

AzaBenzannulated PeryleneDiimide Multimers as Electron Acceptors

Aline Makhoutah,^{†a} Anderson Hoff,^{†b} Antoine Goujon,^{*a} Gregory C. Welch,^{*b} Piétrick
Hudhomme^{*a}

a Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F- 49000 Angers, France.

[†]These authors contributed equally

b Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4,
Canada.

E-mail: antoine.goujon@univ-angers.fr

pietrick.hudhomme@univ-angers.fr

gregory.welch@ucalgary.ca

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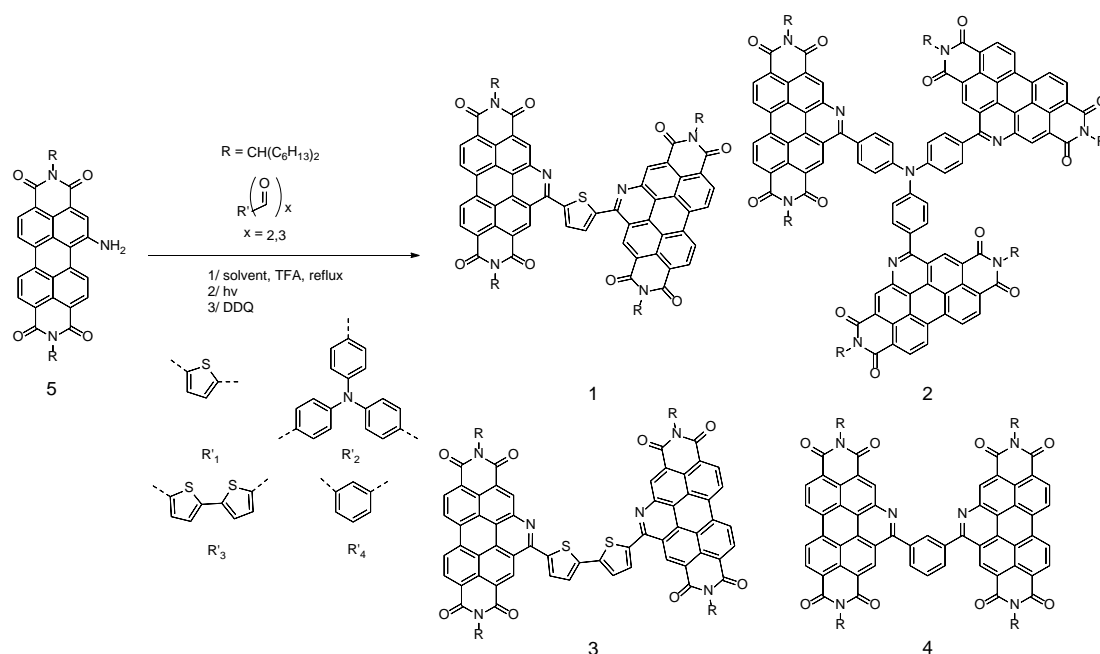
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1. Materials and Methods

Materials and General Methods. Thin Layer Chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm MerckAlugram SIL G/UV254 with fluorescent indicator UV254. Column chromatography was carried out using Sigma-Aldrich silica gel 60 (particle size 63-200 μm). Preparative SEC separation was performed on a JAI recycling SEC HPLC equipped with two HR-2 columns at 10 mL/min in chloroform. UV-Vis absorptions were recorded on a Shimadzu UV-1800 UV-Vis spectrophotometer using quartz cell (pathlength of 1 cm). Cyclic voltammetry experiments were carried out at room temperature with a Bio-Logic SAS SP-150 potentiostat. Nuclear magnetic resonance (NMR) ^1H and ^{13}C spectra were obtained on a Bruker 300 MHz Avance III spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) or 500 MHz Avance III HD spectrometer (125 MHz for ^{13}C). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (CDCl_3 : $\delta\text{H} = 7.26$ ppm). Coupling constants (J) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad signal). Carbon spectra were acquired with a complete decoupling for the proton. High resolution mass spectrometry (HRMS) was performed with a JEOL JMS S3000, MALDI ionisation and SPIRAL TOF detector. TGA was performed with a TA Instruments Q500. Photocyclizations were carried out by introducing the reaction flasks in a homemade photoreactor consisting of a plastic cylinder in which the inside wall was covered by a 1.5 meters white LEDs ribbon (~ 100 LEDs), power of 7 W. Chemicals were purchased from Sigma Aldrich, Acros Organics, Fisher Scientific, Alfa Aesar, Fluorochem, and were used as received. Solvents were purchased from Sigma Aldrich, Fluorochem, or Fischer Scientific, deuterated solvents from Sigma Aldrich. Bio-BeadsTM S-X3 resin was purchased from Bio-Rad.

Abbreviations. AzaBPDI : AzaBenzannulatedPerylenediimide; DDQ : 2,3-dichloro-5,6-dicyanobenzoquinone; equiv: equivalent; HOMO : highest occupied molecular orbital; HPLC-SEC: High-performance liquid chromatography - Size exclusion chromatography; HRMS : high resolution mass spectrometry; LUMO : lowest unoccupied molecular orbital; NMR : Nuclear Magnetic Resonance; PDI : perylenediimide; rt : room temperature; TFA : Trifluoroacetic Acid.

2. Synthesis



Scheme S1. Synthesis of AzaBPDI **1**, **2**, **3** and **4**.

Compound 1. This dye was prepared according to previously reported procedure.¹

Compound 2. Compound 5 (380 mg, 0.5 mmol, 6 equiv.) was dissolved in toluene (13 mL) along with [2,2'-bithiophene]-5,5'-dicarbaldehyde (18 mg, 0.08 mmol, 1 equiv.) and 160 μL of TFA. The solution was refluxed for one hour. The solvent was evaporated under vacuum. The purple residue was taken back in CH_2Cl_2 (150 mL) and stirred at room temperature (rt) while being exposed to visible light (white LED, 7 W) overnight. The resulting dark green solution was stirred at rt with DDQ (38 mg, 0.17 mmol, 2 equiv.) for 2 min. A mixture containing both bis- and trisAzaBPDI was obtained. The solvents were removed under vacuum, and the residue was purified on column chromatography (SiO_2 , CH_2Cl_2) and precipitated from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. The bis- and tris-AzaBPDI were separated using HPLC-SEC coupled with UV to finally afford compound **2** as a yellow brown solid (38 mg, 18%). ^1H NMR (300 MHz, CDCl_3) δ 9.99 – 9.73 (br, 3H), 9.72 – 9.72 (br, 3H), 9.46 – 8.90 (m, 12H), 8.34 – 8.09 (m, 6H), 8.06 – 7.83 (m, 6H), 5.46 – 5.20 (m, 6H), 2.53 – 2.20 (s, 12H), 2.18 – 1.83 (m, 12H), 1.58 – 0.96 (m, 96H), 0.98 – 0.54 (m, 36H). ^{13}C NMR (125 MHz, CDCl_3) δ 164.8, 163.6, 160.6, 148.8, 144.4, 134.7, 134.5, 134.3, 133.7, 132.7, 131.5, 130.8, 129.7, 129.5, 129.2, 128.3, 126.6, 125.9, 125.4, 123.8, 123.3, 123.1, 122.9, 122.1, 121.9, 118.4, 55.3, 32.6, 31.9, 29.4, 27.2, 22.7, 14.2 HRMS (MALDI-TOF) m/z : calcd for $\text{C}_{171}\text{H}_{193}\text{N}_{10}\text{O}_{12}$ ($[\text{M}+\text{H}]^+$): 2577.4721; found: 2578.4794 (1.92 ppm error).

Compound 3. Compound 5 (197 mg, 0.256 mmol, 3.6 equiv.) was dissolved in toluene (2,5 mL) along with [2,2'-bithiophene]-5,5'-dicarbaldehyde (18 mg, 0.08 mmol, 1 equiv.) and 160 μ L of TFA. The solution was refluxed for one hour. The solvent was evaporated under vacuum. The purple residue was taken back in CH₂Cl₂ (150 mL) and stirred at rt while being exposed to visible light (white LED, 7 W) overnight. The resulting dark green solution was stirred at rt with DDQ (33.6 mg, 0.16 mmol, 2 equiv.) for 2 min. The solvents were removed under vacuum. The residue was purified using Bio-BeadsTM S-X3 resin with toluene as an eluent to recover and recycle the excess of amine. The final product was further purified on column chromatography (SiO₂, n-pentane/diethyl ether 4:1) to provide compound 3 as a red solid (108 mg, 78% over three steps). ¹H NMR (500 MHz, CDCl₃) δ 10.07 (s, 1H), 10.05 (s, 1H), 9.13 – 8.83 (m, 10H), 8.05 (s, 2H), 7.81 (d, *J* = 3 Hz, 2H), 5.47 – 5.33 (m, 2H), 5.27 – 5.18 (m, 2H), 2.55 – 2.42 (m, 4H), 2.40 – 2.29 (m, 4H), 2.12 – 2.00 (m, 8H), 1.56 – 1.20 (m, 64H), 0.94 – 0.76 (m, 24H). ¹³C NMR (125 MHz, CDCl₃) δ 164.5, 163.5, 153.0, 143.9, 142.2, 141.9, 133.60, 132.5, 131.2, 128.9, 128.2, 126.5, 126.2, 123.6, 123.0, 122.5, 120.6, 117.5, 55.4, 32.7, 32.0, 29.5, 29.4, 27.3, 27.3, 22.8, 22.7, 14.2, 14.2. HRMS (MALDI-TOF) *m/z*: calcd for C₁₁₀H₁₂₅N₆O₈S₂ ([M+H]⁺): 1721.8922 ; found: 1721.8994 (0.81 ppm error).

Compound 4. Compound 5 (150 mg, 0.2 mmol, 2,4 equiv.) was dissolved in toluene (2 mL) along with isophthalaldehyde (10,9 mg, 0.08 mmol, 1 equiv.) and 128 μ L of TFA. The solution was refluxed for one hour. The solvent was evaporated under vacuum. The purple residue was taken back in CH₂Cl₂ (150 mL) and stirred at rt while being exposed to visible light (white LED, 7 W) overnight. The resulting dark green solution was stirred at rt with DDQ (33,6 mg, 0.16 mmol, 2 equiv.) for 2 min. The solvent was removed under vacuum. The residue was purified using Bio-BeadsTM S-X3 resin with toluene as an eluent to recover and recycle the excess of amine. The final product was further purified on column chromatography (SiO₂, n-pentane/diethyl ether 4:1) to provide compound 4 as a yellow solid (73.6 mg, 56% over three steps). ¹H NMR (500 MHz, CDCl₃) δ 9.91 (s, 2H), 9.62 – 9.43 (br, 2H), 9.24 – 8.91 (m, 9H), 8.40 (d, *J* = 8 Hz, 2H), 8.16 (t, *J* = 8 Hz, 1H), 5.32 – 5,14 (m, 4H), 2,38 – 2,10 (m, 8H), 1,96 – 1,78 (m, 8H), 1,47 – 0,98 (m, 64H), 0,92 – 0,61 (m, 24H). ¹³C NMR (125 MHz, CDCl₃) δ 164.7, 163.5, 160.4, 144.5, 139.6, 135.3, 134.6, 134.1, 133.9, 133.1, 132.5, 131.3, 130.5, 129.9, 129.6, 129.3, 128.3, 126.6, 125.9, 124.6, 123.8, 123.4, 122.9, 122.1, 118.7, 55.2, 32.5, 31.8, 29.3, 27.1, 22.6, 14.1. HRMS (MALDI-TOF) *m/z*: calcd for C₁₀₈H₁₂₅N₆O₈ ([M+H]⁺): 1632,9481; found: 1633.9570 (1.02 ppm error).

Compound 5. This compound was prepared according to previously reported procedure.²

3. NMR

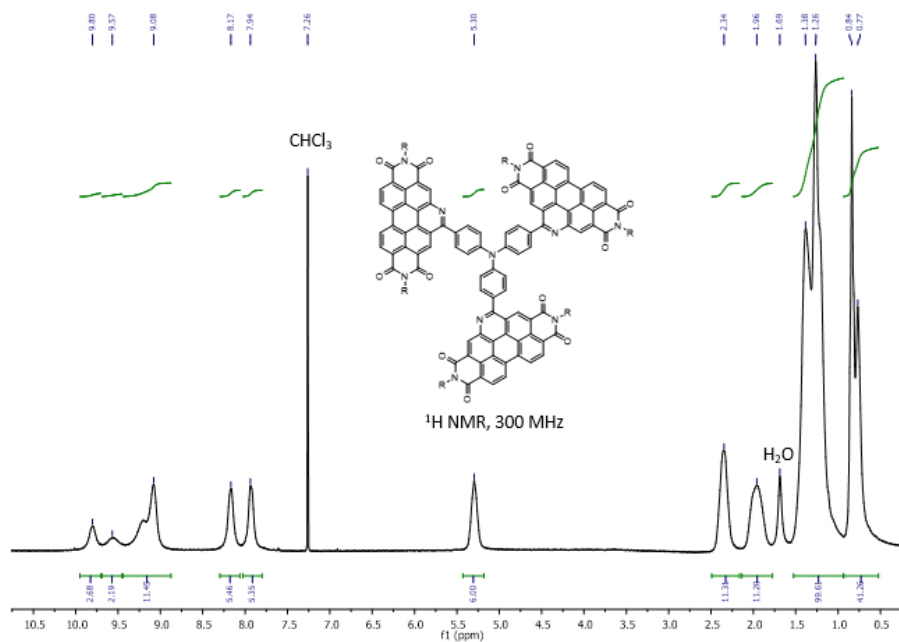


Figure S1. ¹H NMR (300 MHz) spectrum of compound **2** in CDCl₃, R=CH(C₆H₁₃)₂.

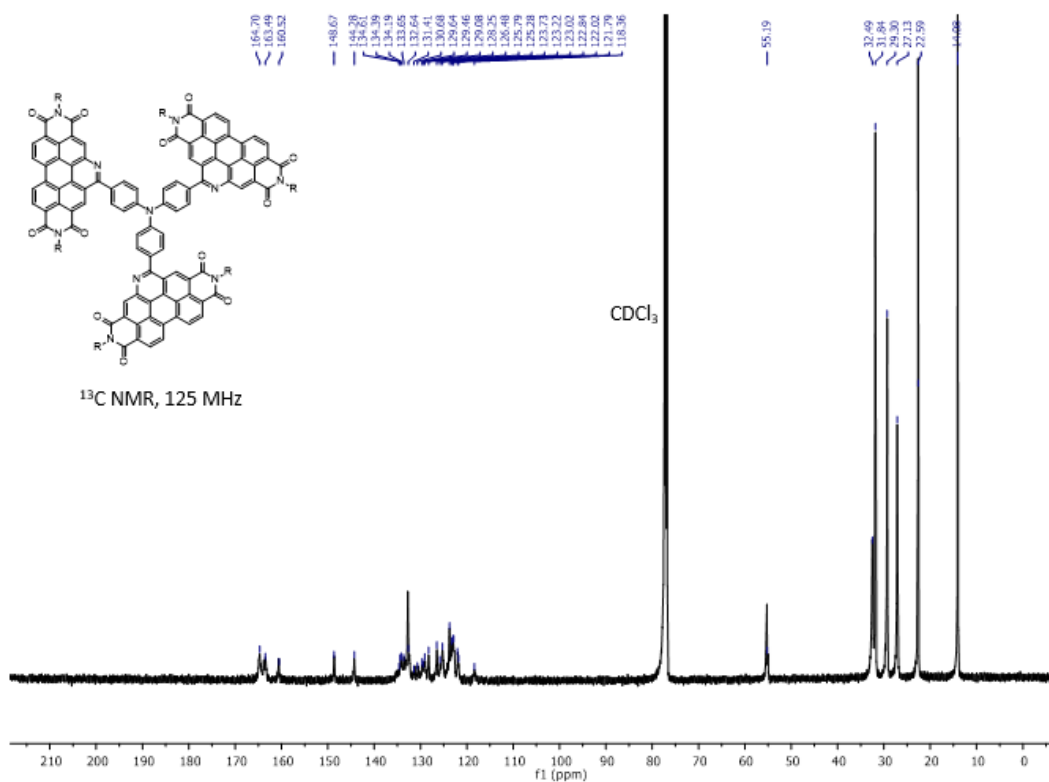


Figure S2. ¹³C NMR (125 MHz) spectrum of compound **2** in CDCl₃, R=CH(C₆H₁₃)₂.

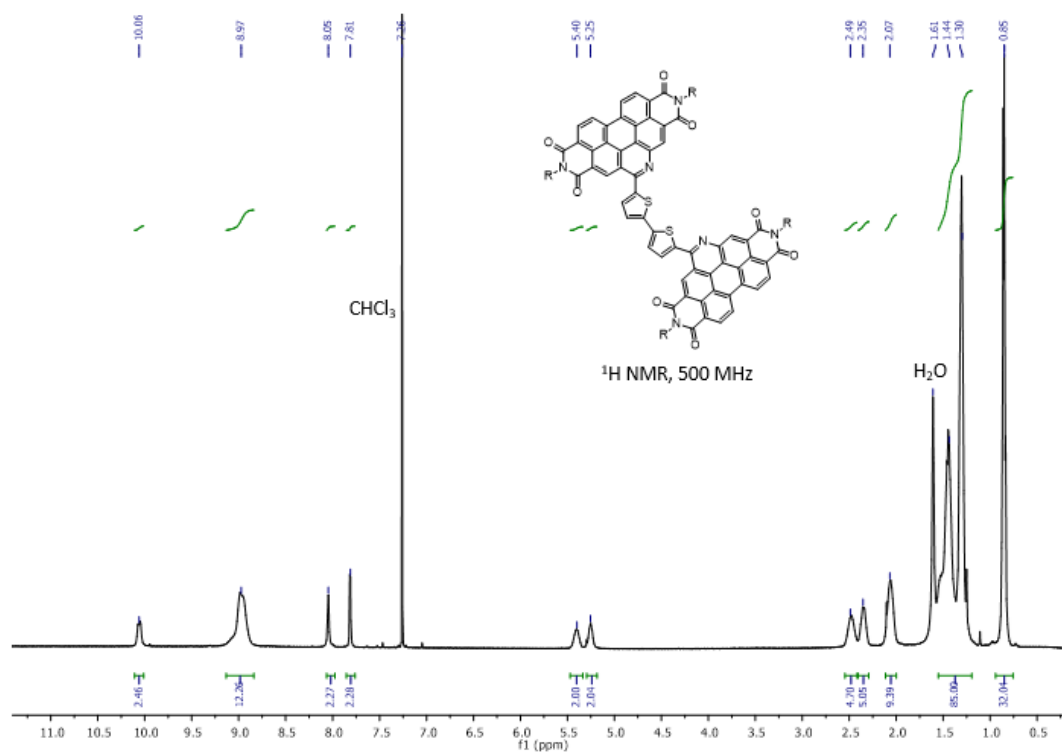


Figure S3. ¹H NMR (500 MHz) spectrum of compound **3** in CDCl₃, R=CH(C₆H₁₃)₂.

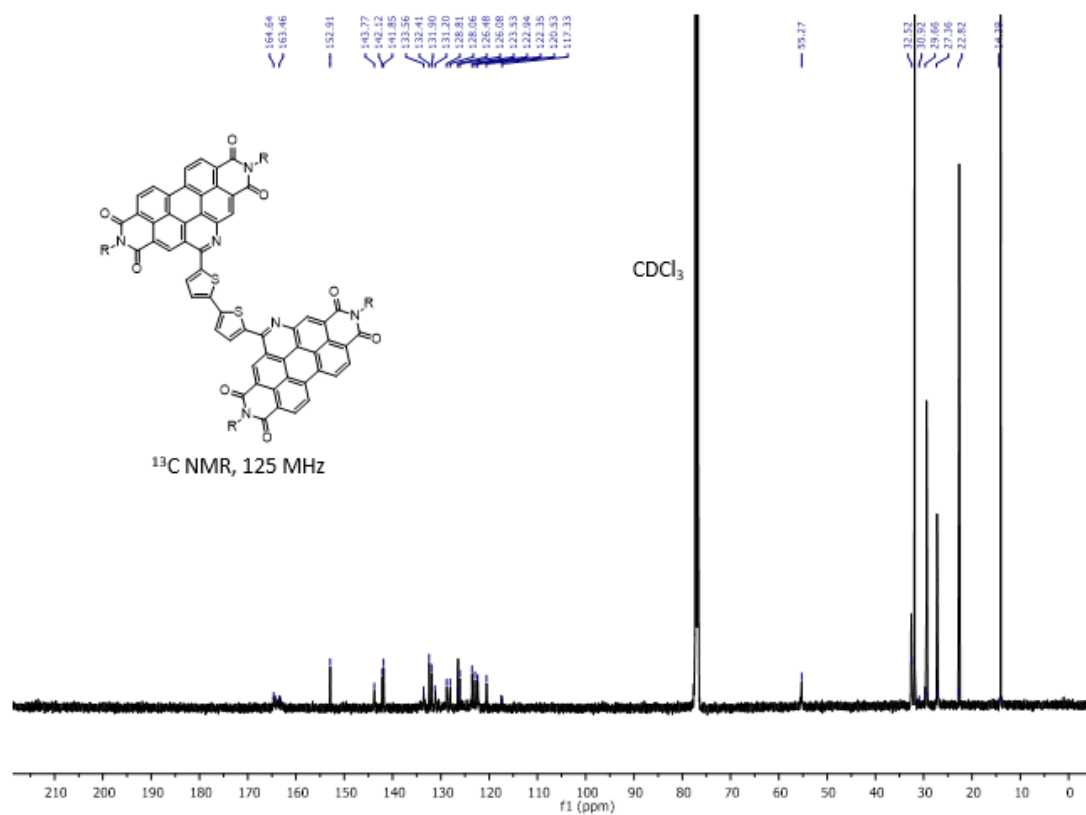


Figure S4. ¹³C NMR (125 MHz) spectrum of compound **3** in CDCl₃, R=CH(C₆H₁₃)₂.

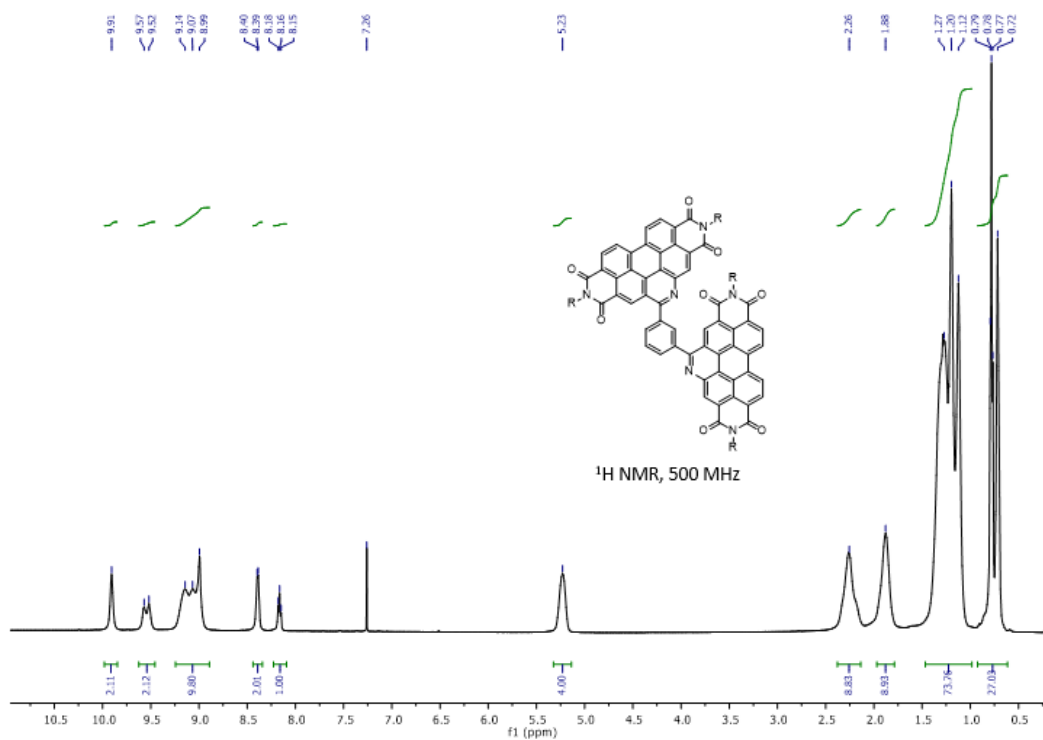


Figure S5. ¹H NMR (500 MHz) spectrum of compound **4** in CDCl₃, R=CH(C₆H₁₃)₂.

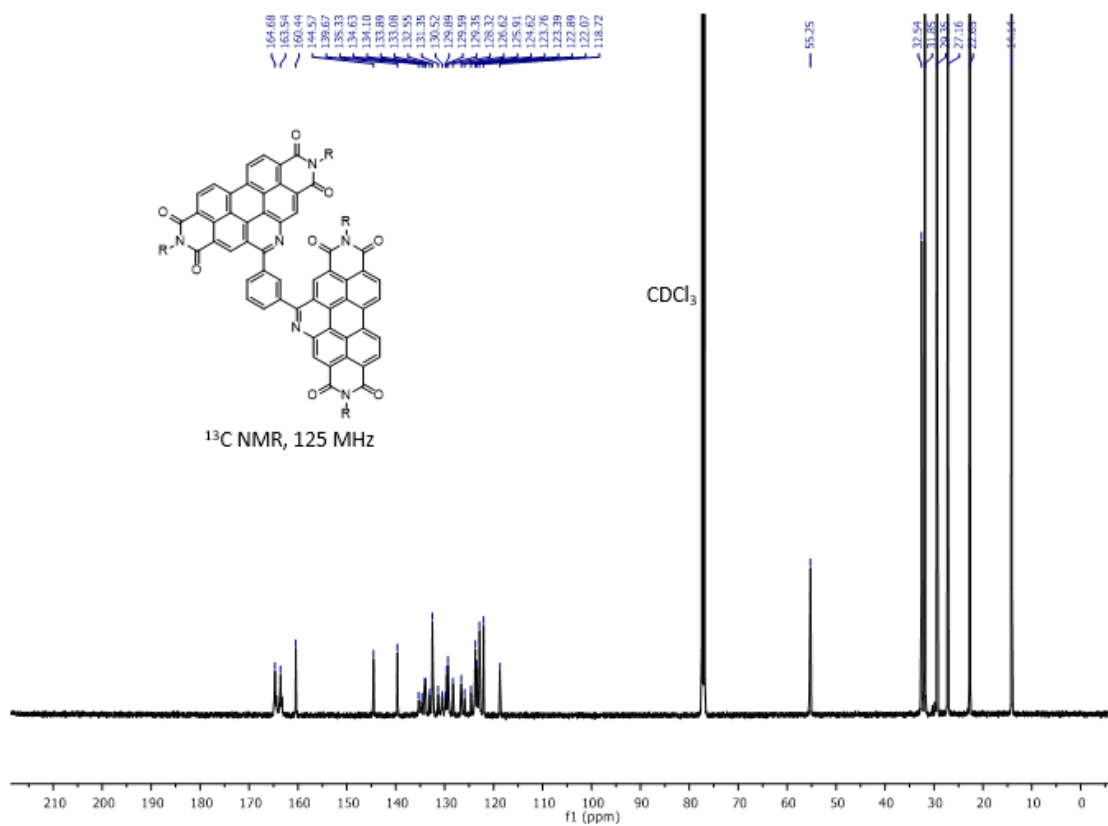


Figure S6. ¹³C NMR (125 MHz) spectrum of compound **4** in CDCl₃, R=CH(C₆H₁₃)₂.

4. High Resolution Mass Spectrometry

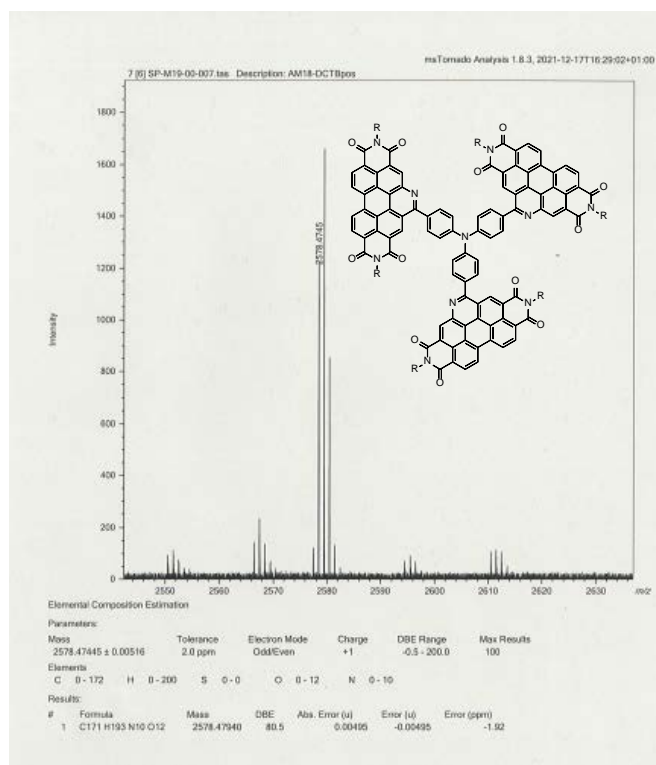


Figure S7. HRMS spectrum of compound 2.

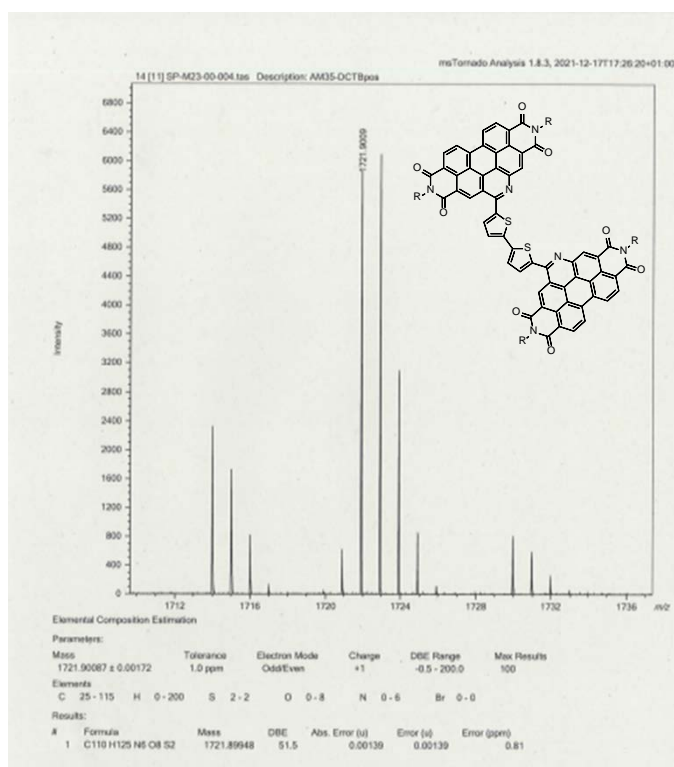


Figure S8. HRMS spectrum of compound 3.

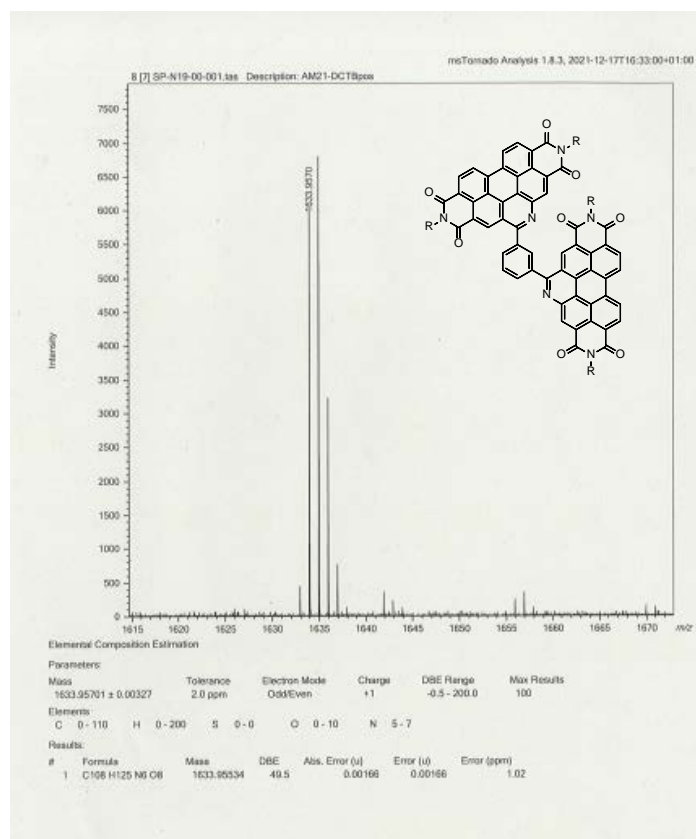


Figure S9. HRMS spectrum of compound **4**.

5. Thermogravimetric Analysis

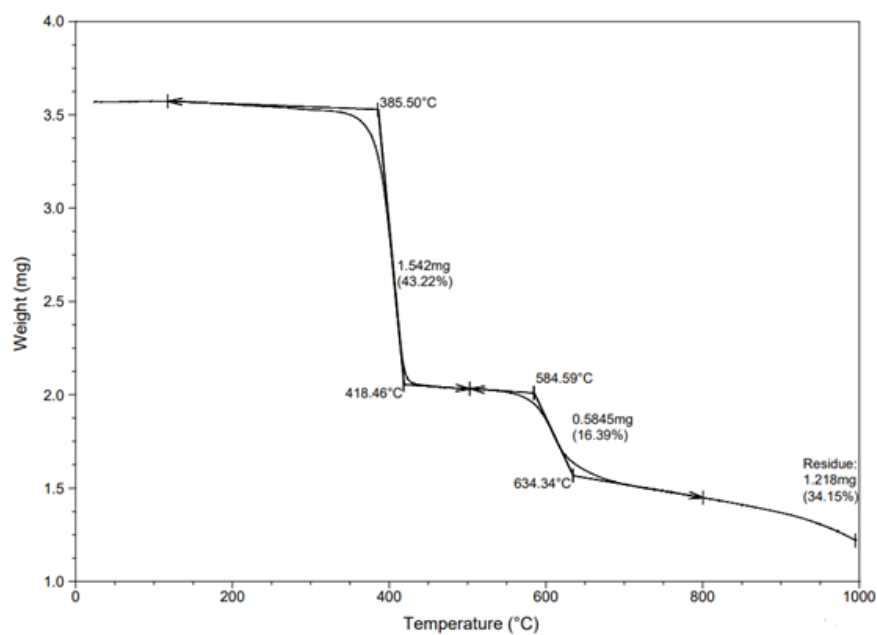


Figure S10. Thermogravimetric analysis of compound **1**.

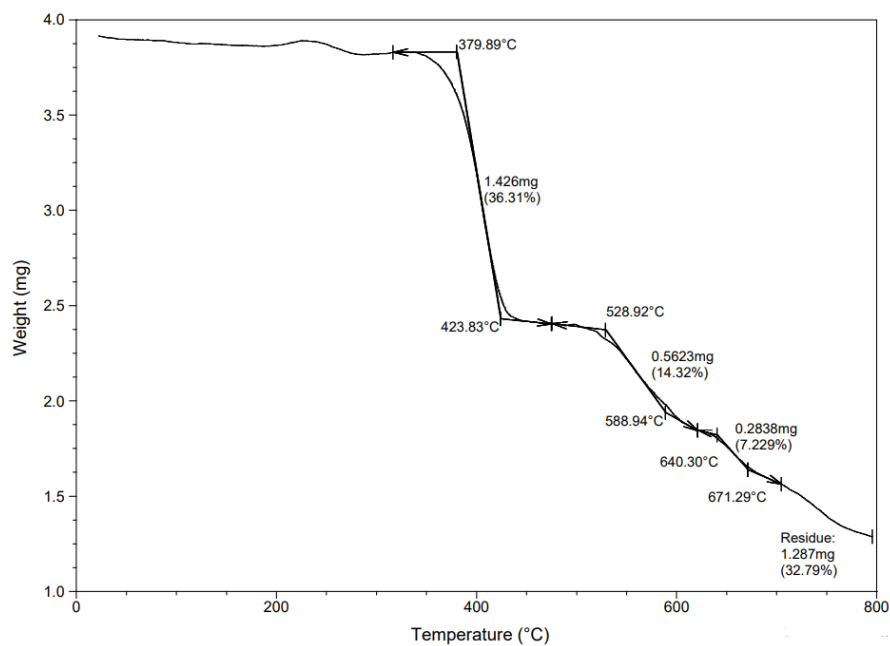


Figure S11. Thermogravimetric analysis of compound **2**.

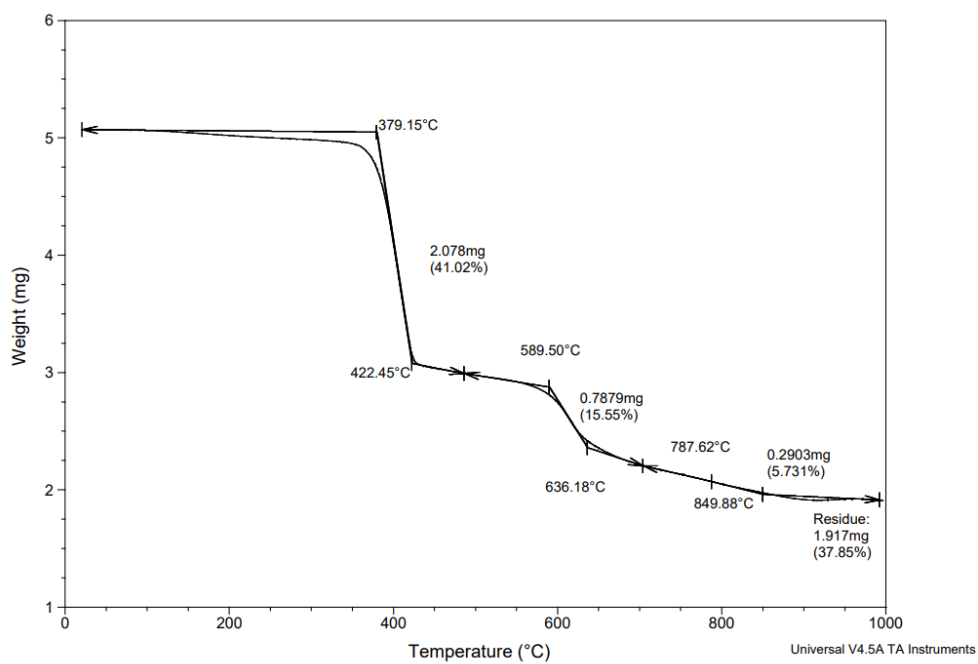


Figure S12. Thermogravimetric analysis of compound **3**.

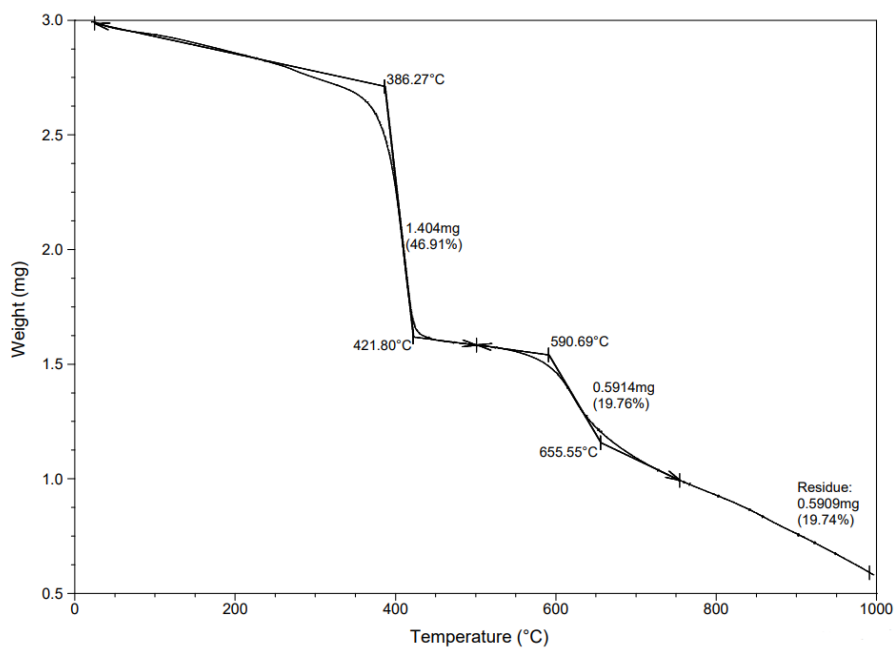


Figure S13. Thermogravimetric analysis of compound **4**.

6. UV-Visible Spectroscopy in solution and on thin films

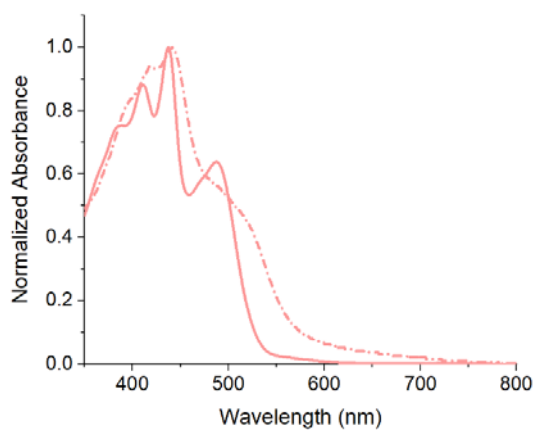


Figure S14. Normalized absorption spectra recorded in solution (CHCl_3 , full line) and films (dashed lines) of compound **1**.

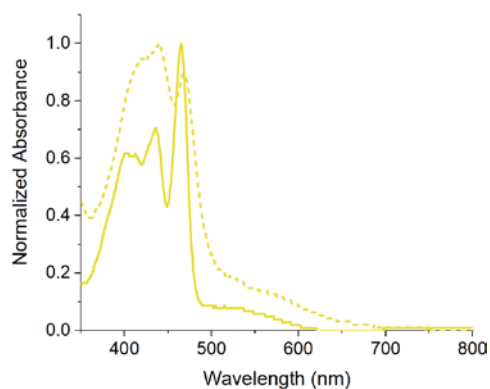


Figure S15. Normalized absorption spectra in recorded in solution (CHCl_3 , full line) and films (dashed lines) of compound **2**.

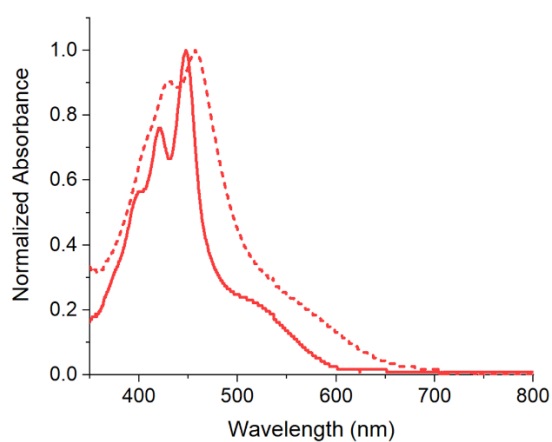


Figure S16. Normalized absorption spectra in recorded in solution (CHCl_3 , full line) and films (dashed lines) of compound **3**.

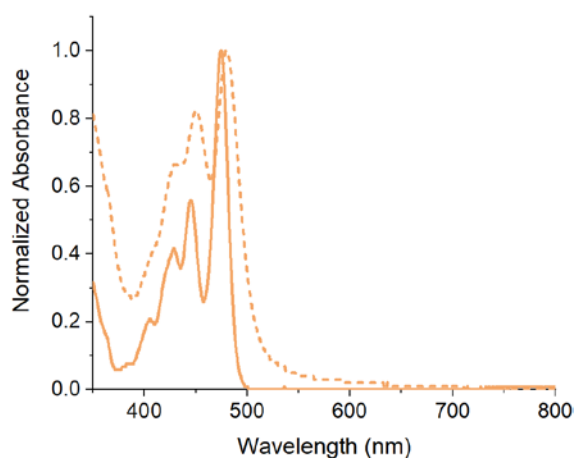


Figure S17. Normalized absorption spectra in recorded in solution (CHCl_3 , full line) and films (dashed lines) of compound **4**.

7. Electrochemistry

Cyclic voltammetry was carried out on a Bio-Logic SAS SP-150 potentiostat with a three electrodes configuration, using a Pt reference electrode, a Pt wire as counter electrode, and a Pt electrode as working electrode. Samples ($C = 10^{-3}$ M) were dissolved in a 0.1 M Bu_4NPF_6 solution in CH_2Cl_2 as supporting electrolyte and ferrocene was used as internal reference. The scan rate is $200 \text{ mV}\cdot\text{s}^{-1}$. The solutions were degassed by bubbling argon for 2 min before measurements.

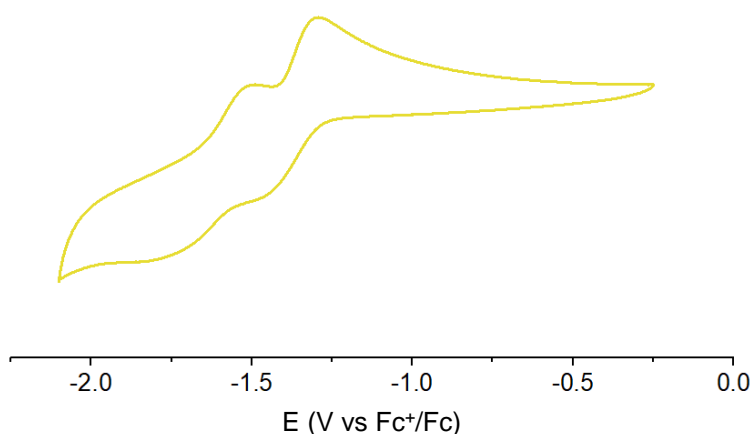


Figure S18. Cyclic voltammogram of compound **2**, V vs Fc^+/Fc .

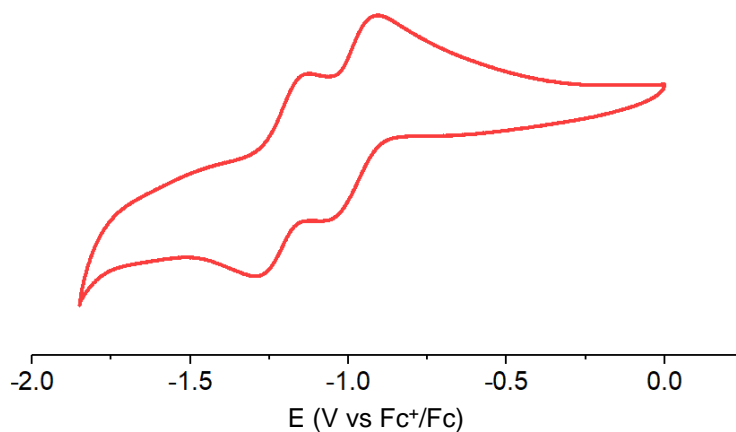


Figure S19. Cyclic voltammogram of compound **3**, V vs Fc^+/Fc .

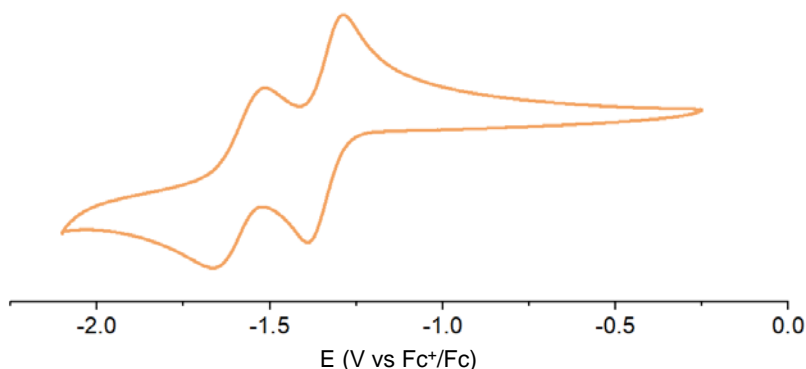


Figure S20. Cyclic voltammogram of compound **4**, V vs Fc⁺/Fc.

8. Optical and Electronic Properties

Compound	λ_{abs}/nm^a sol.	λ_{abs}/nm^a film	$\epsilon/10^3 M^{-1}cm^{-1b}$	$E_{1/2}^{red1}/V^d$	E^{LUMO}/eV^e	E^{HOMO}/eV^e
1	488	635	62.4	-1.17	-3.63	-5.58
2	466	470	81.8	-1.25	-3.55	-6.04
3	448	453	120.8	-1.14	-3.6	-5.96
4	474	480	135.2	-1.27	-3.53	-5.95

Table S1. Optical and Electronic properties of clicked compounds **1**, **2**, **3** and **4**.

Absorption spectra recorded in CHCl₃, reduction potentials data recorded in CH₂Cl₂ at rt.

^aMaximum wavelength of the lowest energy absorption band. ^bExtinction coefficient of the lowest energy absorption band. ^cRecorded using 0.1 M *n*-Bu₄NPF₆. ^dCalculated from the formula $E^{LUMO} = -[E_{1/2}^{red1} + 4.8]$ eV. ^eCalculated from the formula $E^{gap} = E^{LUMO} - E^{HOMO}$.

9. Organic Solar Cells Fabrication and Characterizations

OSC Device Fabrication. OSCs were fabricated and tested under ambient conditions using a bottom-anode top-cathode (conventional) architecture comprised of ITO/PEDOT:PSS/PM6:AzaBPDI/BCP/Ag. The patterned indium-tin-oxide (ITO) substrates were cleaned via sonication in deionized water, acetone and isopropyl alcohol (15 minutes each), dried with pressurized air and treated with UV-ozone for 30 min. The PEDOT-PSS (Al-4083, Heraeus) solution was filtered through a 0.45 μ m PVDF filter and spin-coated on treated ITO at 4000 rpm for 60 s, and then thermally annealed at 140 °C for 20 min at ambient conditions to remove the residual solvent. The active layer solutions, comprised of the polymer donor PM6 (purchased from Brilliant Matters) and the respective AzaBPDI NFA, were dissolved in chloroform (1:1.2 w/w, total concentration = 16 mg mL⁻¹) and 0.5% v/v 1-chloronaphthalene as solvent additive. Each active layer solution was stirred at 60 °C overnight

prior to spin-coating at 3500 rpm for 30 s. The wet active layer films were annealed at 110 °C for 10 minutes. The bathocuproine (BCP, from Sigma-Aldrich) cathode interlayer material was dissolved by stirring in ethanol for 4 h at a concentration of 0.5 mg mL⁻¹, and then spin-coated at 4000 rpm for 60 s on top of the PM6:AzaBPDI layer. To complete device fabrication, a 100 nm Ag layer was evaporated under vacuum of 1×10⁻⁵ Torr through a shadow mask. The active area of device is 14 mm² (rectangular shaped, 7 × 2 mm) defined by the overlap between the ITO and Ag electrodes.

OSC Device Characterization. Performance of the PM6:AzaBPDI-based devices was measured under ambient conditions using a Keithley 2420 Source Measure Unit, at simulated 1.5 G solar illumination (Newport, Model 92251A-1000) with an irradiation intensity of 100 mW/cm², measured by a calibrated silicon solar cell and a readout meter (Newport, Model 91150V). The active area of each device is 14 mm² (rectangular shaped, 7 × 2 mm) as defined by the overlap between the ITO and Ag electrodes. External Quantum Efficiency (EQE) was measured in a QEX7 Solar Cell Spectral Response/QE/IPCE Measurement System (PV Measurement, Model QEX7, USA) with an area of 0.04 cm², smaller than the cell. Optical absorption and photoluminescence (PL) spectra of the PM6:AzaBPDI films were recorded using an Agilent Technologies Cary 60 UV–vis spectrometer and an Agilent Technologies Cary Eclipse fluorescence spectrophotometer, at room temperature. AFM images were acquired using a TT-2 AFM (AFM Workshop, USA) in the tapping mode.

XRD measurements. XRD experiments were performed on a PROTO AXRD Benchtop Diffractometer using coupled 2θ/θ scans and CuK-α radiation source with wavelength of 0.15418 nm. The PM6:AzaBPDI films were coated on top of glass substrates at same condition employed for the solar cell fabrication.

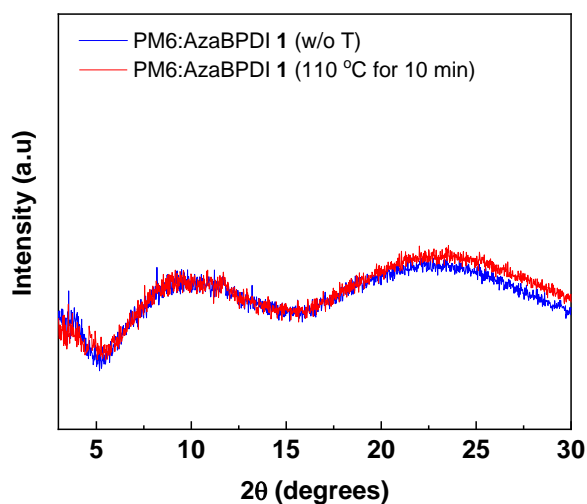


Figure S21. XRD measurements of PM6:AzaBPDI 1 BHI film before (blue line) and after annealing at 110 °C for 10 min (red line).

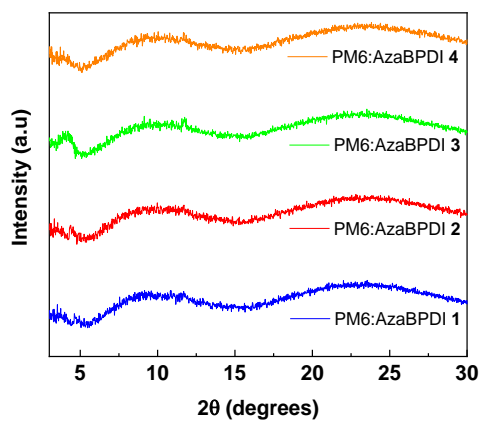


Figure S22. XRD measurements of BHI films with PM6:AzaBPDI 1 (blue), PM6:AzaBPDI 2 (red), PM6:AzaBPDI 3 (green), PM6:AzaBPDI 4 (orange).

10. References

1. A. Goujon, L. Rocard, T. Cauchy, P. Hudhomme, An imine photocyclization as an alternative to the Pictet–Spengler reaction for the synthesis of AzaBenzannulated Perylenediimide dyes, *J. Org. Chem.*, 2020, 85, 7218-7224.
2. H. Langhals, S. Kirner, Novel Fluorescent Dyes by the Extension of the Core of Perylenetetracarboxylic Bisimides, *Eur. J. Org. Chem.*, 2000, 2, 365-380.