Electronic Supplementary Information

Isomeric Anthracene Diimide Polymers

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Experimental section

Materials. All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, Alfa, SunaTech Inc and aladdin) and used without further purification unless stated otherwise. Reagent grade solvents were dried when necessary and purified by distillation. 2,6,9,10-Tetrabromoanthracene (**7**),[1] 9,10-anthracenedicarboxylic acid (**2**),[2] and 9,10-anthracene acid chloride (**3**)[2] were prepared according to literature procedures.

Instrumentations and measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHZ) were carried out on an AVANCE III 400 MHz (room temperature analyses). The spectra were referenced on the internal standard TMS. The MALDI-TOF were carried out on AB SCIEX TOF/TOF 5800 equipped with an Nd: YAG laser (355 nm wavelength) in positive reflection modes, and using DBH as matrix. The GPC measurements were carried out on three PLgel 10 µm MIXED-B LS 300×7.5 mm columns, with the 1,2,4-trichlorobenzene (TCB) as the eluent. UV-Vis absorption spectra were recorded on a Cary 5000, Varian Inc, USA. The TGA and DSC were characterized on SETSYS 1750 and DSC204 HP, respectively. Cyclic voltammetry measurements were carried out using a CHI 660 epotentiostat equipped with a standard three-electrode configuration. Typically, a three-electrode cell equipped with a glassy carbon working electrode, an Ag/$AgNO_3$ (0.01 M in anhydrous acetonitrile) reference electrode, and a Pt counter electrode was employed. Polymer films were drop cast onto the glassy carbon electrode from a 3 mg/mL toluene solution and dried at room temperature prior to measurements. The potential of Ag/$AgNO_3$ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The LUMO and HOMO energy levels were calculated according to the following Equations S1 and S2:

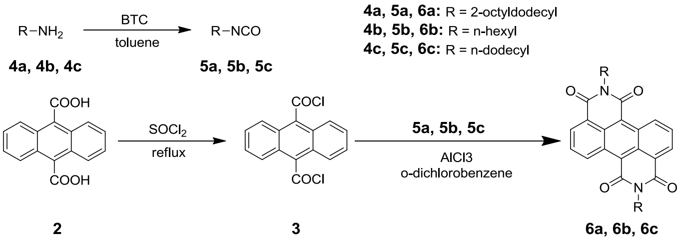
$$\mathrm{E}_{LUMO} = -[4.8\ \mathrm{eV} + \mathrm{e}\,(E_{red} - E_{Fc/Fc^{+}})] \qquad \text{Equation S1}$$

$$E_{HOMO} = E_{LUMO} - E_g$$

Equation S2

Grazing incidence X-ray diffraction (GIXD) measurements were performed using the beamline BL14B1 at the Shanghai Synchrotron Radiation Facility (SSRF) with the incident photon energy of 10 keV (wavelength of 1.2398 angstrom) at an incident angle 0.16° and an exposure time of 30 s. The films for the GIXD measurement were prepared on Si wafer substrates at room temperature or annealed at 70 °C for 10 min.

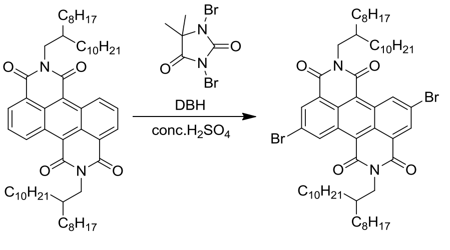
Synthetic details



*Synthesis of compound **6a**:* A solution of compound **4a** (112.5 mmol, 33.4766 g) in dry toluene (112.5 mL) was slowly added into a solution of bis(trichloromethyl) carbonate (BTC, 90 mmol, 17.8050 g) in dry toluene (90 mL) at 0-5 °C. The resulting mixture was refluxed for 6 h to remove excess BTC. The solvent was then evaporated to afford the compound **5a** which was used for next step without further purification. In argon atmosphere, compound **3** (7.5 mmol, synthesized from 9,10-anthracenedicarboxylic acid (**2**) according to the literature),[2] $AlCl_3$ (44.6 mmol, 5.9520 g) and dry *o*-dicholobenzene (100 mL) were charged into a Schlenk flask, and the mixture was stirred for 15 min at room temperature. The compound **5a** was then added and the mixture was heated at 180 °C for 12 h. After removal of the solvent, the residue was purified by column chromatography over silica gel to afford compound **6a** as an orange solid (0. 3422 g). The total yield of two reactions from **2** to **6a** is 5.2%. ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 10.34 (d, J = 9.12 Hz, 2H), 8.86 (d, J = 7.0 Hz, 2H), 8.04 (dd, J = 9.16 Hz, 7.0 Hz, 2H), 4.24 (d, J = 7.32 Hz, 4H), 2.10-2.03 (m, 2H), 1.44-1.20 (m, 60H), 0.88-0.82 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ =164.65, 163.54, 133.88, 133.63, 130.69, 129.77, 128.84, 122.71, 122.18, 72.47, 64.81, 58.32, 44.99, 36.60, 31.90, 31.87, 31.74, 30.05, 29.64, 29.61, 29.60, 29.55, 29.32, 29.29, 26.47, 22.68, 22.65, 14.11, 14.10. HRMS (MALDI/TOF) m/z: $(M+H)^+$ Calcd. for $C_{58}H_{88}N_2O_4$: 878.3303; Found: 878.3579.

*Synthesis of compound **6b**:* The **6b** is synthesized following the same procedure as that of **6a**, where the **4b** (112.5 mmol, 11.3839 g) is used. The total yield of two reactions from **2** to **6b** (0.708 g) is 19.48%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.32 (d, J = 9.12 Hz, 2H), 8.83 (d, J = 5.92 Hz, 2H), 8.01 (dd, J = 9.16 Hz, 7.04 Hz, 2H), 4.28 (t, J = 7.76 Hz, 4H), 1.84-1.77 (m, 4H), 1.62-1.25 (m, 12H), 0.93 (t, J = 7.04 Hz,6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ =164.25, 163.04, 133.84, 133.55, 130.59, 129.75, 128.71, 122.65, 122.04, 41.19, 31.55, 28.03, 26.89, 22.60, 14.07.

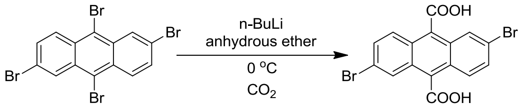
*Synthesis of compound **6c**:* The **6c** is synthesized following the same procedure as that of **6a**, where the **4c** (112.5 mmol, 20.8530 g) is used. The total yield of two reactions from **2** to **6c** (2.4510 g) is 50.05%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.31 (d, J = 9.12 Hz, 2H), 8.82 (d, J = 7.04 Hz, 2H), 8.00 (dd, J = 9.12 Hz, 7.04 Hz, 2H), 4.27 (t, J = 7.72 Hz, 4H), 1.84-1.76 (m, 4H), 1.50-1.25 (m, 36H), 0.89 (t, J = 7.04 Hz,6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ =164.22, 163.01, 133.82, 133.54, 130.55, 129.73, 128.68, 122.63, 122.00, 41.19, 31.92, 29.66, 29.64, 29.62, 29.58, 29.39, 29.36, 28.09, 27.24, 22.69, 14.13.



6a **3,7-2Br-ADI**

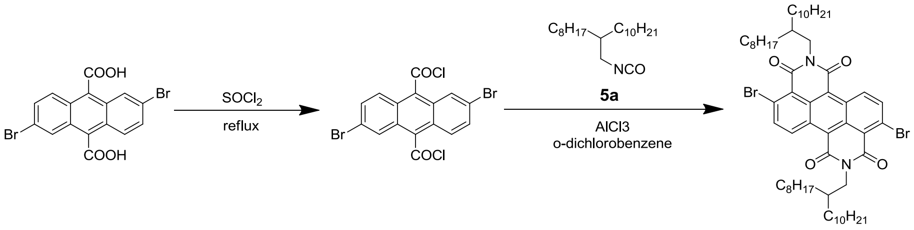
Synthesis of 3,7-2Br-ADI: In a single-necked RB flask, compound **6a** (2.06 mmol, 1.8073 g) was dissolved in concentrated sulfuric acid (8 mL) and stirred at 65 °C for 6 h. After cooling down to room temperature, DBH (10 equiv, 20.6 mmol, 5.8907 g) was added in portions over a period of 1 h. The resulting red solution was stirred at 65 °C for 24 h. The mixture was poured into ice water then extracted with dichloromethane, dried over MgSO$_4$, and finally concentrated by rotary evaporation. The crude product was purified by column chromatography over silica gel to afford 3,7-2Br-ADI as a red solid (0.4400 g, 22%). ^{1}H NMR (400 MHz, CDCl$_3$): δ =10.54 (s, 2H), 8.88 (s, 2H), 4.21 (d, J = 7.3 Hz, 4H), 2.06-2.00 (m, 2H), 1.43-1.22 (m, 60H), 0.88 (q, J = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, CDCl$_3$): δ =163.90, 162.17, 137.15, 135.42, 131.19, 127.76, 125.98, 123.88, 121.17, 54.62, 45.25, 36.50, 31.91, 31.88, 31.65, 31.31, 30.04, 29.71, 29.65, 29.62, 29.56, 29.34, 29.30, 28.40, 26.41, 25.04, 22.68, 22.66, 14.12. HRMS (MALDI/TOF) m/z:

(M+H)$^+$ Calcd. for $C_{58}H_{86}Br_2N_2O_4$: 1036.1224; Found: 1036.1125.



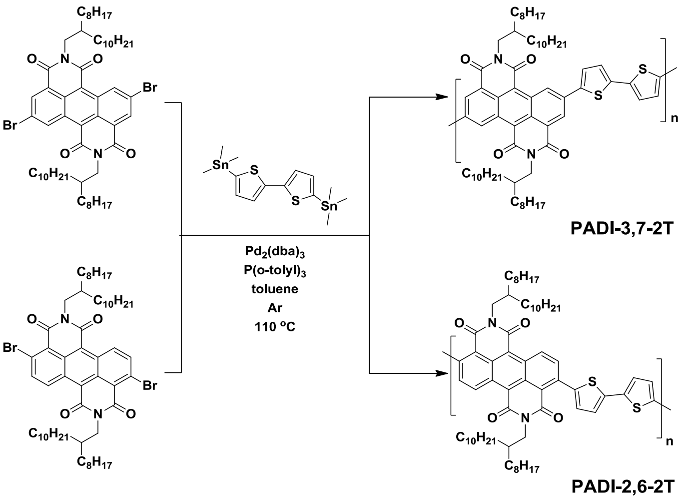
7 8

Synthesis of compound ***8****:* N-butyllithium (50.84 mmol, 31.7 mL, 1.6 M) was added to a suspension of compound **7** (24.8 mmol, 12.2467 g) in anhydrous ether (70 mL) under argon, and the mixture was stirred for 2 h at room temperature. Excessive dry ice was then added into the mixture. After stirring for 2 h, water and diethyl ether were added into the mixture and the aqueous phase was separated and acidified with 6 M HCl. The resulting yellow product was filtered off and dried at 80 °C in vacuum to give compound **8** (6.6606 g, 63%).



8 9 **2,6-2Br-ADI**

Synthesis of 2,6-2Br-ADI: The compound **9** was synthesized by refluxing the compound **8** (7.5 mmol, 3.180g) with thionyl chloride ($SOCl_2$) for 6 h. After removal of the excessive $SOCl_2$ by distillation, the compound **9** was obtained and used for next step without further purification. The synthetic procedure of 2,6-2Br-ADI was the same as that of compound **6a**. The compound **9** instead of compound **3** was used. The 2,6-2Br-ADI was obtained as a yellow solid (0.3320 g). The total yield of the two reactions from compound **8** to 2,6-2Br-ADI is 4.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.09 (d, J = 9.8 Hz, 2H), 7.95 (d, J = 9.8 Hz, 2H), 4.25 (t, J = 7.4 Hz, 4H), 2.07-2.04 (m, 2H), 1.42-1.21 (m, 60 Hz), 0.88 (q, J = 7.2 Hz, 12H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.60, 161.35, 142.66, 140.97, 134.57, 133.42, 129.68, 118.44, 117.92, 64.55, 55.42, 38.38, 36.53, 31.91, 31.88, 31.68, 30.07, 29.65, 29.62, 29.59, 29.54, 29.34, 29.31, 26.38, 22.68, 22.66, 20.12, 14.12, 14.11. HRMS (MALDI/TOF) m/z: (M+H)$^+$ Calcd. for $C_{58}H_{86}Br_2N_2O_4$: 1036.1224; Found: 1036.1720.



Synthesis of polymers: A mixture of 3,7-2Br-ADI or 2,6-2Br-ADI (103.51 mg, 0.1 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (49.18 mg, 0.1 mmol), $Pd_2(dba)_3$ (3.66 mg, 0.004 mmol) and P(*o*-tolyl)$_3$ (2.43 mg, 0.008 mmol) in anhydrous toluene (8 mL) was stirred at 110 ^{o}C for 1 day under argon. Bromobenzene (0.3 mL) was then added and the mixture was stirred for an additional 6 h. The mixture was cooled down to room temperature and poured into HCl (1M)/MeOH (V:V=1:10, 70 mL). The obtained solid was purified by Soxhlet extraction with acetone, hexane, and chloroform, respectively. The chloroform portion was precipitated in MeOH (50 mL), and the precipitate was collected by filtration and dried in vacuum. The PADI-3,7-2T (70 mg, 65%) was obtained as green solid with M_n=17.8 KDa and M_w/M_n=2.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.50 (s), 10.11 (br), 9.04 (s), 8.63 (br), 4.35 (br), 2.35-0.81 (m). The PADI-2,6-2T (68 mg, 64%) was obtained as dark green solid with M_n=14.2 KDa and M_w/M_n=2.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.17 (br), 9.66 (br), 7.95 (br), 7.78 (br), 4.22 (br), 2.11-0.84 (m).

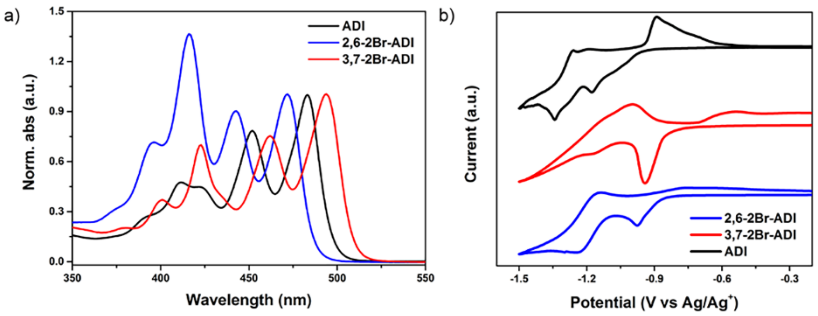


Figure S1. (a) UV-Vis absorption spectra and (b) cyclic voltammograms of ADI, 3,7-2Br-ADI and 2,6-2Br-ADI.

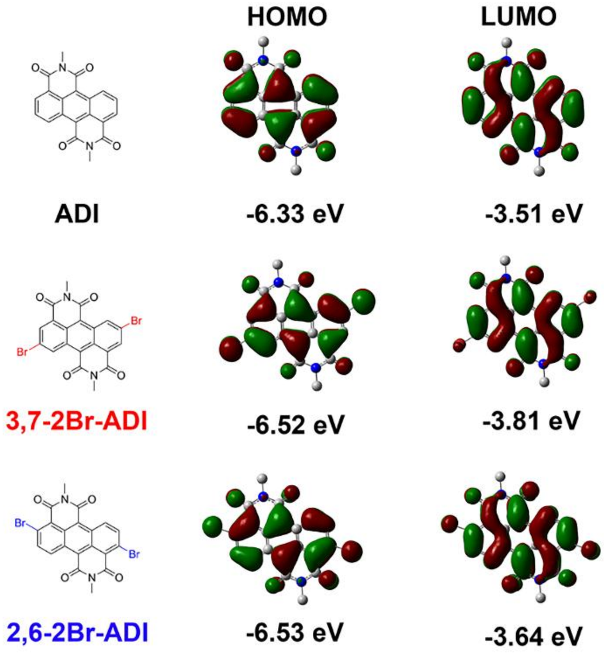


Figure S2. Frontier molecular orbitals of ADI, 3,7-2Br-ADI and 2,6-2Br-ADI calculated via DFT.

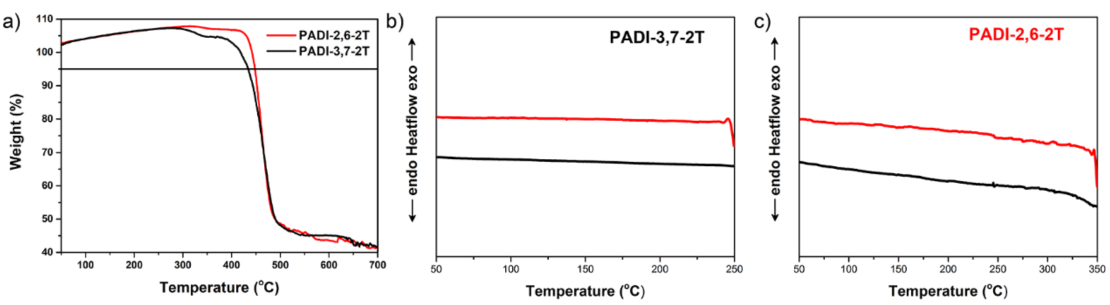


Figure S3. (a) TGA curves of PADI-2,6-2T and PADI-3,7-2T, and the DSC curves of (b) PADI-3,7-2T and (c) PADI-2,6-2T (at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere).

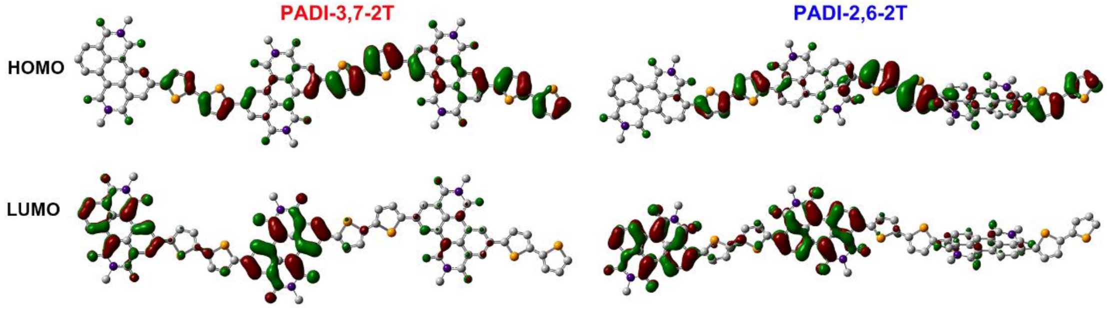


Figure S4. Frontier molecular orbitals of PADI-3,7-2T and PADI-2,6-2T calculated via DFT.

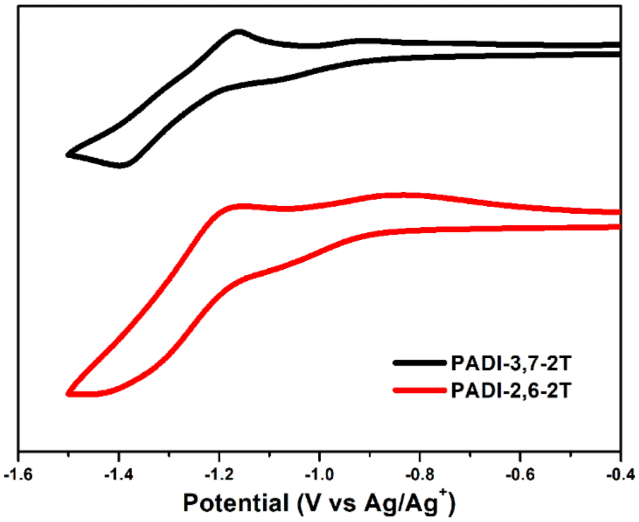


Figure S5. Cyclic voltammograms of PADI-3,7-2T and PADI-2,6-2T.

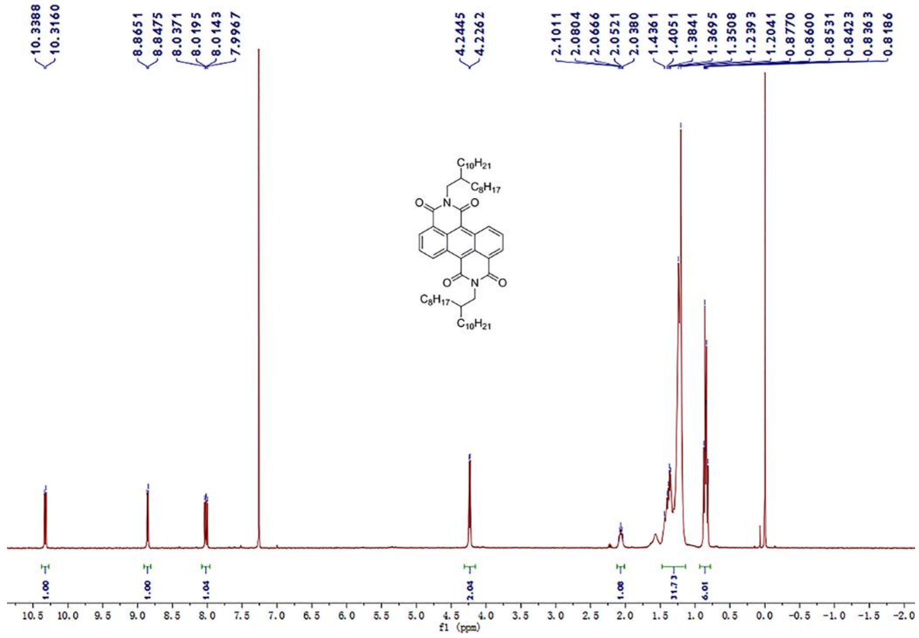


Figure S6. ^{1}H NMR spectrum of compound **6a**.

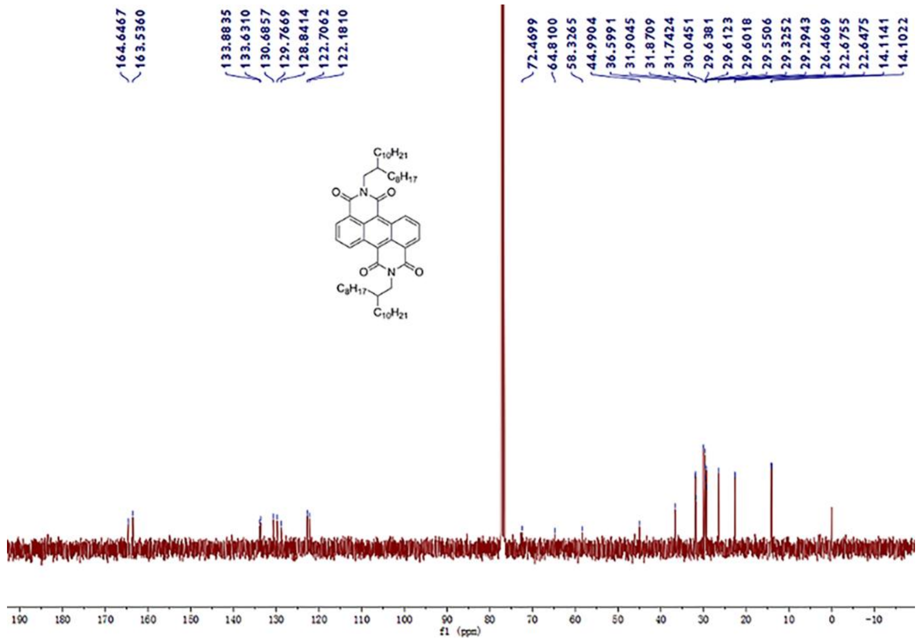


Figure S7. ^{13}C NMR spectrum of compound **6a**.

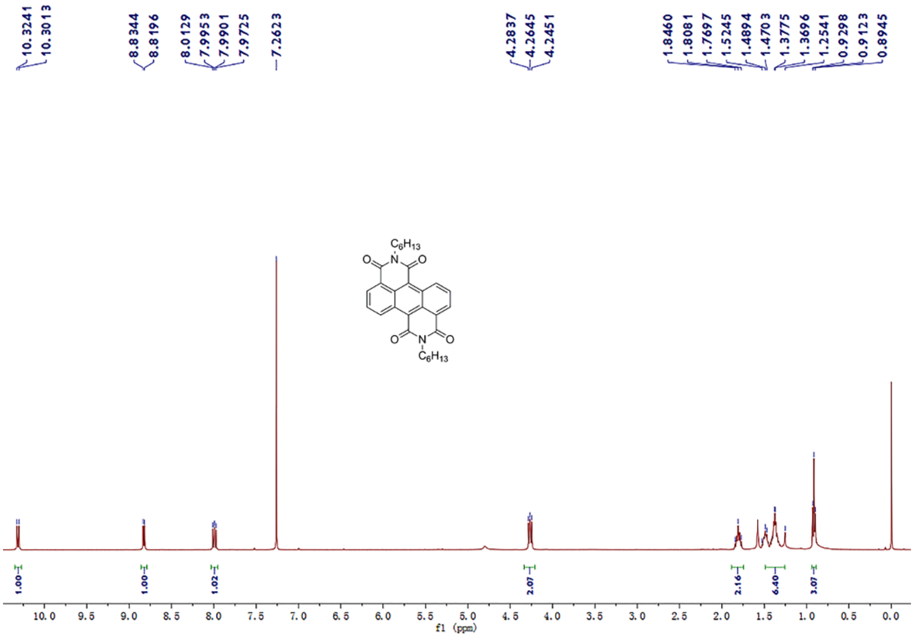


Figure S8. ^{1}H NMR spectrum of compound **6b**.

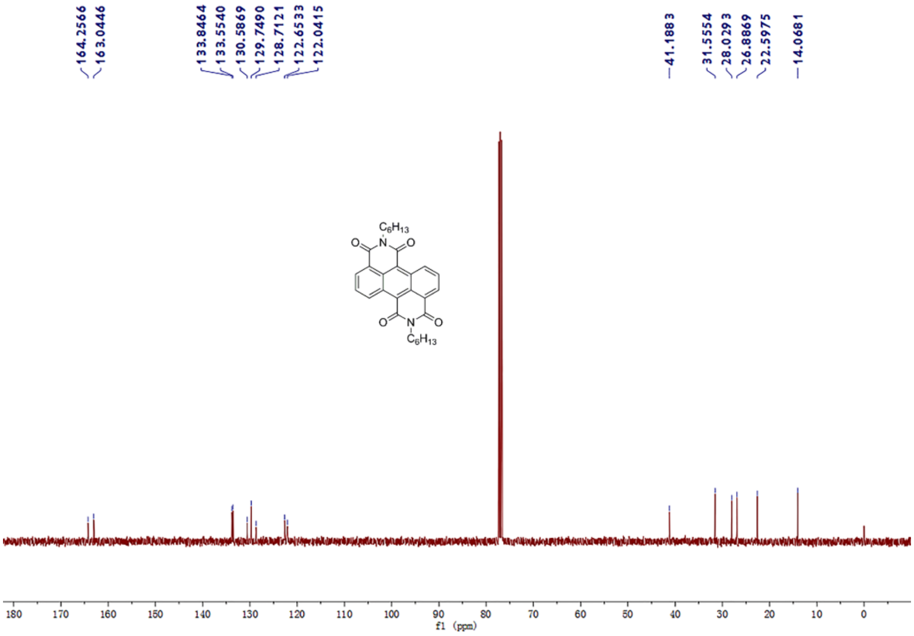


Figure S9. ^{13}C NMR spectrum of compound **6b**.

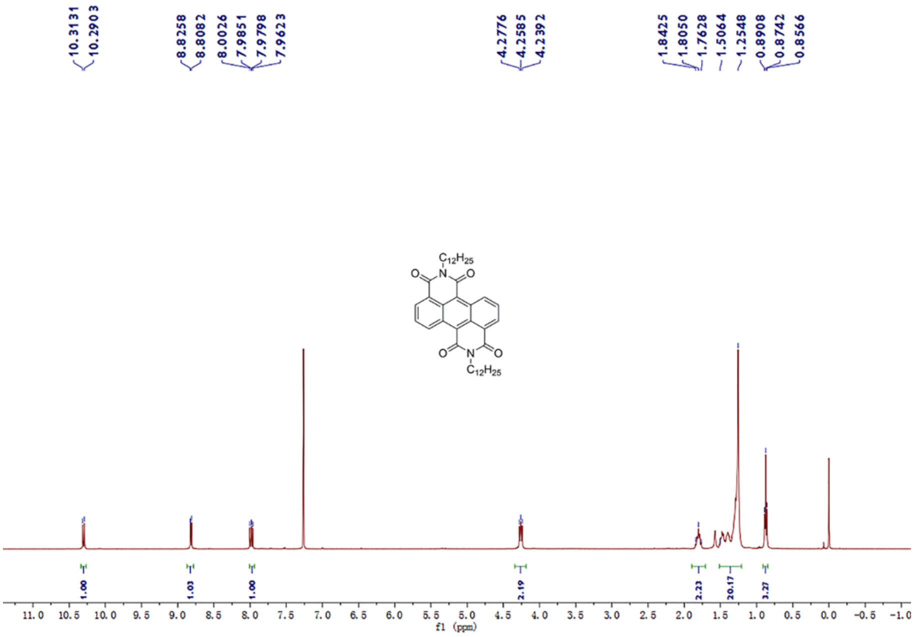


Figure S10. ^{1}H NMR spectrum of compound **6c**.

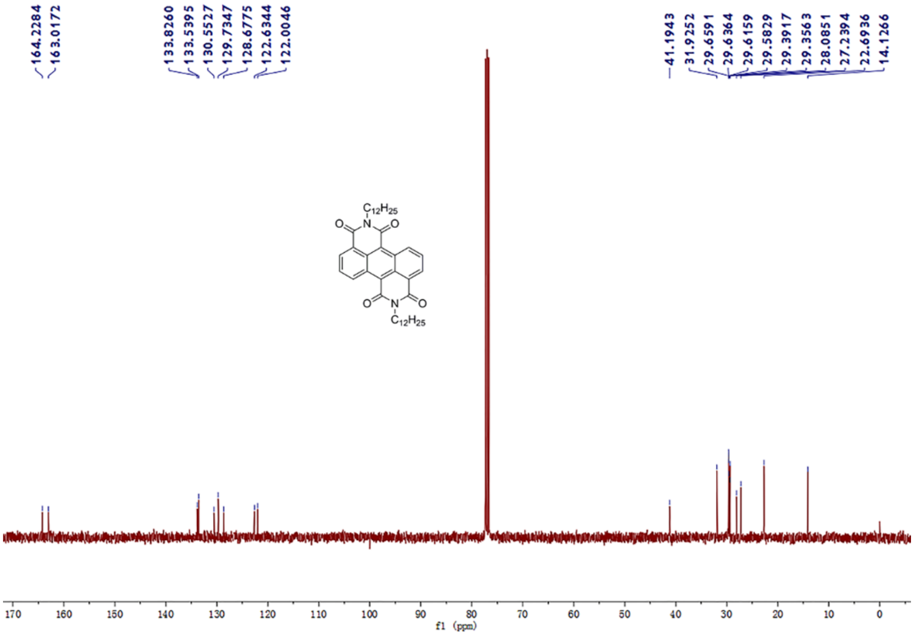


Figure S11. ^{13}C NMR spectrum of compound **6c**.

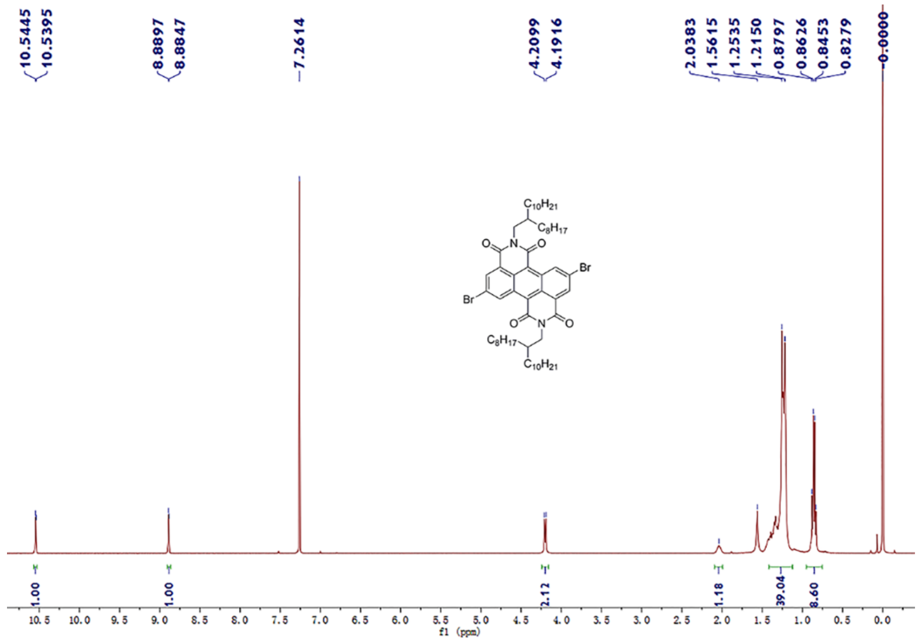


Figure S12. ^{1}H NMR spectrum of 3,7-2Br-ADI.

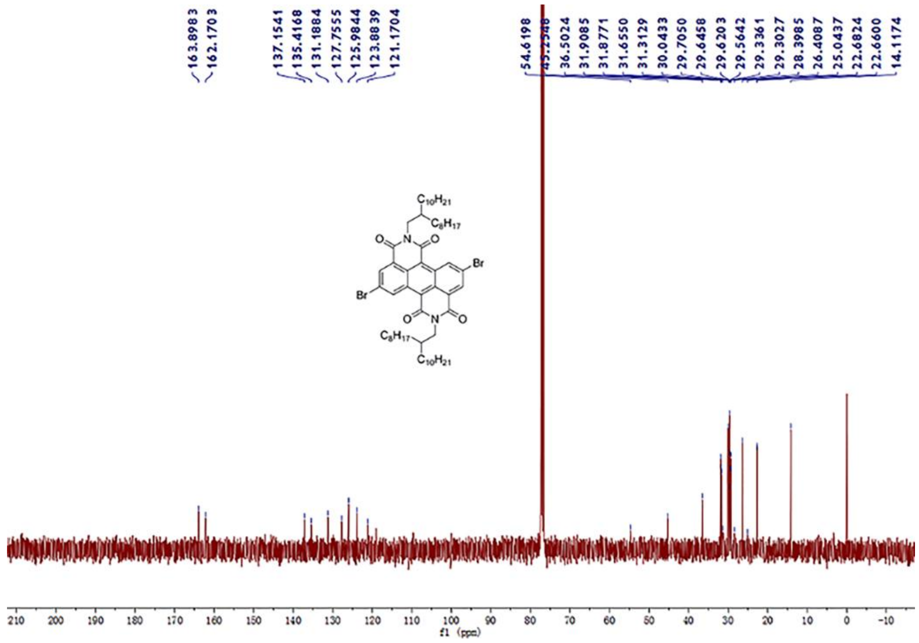


Figure S13. ^{13}C NMR spectrum of 3,7-2Br-ADI.

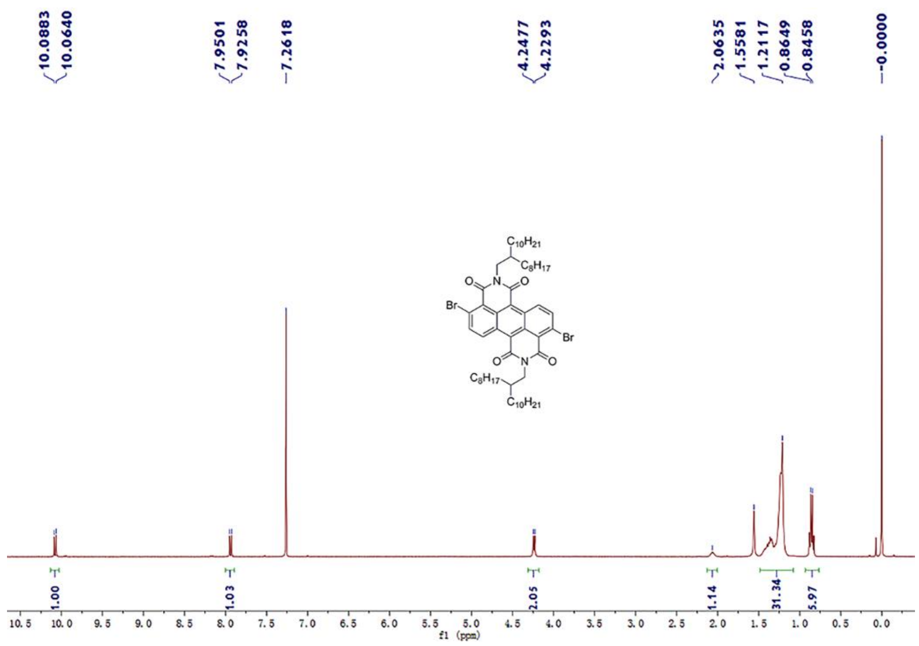


Figure S14. ^{1}H NMR spectrum of 2,6-2Br-ADI.

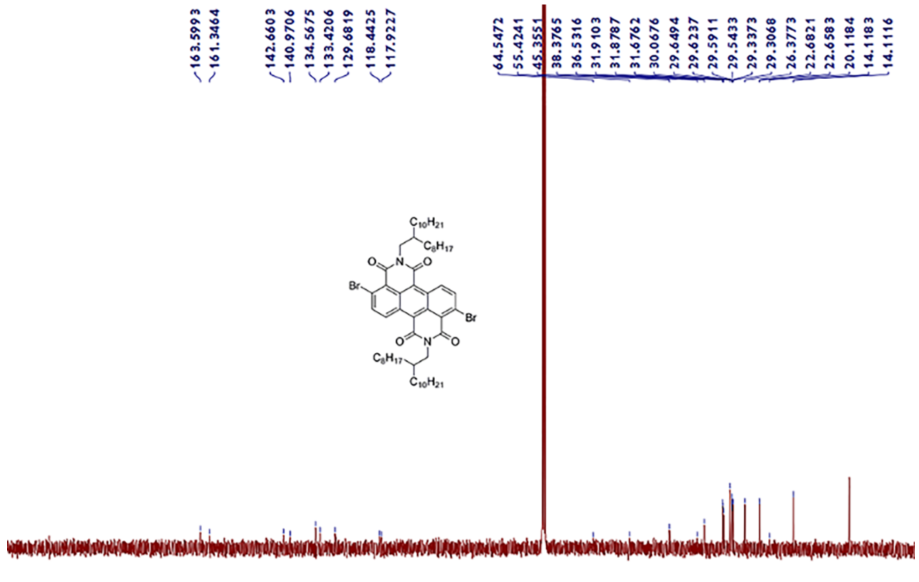


Figure S15. ^{13}C NMR spectrum of 2,6-2Br-ADI.

Table S1. Optimization of the post-bromination conditions.

Entry	Temp/^{o}C	dose	Time/h	pretreatment	Product/yield
1	80	2 equiv	10	rt stir 20min	trace
2	50	1.5 equiv	24	rt stir 20min	trace
3	50	2.5 equiv	48	rt stir 20min	trace
4	50	7.5 equiv	72	rt stir 20min	trace
5	60	5 equiv	60	rt stir 20min	trace
6	65	8 equiv	24	65 ^{o}C stir 5h	26%
7	65	10 equiv	60	65 ^{o}C stir 4h	22%

After screening different bromination reagent/solvent: Br_2/nitrobenzene, Br_2/conc. H_2SO_4, and DBH/conc. H_2SO_4, the DBH/conc. H_2SO_4 was chosen as the bromination reagent/solvent.

Table S2. Crystal coherence length (CCL), d spacing distance (d) of PADI-3,7-2T and PADI-2,6-2T, obtained by the GIXD measurement.

polymer	d^{a} [100] (nm)	CCL^{b} [100] (nm)	d^{a} [010] (nm)	CCL^{b} [010] (nm)
	IP/OOP	IP/OOP	IP/OOP	IP/OOP
PADI-3,7-2T (as cast)	2.38/2.31	10.3/9.1	0.35/0.35	2.9/2.5
PADI-3,7-2T (TA)	2.37/2.38	6.8/10.7	0.35/0.35	3.9/2.9
PADI-2,6-2T (as cast)	2.32/2.32	13.4/11.3	0.38/0.38	5.3/3.4
PADI-2,6-2T (TA)	2.32/2.34	11.7/13.6	0.38/0.38	5.8/4.1

^{a}Calculated from equation: $d=2\pi/q$. ^{b}Calculated from Scherrer equation: $CCL=2\pi K/\Delta q$, where Δq is the full-width at half-maximum of the peak and K is a shape factor (0.9 was used here).

References

1. P. G. Del Rosso, M. F. Almassio, M. Bruno and R. O. Garay, *Tetrahedron Lett.*, 2010, **51**, 6730-6733.

2. U. Herrmann, B. Tummler, G. Maass, P. K. T. Mew and F. Vogtle, *Biochem.*, 1984, **23**, 4059-4067.