

Azido-Perylenediimide : A Versatile Building Block for CuAAC Reactions and an Alternative Precursor for N-Annulation

Antoine Goujon,* Lou Rocard, Heorhii Melnychenko and Piétrick Hudhomme.*

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

antoine.goujon@univ-angers.fr

pietrick.hudhomme@univ-angers.fr

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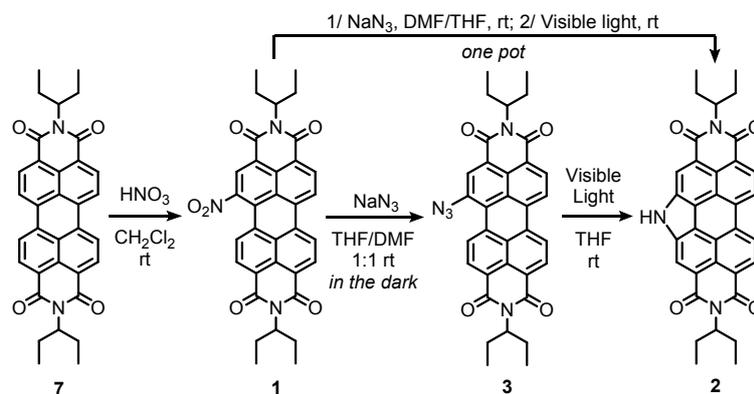
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1. Materials and Methods

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). UV-Vis absorptions were recorded on a Shimadzu UV-1800 UV-Vis spectrophotometer using quartz cell (pathlength of 1 cm). Fluorescence was measured on a Shimadzu RF-6000 Spectrophotometer using quartz cell (pathlength of 1 cm). Quantum Yield were measured on a Jasco FP-8500 Spectrophotometer equipped with an ILF-835 integration sphere. 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), dd (doublet of doublets), 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-700 B/E. TGA analysis were performed on a TGA Q500 setup under nitrogen atmosphere using a platinum crucible. 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 while deuterated solvents from Sigma Aldrich.

Abbreviations. CV : cyclic voltammetry; DMF : dimethylformamide; HRMS : high resolution mass spectrometry; LUMO : lowest unoccupied molecular orbital; NMR : nuclear magnetic resonance; PDI : perylenediimide; PMDTA : N,N,N',N'',N''-pentamethyldiethylenetriamine; rt : room temperature; TGA : thermogravimetric analysis; THF : tetrahydrofuran, TLC : thin layer chromatography.

2. Synthesis



Scheme S1. Synthesis of NO₂-PDI **1**, intermediate N₃-PDI **3** and N-annulated derivative **2**.

Sodium azide is a hazardous reagent (explosive) and should be handled with care.

Compound 1. PDI **7**¹ (3 g, 5.65 mmol) was dissolved in CH₂Cl₂ (400 mL) before fuming HNO₃ was added (5.8 mL, 140 mmol). The mixture was stirred at rt until the starting material was completely converted into the mono-nitrated compound (according to TLC, around 30 min). Water was added (400 mL) and the organic phase was separated and washed with NaHCO₃ sat. (400 mL). The organic phase was dried on MgSO₄, filtered and evaporated to afford a red solid. The crude was taken back in a minimum of CH₂Cl₂ to which MeOH was added until precipitation. The suspension was cooled down to 0°C with an ice bath 15 min. Filtration afforded a red solid which was washed with MeOH and dried to afford **1** as a deep red solid (3.2 g, 98% yield). Characterizations were in accordance with previous reports.¹

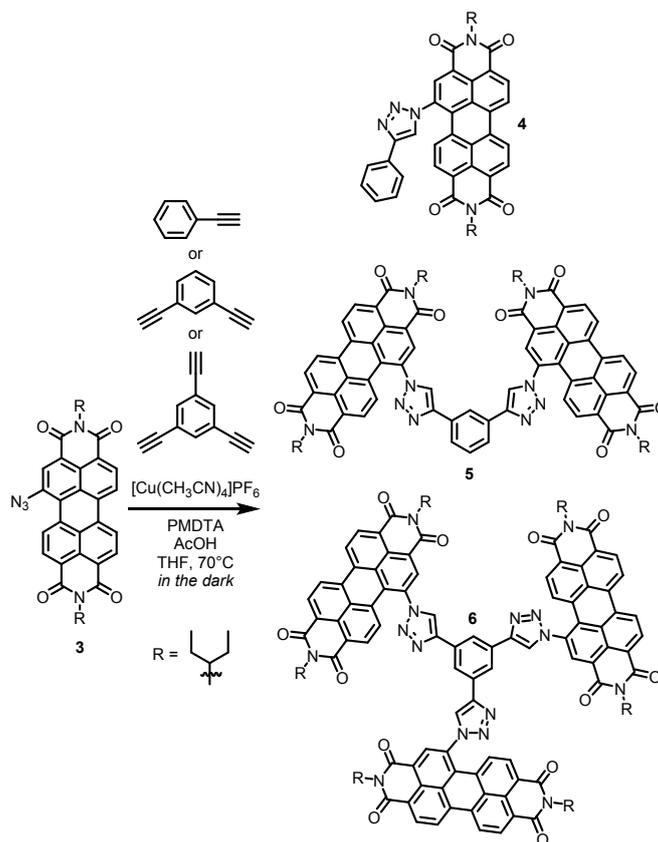
Compound 2. Two strategies:

One pot procedure. Compound **1** (1 g, 1.73 mmol) was dissolved in THF/DMF 1:1 (30 mL) and hidden from ambient light with aluminum foil. NaN₃ (135 mg, 2.08 mmol) was added in one portion and the solution was stirred 30 min at rt, at which point TLC analysis showed complete disappearance of the starting material to the profit of intermediate **3**. The solution was then stirred while exposed to white light LEDs until complete conversion into compound **2**. Water was added (50 mL) and the solution was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic phase were dried on MgSO₄ and evaporated. The red crude was dissolved in CHCl₃ and pentane was added until precipitation. The solid was recovered by filtration and washed with cold pentane to afford **2** as a deep red solid (870 mg, 95% yield). Characterizations were in accordance with previous reports.¹

Two steps procedure. Compound **1** (1 g, 1.73 mmol) was dissolved in THF/DMF 1:1 (30 mL) and hidden from ambient light with aluminum foil. NaN₃ (135 mg, 2.08 mmol) was added in one portion and the solution was stirred 30 min at rt, at which point TLC analysis showed complete disappearance

of the starting material to the profit of the intermediate **3**. Water was added (50 mL) and the suspension was cooled down to 0°C with an ice bath 15 min. The suspension was filtered and the solid washed with water to afford intermediate **3** as a deep purple solid (940 mg, 95% yield), stable under ambient conditions. ¹H NMR (300 MHz, CDCl₃): δ 9.75 (d, *J* = 8.4 Hz, 1H), 8.71 – 8.52 (m, 6H), 5.14 – 4.99 (m, 2H), 2.35 – 2.17 (m, 4H), 2.03 – 1.86 (m, 4H), 0.93 (t, *J* = 7.5 Hz, 12H). IR (cm⁻¹, powder) : 2958 (w), 2932 (w), 2871 (w), 2106 (m), 1693 (s), 1652 (s), 1594 (s), 1533 (m), 1457 (m), 1404 (s), 1329 (s), 1246 (s), 1194 (s), 1084 (s).

Compound **3** (940 mg, 1.64 mmol) was dissolved in THF (30 mL) and exposed to white light LEDs until complete conversion into compound **2** (around 30 min). Water was added (50 mL) and the solution was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic phase were dried on MgSO₄ and evaporated. The red crude was dissolved in CHCl₃ and pentane was added until precipitation. The solid was recovered by filtration and washed with cold pentane and MeOH to afford **2** as a deep red solid (885 mg, quantitative yield). Characterizations were in accordance with previous reports.¹



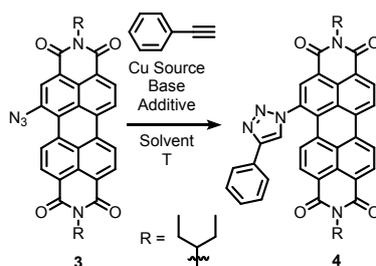
Scheme S2. Synthesis of clicked compounds **4**, **5** and **6**.

Compound 4. Intermediate **3** (100 mg, 0.17 mmol) was dissolved in THF (6 mL) in a Schlenk flask and hidden from ambient light by aluminum foil. To the solution were added phenylacetylene (18 μL, 0.26 mmol), [Cu(CH₃CN)₄]PF₆ (64 mg, 0.17 mmol), PMDTA (35 μL, 0.17 mmol) and glacial AcOH (38 μL, 68 mmol). The flask was flushed with argon and the mixture was stirred 6 hours at 75 °C. The

mixture was added to a separating funnel along with water (20 mL) and CH₂Cl₂ (20 mL). The organic phase was washed with water (2 x 20 mL), dried on MgSO₄ and evaporated. The crude was purified on column chromatography (SiO₂, CH₂Cl₂/Et₂O 98:2) to afford click product **4** as a red solid (105 mg, 92% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.85-8.83 (m, 1H), 8.80-8.66 (m, 4H), 8.31-8.29 (d, *J* = 8.3 Hz, 1H), 8.14 (s, 1H), 8.04-7.94 (m, 2H), 7.61-7.50 (m, 2H), 7.53-7.42 (m, 1H), 6.87-6.84 (d, *J* = 8.3 Hz, 1H), 5.15-4.97 (m, 2H), 2.37-2.17 (m, 4H), 1.96-1.85 (m, 4H), 1.00-0.88 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7, 150.4, 135.4, 133.8, 133.6, 132.5, 131.4, 131.3, 131.0, 129.6, 129.5, 129.2, 129.2, 129.2, 128.2, 127.6, 127.1, 126.1, 124.3, 123.7, 120.0, 58.2, 57.9, 25.0, 11.4. HRMS calcd. for C₄₂H₃₄N₅O₄ ([M-H]⁺): 672.2605 found: 672.2615 (1.49 ppm error).

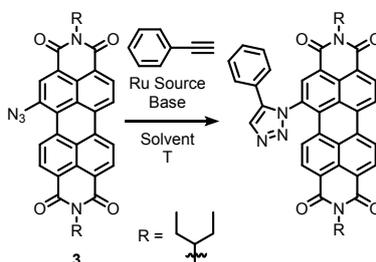
Compound 5. Intermediate **3** (100 mg, 0.17 mmol) was dissolved in THF (6 mL) in a Schlenk flask and hidden from ambient light by aluminum foil. To the solution were added 1,3-diethynylbenzene (23 μL, 0.09 mmol), [Cu(CH₃CN)₄]PF₆ (64 mg, 0.17 mmol), PDMTA (35 μL, 0.17 mmol) and glacial AcOH (38 μL, 68 mmol). The flask was flushed with argon and the mixture was stirred 6 hours at 75 °C. The mixture was added to a separating funnel along with water (20 mL) and CH₂Cl₂ (20 mL). The organic phase was washed with water (2 x 20 mL), dried on MgSO₄ and evaporated. The crude was purified on column chromatography (SiO₂, CH₂Cl₂/Et₂O 98:5) to afford click product **5** as a red solid (94 mg, 88% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.73-8.67 (d, *J* = 8.0 Hz, 2H), 8.66 – 8.53 (m, 8H), 8.45 (s, 1H), 8.24 (s, 2H), 8.23 (d, *J* = 7.9 Hz, 2H), 7.96-7.92 (d, *J* = 7.9 Hz, 2H), 7.6-7.55 (t, *J* = 7.8 Hz, 1H), 6.75-6.71 (d, *J* = 8.3 Hz, 2H), 5.03-4.84 (m, 4H), 2.30-1.99 (m, 8H), 1.92-1.72 (m, 8H), 0.92 (t, *J* = 7.4 Hz, 12H), 0.84 (t, *J* = 7.4 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7, 149.8, 135.3, 133.6, 133.4, 132.5, 131.4, 131.3, 130.9, 130.4, 130.1, 129.6, 129.1, 129.1, 128.3, 128.1, 127.5, 127.0, 126.5, 124.3, 124.1, 123.7, 123.6, 123.4, 120.6, 58.1, 57.8, 25.0, 11.4, 11.4. HRMS calcd. for C₇₈H₆₆N₆O₈ ([M-4N]⁺): 1212.4780 found: 1212.4764 (1.31 ppm error).

Compound 6. Intermediate **3** (100 mg, 0.17 mmol) was dissolved in THF (6 mL) in a Schlenk flask and hidden from ambient light by aluminum foil. To the solution were added 1,3,5-triethynylbenzene (8.5 mg, 0.06 mmol), [Cu(CH₃CN)₄]PF₆ (64 mg, 0.17 mmol), PDMTA (35 μL, 0.17 mmol) and glacial AcOH (38 μL, 68 mmol). The flask was flushed with argon and the mixture was stirred 6 hours at 75 °C. The mixture was added to a separating funnel along with water (20 mL) and CH₂Cl₂ (20 mL). The organic phase was washed with water (2 x 20 mL), dried on MgSO₄ and evaporated. The crude was purified on column chromatography (SiO₂, CH₂Cl₂/Et₂O 98:5) to afford click product **6** as a red solid (92 mg, 87% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.75-8.7 (d, *J* = 8.0 Hz, 3H), 8.69 – 8.55 (m, 15H), 8.39 (s, 3H), 8.22-8.17 (d, *J* = 8.2 Hz, 3H), 6.81-6.76 (d, *J* = 8.3 Hz, 3H), 5.08-4.82 (m, 6H), 2.29-2.02 (m, 12H), 1.92-1.72 (m, 12H), 0.93 (t, *J* = 7.4 Hz, 18H), 0.86 (t, *J* = 7.4 Hz, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7, 149.3, 135.4, 133.6, 133.5, 132.5, 131.4, 131.3, 131.2, 131.0, 129.7, 129.2, 128.2, 127.6, 127.1, 124.4, 124.2, 123.8, 123.7, 123.5, 121.2, 58.2, 57.9, 25.0, 11.4. HRMS calcd. for C₁₁₄H₉₃N₉O₁₂ ([M-6N]⁺): 1779,6949 found: 1779,6953 (0.19 ppm error).



Entry	Cu source	Base	Ligand	Additive	Solvent	T	Outcome
1	CuSO ₄ ·5H ₂ O	/	/	NaAscorbate	THF/H ₂ O	rt	No conversion
2	CuI	NEt ₃	/	/	THF	rt	Low conversion + side products
3	CuI	NEt ₃	/	/	THF	Reflux	Low conversion + side products
4	CuBr	/	PMDTA	/	DMF	rt	Low conversion + side products
5	CuBr	/	PMDTA	/	DMF	80°C	Low conversion + side products
6	[Cu(CH ₃ CN) ₄]PF ₆	1,6-lutidine	/	/	THF	Reflux	Conversion Low rate
7	[Cu(CH ₃ CN) ₄]PF ₆	/	PMDTA	AcOH	THF	Reflux	Full conversion in 6h

Table S1. Conditions screening for the CuAAC reactions involving azide **3**.



Entry	Ru source	Base	Solvent	T	Outcome
1	Cp*RuCl(PPh ₃) ₂ , RuCl ₂ (PPh ₃) ₂	/	Toluene or THF	rt	Decomposition
2	Cp*RuCl(PPh ₃) ₂ , RuCl ₂ (PPh ₃) ₂	/	Toluene or THF	reflux	Decomposition
3	Cp*RuCl(PPh ₃) ₂ , RuCl ₂ (PPh ₃) ₂	NEt ₃	Toluene or THF	reflux	Decomposition
4	[RuCp*(MeCN) ₃]PF ₆	/	Toluene or THF	rt	Decomposition
5	[RuCp*(MeCN) ₃]PF ₆	/	Toluene or THF	reflux	Decomposition
6	[RuCp*(MeCN) ₃]PF ₆	NEt ₃	Toluene or THF	reflux	Decomposition
7	Cp*RuCl(cod)	/	Toluene or THF	rt	Decomposition
8	Cp*RuCl(cod)	/	Toluene or THF	Reflux	Decomposition
9	Cp*RuCl(cod)	NEt ₃	Toluene or THF	Reflux	Decomposition

Table S2. Conditions screening for the RuAAC reactions involving azide **3**.

3. Absorption and Emission Spectroscopy

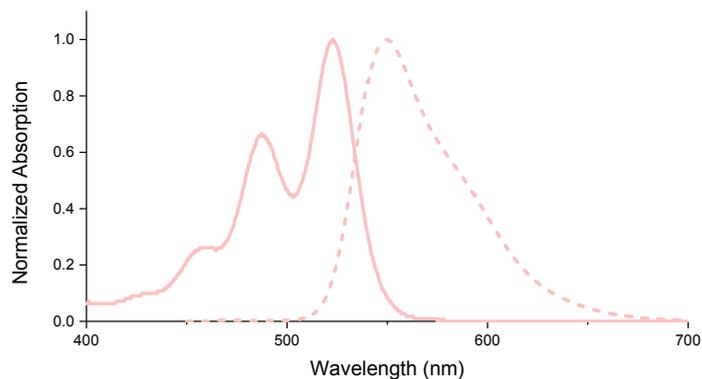


Figure S1. Normalized absorption (full line) and emission (dashed line) spectra of **4** in CH_2Cl_2 , $5 \cdot 10^{-5}$ M.

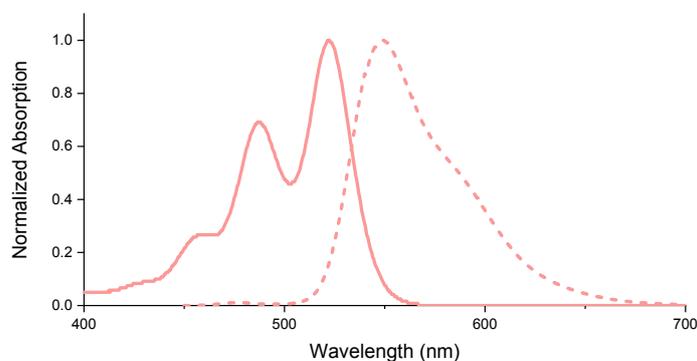


Figure S2. Normalized absorption (full line) and emission (dashed line) spectra of **5** in CH_2Cl_2 , $5 \cdot 10^{-5}$ M.

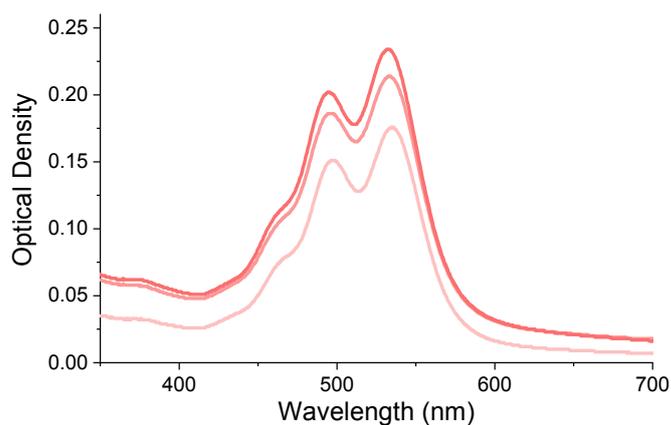


Figure S3. Absorption spectra in thin films of **4**, **5** and **6** (from bottom to top). Spin-coated at 2000 rpm from $3 \text{ mg} \cdot \text{mL}^{-1}$ solution in CH_2Cl_2 .

4. Electrochemistry

Cyclic voltammetry was performed with Pt as a working electrode, an Ag/AgNO₃ reference electrode (calibrated to the Fc/Fc⁺ couple) and a Pt wire as counter electrode, with Bu₄NPF₆ 0.1M in CH₂Cl₂, 100 mV/s, solutions degassed 2 min with argon prior to measurements.

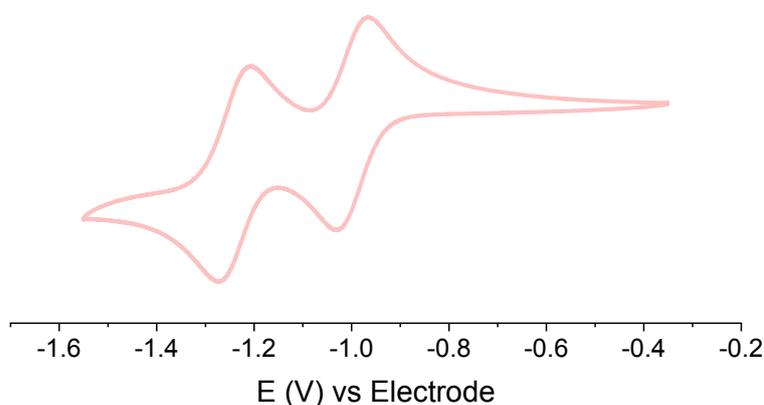


Figure S4. Cyclic voltammogram of compound **4**.

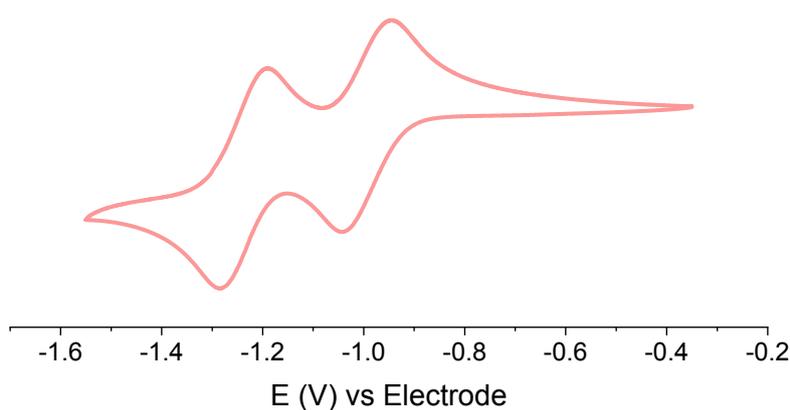


Figure S5. Cyclic voltammogram of compound **5**.

5. Optical and Electronic Properties

Compound	λ_{abs}/nm^a sol.	λ_{abs}/nm^a film	$\epsilon/10^3 M^{-1}cm^{-1b}$	λ_{em}/nm	Φ_f^c	$E_{1/2}^{red1}/V^d$	E^{LUMO}/eV^e
4	522	535	81.8	550	0.75	-0.98	-3.82
5	523	533	120.8	549	0.74	-0.98	-3.82
6	522	532	135.2	550	0.53	-0.98	-3.82

Table S3. Optical and Electronic properties of clicked compounds **4**, **5** and **6**.

Absorption and emission spectra, reduction potentials data recorded in CH₂Cl₂ at rt. ^aMaximum wavelength of the lowest energy absorption band. ^bExtinction coefficient of the lowest energy absorption band. ^cFluorescence Quantum Yields measured with an integration sphere.

^dRecorded using 0.1 M *n*-Bu₄PF₆. ^eCalculated from the formula $E^{LUMO} = - [E_{1/2}^{red1} + 4.8] eV$.

6. Thermogravimetric Analysis

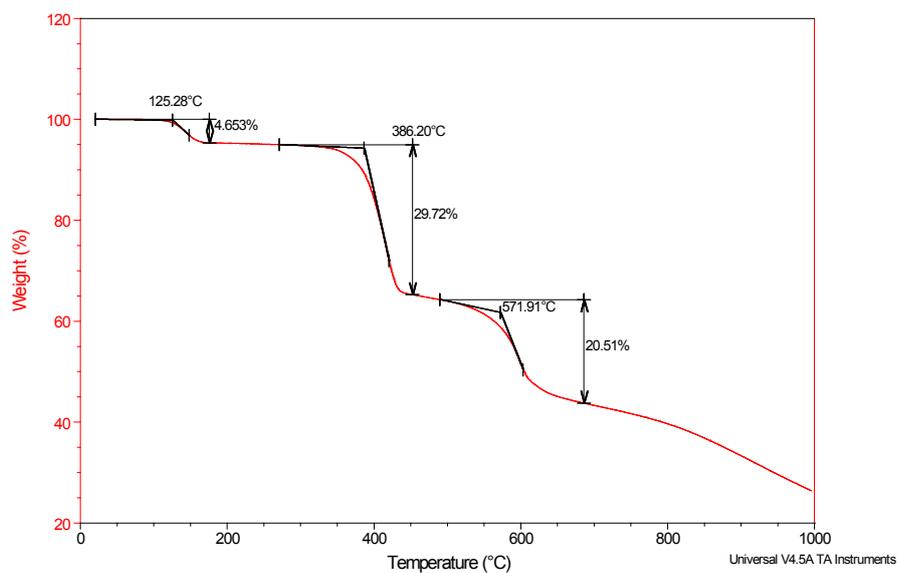


Figure S6. Thermogravimetric analysis of compound 2.

7. Infrared Spectroscopy

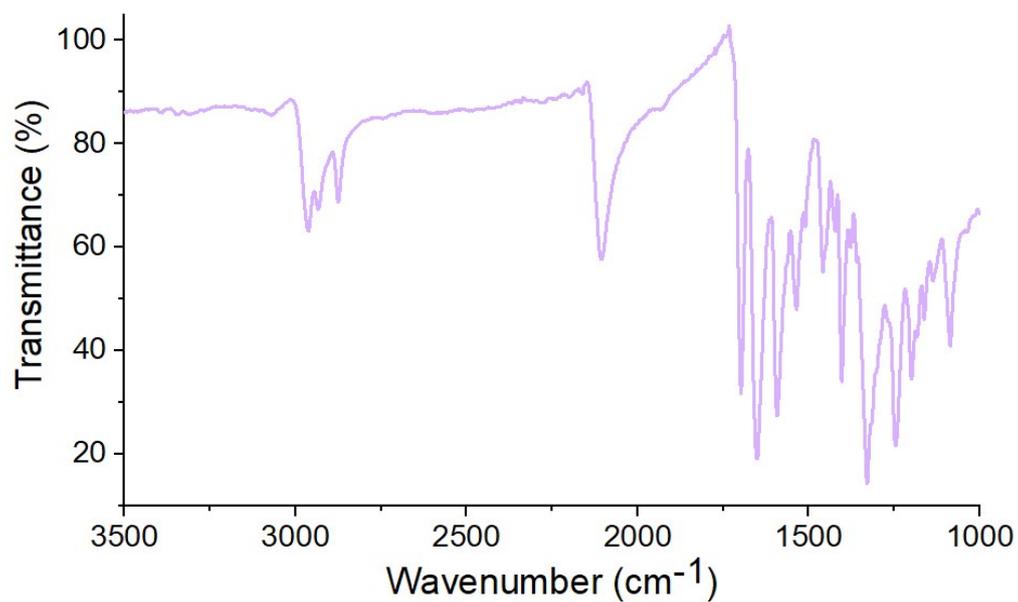


Figure S7. Infrared spectrum of compound 3.

8. NMR

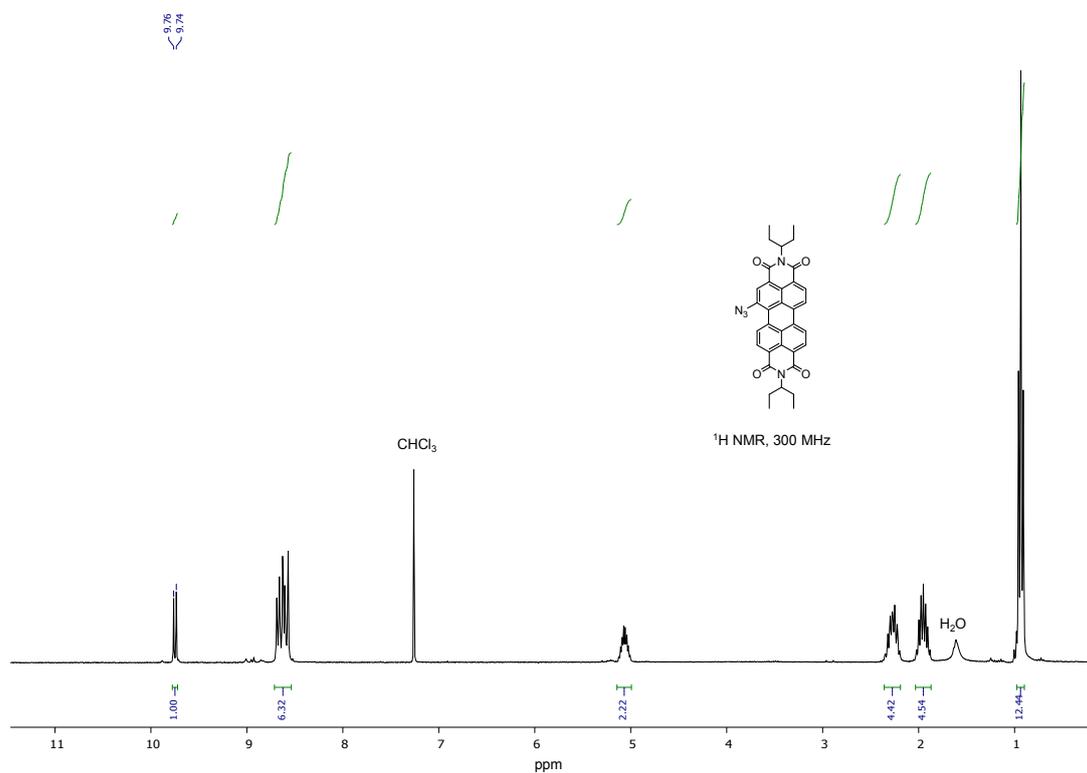


Figure S8. ¹H NMR (300 MHz) spectrum of compound **3** in CDCl₃.

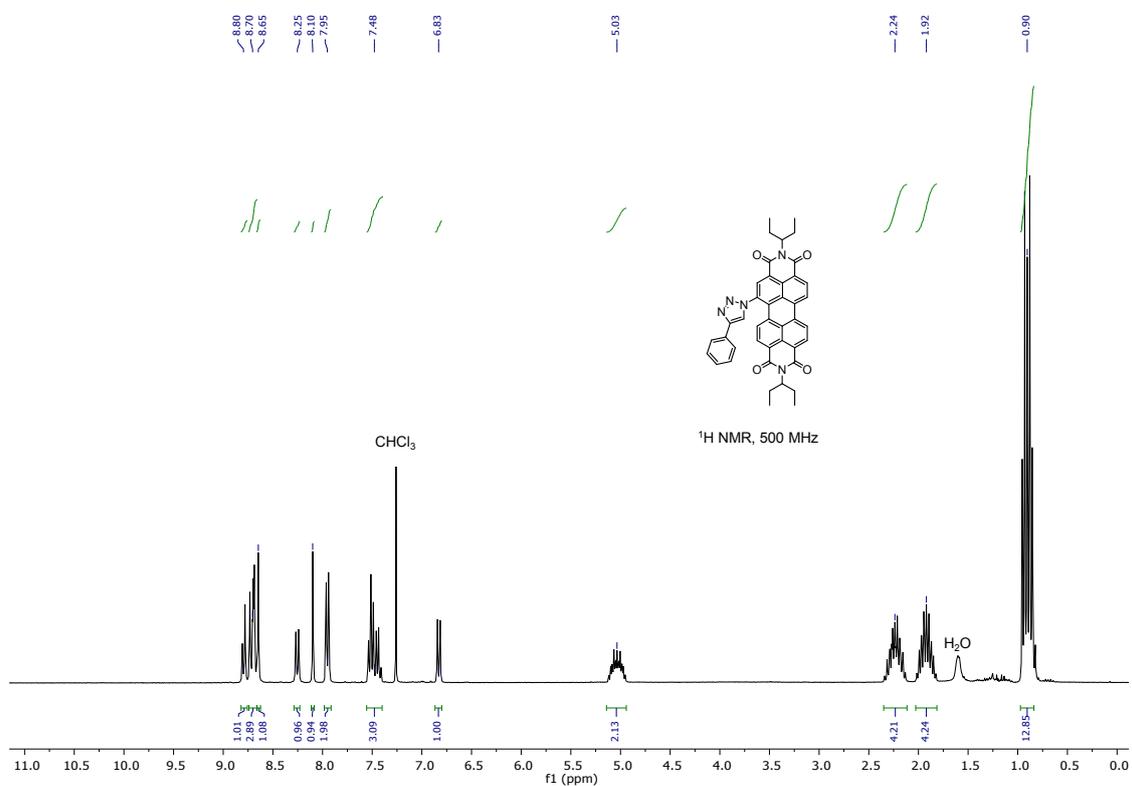


Figure S9. ¹H NMR (500 MHz) spectrum of compound **4** in CDCl₃.

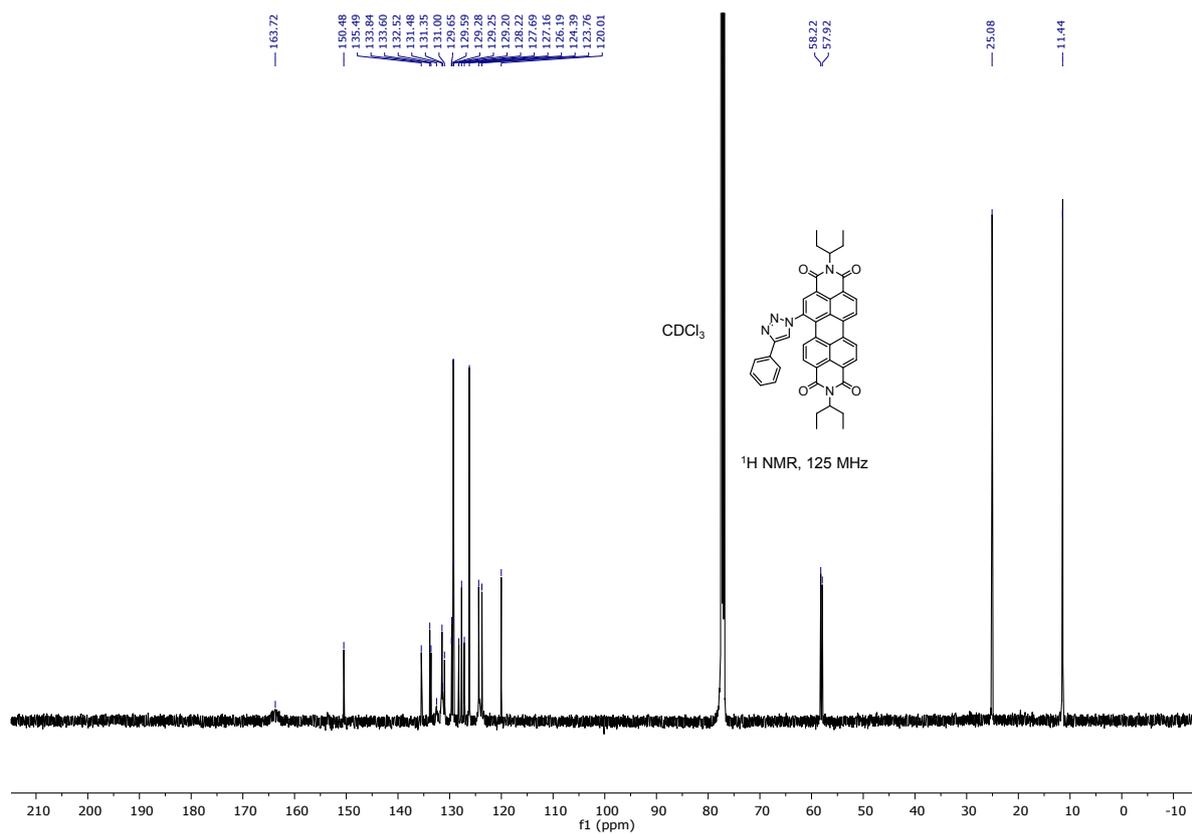


Figure S10. ^{13}C NMR (125 MHz) spectrum of compound **4** in CDCl_3 .

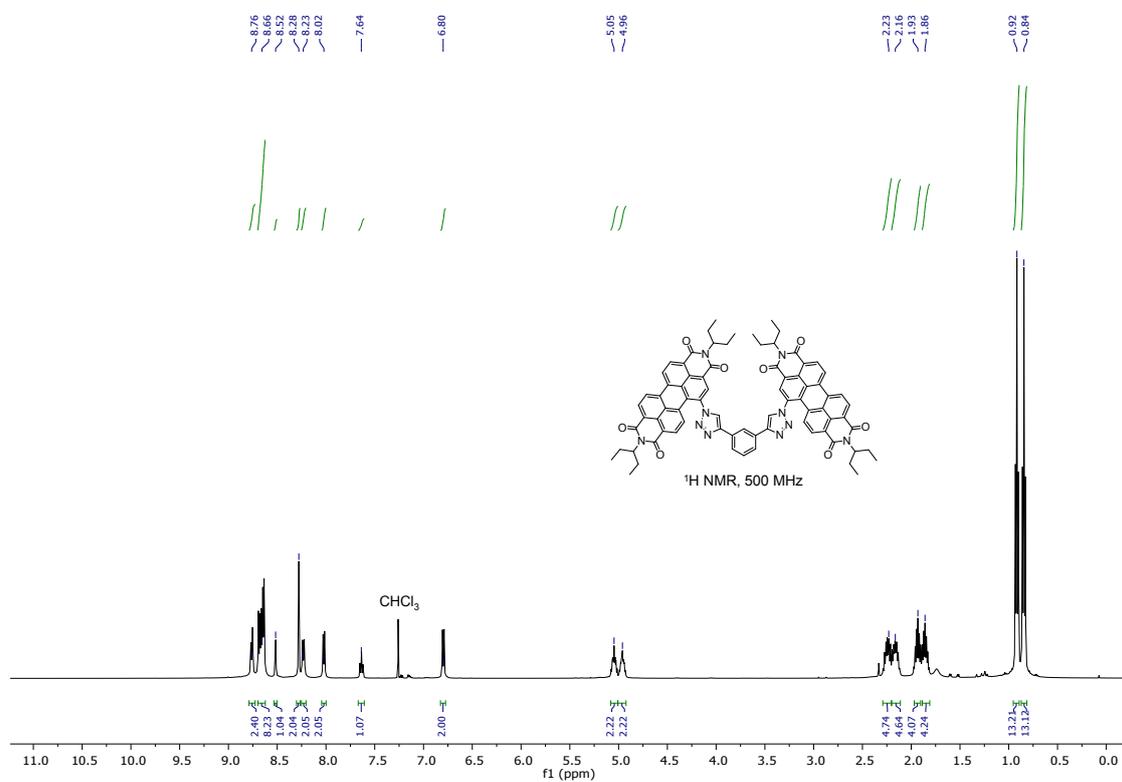


Figure S11. ^1H NMR (500 MHz) spectrum of compound **5** in CDCl_3 .

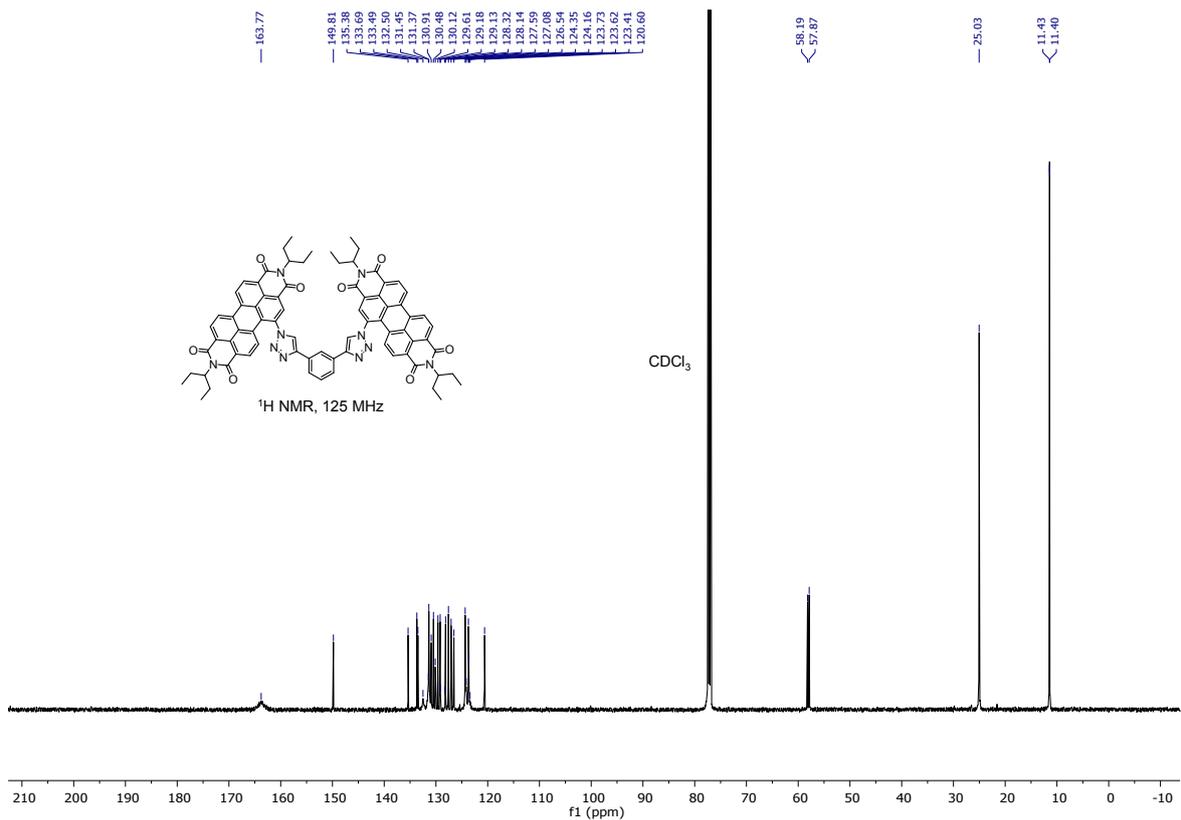


Figure S12. ¹³C NMR (125 MHz) spectrum of compound **5** in CDCl₃.

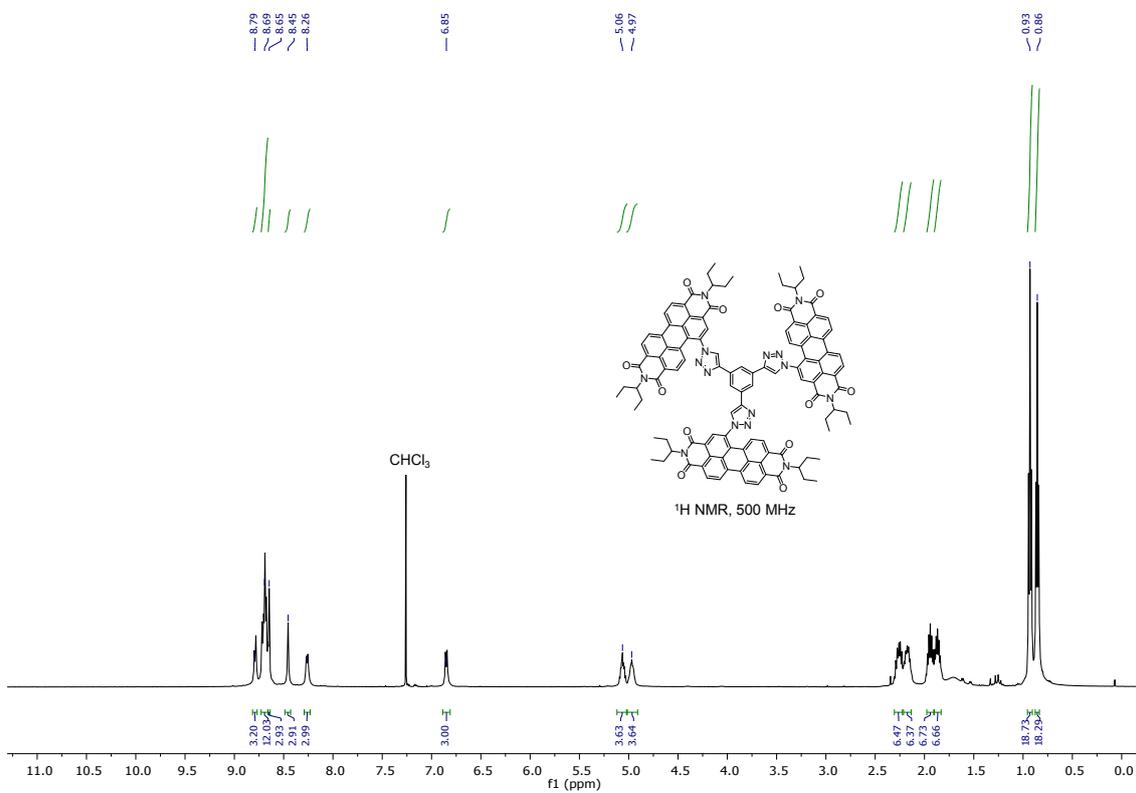


Figure S13. ¹H NMR (500 MHz) spectrum of compound **6** in CDCl₃.

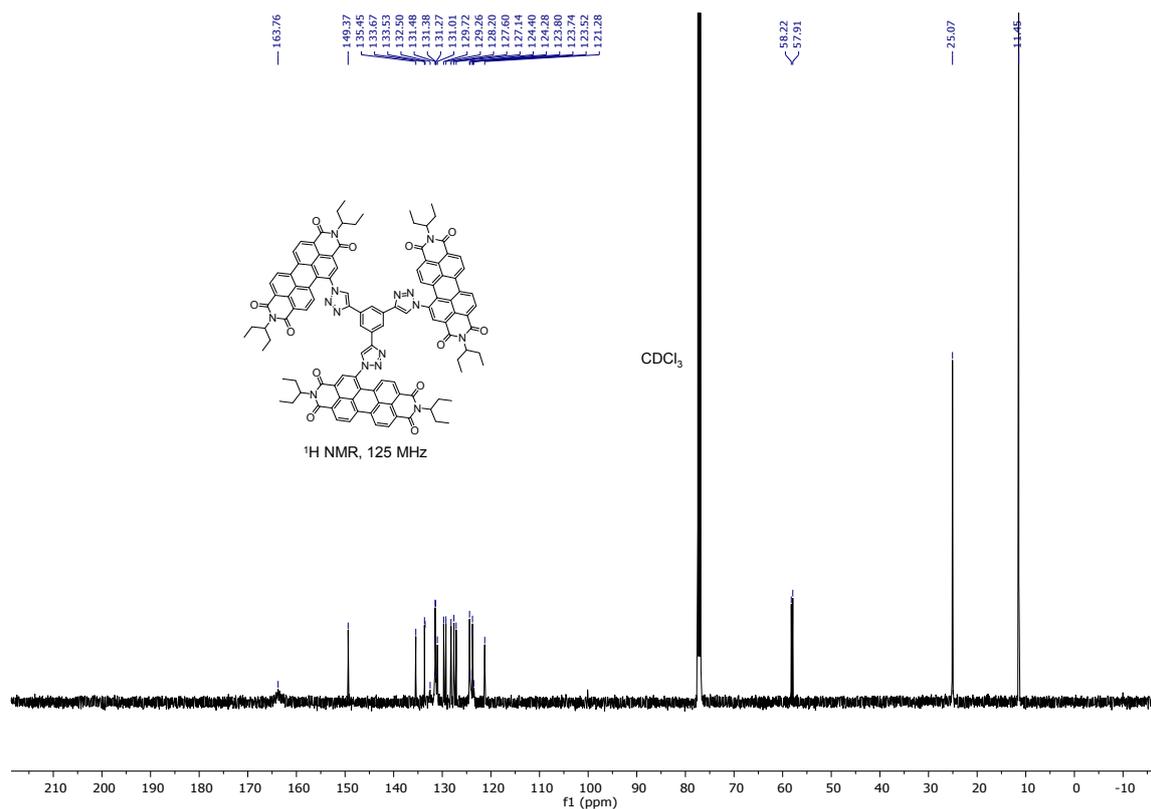


Figure S14. ¹³C NMR (125 MHz) spectrum of compound **6** in CDCl₃.

9. High Resolution Mass Spectrometry

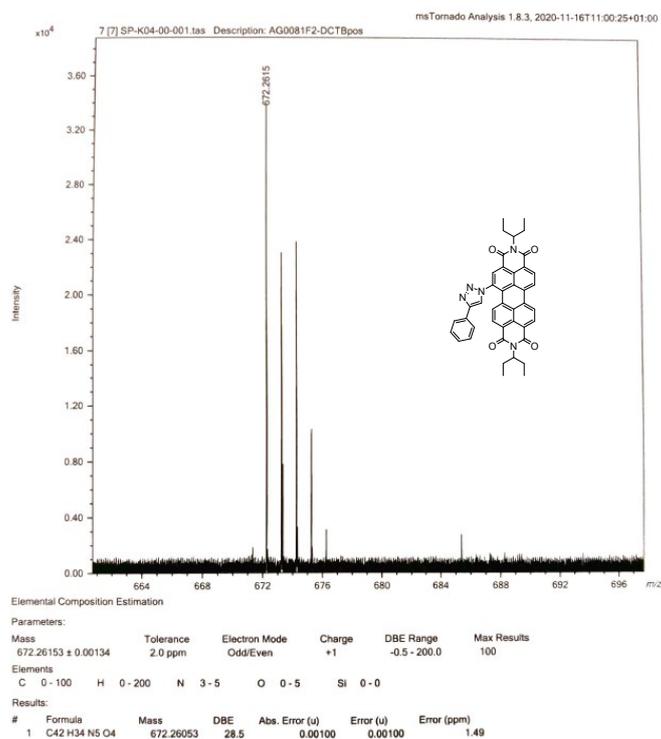


Figure S15. HRMS spectrum of compound 4.

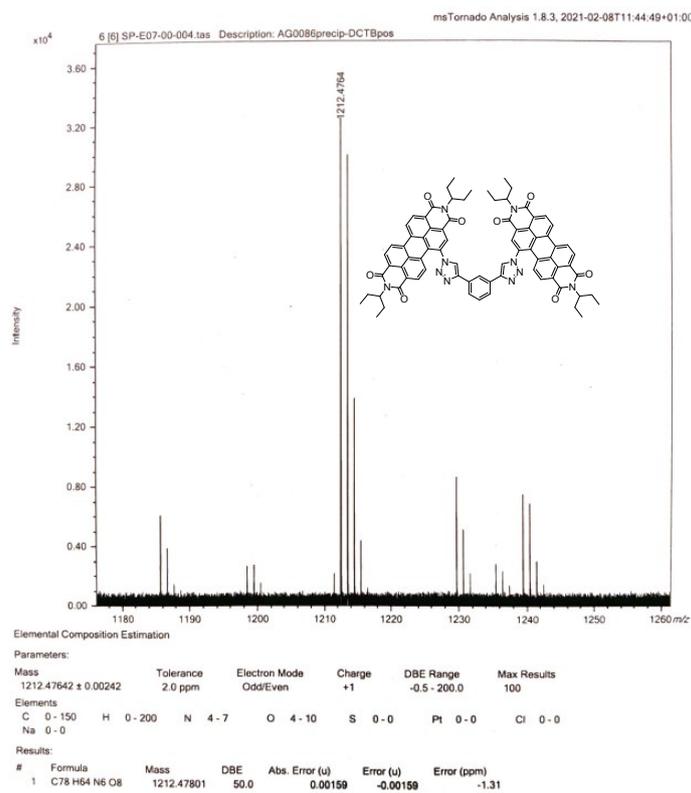


Figure S16. HRMS spectrum of compound 5.

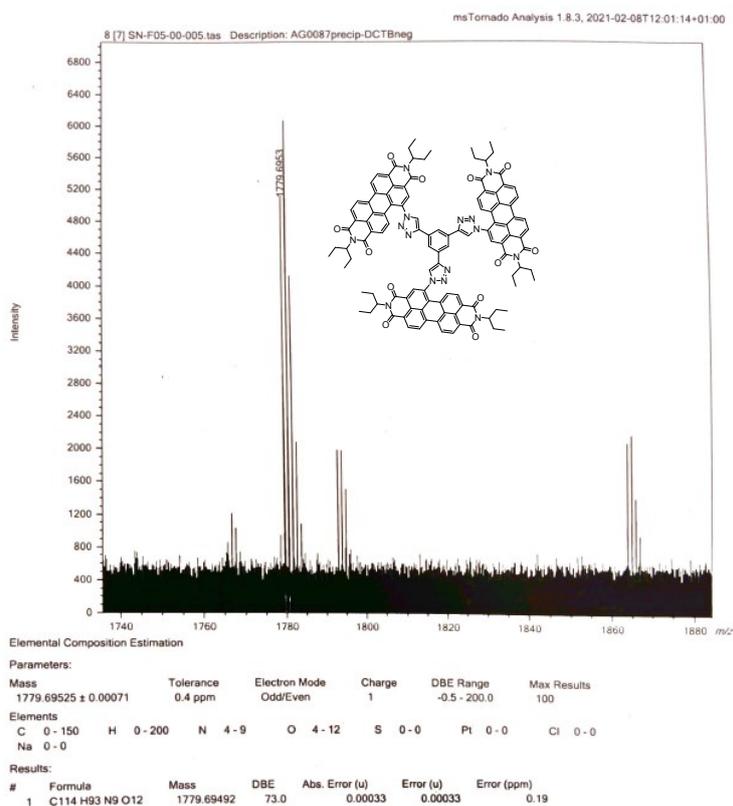


Figure S17. HRMS spectrum of compound **6**.

10. References

1. A. D. Hendsbee, J.-P. Sun, W. K. Law, H. Yan, I. G. Hill, D. M. Spasyuk and G. C. Welch, *Chem. Mater.*, 2016, **28**, 7098.