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**Supporting Information for** 

# An Electron-Deficient Nanosized Polycyclic Aromatic Hydrocarbon with Enhanced Anion-π Interactions

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#### 1. Materials and measurements

2, 6-diisopropylaniline (97%), propionic acid, dimethyl sulfoxide (DMSO), cuprous iodide (98%), L-proline (98%) and graphite felt were obtained from the commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. PDI **1**, as well as the intermediates benzo[ghi]perylene-1, 2, 4, 5, 10, 11-hexacarboxylic trianhydride (BPTA) and 7, 8-dichlorobenzo[ghi]perylenetriimide were prepared according to the previous literatures. <sup>[S1]</sup>

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 and 500 spectrometer, with working frequencies of 400 and 500 MHz. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. <sup>1</sup>H coupling constants *J* are given in Hertz (Hz). High-resolution mass spectra (HRMS) were acquired on the Thermo Scientific Exactive Plus Mass spectrometer equipped with electrospray ionization (ESI) source. The UV/Vis/NIR spectra were recorded on a Perkins Elmer Lambda 900 spectrometer equipped with a PTP-1 Peltier temperature controller and steady-state emission spectra were acquired using Edinburgh Instruments, FLS920 spectrometer. Fourier Transform Infrared Spectrometer (FT-IR) was investigated by Thermo Scientific Nicolet iS50. Diffusion NMR experiments were carried out on a Bruker Avance III 500 MHz instrument using a BBO Probe with z-gradient. <sup>1</sup>H-DOSY Spectra were recorded using the bipolar pulse pairs stimulated echo pulse sequence with LED (Longitudinal-Eddy-current Delay) in a 5-mm NMR tube at 30°C with 60 ms diffusion delay, 24 linear increments for gradient levels and 8 transients. Sample concentrations of 1 mM were used. The cyclic voltammetry (CV) experiments were carried out at room temperature in argon purged solutions of CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> was freshly distilled prior to use) and recorded on an electrochemical workstation (CHI 660D, CH Instruments, China). All CVs experiments were performed using a glassy carbon disk as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. The concentration of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), were 0.5 mM and 0.1 M, respectively.

#### 2. Syntheses and characterizations



Scheme S1 Synthesis of PAHs 2 and 3

Synthesis of 2: A mixture of benzo[ghi]perylene-1, 2, 4, 5, 10, 11-hexacarboxylic trianhydride (BPTA) (1.0 g, 2.1 mmol), 2,6-diisopropylaniline (4.0 ml, 21 mmol), and propionic acid (110 ml) were degassed by three vacuum/argon cycles and heated at 130 °C for 24 h under an argon atmosphere. After being cooled to room temperature, the reaction mixture was poured into a 1000 ml of water and washed with saturated sodium bicarbonate solution to removed residual propionic acid and then washed with water until pH-neutral. The crude product was purified by column chromatography (SiO<sub>2</sub>, dichloromethane / petroleum ether, 2:1) and removal of the solvent with rotary evaporator, 1.7 g (0.12 mmol, 86 % yield) of an orange solid product were obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.67 (s), 9.63 (d, *J* = 8.4 Hz, 2H), 9.35 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.47 – 7.32 (m, 4H), 3.02 – 2.76 (m, 6H), 1.31 – 1.17 (m, 36H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.10, 163.70, 163.20, 147.47, 145.67, 134.06, 131.12, 131.04, 130.62, 130.39, 129.91, 128.83, 128.38, 127.73, 126.46, 125.52, 125.42, 124.57, 124.25, 124.21, 124.08, 123.10, 29.66, 29.38, 24.23, 24.12, 24.10. ESI-MS M/z calculated for [C<sub>64</sub>H<sub>57</sub>N<sub>3</sub>O<sub>6</sub> – H<sup>+</sup>] · 963.4247, [M]<sup>-</sup> found 963.4266.

**Synthesis of 3:** A mixture of the intermediate 7, 8-dichlorobenzo[ghi]perylenetriimide (400 mg, 0.38 mmol), CuI (440 mg, 2.3 mmol), L-proline (320 mg, 2.8 mmol), K<sub>2</sub>CO<sub>3</sub> (540 mg, 1.9 mmol) in 25 mL DMSO were degassed by three vacuum/argon cycles and heated at 75 °C for 10 h under an argon atmosphere. The solution was cooled down and quenched with 2 M HCl (250 mL), and extracted with ethylacetate. The organic layers were separated, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>. After column chromatography (SiO<sub>2</sub>, dichloromethane / petroleum ether, 1:4) and removal of the solvent by rotary evaporator, 85 mg (0.045 mmol, 23.7 % yield) of a crimson solid product were obtained. <sup>1</sup>H NMR (500 MHz, 1,2-

dichlorobenzene-*d*<sub>4</sub>, 273 K) δ 11.92 (s, 2H), 11.71 (s, 2H), 11.47 (s, 2H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.69 – 7.62 (m, 4H), 7.62 – 7.54 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.45 (s, 4H), 4.22 (s, 2H), 3.55 (dd, J = 13.1, 6.4 Hz, 4H), 3.31 (m, 4H), 3.02 (s, 2H), 2.04 – 1.15 (m, 72H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.29, 164.31, 163.58, 163.39, 147.61, 139.28, 136.73, 132.36, 130.79, 130.71, 130.65, 129.94, 129.85, 129.07, 128.99, 128.53, 127.91, 127.56, 127.32, 127.31, 126.50, 126.10, 125.62, 125.25, 124.92, 124.77, 124.50, 124.34, 124.18, 123.16, 121.77, 121.31, 120.73, 119.72, 114.08, 33.83, 31.94, 30.17, 29.79, 29.71, 29.67, 29.64, 29.53, 29.37, 29.17, 28.97, 24.60, 24.36, 24.15, 24.03, 22.70, 14.12. ESI-MS M/z calculated for [C<sub>128</sub>H<sub>108</sub>N<sub>6</sub>O<sub>12</sub> – H<sup>+</sup>]<sup>-</sup> 1921.8058, [M]<sup>-</sup> found 1921.8104.

### 3. NMR and HRMS spectra



Figure S1. <sup>1</sup>H NMR spectrum of 2 and the assignment of its protons (400 MHz, CDCl<sub>3</sub>, 298K)



Figure S2. <sup>13</sup>C NMR spectrum of 2 (100 MHz, CDCl<sub>3</sub>, 298K)



Figure S3. <sup>1</sup>H NMR spectrum of 3 (500 MHz, 1,2-dichlorobenzene-d4, 273K, ppm).



Figure S4. <sup>13</sup>C NMR spectrum of 3 (100 MHz, CDCl<sub>3</sub>, 298K)



*Figure S5.* 2D <sup>1</sup>H DOSY NMR spectrum of **1** (black), **2** (red) and **3** (blue) (500 MHz, 1,2-dichlorobenzene-*d*4, 298 K). (Diffusion coefficients of **3**, **2** and **1** are  $1.49*10^{-10}$  m<sup>-2</sup>/s,  $1.99*10^{-10}$  m<sup>-2</sup>/s, and  $2.32*10^{-10}$  m<sup>-2</sup>/s, respectively.)



*Figure S6.* 2D <sup>1</sup>H–<sup>1</sup>H NOESY (correlation NMR spectroscopy) NMR spectrum of **3** (500 MHz, 1,2-dichlorobenzene-*d*4, 273 K)



*Figure S7.* ESI mass spectrum of **2** in  $CH_2Cl_2$  in negative mode; Inset: Zoomed spectrum of the [M]<sup>-</sup> base peak (up) and the simulated spectrum (down) **2**.



*Figure S8.* ESI mass spectrum of **3** in  $CH_2Cl_2$  in negative mode; Inset: Zoomed spectrum of the [M]<sup>-</sup> base peak (up) and the simulated spectrum (down) **3**.

#### 4. X-ray diffraction analyses

Single crystals of **2** and **3** (co-crystals of nanographene **3** with naphthalene) suitable for X-ray diffraction analyses were obtained by dissolving each of them in a solvent mixture (dichloromethane/ethanol = 90:10 by volume), followed by slow evaporation of the solvents within several days.

Suitable single crystals of **2** and **3** (co-crystals of nanographene **3** with naphthalene) were mounted on glass fiber for the X-ray measurement. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD area-detector system. The measurement was made by using graphic monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 153 K under a cold nitrogen stream. The frame data were integrated and absorption correction using a Rigaku CrystalClear program package. All calculations were performed with the SHELXTL-97 program package <sup>[S2]</sup>, and structures were solved by direct methods and refined by full-matrix least-squares against F2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. Crystals of 1 and 2 had voids with badly disordered solvents and the crystallographic refinement for them was completed with the solvent contribution subtracted from the data using SQUEEZE in PLATON package of crystallographic software. <sup>[S3]</sup> Crystall ographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication number CCDC 1568405 and 1568403 for **2** and **3**, respectively, which can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/

Crystals data for **2**: moiety formula  $C_{64}H_5N_3O_6$ ,  $CH_2Cl_2$ , sum formula  $C_{65}H_{59}Cl_2N_3O_6$ , formula weight 1049.05, T = 293.15 K, wavelength 0.71073 Å, crystal system: monoclinic, space group P 21/c, unit cell dimensions a = 22.793 (5) Å, b = 19.106 (4) Å, c = 14.475 (3) Å,  $\alpha = 90$ ,  $\beta = 107.05$  (3),  $\gamma = 90$ , V = 6027 (2) Å<sup>3</sup>, Z = 4,  $\rho cal = 1.156$  g / cm<sup>3</sup>, absorption coefficient, 0.159 mm<sup>-1</sup>, F(000) = 2208, crystal size  $0.20 \times 0.20 \times 0.20$  mm<sup>3</sup>, theta range for data collection 6.974 to 55.788 deg, index ranges -27<=h<=29; -18<=k<=24; -18<=l<=18, reflections collected 49214, independent reflections, 13799 [R(int) = 0.0840], GooF(F\_2) = 1.490, R<sub>1</sub> = 0.1842 wR<sub>2</sub> = 0.4773 for I > 2sigma (I), R<sub>1</sub> = 0.2530 wR<sub>2</sub> = 0.5113 for all data, data completeness 0.958 and largest diff. peak and hole, 0.41 and -0.48 e. Å<sup>-3</sup>.

Co-crystals data for **3** and naphthalene: moiety formula  $C_{128}H_{108}N_6O_{12}$ ,  $C_2H_6O_5$ ,  $C_{10}H_6$ ,  $C_2H_5O_5$ , sum formula  $C_{147}H_{128}N_6O_{14}$ , formula weight 2202.55, T = 173.15 K, wavelength 0.71073 Å, crystal system: triclinic, space group P-1, unit cell dimensions a = 18.348 (4) Å, b = 18.837 (4) Å, c = 21.554 (4) Å,  $\alpha = 97.90$  (3),  $\beta = 100.31$  (3),  $\gamma = 114.63$  (3), V = 6472 (3) Å<sup>3</sup>, Z = 2, pcal = 1.130 g / cm<sup>3</sup>, absorption coefficient, 0.072 mm<sup>-1</sup>, F(000) = 2328, crystal size 0.40 × 0.30 × 0.20 mm<sup>3</sup>, theta range for data collection 4.128 to 62.092 deg, index ranges -24<=h<=25; -22<=k<=26; -27<=l<=26, reflections collected 60077, independent reflections, 32045 [R(int) = 0.0424], GooF(F\_2) = 0.914, R\_1 = 0.0952 wR\_2 = 0.2466 for I > 2sigma (I), R\_1 = 0.1922 wR\_2 = 0.2833 for all data, data completeness 0.773 and largest diff. peak and hole, 0.67 and -0.50 e.



Figure S9. Molecular packing of 2 in the crystals



*Figure S10.* Molecular packing of **3** in the crystals

# 5. UV-Vis and fluorescence spectra



*Figure S11.* UV/Vis absorption (solid line) and emission spectra (dotted line) of **1** (a,  $\lambda_{ex} = 527$  nm) and **2** (b,  $\lambda_{ex} = 467$  nm) in DCM (c  $\approx 1 \times 10^{-5}$  M) at room temperature.



*Figure S12.* UV-Vis absorption spectral changes of **1** in DCM ( $10^{-5}$  M) with increasing amounts of TBAF (a), TBAOH (b); and UV-Vis absorption spectral changes of **1** and 100 folded TBAOAc (c) or LiTFSI (d) or TBAPF<sub>6</sub> (e) in DCM ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].



*Figure S13.* UV-Vis absorption spectral changes of **2** in DCM ( $10^{-5}$  M) with increasing amounts of TBAF (a), TBAOH (b); and UV-Vis absorption spectral changes of **2** and 100 folded TBAOAc (c) or LiTFSI (d) or TBAPF<sub>6</sub> (e) in DCM ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].



*Figure S14.* UV-Vis absorption spectral changes of **3** in DCM ( $10^{-5}$  M) with increasing amounts of TBAOH (a), TBAOH (b); and UV-Vis absorption spectral changes of **3** and 100 folded TBAOAc (c) or LiTFSI (d) or TBAPF<sub>6</sub> (e) in DCM ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].



*Figure S15.* UV-Vis absorption spectral changes of **1** in DOL/DME ( $10^{-5}$  M) with increasing amounts of TBAF (a), TBAOH (b); and UV-Vis absorption spectral changes of **1** and 100 folded TBAOAc (c) or LiTFSI (d) or TBAPF<sub>6</sub> (e) in DOL/DME ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].



*Figure S16.* UV-Vis absorption spectral changes of **2** in DOL/DME ( $10^{-5}$  M) with increasing amounts of TBAF (a), TBAOH (b); and UV-Vis absorption spectral changes of **2** and 100 folded TBAOAc (c) or LiTFSI (d) or TBAPF<sub>6</sub> (e) in DOL/DME ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].



*Figure S17.* UV-Vis absorption spectral changes of **3** in DOL/DME ( $10^{-5}$  M) with increasing amounts of TBAF (a), TBAOH (b) or TBAOAc (c); and spectral changes of **3** and 100 folded LiTFSI (d) or TBAPF<sub>6</sub> (e) in DOL/DME ( $10^{-5}$  M) without and with the UV lamp irradiation or with time; as well as spectral changes of **3** and 100 folded TBAPF<sub>6</sub> in EC/DMC ( $10^{-5}$  M) without and with the UV lamp irradiation or with time [7 days, d represents days in figures].

# 6. Dissolving photographs



Figure S18. Digital photos of the 0.03 M PAHs 1-3 dissolving in DOL/DME (1:1 in volume, a) with 1.0 M LiTFSI and their digital photos after

10 h

### 7. Theoretical calculations

Density functional theory (DFT) calculations of **1-3** were performed with the Gaussian 09 program package.<sup>[S4]</sup> The geometries of the molecule were first fully relaxed in gas phase at the B3LYP <sup>[S5]</sup> level starting from a planar configuration, then the most stable configuration were obtained at the B3LYP/6-31 G(d) level. The calculated HOMOs and LUMOs are shown in Figure S19.



*Figure S19*. The chemical structures of PAHs 1-3 and their calculated LUMO+1, LUMO, HOMO and HOMO-1 energies by the DFT calculations (for simplification, the methyl are used to replace substituents in both compounds)

# 8. FTIR spectra



Figure S20. FT-IR spectra of 1, 2 and 3.

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