

Supporting Information

Dodecatwistarene Imides with Zigzag-Twisted Conformation for Organic Electronics

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Materials and Methods:

^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on Bruker AVANCE 400 NMR Spectrometer and Bruker Ascend 500WB NMR Spectrometer. ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer, and High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Fluorescence emission spectra were recorded with a Jasco FP-660 Spectrofluorometer at room temperature. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) dissolved in CH_2Cl_2 was employed as the supporting electrolyte. CH_2Cl_2 was freshly distilled prior to use.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Starting materials **1** and **4** were synthesized according to a literature.^[1]

Synthesis and characterization

Compound 3:

A mixture of compound **1** (1 g for 1a and 1b, 1 equiv), compound **2** (1.4 g for 2a and 1.2 g for 2b, 1.2 equiv), $\text{Pd}(\text{PPh}_3)_4$ (150 mg for 3a and 132 mg for 3b, 0.1 equiv), CuI (50 mg for 3a and 43 mg for 3b, 0.2 equiv) in 70 ml dry toluene was stirred at 110 °C for 10 h under argon. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ CH_2Cl_2 , 1:1 to 1:5, v/v) to yield the dark violet solid product (1 g for 3a and 3b, 60%).

Compound 3a: ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 9.63 (s, 2H), 9.02 (s, 2H), 8.91 (s, 2H), 4.32-4.23 (m, 8H), 1.94-1.75 (m, 8H), 1.53-1.25 (m, 60H), 0.86 (t, 12H); ^{13}C NMR (100 MHz, CDCl_3 , 298K, ppm): δ = 163.2, 163.1, 162.5, 162.1, 135.7, 134.9, 134.4, 134.1, 132.7, 130.8, 127.6, 127.2, 126.8, 126.4, 126.3, 125.4, 123.7, 121.8, 120.7, 41.9, 41.1, 31.9, 31.8, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 29.1, 28.1, 27.2, 22.7, 22.6, 14.1. MS (MALDI-TOF): m/z (M^+) = 1283.0 (calcd for $\text{C}_{78}\text{H}_{90}\text{Cl}_2\text{N}_4\text{O}_8$: 1282.5).

Compound 3b: ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K, ppm): δ = 9.69 (s, 2H), 9.13 (s, 2H), 8.98 (s, 2H), 7.54-7.47 (m, 4H), 7.42-7.39 (t, 4H), 7.34 (d, 2H), 7.25 (d, 2H), 3.36-3.32 (m, 2H), 2.95-2.90 (m, 2H), 2.67-2.61 (m, 2H), 2.47-2.41 (m, 2H), 1.51-1.47 (m, 8H), 1.41-1.35 (m, 9H), 1.31-1.18 (m, 19H), 1.12-1.08 (m, 12H), 0.97-0.93 (m, 8H). ^{13}C NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K, ppm): δ = 162.6, 162.5, 162.4, 162.2, 146.8, 146.4, 145.8, 145.1, 136.2, 136.1, 134.9, 134.5, 133.0, 131.2, 130.7, 130.4, 129.7, 129.4, 128.3, 127.7, 127.6, 127.3, 126.6, 126.2, 124.3, 124.3, 124.0, 123.9, 121.4, 121.3, 30.0, 29.6, 29.3, 24.5, 24.5, 24.1, 23.9, 23.9, 23.8. MS (MALDI-TOF): m/z (M^+) = 1360.4 (calcd for $\text{C}_{86}\text{H}_{74}\text{Cl}_2\text{N}_4\text{O}_8$: 1360.5).

Compound 5:

A mixture of compound **3** (240 mg for 3a and 3b, 1 equiv), compound **4** (200 mg for 4a and 4b, 1 equiv), $\text{Pd}(\text{PPh}_3)_4$ (20 mg for 5a and 5b, 0.1 equiv), CuI (8 mg for 5a and 5b, 0.2 equiv) in 20 ml dry toluene was stirred at 115 °C for 8 h under argon. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (CH_2Cl_2 /THF, 100:1) to yield the dark green solid (80 mg, 30% for 5a, 100 mg, 40% for 5b).

Compound 5a: ^1H NMR (400 MHz, CDCl_3 , 298K, ppm): δ = 10.03 (s, 4H), 10.02 (s, 4H), 9.08 (s, 4H), 4.56-4.53 (m, 4H), 4.35 (m, 16H), 2.32 (m, 4H), 1.96-1.86 (m, 16H), 1.62-1.25 (m, 158H), 0.90-0.85 (m, 34H); ^{13}C NMR (100 MHz, CDCl_3 , 298K, ppm): δ = 163.6, 163.5, 163.4, 162.2, 136.3, 135.6, 134.8, 132.7, 127.9, 127.7, 127.6, 127.5, 127.4, 126.9, 126.3, 122.2, 122.0, 121.1, 120.7, 42.1, 41.3, 32.0, 31.9, 29.7, 29.5, 29.3, 29.2, 28.6, 28.3, 28.2, 27.5, 27.4, 27.2, 22.6, 14.1. HRMS: calcd for $\text{C}_{186}\text{H}_{214}\text{N}_{10}\text{O}_{20}^-$ [M]: 2907.6041; found 2907.6046.

Compound 5b: ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K, ppm): δ = 10.14 (s, 4H), 9.99 (s, 4H), 9.15 (s, 4H), 7.52-7.44 (m, 8H), 7.36-7.30 (m, 18H), 7.19 (d, 4H), 2.91-2.80 (m, 20H), 1.25-1.11 (m, 120H). ^{13}C NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K, ppm): δ = 162.8, 162.6, 162.2, 161.8, 146.4, 145.9, 137.4, 136.0, 135.8, 132.9, 131.3, 130.5, 130.4, 129.6, 129.1, 128.1, 127.9, 127.6, 127.5, 127.3, 123.9, 123.7, 122.1, 121.5, 121.2, 29.6, 29.2, 24.3, 24.2, 23.8. HRMS: calcd for $\text{C}_{210}\text{H}_{182}\text{N}_{10}\text{O}_{20}^-$ [M]: 3163.3537; found 3163.3583.

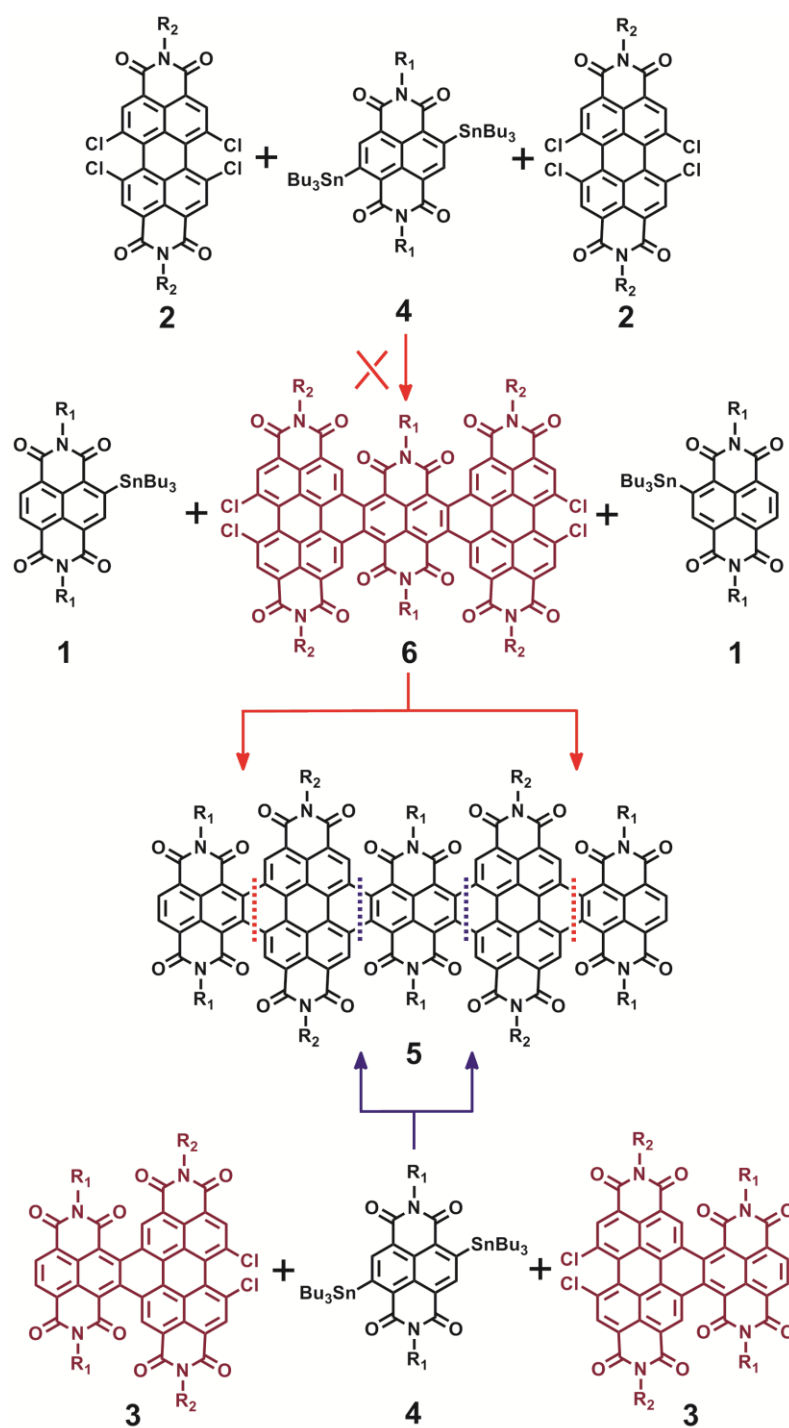


Figure S1. Two different synthetic strategies based on different building blocks for dodecatwistarene imides **5**.

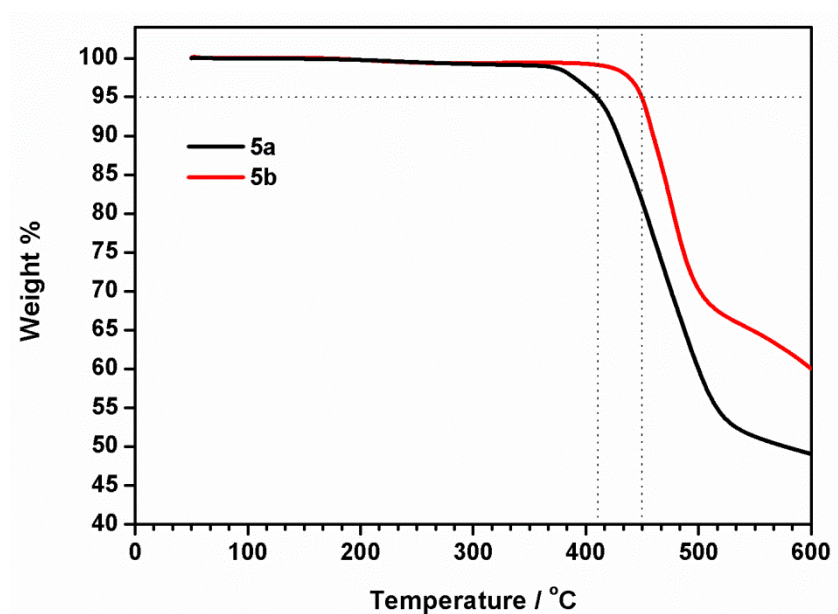


Figure S2. TGA curves of **5a** and **5b** under nitrogen flow.

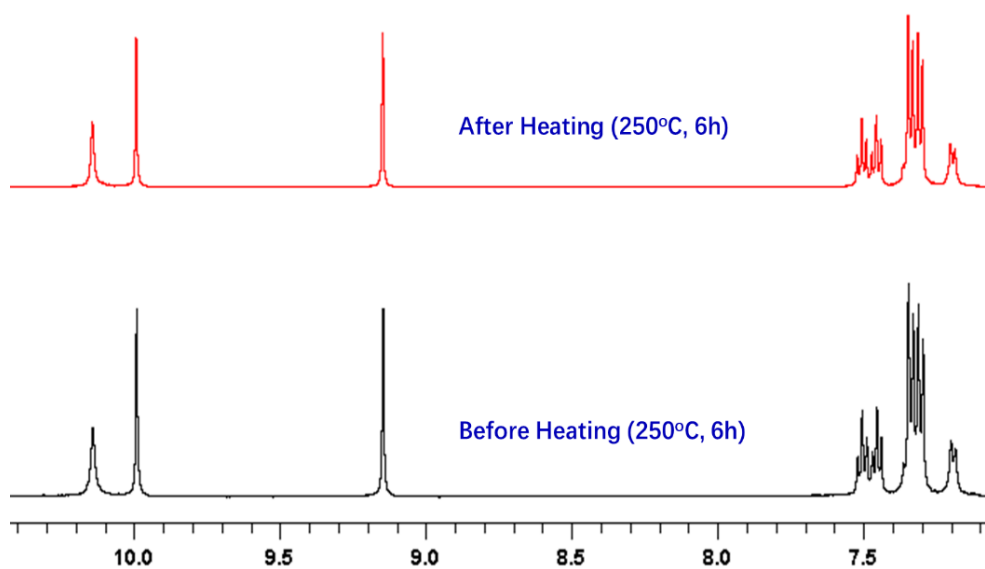


Figure S3. ¹H NMR spectra of **5b** before and after heating in diphenyl ether. (500 MHz, C₂D₂Cl₄, 373 K)

DFT Calculation

The aromaticity of dodecatwistarene imides **5** was evaluated using nucleus independent chemical shifts (NICS).^[2,3] The values of the magnetic shieldings were calculated for ghost atoms placed on the geometric center of the ring. The values of the chemical shifts obtained are a consequence of the electron delocalization in a cyclic ring and, hence, aromaticity. Rings with more negative chemical shifts, caused by enhanced diatropic ring currents, are more aromatic according to this criterion. In this work, the magnetic shieldings were calculated by the standard GIAO procedure,^[4,5] using density functional theory with the hybrid exchange correlation functional B3LYP^[6] and the 6-311+G** basis set. The CAM-B3LYP optimized geometries were used for the computation of the magnetic shieldings. For the NICS at the center of the ring was considered the isotropic value (NICS(0)). All the calculations were performed with the Gaussian 16 Rev. A.03 quantum chemistry package.^[7]

The conformation of each PDI + NDI unit are almost the same in the dodecatwistarene imides **5**, therefore we considered the dimer model shown in figure S4 to estimate the energy barrier for conformational changes. The barrier is associated with an almost planar and highly strained transition state structure in which the carbonyl oxygen of the naphthalene moiety and the perylene hydrogen experience a huge steric repulsion. Such barrier is as large as 61 kcal/mol (figure S4). Therefore, it is not surprising that for the dodecatwistarene imides the inversion between possible different isomers does not occur since the barrier in this latter case is expected to be even larger.

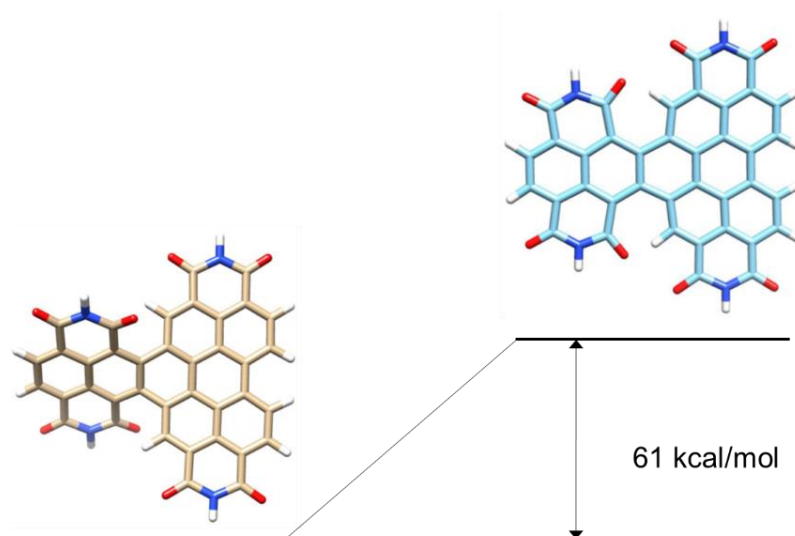


Figure S4. The energy barrier of conformation changes calculation using the B3LYP/6-311+G**.

X-ray crystallographic analysis

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1940982 (**5b**). The measurements were made on a Bruker SMART CCD area detector with graphite monochromated CuK α radiation ($\lambda = 1.54178$). All calculations were performed using the SHELXL-97 and the CrystalStructure crystallographic software package. The crystallographic data was summarized in Table S1.

Table S1. Crystallographic data of dodecatwistarene imides.

Compound Reference	5b
Chemical formula	C ₂₁₀ H ₁₈₂ N ₁₀ O ₂₀
Formula weight	3165.65
Crystal system	monoclinic
Space group	P 21/c
Calculated density	0.733 g/cm ³
<i>a</i> (Å)	31.5545 (13)
<i>b</i> (Å)	13.0465 (4)
<i>c</i> (Å)	37.9844 (18)
α (°)	90
β (°)	113.427(5)
γ (°)	90
Unit cell volume (Å ³)	14348.2(11)
Temperature (K)	169.99(10)
No. of formula units per unit cell	2
No. of reflections measured	29220
No. of independent reflections	11164
R _{int}	merged
Final R1 [<i>I</i> > 2 σ (<i>I</i>)]	0.1124

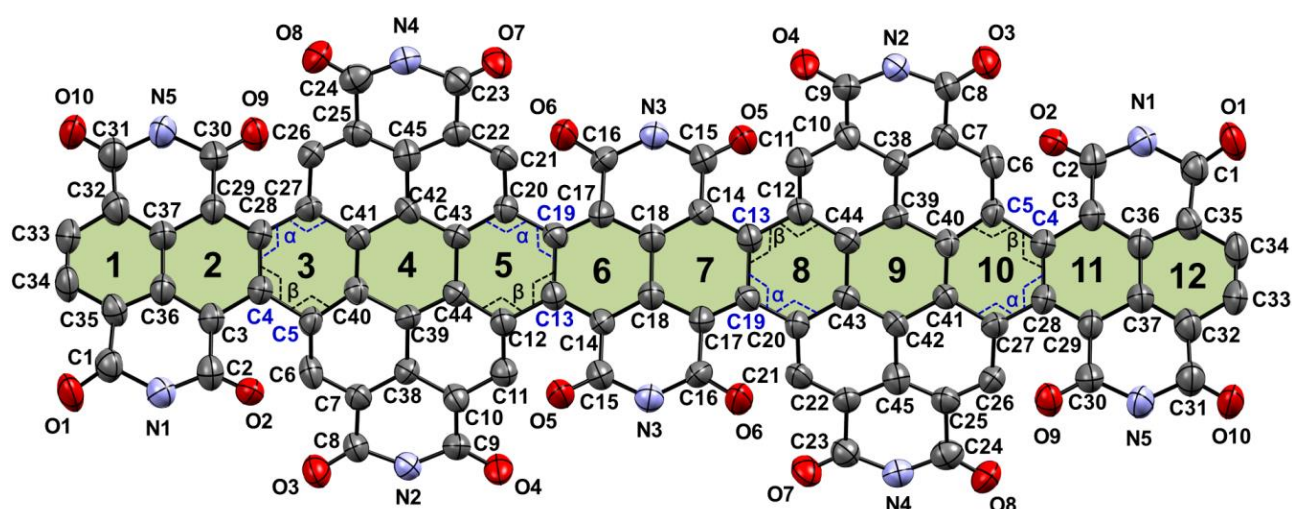


Figure S5. Single-crystal backbone structure of dodecatwistarene imides **5b** with label atoms and torsion angles.

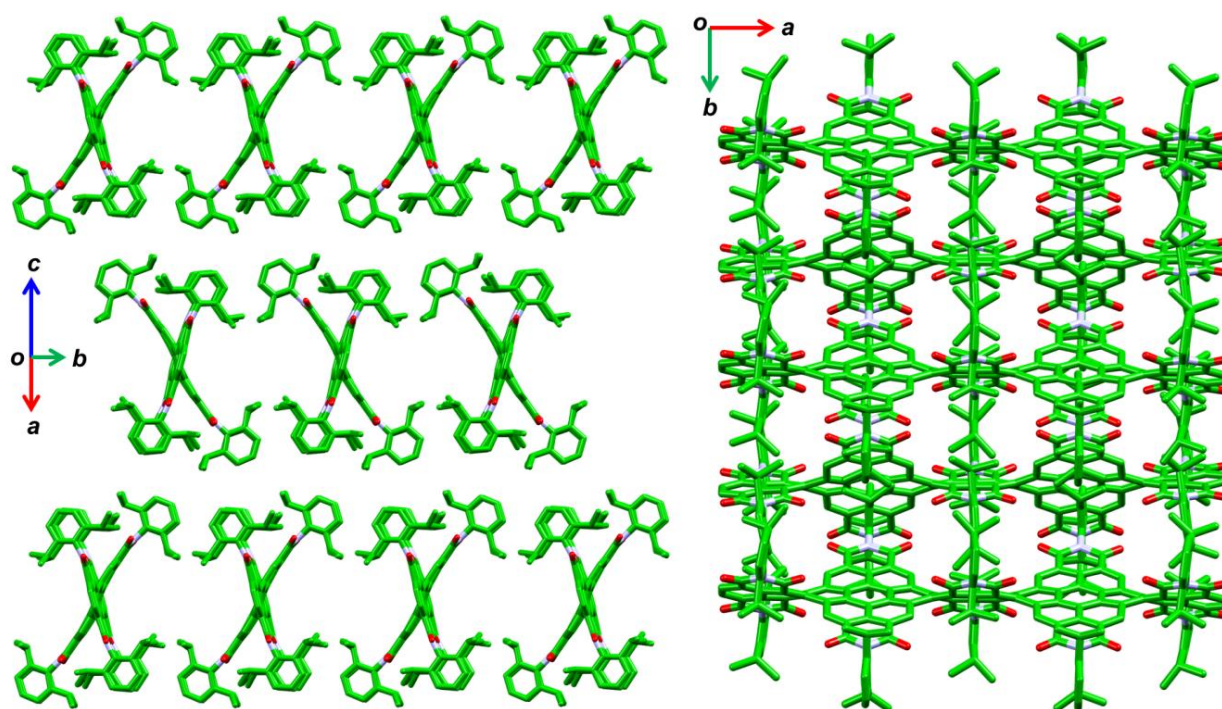


Figure S6. Crystal-packing pattern of **5b** viewed from a^* and c axis.

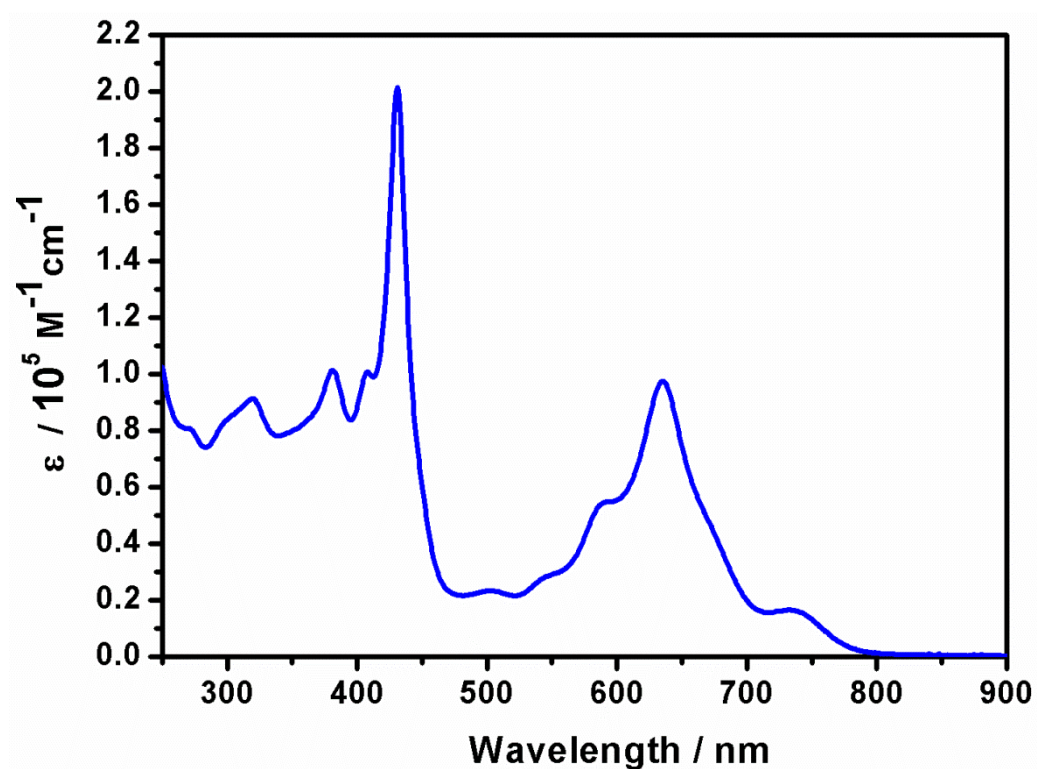


Figure S7. UV/Vis absorption spectrum of **5b** in CHCl_3 at room temperature ($1 \times 10^{-5} \text{ M}$).

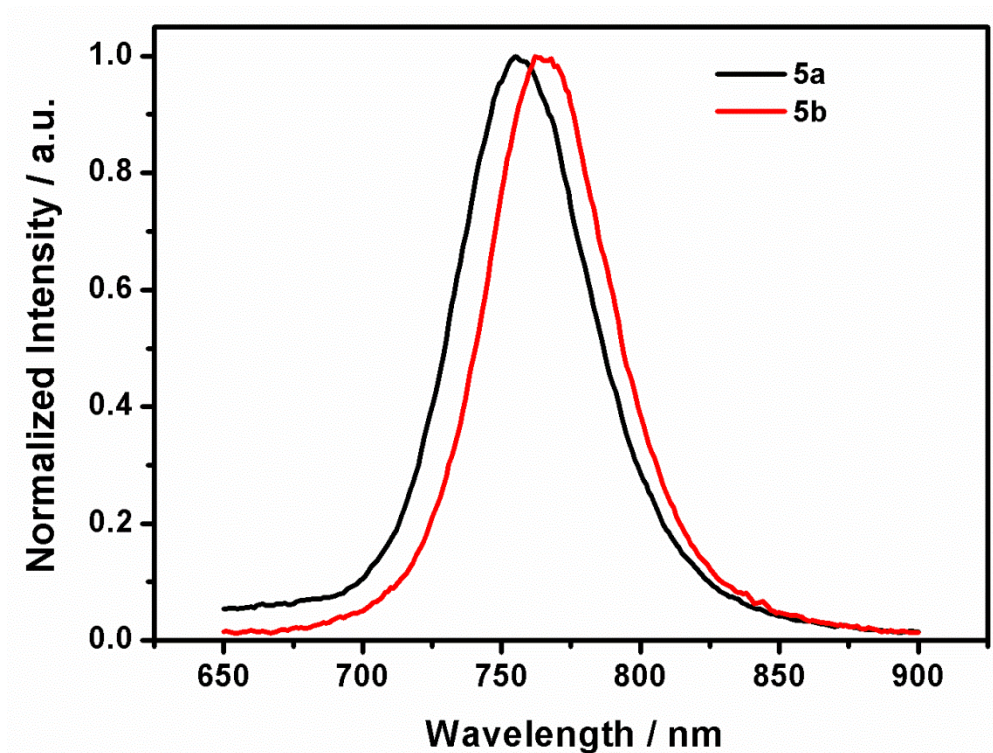


Figure S8. Fluorescence spectra of **5a** and **5b** in CHCl_3 .

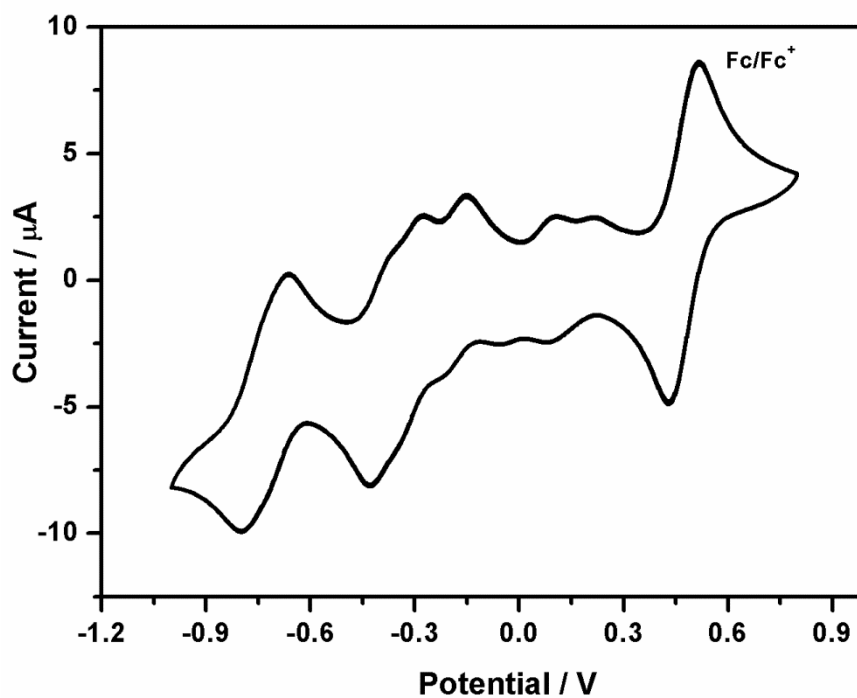


Figure S9. Cyclic voltammogram of **5a** in dry CH_2Cl_2 with ferrocene as an internal potential marker. Scan rate = 0.1 V/s (Ag/AgCl, electrolyte, 0.1 M TBAPF6).

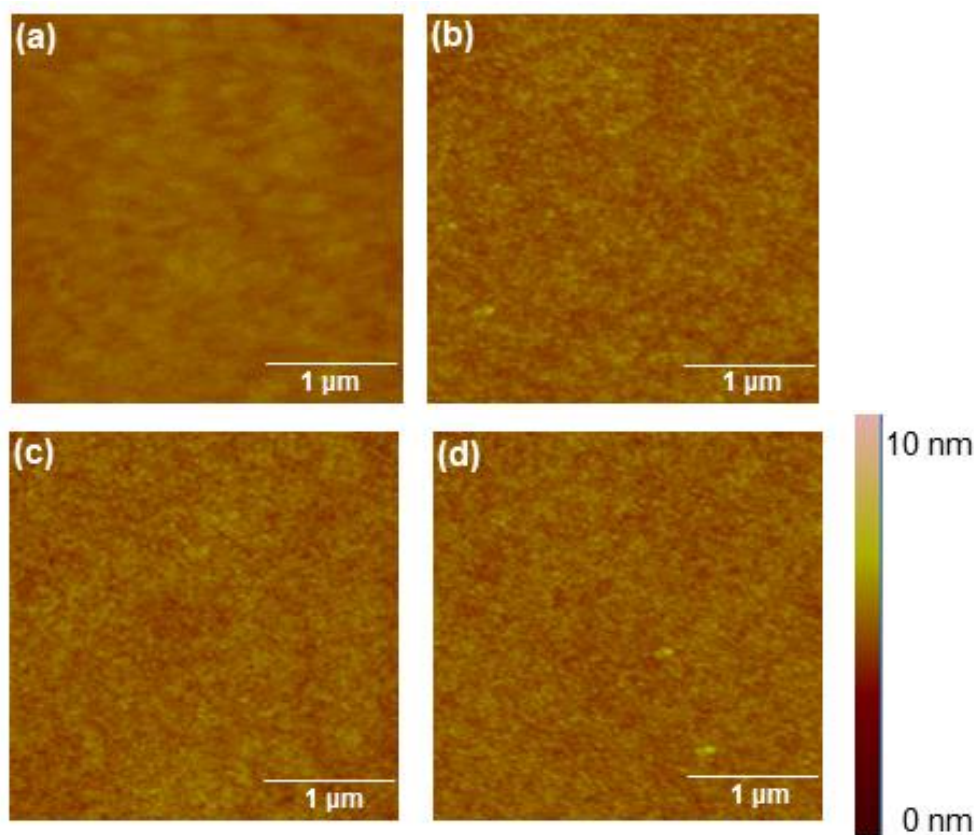


Figure S10. AFM images of thin films of **5a** annealed at (a) 25 °C, $R_q = 0.193$ nm; (b) 180 °C, $R_q = 0.284$ nm; (c) 200 °C, $R_q = 0.291$ nm; (d) 220 °C, $R_q = 0.295$ nm.

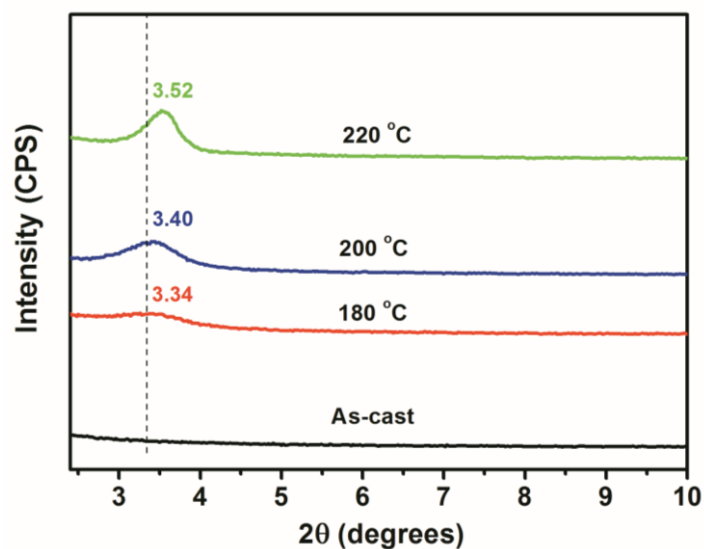


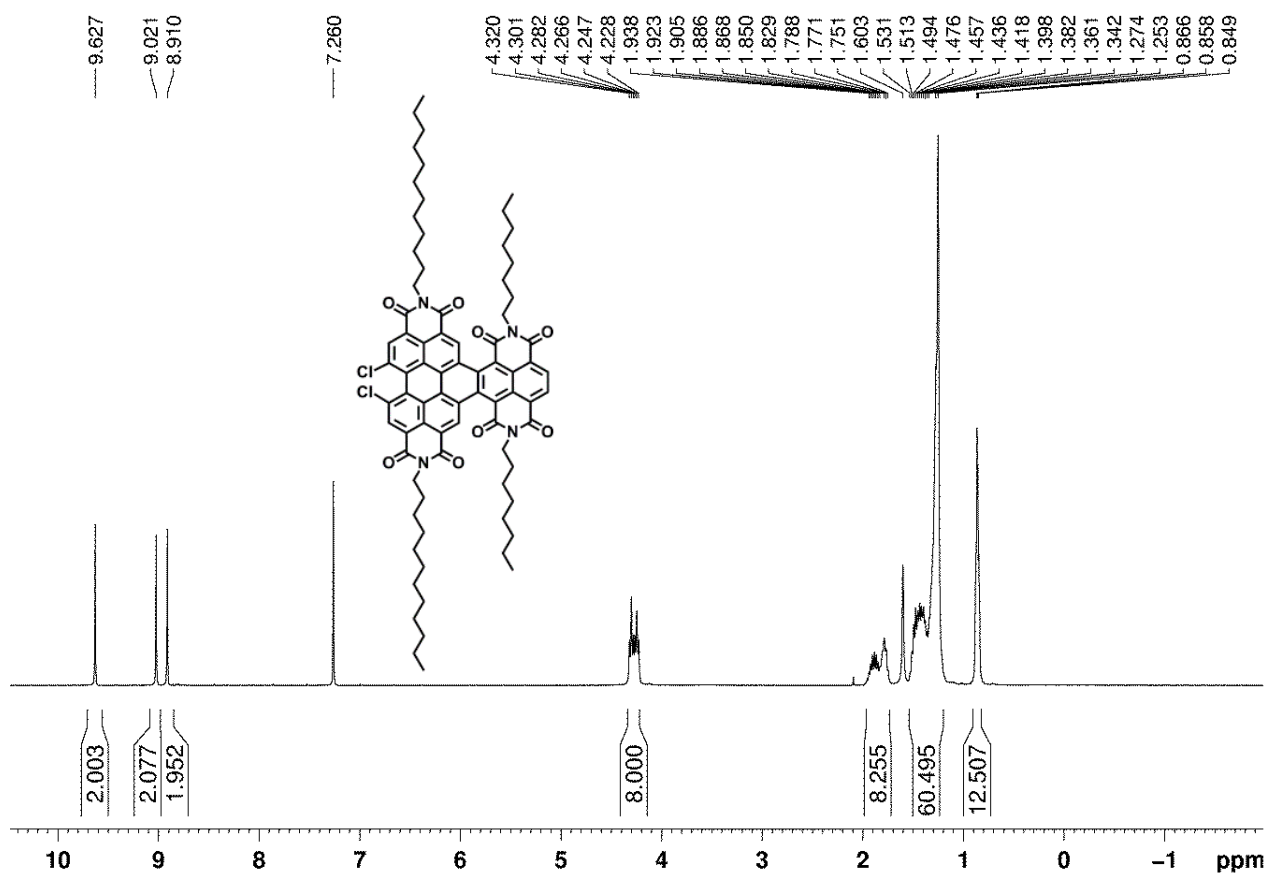
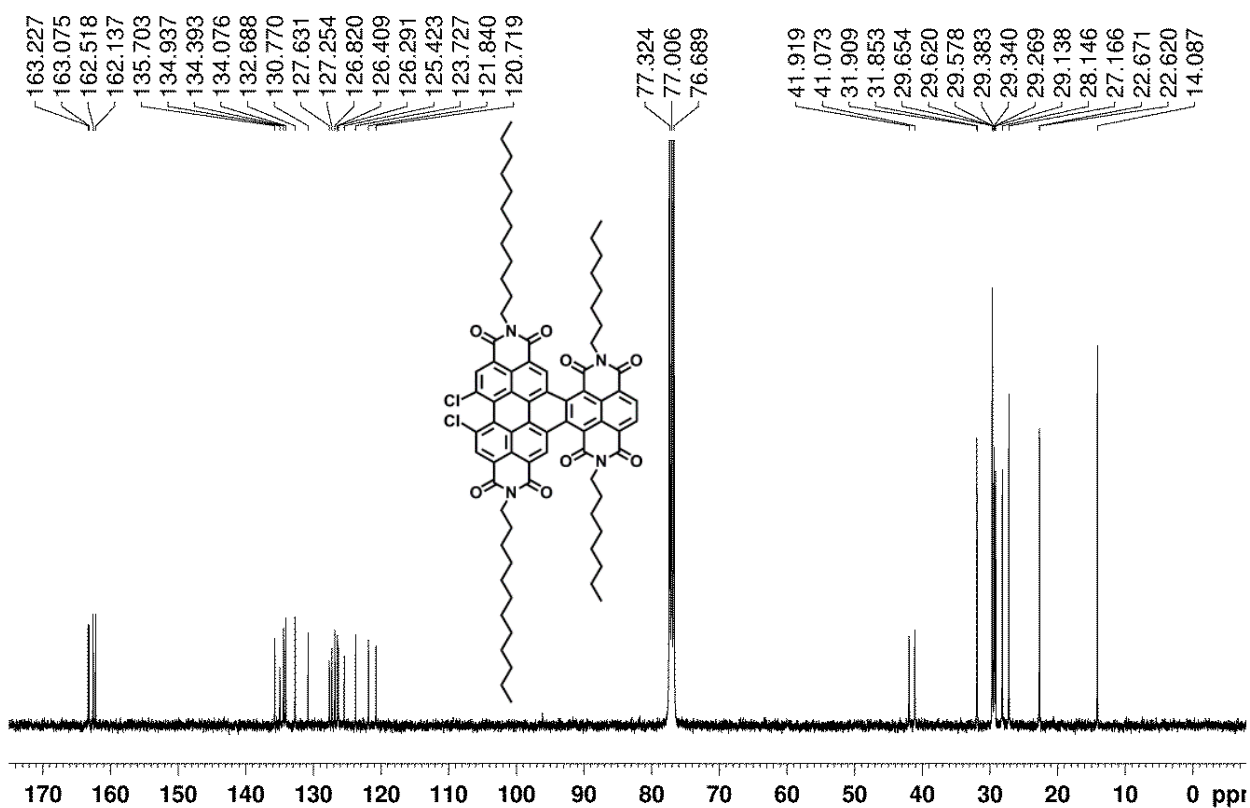
Figure S11. The out of plane X-ray diffraction patterns of **5a** thin films at different annealing temperature.

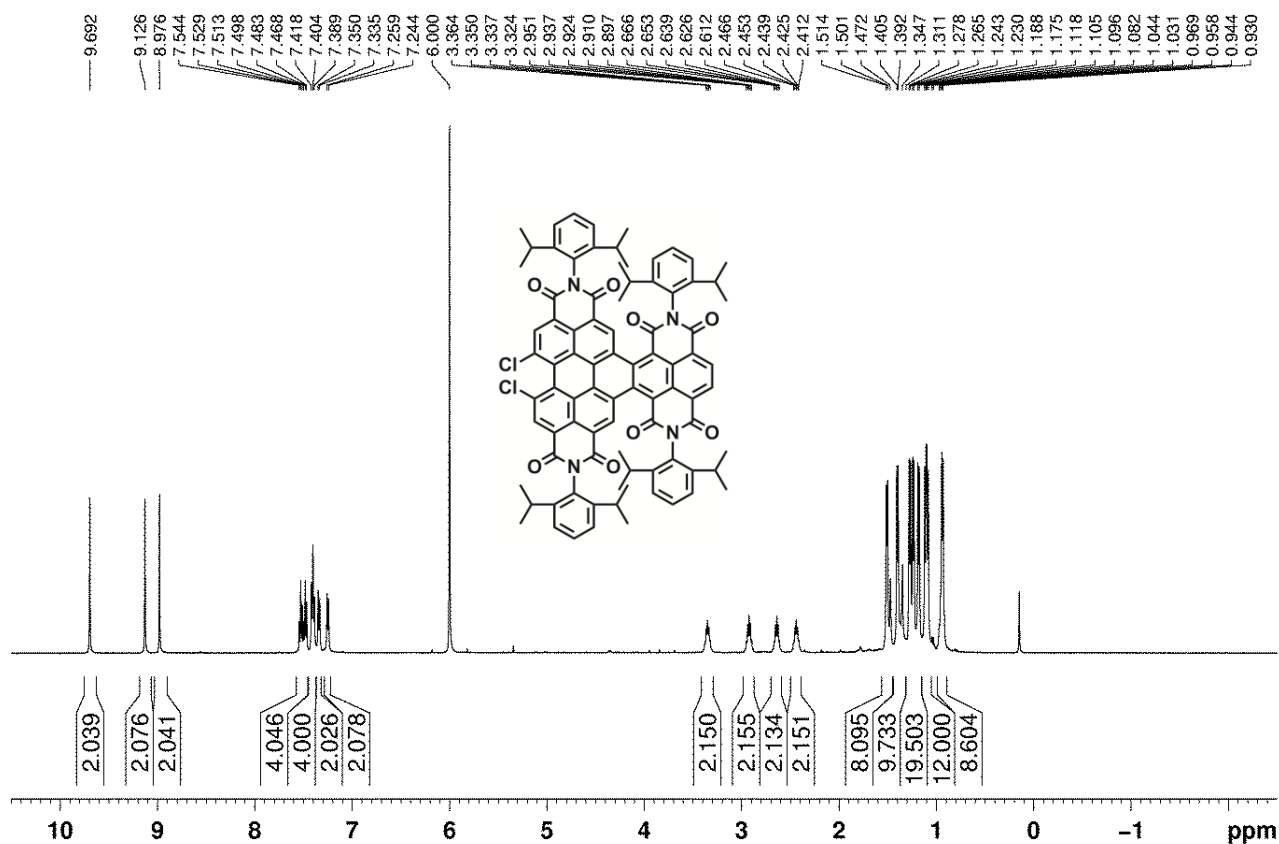
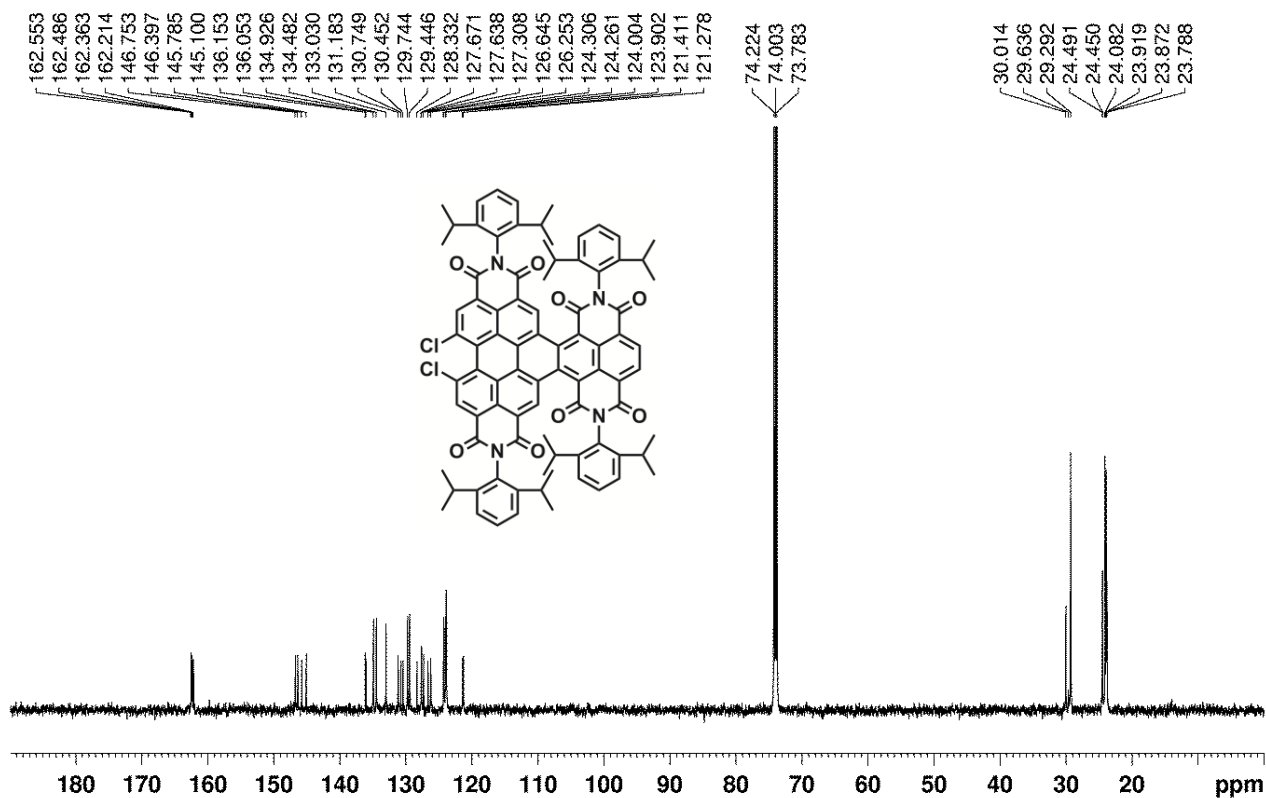
Table S2. Thin film OFET Parameters based on ten devices

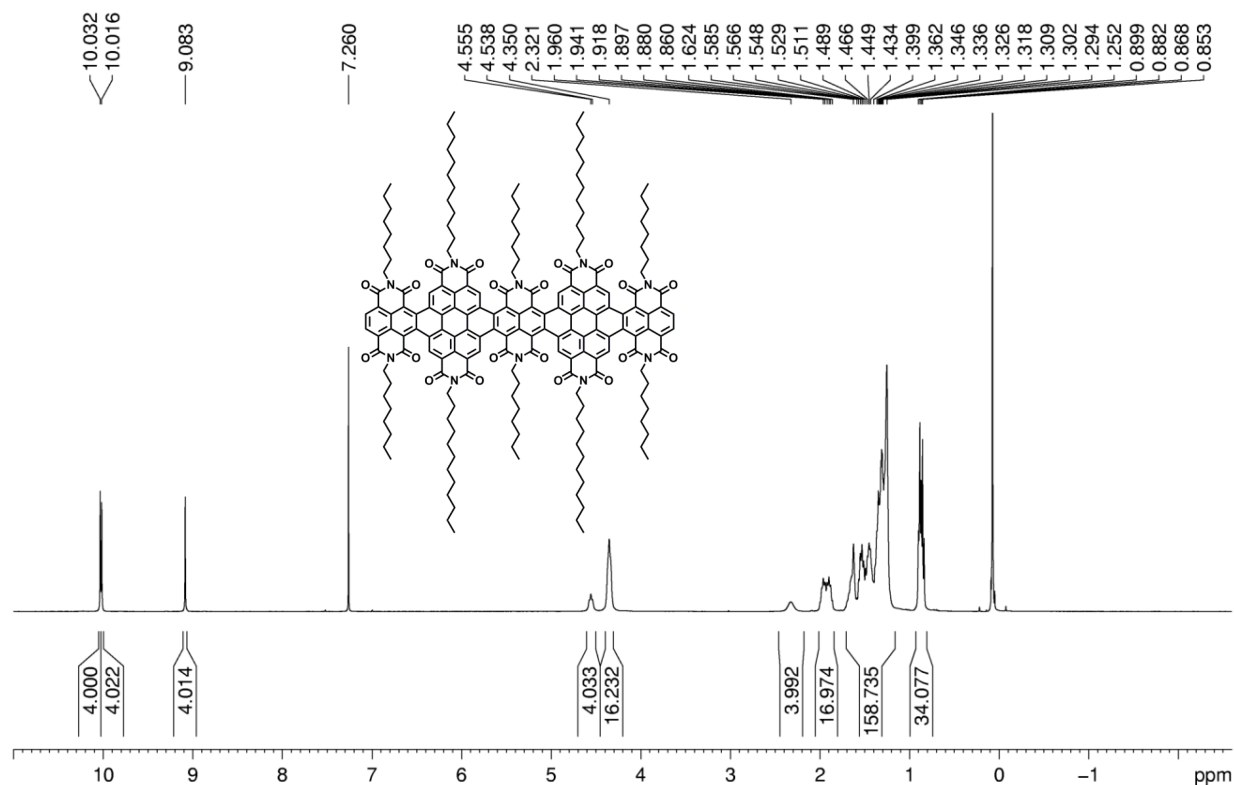
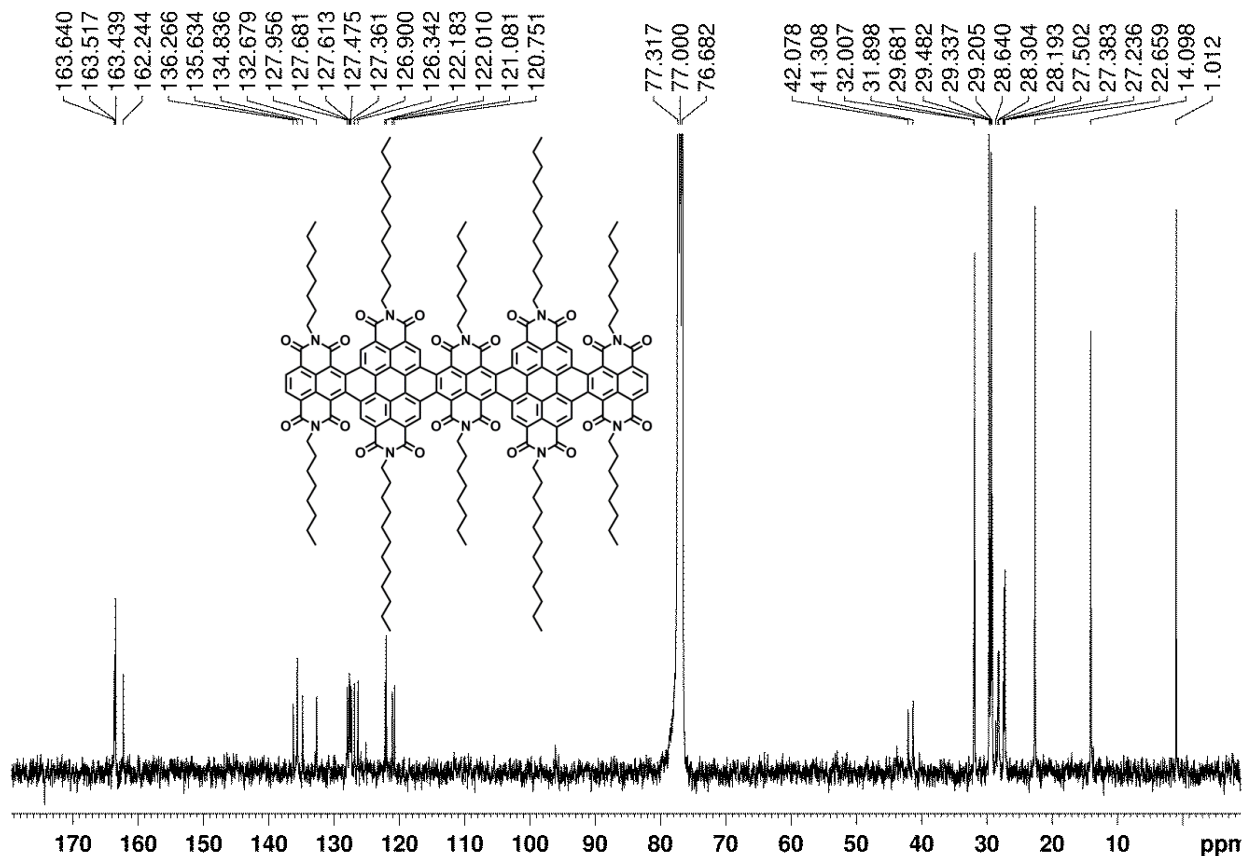
Comp.	W/L (μm)	Atm.	μ_e^{\max} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_t / V	On/off Ratio
5a	200/25	Air	1.50	9.28	8.3×10^8
			1.49	12.3	1.3×10^8
			1.19	11.9	1.1×10^8
			1.13	8.16	8.1×10^7
			1.35	8.64	3.3×10^8
			1.31	9.40	4.9×10^8
			1.15	11.2	1.5×10^8
			1.18	9.07	3.8×10^8
			1.27	9.25	1.4×10^8
			1.34	9.15	3.6×10^8
			$\mu_e^{\text{ave}} = 1.30 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$		

References

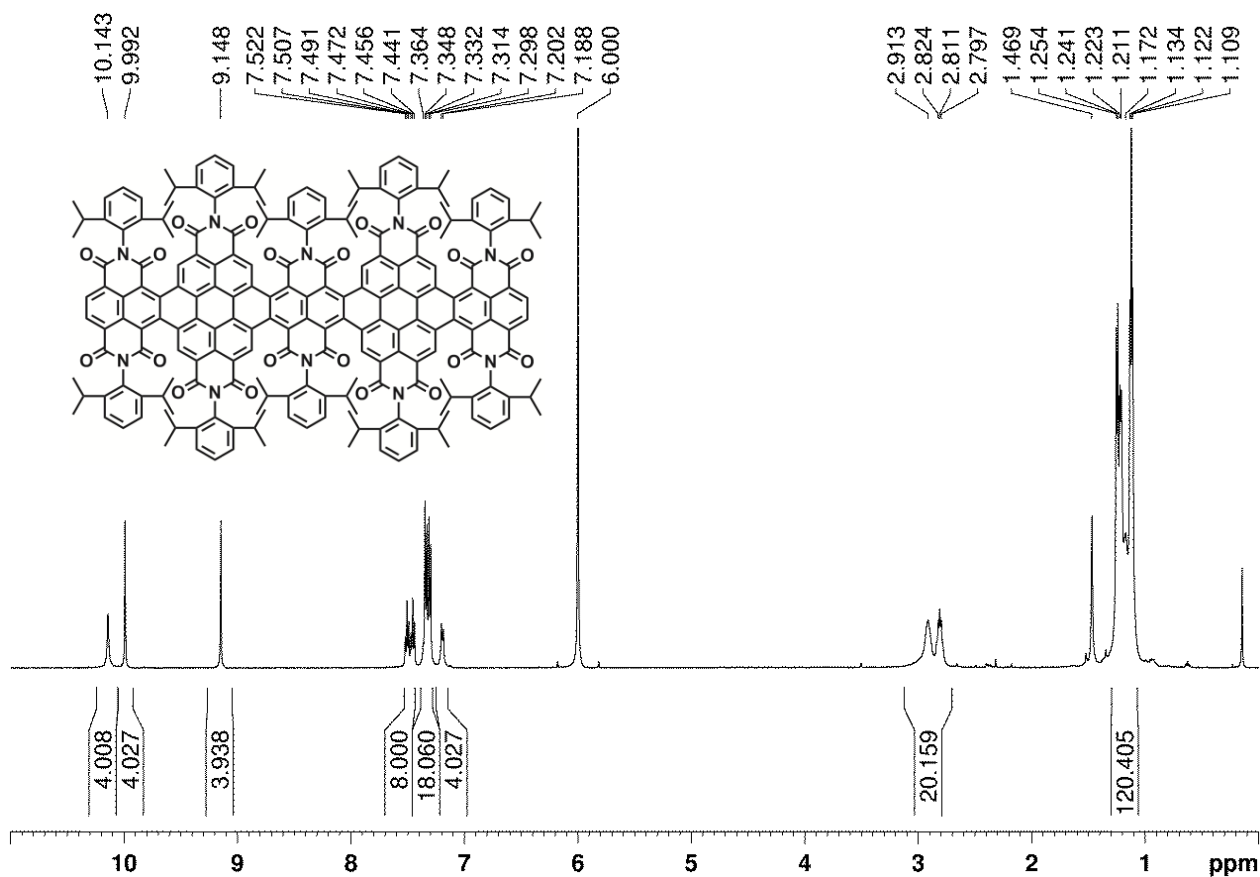
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^1H NMR spectrum of **3a** (400 MHz, CDCl_3 , 298 K) ^{13}C NMR spectrum of **3a** (100 MHz, CDCl_3 , 298 K)

¹H NMR spectrum of **3b** (500 MHz, C₂D₂Cl₄, 373 K)¹³C NMR spectrum of **3b** (125 MHz, C₂D₂Cl₄, 373 K)

^1H NMR spectrum of **5a** (400 MHz, CDCl_3 , 298 K) ^{13}C NMR spectrum of **5a** (100 MHz, CDCl_3 , 298 K)

^1H NMR spectrum of **5b** (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K)



^{13}C NMR spectrum of **5b** (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K)

