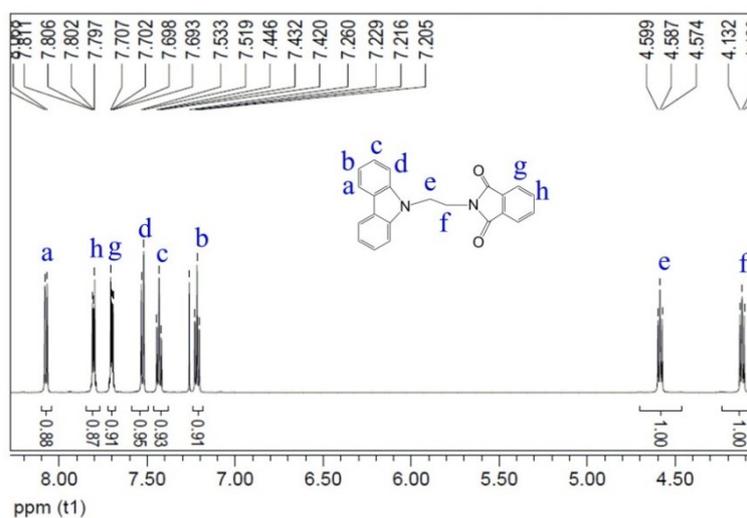


Fig. S5. ¹H NMR spectrum of N-(2-carbazol-9-ylethyl) phthalimide (Cz-2PAK) in CDCl₃.

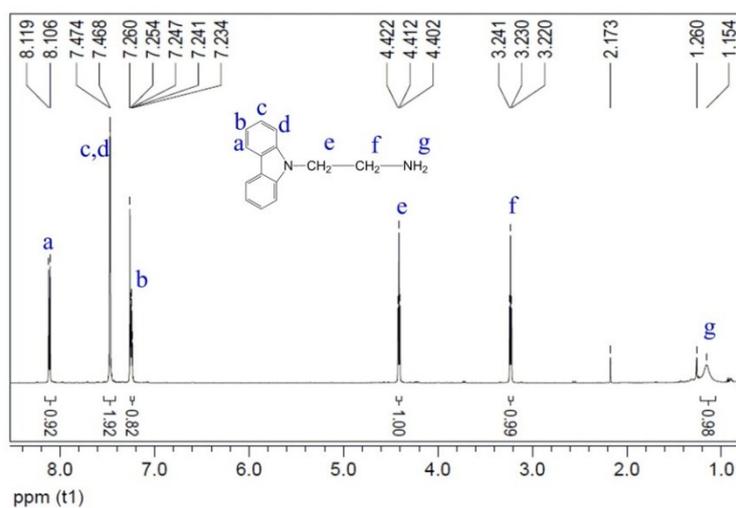


Fig. S6. ¹H NMR spectrum of 2-carbazol-9-ylethylamine (Cz-2NH₂) in CDCl₃.

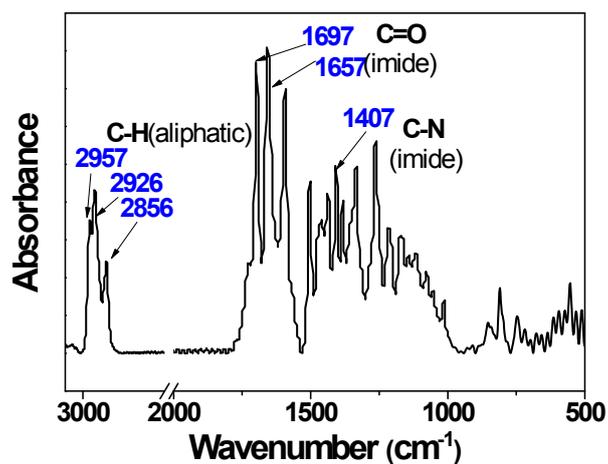


Fig. S7. The FT-IR spectrum of N, N'-(6-carbazole hexyl) - 1, 7-di(4-tert-butylphenoxy) perylene - 3,4;9,10- tetra-carboxylic diimide (PDI-6Cz)

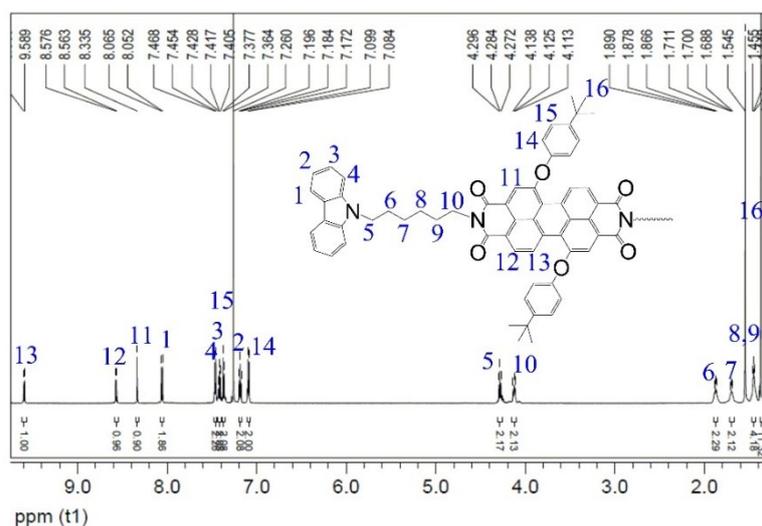


Fig. S8. ^1H NMR spectrum of N, N'-(6-carbazole hexyl) - 1, 7-di(4-tert-butylphenoxy) perylene - 3,4;9,10- tetra-carboxylic diimide (PDI-6Cz) in CDCl_3 .

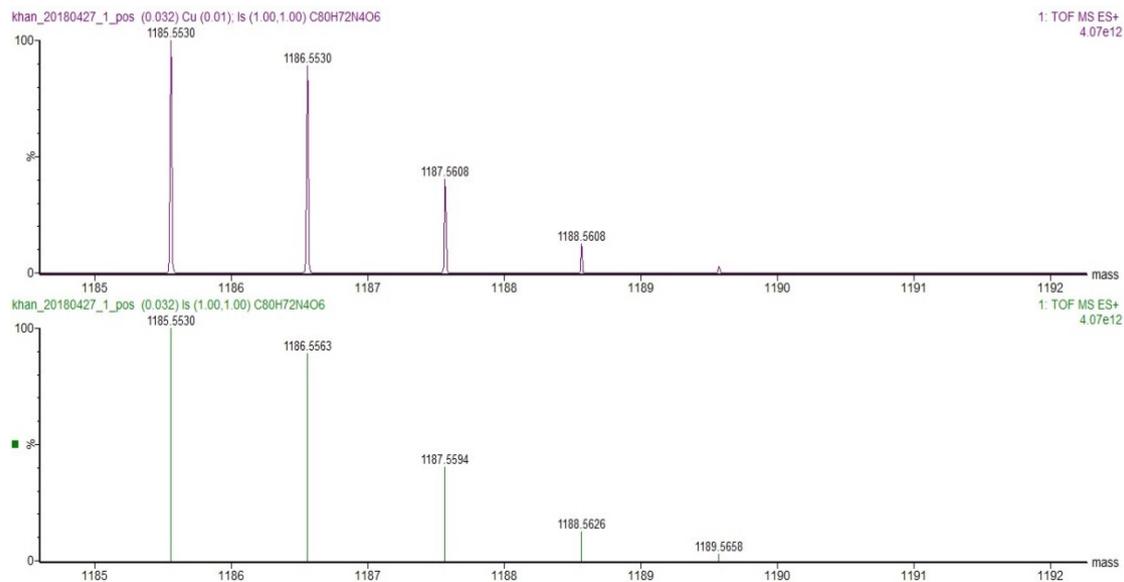


Fig. S9. $[M]^+$ Ionization Peaks of PDI-6Cz

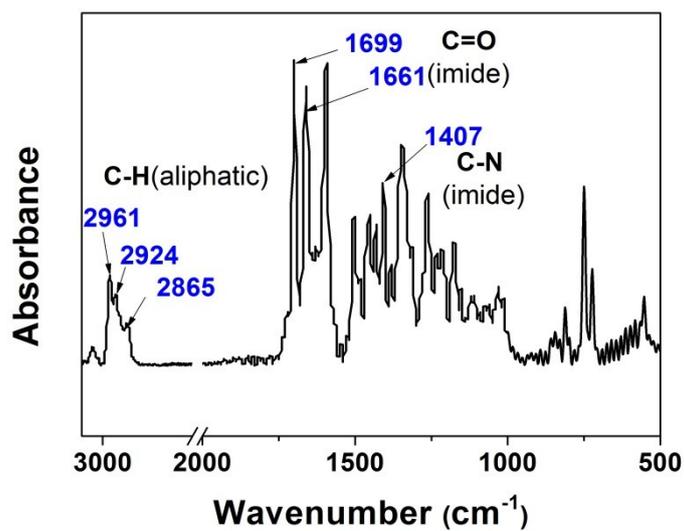


Fig. S10 The FI-IR spectrum of N, N'-(2-carbazole ethyl)-1, 7-(4-tert-butylphenoxy) perylene-3, 4:9, 10- dicarboximide derivative

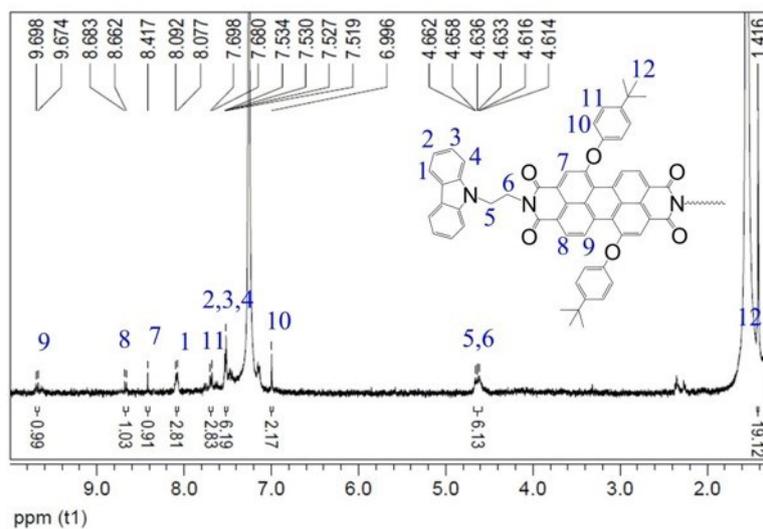


Fig. S11. ^1H NMR spectrum of N, N'-(2-carbazole ethyl)-1,7-(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic diimide (PDI-2Cz) in CDCl_3 .

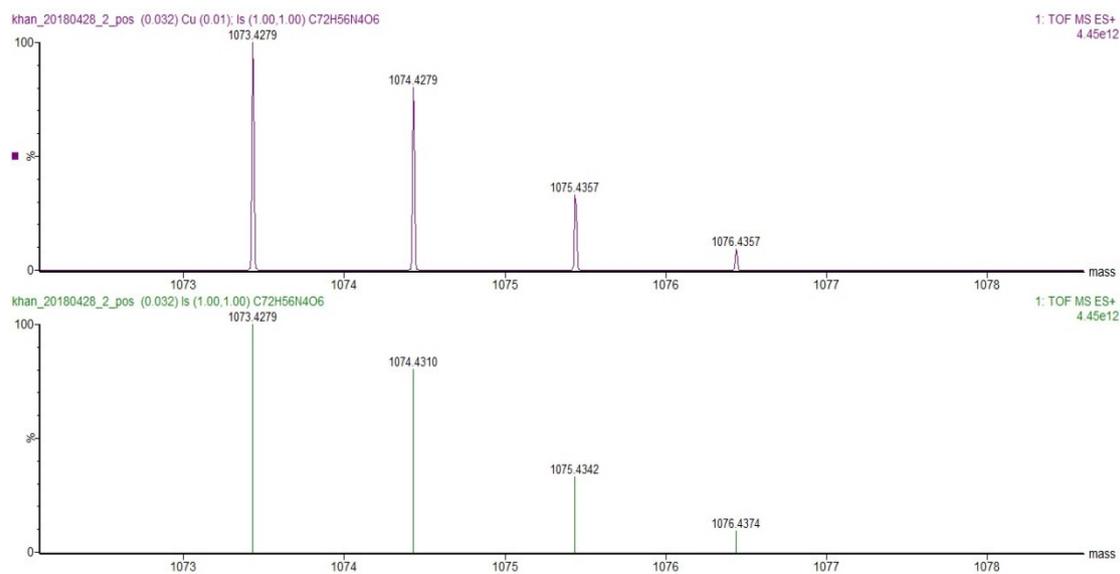


Fig. S12. $[\text{M}]^+$ Ionization Peaks of PDI-6Cz

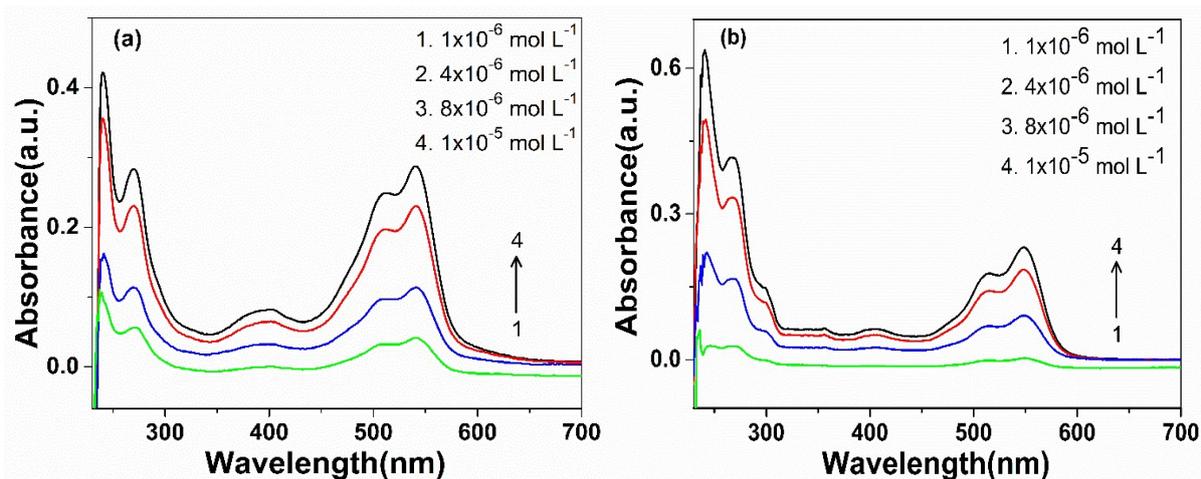


Fig. S13. UV-Vis absorption spectra of (a) PDA-TBP and (b) PDI-6Cz measured in chloroform with different concentrations

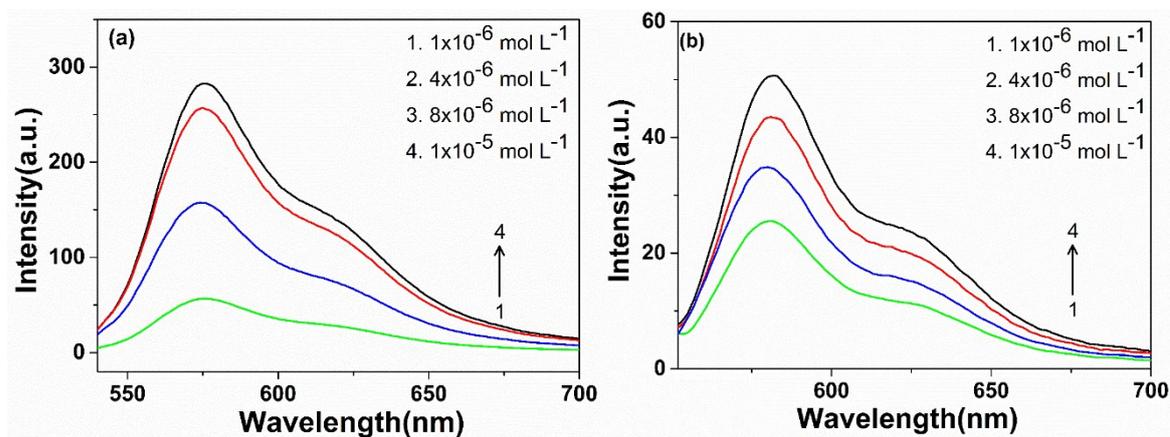


Fig. S14. (a) Fluorescence spectra of PDA-TBP and (b) fluorescence spectra of PDI-6Cz measured in chloroform with different concentrations.

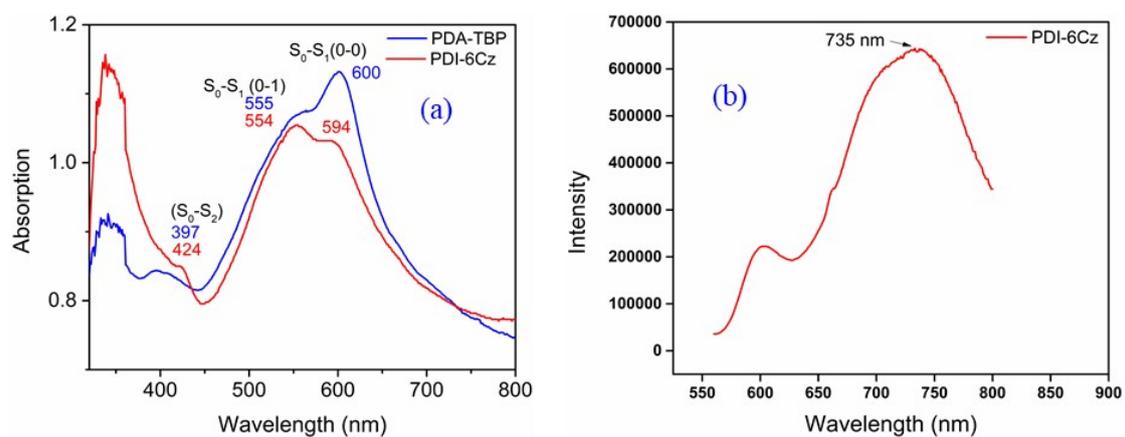


Fig. S15. (a) UV-Vis absorption spectra of PDA-TBP and PDI-6Cz thin film coated on the ITO glass and (b) fluorescence spectra of PDI-6Cz thin film on the quartz glass.