

Synthesis of acenaphthene fused azabenzannulated perylene diimide for ambipolar organic field-effect transistors

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1. General information

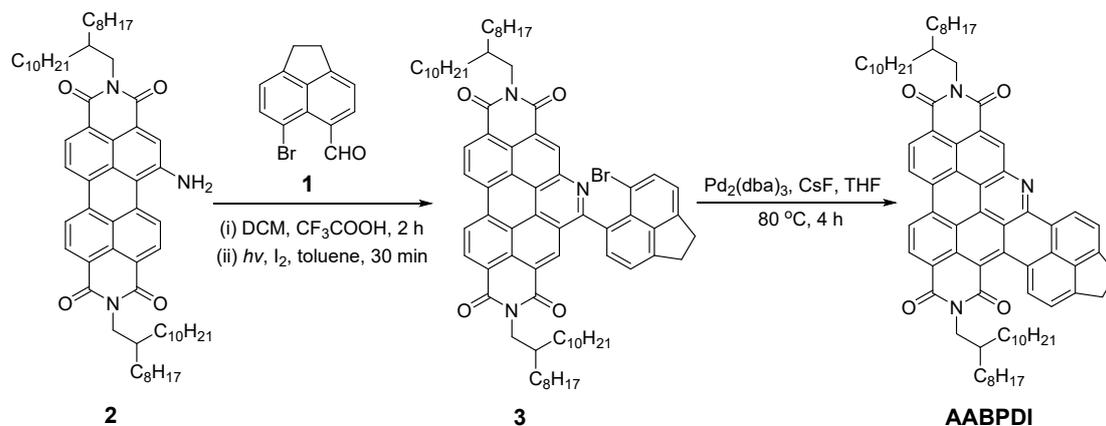
All chemical reactions were conducted in oven-dried or flame-dried glassware. All the chemicals and starting materials were purchased from commercial sources without further treatment unless specially noted. Anhydrous THF was dried over sodium shavings. Compounds **1** and **2** was synthesized according to literature procedures.¹⁻⁴

¹H NMR and ¹³C NMR spectra were measured on Bruker Avance IIIHD. MALDI-TOF Mass spectrum was measured with AB Sciex 5800. UV-vis spectrum was recorded on Shimadzu UV-1800. Cyclic voltammograms (CVs) were obtained on CHI660E electrochemical workstation. A three-electrode one-compartment cell containing a solution of the analyte and supporting electrolyte (tetrabutylammonium, ([NBu₄]PF₆), 0.1 M) in dry CH₂Cl₂ was utilized. The three-electrode were a 500 μm diameter platinum-disk as working electrode, a platinum-wire as counter electrode, and an Ag/AgCl as reference electrode. The measurements were obtained under a scanning rate of 100 mV/s. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q-600 under a nitrogen atmosphere at a heating rate of 10 °C/min.

The bottom-gate-top-contact (BGTC) OFET devices with **AABPDI** as channel materials was fabricated to evaluate their semiconducting properties. A highly doped silicon wafer, with a thermally grown SiO₂ layer of 300 nm thickness ($C_i = 11 \text{ nF cm}^{-2}$), under the following pretreatment process: ultrasonic cleaning of the substrate using deionized water, acetone, and isopropyl alcohol (IPA) for 15 minutes, respectively. Subsequently, treatment in piranha solution (composed of H₂SO₄/H₂O₂ in a ratio of 7:3 v/v) for 30 minutes followed by rinsing with deionized water and IPA; deposition of Octadecyltrichlorosilane (OTS) on the piranha solution treated substrate to passivate the hydroxyl groups. Solutions containing concentrations of 5 mg mL⁻¹ for both compounds were prepared using chloroform as the solvent and stirred at room temperature for 5 h. Thin films were then spin-coated onto the OTS modified SiO₂ dielectric layer at a speed of 6000 rpm for 50 seconds. Gold source/drain electrodes (W/L = 150 μm/2000 μm) with a thickness of 30 nm were thermally evaporated onto

either the as-casted or thermally annealed semiconducting layers to complete OFET fabrication.

2. Material Synthesis



Scheme S1 Synthetic pathway toward AABPDI.

Compound **3**: Compound **1** (261 mg, 1 mmol) and Compound **2** (966 mg, 1 mmol) were dissolved in CH₂Cl₂ (48 mL) under air atmosphere, then trifluoromethanesulfonic acid (0.5 mL) was added under stirring. After stirring at room temperature for 2 h, the organic solvent was removed by vacuum rotary evaporator, and the remaining solid was dissolved in toluene with iodine (100 mg). The reaction mixture solution was drawn into a home-built flow reactor for photocyclization reaction. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (PE:CH₂Cl₂ = 1:2, v/v). Compound **3** (990 mg, 82%) was obtained as a red solid. ¹H NMR (500 MHz, Chloroform-*d*) δ (ppm) 9.60 (s, 1H), 9.33-9.32 (m, 2H), 9.16 (d, *J* = 8.2 Hz, 1H), 9.15-9.05 (m, 1H), 9.05 (s, 1H), 7.78 (dd, *J* = 6.8, 2.8 Hz, 1H), 7.58 (dd, *J* = 14.1, 7.2 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 4.24 (d, *J* = 6.9 Hz, 2H), 4.15 (d, *J* = 7.2 Hz, 2H), 3.63-3.61 (m, 2H), 3.63-3.51 (m, 2H), 2.12-2.08 (m, 1H), 2.02-1.97 (m, 1H), 1.26-1.18 (m, 64H), 0.84-0.81 (m, 12H). ¹³C NMR (126 MHz, Chloroform-*d*) δ (ppm) 163.8, 163.7, 163.5, 162.6, 149.1, 147.0, 143.5, 141.4, 134.4, 134.2, 132.9, 132.6, 132.6, 130.8, 129.3, 129.2, 128.1, 128.0, 126.3, 125.6, 125.4, 123.7, 123.4, 123.4, 122.8, 122.7, 122.3, 121.2, 119.8, 114.0, 36.9, 36.7, 31.9, 31.9, 31.8, 31.7, 31.7, 30.1, 30.1, 30.1, 29.7, 29.6, 29.6, 29.6, 29.3, 29.3, 29.3, 26.6, 26.5, 22.7, 22.6, 14.1. HRMS (MALDI-TOF) *m/z* [M+H]⁺ calcd for C₇₇H₉₆BrN₃O₄ 1206.6662; found 1206.6667.

Compound AABPDI: Compound **3** (1.21 g, 1 mmol) was added to a 100 mL two-neck round bottom flask. The flask was purged with N₂ for 30 min, followed by the addition of Pd₂(dba)₃ (113.7 mg, 0.1 mmol) and THF (36 mL). The resulting mixture

was stirred at 80 °C for 4 h. Water was added to quench the reaction and the reaction mixture was extracted three times with CH₂Cl₂. The organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified on a silica-gel column chromatography with PE:CH₂Cl₂ = 1:2 (v/v). Compound **AABPDI** (754.8 mg, 67%) was obtained as green solid. ¹H NMR (600 MHz, Chloroform-*d*) δ (ppm) 8.55-8.54 (m, 1H), 8.37 (s, 1H), 8.25 (s, 2H), 8.17 (s, 1H), 7.99 (d, *J* = 45.9 Hz, 3H), 7.31-7.28 (m, 2H), 4.09 (s, 4H), 3.54 (s, 4H), 2.12 (s, 1H), 2.02 (s, 1H), 0.89-0.80 (m, 12H). ¹³C NMR (126 MHz, Chloroform-*d*) δ (ppm) 165.4, 163.2, 162.8, 162.6, 153.1, 151.9, 148.5, 142.7, 139.2, 138.4, 135.3, 131.3, 130.3, 128.5, 127.4, 126.2, 124.9, 124.5, 124.3, 122.4, 121.8, 121.3, 120.9, 120.8, 120.2, 120.0, 119.4, 116.2, 115.2, 37.1, 36.9, 32.1, 32.0, 32.0, 31.9, 31.8, 31.6, 31.5, 30.5, 30.4, 30.3, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 26.6, 22.8, 22.7, 22.7, 14.2, 14.1, 14.1. HRMS (MALDI-TOF) *m/z* [M+H]⁺ calcd for C₇₇H₉₆N₃O₄ 1126.7401; found 1126.7436.

3. Optical properties

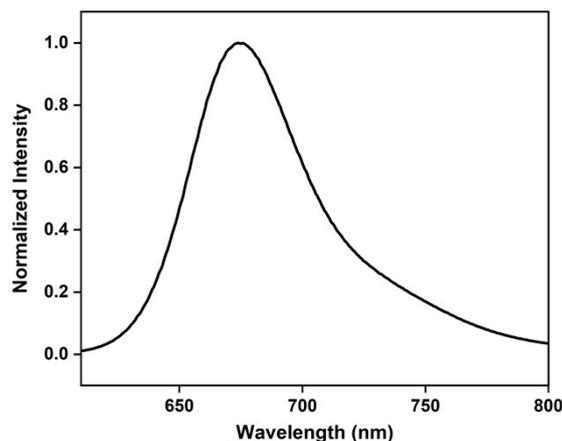


Fig. S1 The normalized emission spectra of **AABPDI** in chloroform solution (1.0×10^{-5} M).

4. Thermogravimetric analysis (TGA):

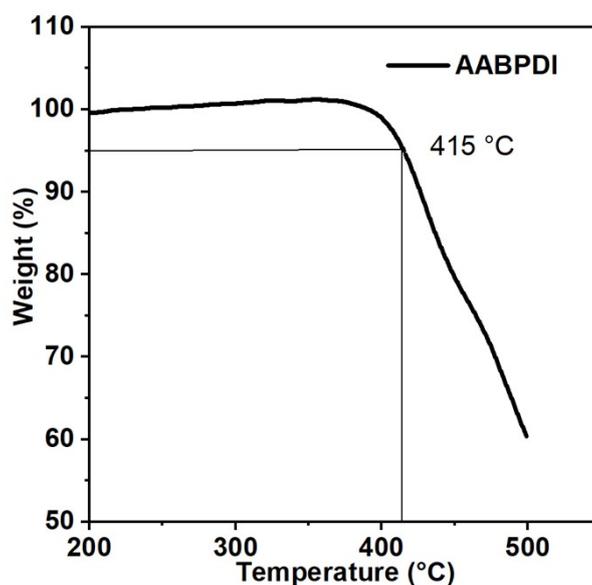


Fig. S2 TGA thermogram of compound AABPDI.

5. Optical and electrochemical properties

Table S1 Optical and electrochemical parameters of compound AABPDI.

compound	ϵ^a $M^{-1} cm^{-1}$	E_{red}^b (V)	E_{ox}^c (V)	E_{HOMO}^d (eV)	E_{LUMO}^d (eV)	$E_g^{opt e}$ (eV)	$E_g^{exp f}$
AABPDI	0.7×10^5 (452 nm)	-0.63	1.1	-5.45	-3.72	1.85	1.73
	0.2×10^5 (626 nm)						

^aThe molar extinction coefficient ϵ were measured in the $CHCl_3$ solutions of a concentration of 5.0

$\times 10^{-6} M$; ^bThe first reduction potential and ^cthe first oxidation potential were measured by CV;

^dHOMO/LUMO levels were calculated by the following equations: $E_{HOMO} = -(E_{ox} - E_{Fc} + 4.8)$ eV,

$E_{LUMO} = -(E_{red} - E_{Fc} + 4.8)$ eV, E_{Fc} is the ferrocene potential of -0.45 V; ^eBand gap values

determined from solution absorption spectra using the equation: $E_g^{\text{opt}} = 1240/\lambda$ (onset) ; ^fThe band gap calculated from the difference between HOMO and LUMO levels according to CV results.

6. The organic field-effect transistors (OFETs) performance of the devices

Table S2 Organic field effect transistor properties of compound **AABPDI** with different annealing temperature.

Compound	Annealing temperature	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	$I_{\text{ON}}/$ I_{OFF}	V_{TH} (V)	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	$I_{\text{ON}}/$ I_{OFF}	V_{TH} (V)
AABPDI	As	-	-	-	5.00×10^{-4}	10^3	43
	60 °C	-	-	-	4.00×10^{-3}	10^4	42
	120 °C	7×10^{-3}	10^3	61	1.17×10^{-1}	10^5	48
	Two steps annealing	1.1×10^{-2}	10^3	60	1.65×10^{-1}	10^5	45

Two steps annealing, The sample was preheated at a low temperature of 60 °C and then annealed at 120 °C.

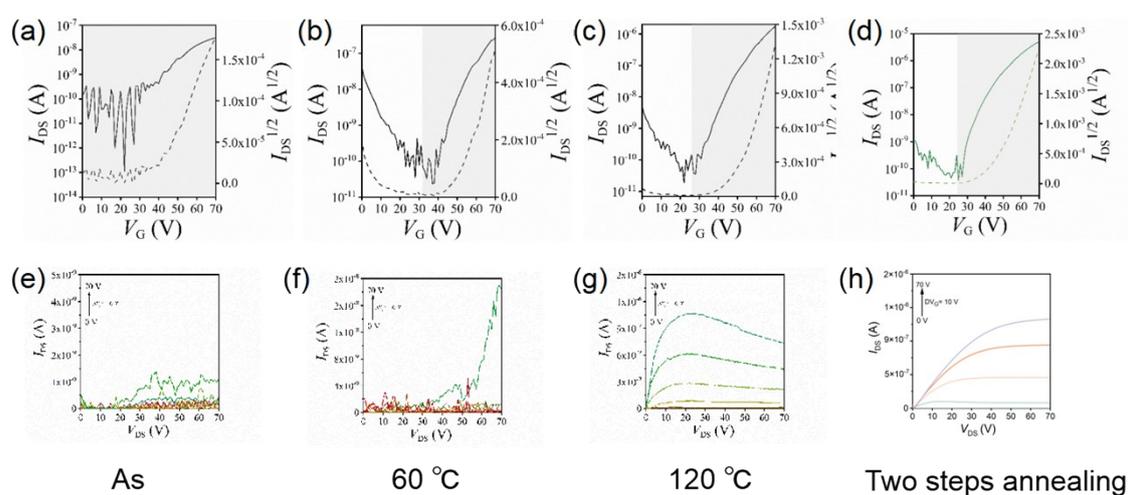


Fig.S3 The transfer characteristics and output characteristics of the thin films n-type OFET

devices of compound **AABPDI**.

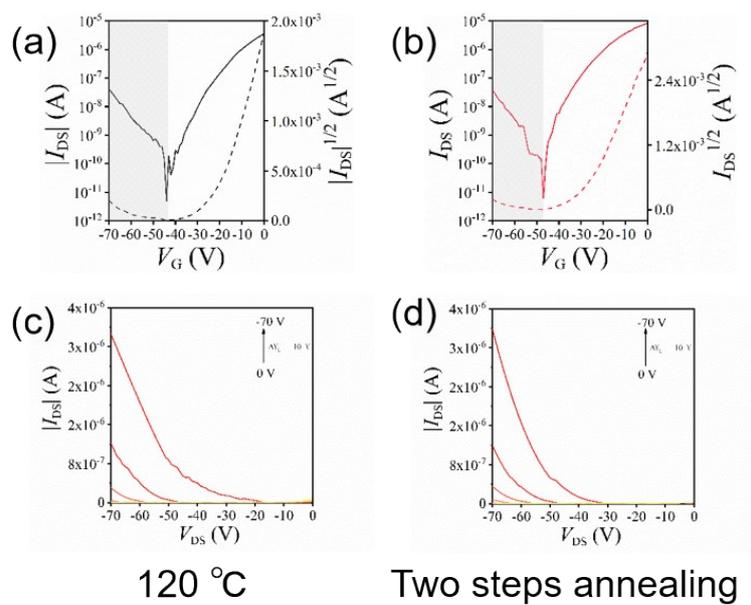


Fig. S4 The transfer characteristics and output characteristics of the thin films p-type OFET devices of compound **AABPDI**.

7. Reference

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8. Appendix

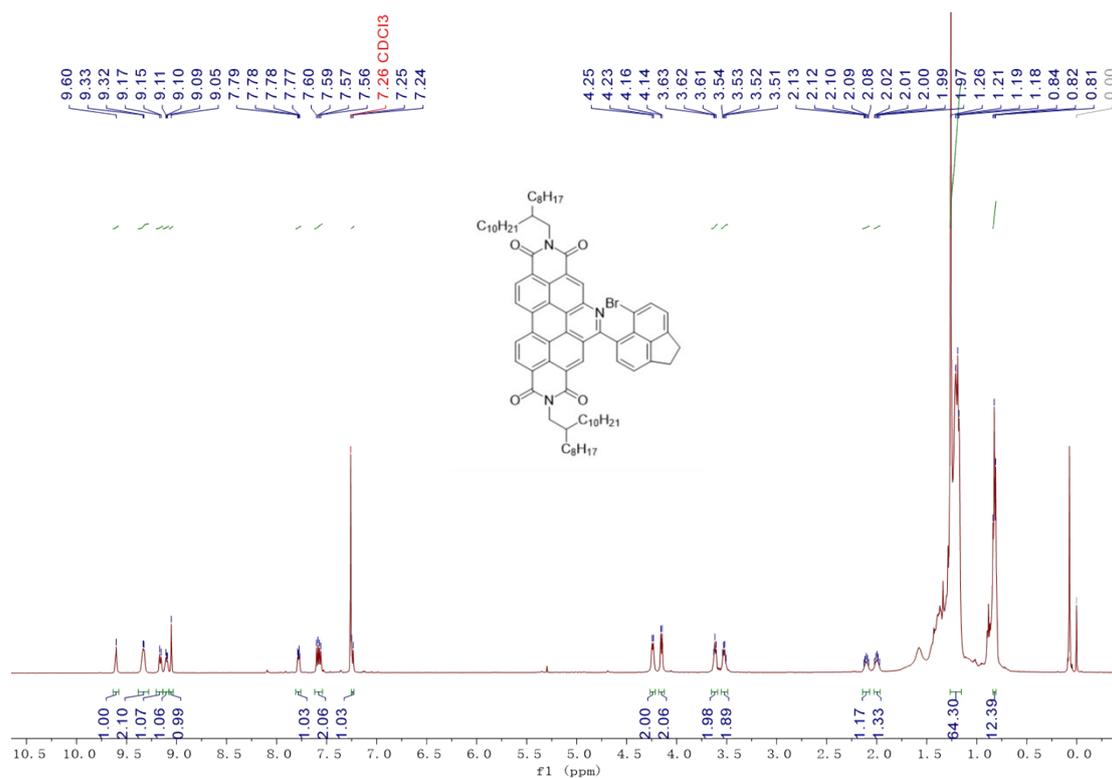


Fig. S5 ¹H NMR spectra for 3.

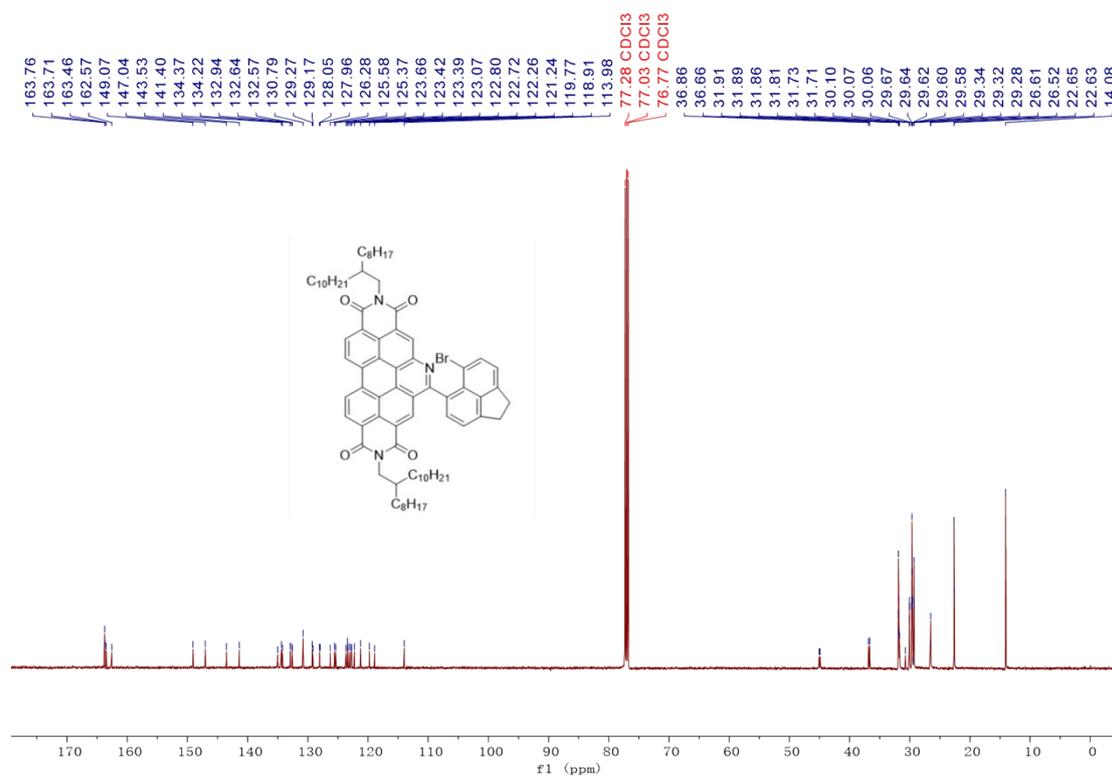


Fig. S6 ¹³C NMR spectra for 3.

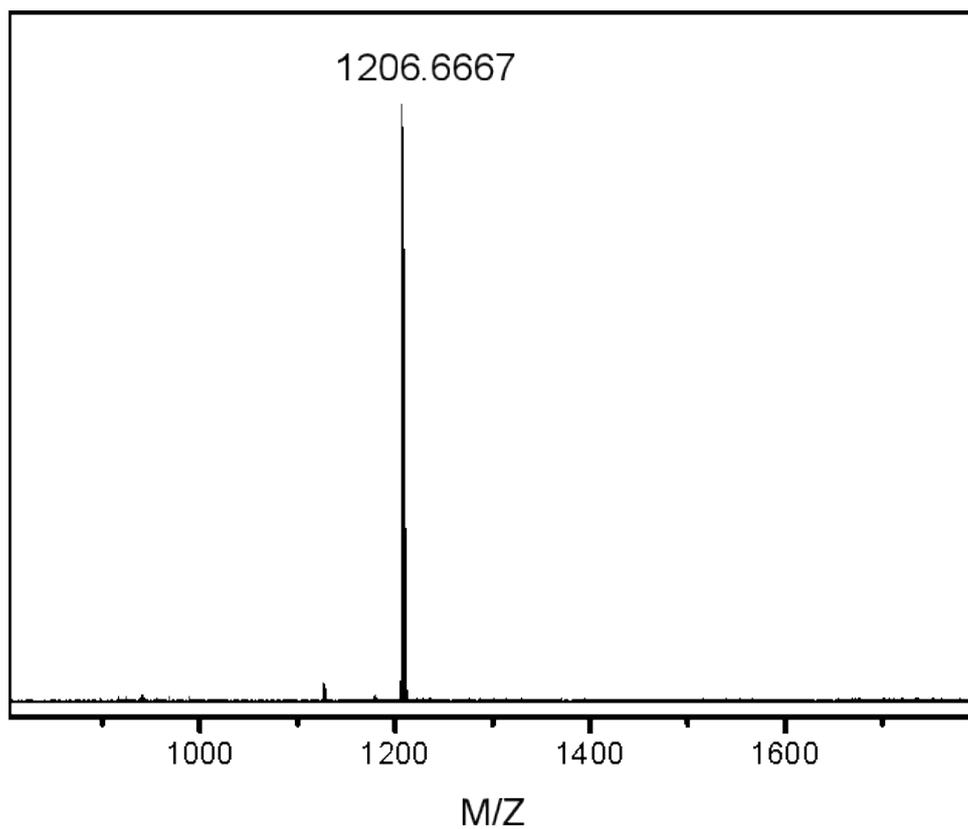


Fig. S7 MALDI-TOF Mass Spectrum for **3**.

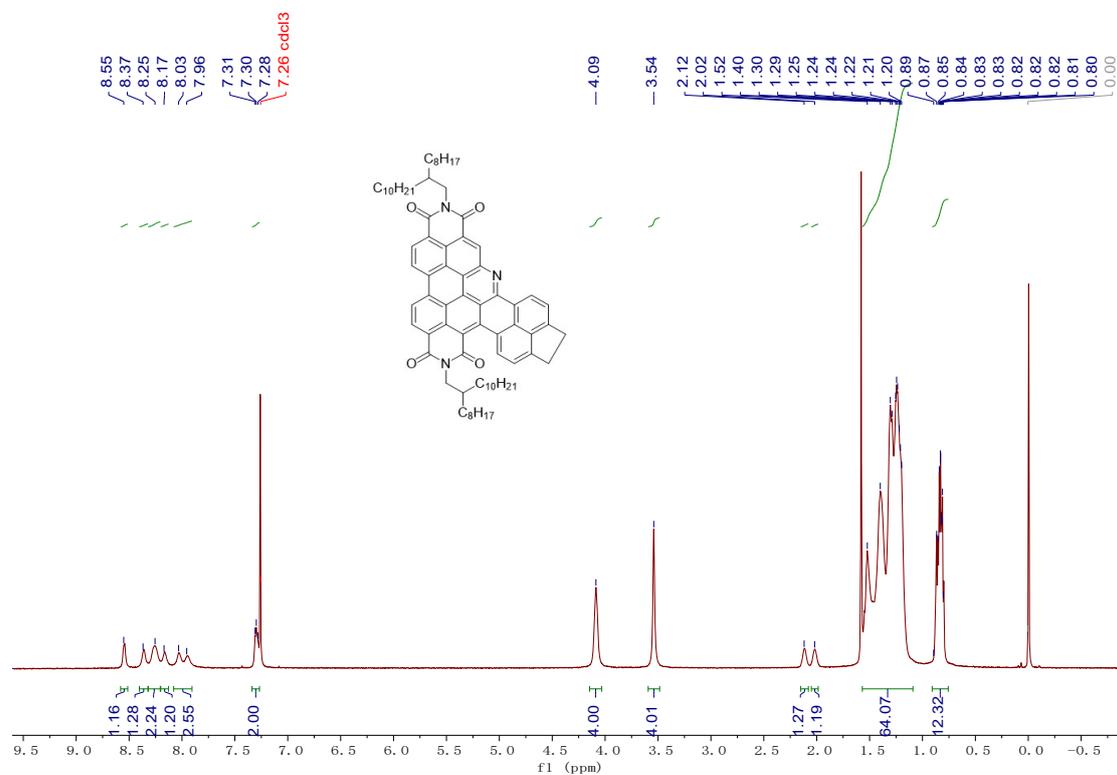


Fig. S8 ^1H NMR spectra for AABPDI.

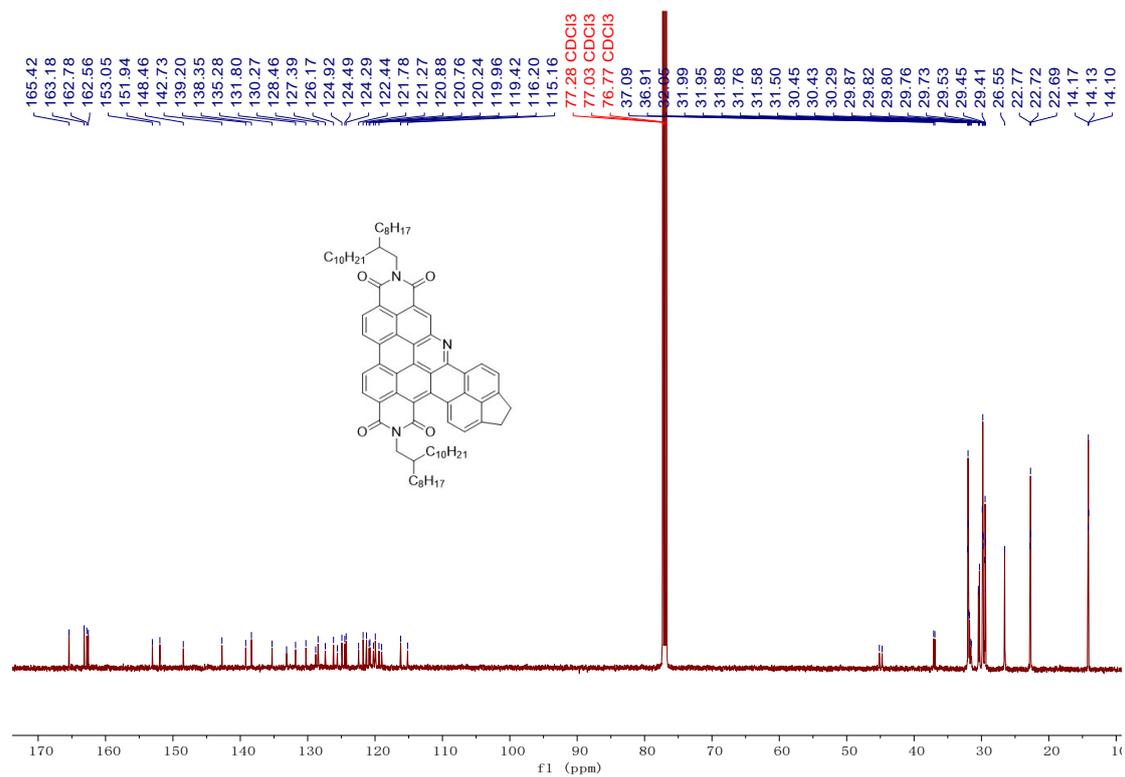


Fig. S9 ¹³C NMR spectra for AABPDI.

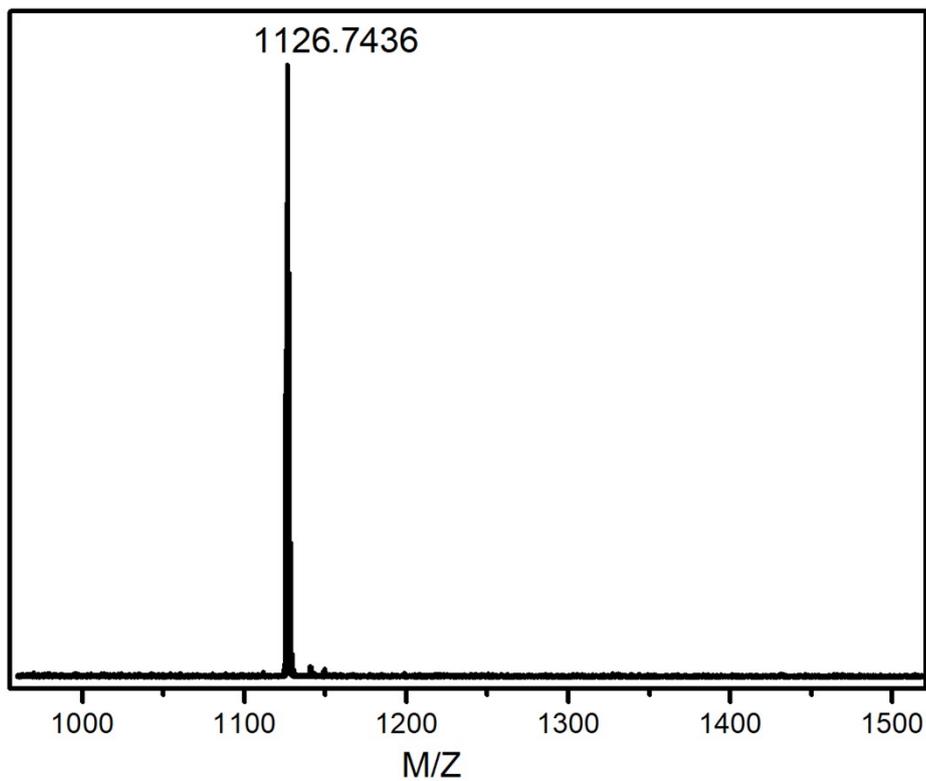


Fig. S10 MALDI-TOF Mass Spectrum for AABPDI.