

## Sidechain Engineering of N-Annulated Perylene Diimide Molecules

Mark Martell,<sup>a</sup> Michael U. Ocheje,<sup>b</sup> Benjamin S. Gelfand<sup>a</sup>, Simon Rondeau-Gagné<sup>b</sup> and Gregory C. Welch<sup>a\*</sup>

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*Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada. E-mail: gregory.welch@ucalgary.ca\**

*Department of Chemistry and Biochemistry, Advanced Materials Centre of Research (AMCOrE), University of Windsor, Ontario, N98 3P4, Canada*

### Supporting Information

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## S.1 Materials and Methods:

**Materials:** All reactants, reagents, and catalysts were purchased from Sigma-Aldrich, Fisher Scientific, Alfa-Aesar or TCI Chemicals unless indicated otherwise. All solvents and materials purchased were used without further purification.

**Nuclear Magnetic Resonance:**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance-500 MHz, 400 MHz or 300 MHz spectrometer at 300 K. All experiments were performed in either chloroform-d. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), doublet of doublets (dd), doublet of quartets (dq), triplet of doublets (td), quartet of doublets (qd), overlapping (ov), and broad (br).

**High-resolution Mass Spectrometry (HRMS):** High-resolution MALDI mass spectrometry measurements were performed courtesy of Jian Jun Li in the Chemical Instrumentation Facility at the University of Calgary. A Bruker Autoflex III Smartbeam MALDI-TOF (Na:YAG laser, 355nm), setting in positive or negative reflective mode, was used to acquire spectra. Operation settings were all typical, e.g. laser offset 62-69; laser frequency 200Hz; and number of shots 300. The target used was Bruker MTP 384 ground steel plate target. Sample solution ( $\sim 1 \mu\text{g/mL}$  in dichloromethane) was mixed with matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldene]malononitrile (DCTB) solution ( $\sim 5\text{mg/mL}$  in methanol). Pipetted  $1\mu\text{l}$  solution above to target spot and dried in the fume hood.

**Cyclic Voltammetry (CV):** All electrochemical measurements were performed using a Model 1200B Series Handheld Potentiostat by CH Instruments Inc. equipped with Ag wire, Pt wire and glassy carbon electrode, as the pseudo reference, counter electrode and working electrode respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry experiments were performed in anhydrous dichloromethane solution with  $\sim 0.1 \text{ M}$  tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte at scan rate 100 mV/s. All electrochemical solutions were purged with dry N<sub>2</sub> for 5 minutes to deoxygenate the system. Solution CV measurements were carried out with a small molecule concentration of  $\sim 0.5 \text{ mg/mL}$  in dichloromethane. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the onsets of oxidation and reduction ( $E_{\text{oxFc/Fc}^+}$ ,  $E_{\text{redFc/Fc}^+}$ ) referenced to a ferrocene internal standard to that of the ionization potential of ferrocene using a conversion value of 4.8 (see: Advanced Materials, 1995, 7 (6), 551-554, Advanced Materials, 2011, 23 (20), 2367-2371).

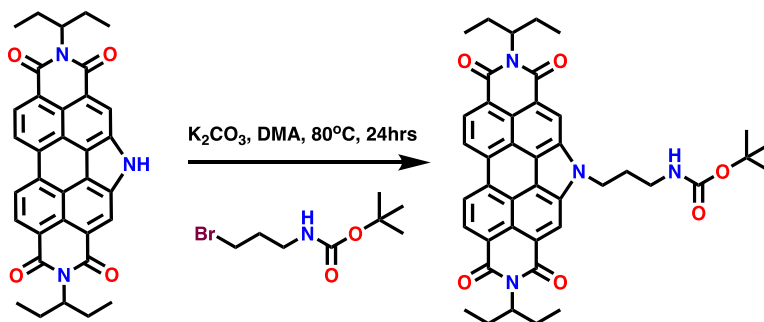
**UV-Visible Spectroscopy (UV-Vis):** All optical absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis experiments were run in CHCl<sub>3</sub> using 10 mm quartz cuvettes. Films were spin-cast into Corning glass micro slides from CHCl<sub>3</sub> solutions (10mg/mL) at 1500 rpm. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

**CHN Analysis:** Elemental analysis was performed by Jian Jun Li in the Chemical Instrumentation Facility at the University of Calgary. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data from a minimum of 3 mg of sample with particle sizes ranging between 0.2 and 0.5 mm in diameter. Results were obtained in duplicate.

**Single Crystal XRD:** Single crystals of **7**, were grown from dichloromethane (1 mL) and methanol (1 mL) at 298K. A suitable crystal was selected and mounted on a glass loop S3 using Paratone oil. Diffraction experiments were performed on a Bruker Smart diffractometer equipped with an Incoatec Microfocus (Cu K $\alpha$ ,  $\lambda = 1.54178 \text{ \AA}$ ) and an APEX II CCD detector. The crystal was kept at 173 K during data collection. Diffractions spots were integrated and scaled with SAINT<sup>1</sup> and the space group was determined with XPREP.<sup>2</sup> Using Olex2<sup>3</sup>, the structure was solved with the ShelXT<sup>4</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>5</sup> refinement package using Least Squares minimisation. This data was collected and solved by Dr. Benjamin S. Gelfand, University of Calgary, X-Ray Crystallography Facility. CCDC# 2108930.

**Organic Field Effect Transistors:** FET devices were fabricated on pre-patterned highly doped n-type Si wafers with a 230 nm thick SiO<sub>2</sub> functionalized with an octyltrichlorosilane (OTS) self-assembled monolayer.<sup>6</sup> Pre-patterned wafers were purchased from Fraunhofer Institute for Photonic Microsystems. To prepare the pre-patterned wafers for spincoating, they were first sonicated in acetone for 5 minutes to remove the photoresist. Following ultrasonication, the wafers rinsed with acetone and then isopropyl alcohol, then dried with nitrogen. After drying, the wafers underwent UV ozone treatment for 15 minutes followed by treatment with OTS according to literature.<sup>1</sup> After OTS treatment, the wafers were rinsed once again with acetone and isopropyl alcohol, and dried with nitrogen prior to spincoating. The organic semiconductor ink was spin-coated into thin-films onto the OTS-treated substrates from solutions in anhydrous 2-methyltetrahydrofuran (10 mg mL<sup>-1</sup>). The thermal annealing process was carried out inside a nitrogen-filled glovebox. All measurements were conducted in a glovebox using a Keithley 4200-SCS Parameter Analyzer.

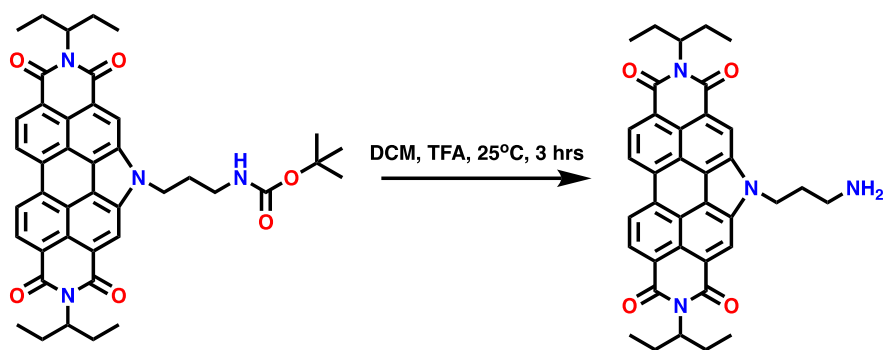
## S.2 Experimental Details



### Synthesis of Boc-HN-C<sub>3</sub>-N-PDI:

H-N-PDI (485 mg, 0.891 mmol), *tert*-butyl-3-bromopropylcarbamate (318 mg, 1.34 mmol) and K<sub>2</sub>CO<sub>3</sub> (308 mg, 2.23 mmol) were added into a 20 mL glass pressure tube. Then 10 mL of *N,N*-dimethylacetamide was added, the tube was seal and the reaction mixture was placed in a LabArmor® bead bath at 80 °C for 24 hours. The reaction mixture was passed through a short Celite plug with dichloromethane then the organic solvent was removed using rotary evaporation. The resulting red solid was precipitated into methanol and allowed to stir for 1 hour and then it was collected by vacuum filtration. **Yield:** 535 mg (86%)

**<sup>1</sup>H-NMR** (500 MHz, chloroform-*d*)  $\delta$ : 9.01-8.96 (ov, 4H), 8.85 (br, 2H), 5.26-5.18 (m, 2H), 4.99-4.94 (t, *J* = 7.3 Hz, 2H), 4.63 (br, 1H), 3.30-3.23 (q, *J* = 6.8 Hz, 2H), 2.47-2.40 (m, 3H), 2.39-2.31 (m, 5H), 2.05-1.95 (m, 5H) 1.41 (s, 9H), 1.01-0.951 (t, *J* = 8.2 Hz, 12H)



### Synthesis of H<sub>2</sub>N-C<sub>3</sub>-N-PDI (1):

Boc-HN-C<sub>3</sub>-N-PDI (360 mg, 0.514 mmol) and 1 mL of trifluoroacetic acid dissolved in 10 mL of dichloromethane were added to a 100 mL round bottom flask. The flask was sealed, and the reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was then extracted with NaOH solution and dichloromethane (3 x 25 mL), combined organic layers were dried over MgSO<sub>4</sub> then filtered through a short Celite plug. The organic solvent was removed by rotary evaporation and the crude solid was purified by silica gel plug, eluted first with 5% acetone in dichloromethane followed by 10% triethylamine in acetone to collect product. The organic solvent was removed by rotary evaporation then the resulting red solid was precipitated into water and vacuum filtered. **Yield:** 272 mg (88%)

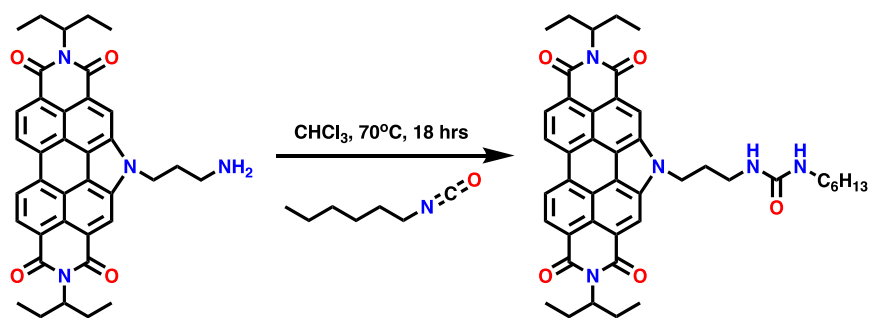
**<sup>1</sup>H-NMR** (500 MHz, chloroform-d)  $\delta$ : 9.09 (s, 2H), 9.03-8.99 (d,  $J = 8.8$  Hz, 2H), 8.87 (br, 2H), 5.27-5.19 (m, 2H), 5.08-5.03 (t,  $J = 7.2$  Hz, 2H), 2.84-2.79 (t,  $J = 6.7$  Hz, 2H), 2.41-2.29 (m, 7H), 2.05-1.95 (m, 5H), 1.01-0.951 (t,  $J = 7.7$  Hz, 13H)

**<sup>13</sup>C-NMR** (125 MHz, chloroform-d)  $\delta$ : 135.0, 132.8, 127.9, 124.8, 123.9, 122.3, 121.9, 119.7, 119.1, 57.8, 44.2, 39.1, 34.5, 25.3, 11.5

Expected <sup>13</sup>C signals: 18 Tabulated <sup>13</sup>C signals: 15

**MALDI-TOF:** m/z [M-H] expected: 599.27 obtained: 599.27

**CHN:** Theoretical (%) C: 73.98 H: 6.04 N: 9.33 Found (%) C: 73.27 H: 5.77 N: 8.92



### Synthesis of Urea-C<sub>3</sub>-N-PDI (2):

H<sub>2</sub>N-C<sub>3</sub>-N-PDI (91.0 mg, 0.151 mmol) and hexyl isocyanate (44 μL, 0.303 mmol) were added to a 10 mL glass pressure tube. Then 5 mL of dry chloroform was added, the tube was sealed, and the reaction mixture was placed in a LabArmor® bead bath at 70 °C for 18 hours. The reaction mixture was then extracted with 0.5 M HCl and dichloromethane (3 x 25 mL). The combined organic layers were dried over MgSO<sub>4</sub> and filtered through a short Celite plug. The organic solvent was removed using rotary evaporation and the resulting red solid was precipitated into water then vacuum filtered. **Yield:** 92.1 mg (82%)

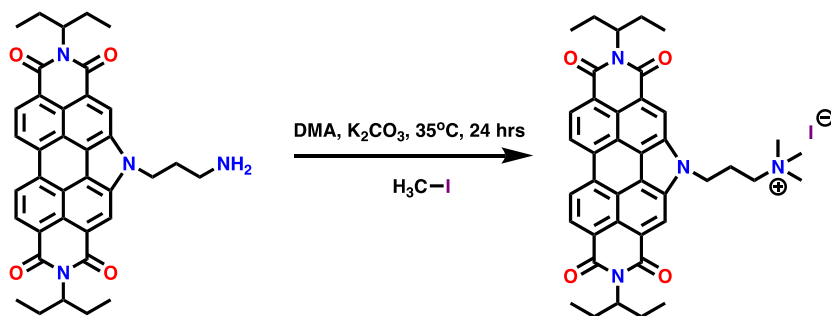
**<sup>1</sup>H-NMR** (500 MHz, chloroform-d) δ: 8.95 (s, 2H), 8.93-8.90 (d, *J* = 8.2 Hz, 2H), 8.84-8.79 (d, *J* = 9.0 Hz, 2H), 5.24-5.17 (m, 2H), 4.98-4.93 (t, *J* = 8.2 Hz, 2H), 4.68-4.63 (br, 1H), 4.53-4.49 (t, *J* = 6.5 Hz, 1H), 3.39-3.33 (q, *J* = 6.4 Hz, 2H), 3.18-3.12 (q, *J* = 6.4 Hz, 2H), 2.46-2.39 (m, 2H), 2.38-2.30 (m, 5H), 2.05-1.95 (m, 5H), 1.51-1.44 (m, 2H), 1.33-1.21 (m, 7H), 1.01-0.953 (t, *J* = 7.3 Hz, 13H), 0.865-0.825 (t, *J* = 5.5 Hz, 3H)

**<sup>13</sup>C-NMR** (125 MHz, chloroform-d) δ: 158.4, 134.6, 132.4, 127.9, 124.5, 123.8, 122.1, 121.5, 119.3, 118.6, 57.9, 44.3, 40.8, 37.9, 32.2, 31.4, 30.2, 26.6, 25.6, 22.6, 13.9, 11.5

Expected <sup>13</sup>C signals: 25 Tabulated <sup>13</sup>C signals: 22

**MALDI-TOF:** m/z [M-H] expected: 726.37 obtained: 726.31

**CHN:** Theoretical (%) C: 72.60 H: 6.79 N: 9.62 Found (%) C: 72.51 H: 6.80 N: 9.09



### Synthesis of Ionic-C<sub>3</sub>-N-PDI (3):

H<sub>2</sub>N-C<sub>3</sub>-N-PDI (105 mg, 0.174 mmol), iodomethane (34  $\mu$ L, 0.548 mmol) and K<sub>2</sub>CO<sub>3</sub> (75.7 mg, 0.548 mmol) were added into a 10 mL glass pressure tube. Then 3 mL of *N,N*-dimethylacetamide was added, the tube was seal and the reaction mixture was placed in a LabArmor® bead bath at 35 °C for 24 hours. The reaction mixture was passed through a short Celite plug with dichloromethane then the organic solvent was removed using rotary evaporation. Then the resulting red solid was precipitated into methanol and vacuum filtered. **Yield:** 99.1 mg (82%)

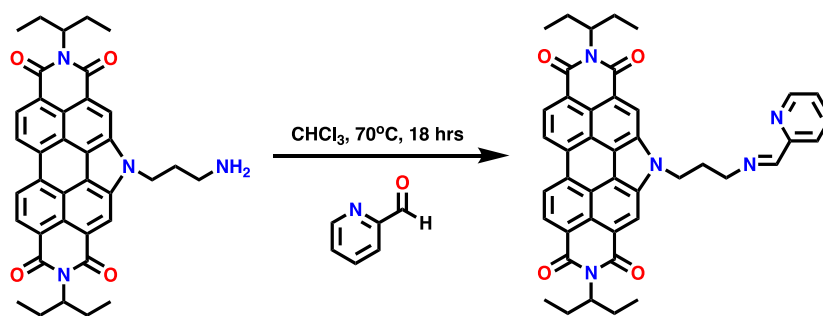
**<sup>1</sup>H-NMR** (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.92 (s, 2H), 8.77-8.69 (d, *J* = 7.9 Hz, 2H), 8.46-8.39 (d, *J* = 7.9 Hz, 2H), 5.13-5.02 (m, 2H), 5.01-4.93 (m, 2H), 3.53-3.44 (m, 2H), 3.06 (s, 8H), 3.38-2.21 (m, 5H), 2.10-1.94 (m, 5H), 1.01-0.892 (t, *J* = 8.6 Hz, 13H)

**<sup>13</sup>C-NMR** (75 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 134.7, 132.1, 124.8, 124.1, 120.9, 118.8, 63.3, 57.4, 53.0, 25.3, 25.2, 12.0

Expected <sup>13</sup>C signals: 19 Tabulated <sup>13</sup>C signals: 12

**MALDI-TOF:** m/z [M-I] expected: 643.81 obtained: 643.33

**CHN:** Theoretical (%) C: 74.62 H: 6.73 N: 8.76 Found (%) C: 60.37 H: 5.64 N: 7.03



### Synthesis of Imine-C<sub>3</sub>-N-PDI (4):

H<sub>2</sub>N-C<sub>3</sub>-N-PDI (105 mg, 0.174 mmol) and 2-pyridinecarboxaldehyde (23  $\mu$ L, 0.261 mmol) were added to a 10 mL glass pressure tube. Then 5 mL of dry chloroform was added, the tube was sealed, and the reaction mixture was placed in a LabArmor® bead bath at 70 °C for 18 hours. The reaction mixture was then diluted in 100 mL of methanol and 10 mL of H<sub>2</sub>O and set to stir for 1 hour. The resulting red precipitate was then vacuum filtered. **Yield:** 103 mg (86%)

**<sup>1</sup>H-NMR** (500 MHz, chloroform-d)  $\delta$ : 9.09 (s, 2H), 9.00-8.97 (d,  $J$  = 8.0 Hz, 2H), 8.86 (br, 2H), 8.49-8.41 (dq,  $J$  = 4.8 Hz and  $J$  = 0.9 Hz, 1H), 8.11 (s, 1H), 7.72-7.69 (d,  $J$  = 8.0 Hz, 1H), 7.76-7.52 (td,  $J$  = 8.0 Hz and  $J$  = 1.7 Hz, 1H), 7.19-7.16 (qd,  $J$  = 4.8 Hz and  $J$  = 1.3 Hz, 1H), 5.26-5.18 (m, 2H), 5.15-5.11 (t,  $J$  = 6.3 Hz, 2H), 3.70-3.66 (t,  $J$  = 5.9 Hz, 2H), 2.73-2.66 (p,  $J$  = 6.9 Hz, 2H), 2.41-2.30 (m, 5H), 2.05-1.95 (m, 4H), 1.00-0.951 (t,  $J$  = 7.4 Hz, 12H)

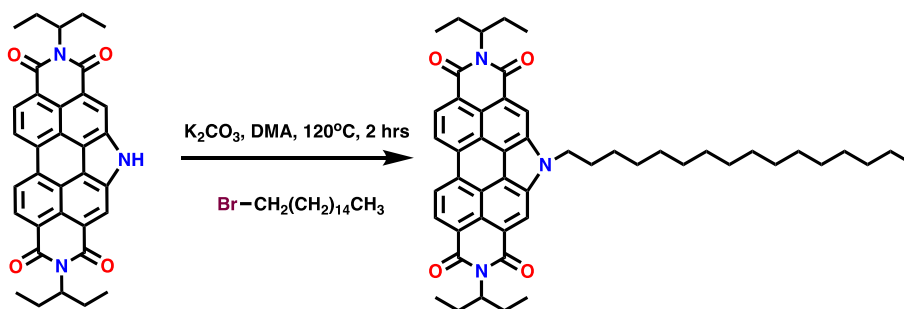
**<sup>13</sup>C-NMR** (125 MHz, chloroform-d)  $\delta$ : 165.5, 162.7, 153.7, 149.2, 136.3, 135.0, 132.8, 127.9, 124.8, 124.6, 123.9, 122.3, 121.9, 121.0, 119.7, 119.2, 57.9, 57.8, 44.9, 31.8, 25.3, 11.5

Expected <sup>13</sup>C signals: 24 Tabulated <sup>13</sup>C signals: 22

**MALDI-TOF:** m/z [M+H] expected: 690.30 obtained: 690.31

**CHN:** Theoretical (%) C: 74.87 H: 5.70 N: 10.15 Found (%) C: 74.77 H: 5.81 N: 9.86





### Synthesis of Hexadecyl-N-PDI (5):

H-N-PDI (120 mg, 0.221 mmol), 1-bromohexadecane (100  $\mu$ L, 0.331 mmol) and  $K_2CO_3$  (76.2 mg, 0.552 mmol) were added into a 10 mL glass pressure tube. Then 5 mL of *N,N*-dimethylacetamide was added, the tube was seal and the reaction mixture was placed in a LabArmor® bead bath at 120  $^{\circ}C$  for 2 hours. The reaction mixture was passed through a short Celite plug with dichloromethane then the organic solvent was removed using rotary evaporation. The crude solid was then passed through a short silica gel plug, eluted first with hexanes then dichloromethane to collect the product. The organic solvent was removed by rotary evaporation then the resulting red solid was precipitated into methanol and vacuum filtered. **Yield:** 148 mg (87%)

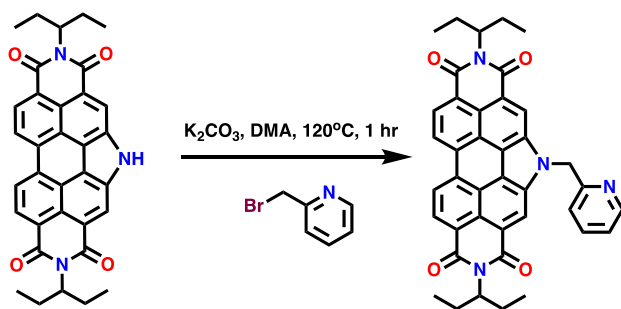
**$^1H$ -NMR** (500 MHz, chloroform-*d*)  $\delta$ : 8.99 (s, 2H), 8.98-8.95 (d,  $J = 8.0$  Hz, 2H), 8.85 (br, 2H), 5.27-5.20 (m, 2H), 4.89-4.84 (t,  $J = 7.6$  Hz, 2H), 2.43-2.32 (m, 4H), 2.23-2.15 (p,  $J = 7.2$  Hz, 2H), 2.08-1.97 (m, 4H), 1.30-1.17 (m, 26H), 1.02-0.966 (t,  $J = 7.6$  Hz, 12H), 0.887-0.842 (t,  $J = 6.5$  Hz, 3H)

**$^{13}C$ -NMR** (125 MHz, chloroform-*d*)  $\delta$ : 134.9, 132.8, 128.0, 124.7, 132.9, 122.4, 121.9, 119.6, 118.6, 57.8, 47.1, 32.0, 31.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 27.3, 25.3, 22.7, 14.1, 11.5

Expected  $^{13}C$  signals: 31 Tabulated  $^{13}C$  signals: 24

**MALDI-TOF:**  $m/z$  [M-H] expected: 766.47 obtained: 766.46

**CHN:** Theoretical (%) C: 78.19 H: 8.01 N: 5.47 Found (%) C: 78.39 H: 8.55 N: 5.21



### Synthesis of 2-(MePy)-N-PDI (6):

H-N-PDI (92.8 mg, 0.171 mmol), 2-(bromomethyl)-pyridine hydrobromide (64.8 mg, 0.256 mmol) and  $K_2CO_3$  (118 mg, 0.855 mmol) were added into a 10 mL glass pressure tube. Then 3 mL of *N,N*-dimethylacetamide was added, the tube was seal and the reaction mixture was placed in a LabArmor® bead bath at 120 °C for 1 hour. The reaction mixture was passed through a short Celite plug with dichloromethane then the organic solvent was removed using rotary evaporation. The resulting red solid was precipitated into methanol and vacuum filtered. **Yield:** 90.7 mg (84%)

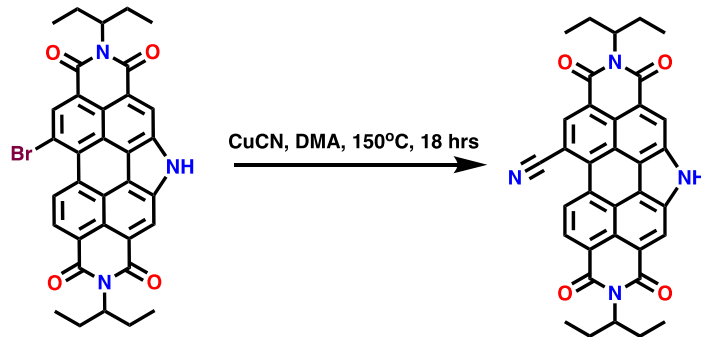
**$^1H$ -NMR** (300 MHz, chloroform-*d*)  $\delta$ : 9.01-8.94 (ov, 4H), 8.89-8.81 (d,  $J = 7.4$  Hz, 2H), 8.62-8.58 (d,  $J = 4.8$  Hz, 1H), 7.66-7.58 (td,  $J = 7.9$  Hz and  $J = 2.2$  Hz, 1H), 7.25-7.21 (br, 2H), 7.12-7.07 (d,  $J = 7.9$  Hz, 1H), 6.16 (s, 2H), 5.26-5.14 (m, 2H), 2.42-2.26 (m, 4H), 2.07-1.91 (m, 4H), 1.01-0.92 (t,  $J = 7.4$  Hz, 12H)

**$^{13}C$ -NMR** (75 MHz, chloroform-*d*)  $\delta$ : 165.4, 155.6, 150.3, 137.4, 135.4, 132.9, 128.1, 125.0, 124.1, 123.4, 122.0, 121.2, 120.0, 119.2, 57.8, 51.9, 25.3, 11.5

Expected  $^{13}C$  signals: 21 Tabulated  $^{13}C$  signals: 18

**MALDI-TOF:**  $m/z$  [M-H] expected: 633.26 obtained: 633.25

**CHN:** Theoretical (%) C: 75.69 H: 5.40 N: 8.83 Found (%) C: 74.86 H: 3.64 N: 8.77



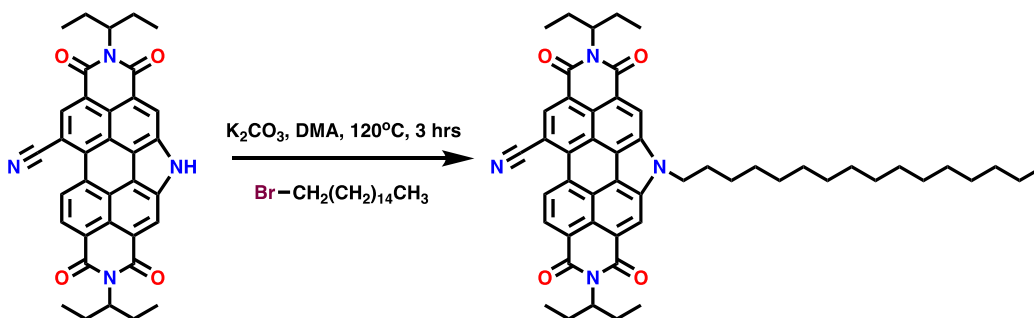
### Synthesis of H-N-PDI-CN

H-N-PDI-Br (307 mg, 0.490 mmol) and CuCN (800 mg, 8.88 mmol) were added to a 10 mL glass pressure tube. Reaction vessel was flushed with N<sub>2</sub> for 15 minutes then 10 mL of dry and N<sub>2</sub> sparged *N,N*-dimethylacetamide was added *via* cannula transfer. Reaction mixture was then placed in a LabArmor® bead bath at 150 °C for 18 hours. Reaction mixture was diluted in 100 mL of methanol and 10 mL of water, followed by the dropwise addition of 1 mL of HCl. The resulting solids were filtered *via* vacuum filtration. The solids were then dissolved in tetrahydrofuran and passed through a silica gel plug. The organic solvent was then removed by rotary evaporation and the resulting red solid was precipitated into methanol and vacuum filtered. **Yield:** 265 mg (95%)

<sup>1</sup>H-NMR (400 MHz, chloroform-d) δ: 10.10-10.06 (d, *J* = 8.3 Hz, 1H), 9.98 (s, 1H), 9.25 (s, 1H) 9.14 (s, 1H), 9.05-8.99 (d, *J* = 9.8 Hz, 1H), 5.28-5.17 (m, 2H), 2.43-2.29 (m, 4H), 2.10-1.98 (m, 3H), 1.04-0.958 (q, *J* = 7.5 Hz, 8H)

<sup>13</sup>C-NMR: Due to the poor solubility of this compound a suitable <sup>13</sup>C-NMR spectrum was not obtained

MALDI-TOF: m/z [M-H] expected: 567.21 obtained: 567.21



### Synthesis of Hexadecyl-N-PDI-CN (7)

H-N-PDI-CN (71.8 mg, 0.126 mmol), 1-bromohexadecane (58  $\mu$ L, 0.189 mmol) and  $K_2CO_3$  (43.6 mg, 0.316 mmol) were added into a 10 mL glass pressure tube. Then 5 mL of *N,N*-dimethylacetamide was added, the tube was seal and the reaction mixture was placed in a LabArmor® bead bath at 100  $^{\circ}C$  for 3 hours. The reaction mixture was passed through a short Celite plug with dichloromethane then the organic solvent was removed using rotary evaporation. The crude solid was then passed through a short silica gel plug, eluted first with hexanes then dichloromethane to collect the product. The organic solvent was removed by rotary evaporation then the resulting red solid was precipitated into methanol and vacuum filtered. **Yield:** 70.0 mg (70%)

**$^1H$ -NMR** (300 MHz, chloroform-*d*)  $\delta$ : 10.07-10.00 (d,  $J$  = 8.5 Hz, 1H), 9.21 (s, 1H), 9.11 (s, 2H), 9.03-8.99 (d,  $J$  = 9.1 Hz, 1H), 5.30-5.17 (m, 2H), 5.03-4.94 (t,  $J$  = 6.7 Hz, 2H), 2.44-2.30 (m, 4H), 2.29-2.20 (m, 3H), 2.12-1.96 (m, 4H), 1.29-1.20 (br, 23H), 1.05-0.954 (m, 12H), 0.908-0.849 (t,  $J$  = 6.1 Hz, 3H)

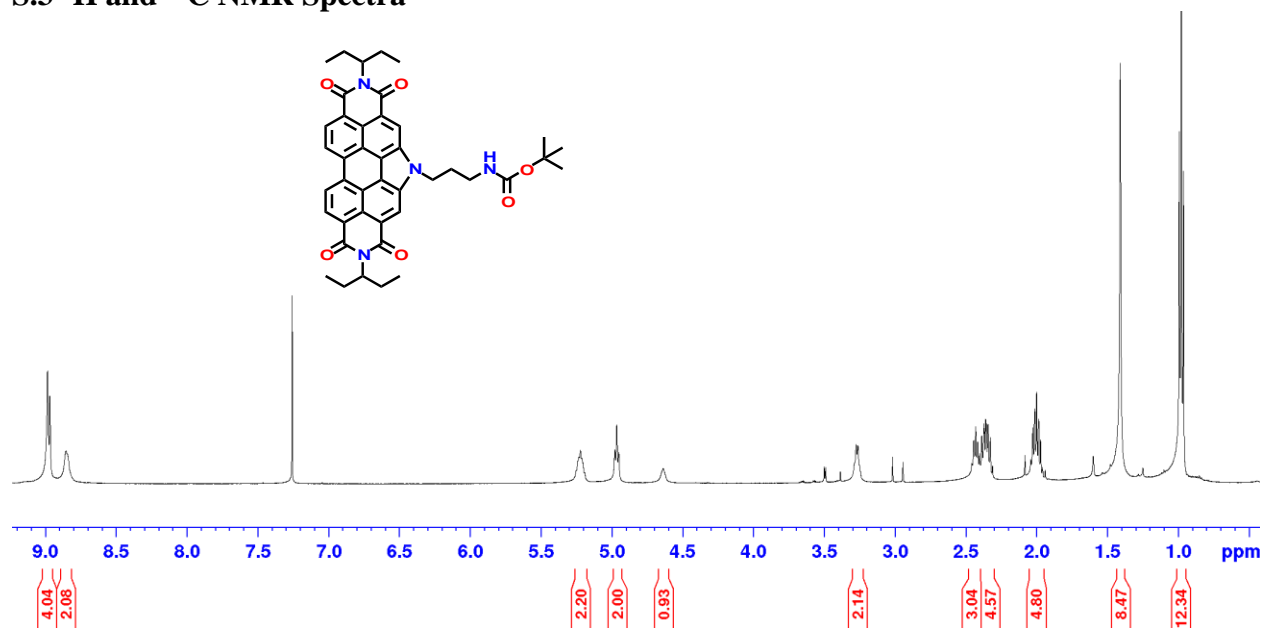
**$^{13}C$ -NMR** (75 MHz, chloroform-*d*)  $\delta$ : 148.9, 140.0, 135.5, 134.8, 133.4, 130.5, 127.3, 126.3, 124.3, 122.0, 119.3, 119.0, 118.9, 106.7, 58.3, 58.1, 47.2, 34.9, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 27.2, 25.2, 25.1, 23.9, 22.7, 14.1, 11.5, 11.4

Expected  $^{13}C$  signals: 44 Tabulated  $^{13}C$  signals: 37

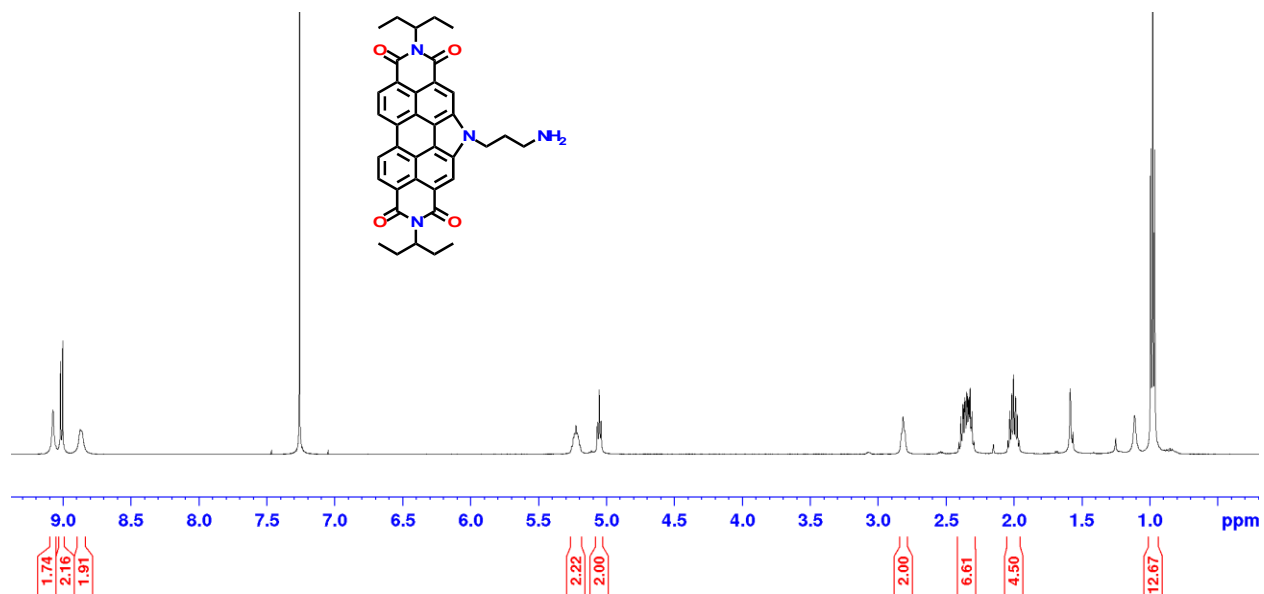
**MALDI-TOF:**  $m/z$  [M-H] expected: 791.43 obtained: 791.46

**CHN:** Theoretical (%) C: 77.24 H: 7.63 N: 7.06

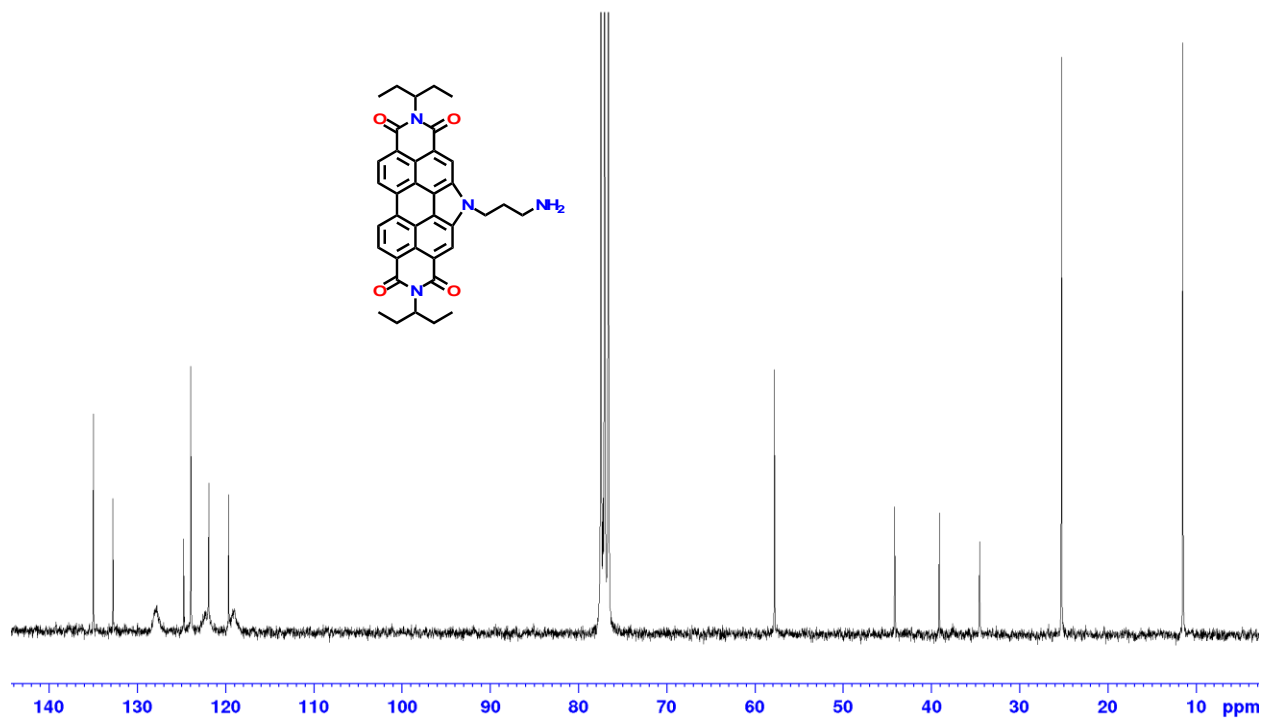
### S.3 $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



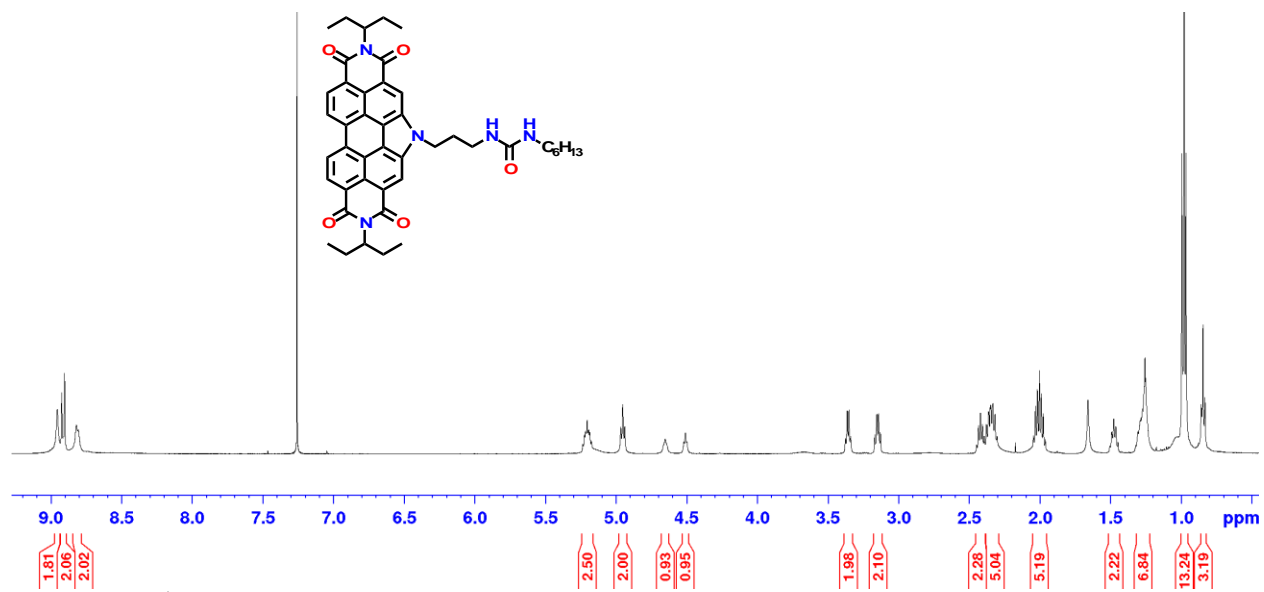
**Figure S1:**  $^1\text{H}$ -NMR spectrum of Boc-HN-C<sub>3</sub>-N-PDI in CDCl<sub>3</sub>



**Figure S2:** <sup>1</sup>H-NMR spectrum of compound **1** in CDCl<sub>3</sub>

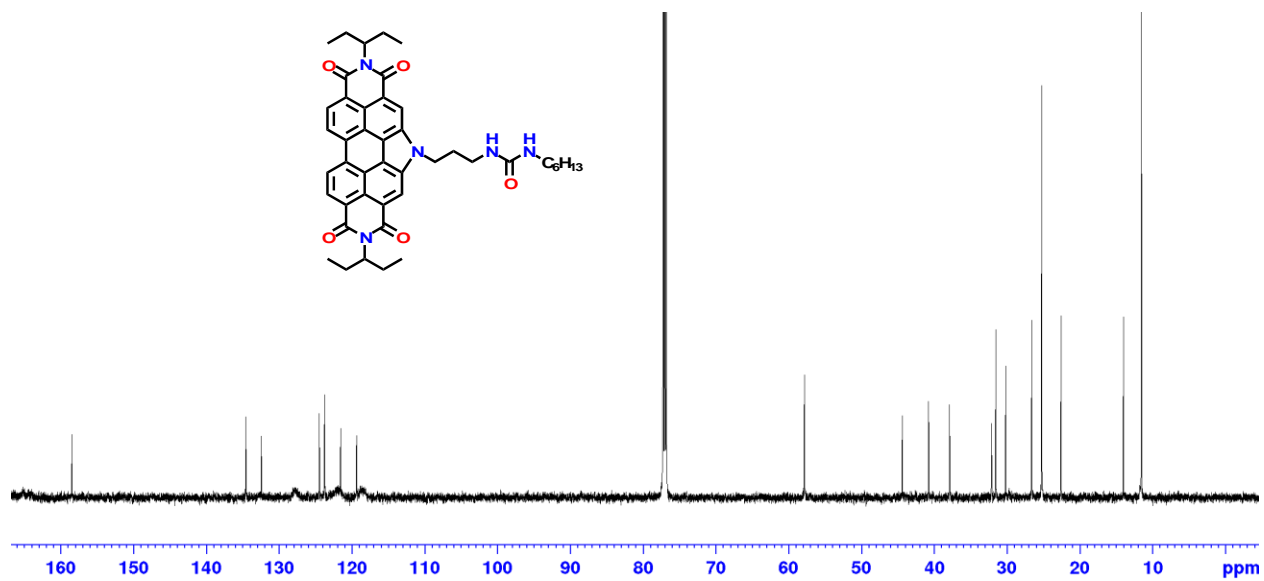


**Figure S3:**  $^{13}\text{C}$ -NMR spectrum of compound **1** in  $\text{CDCl}_3$

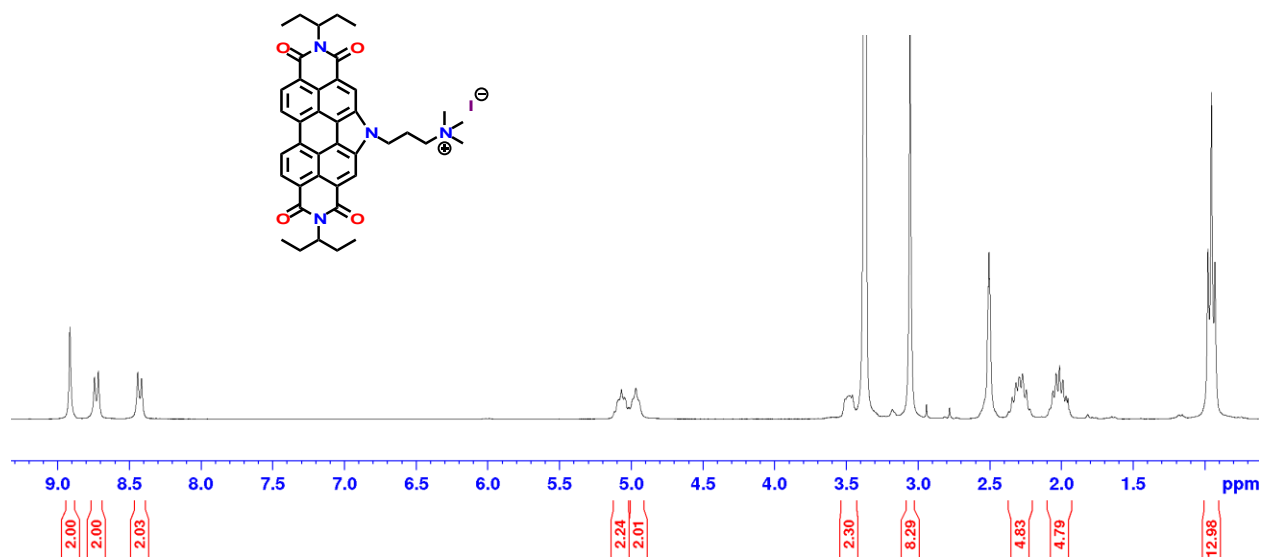


**Figure S4:** <sup>1</sup>H-NMR spectrum of compound **2** in CDCl<sub>3</sub>

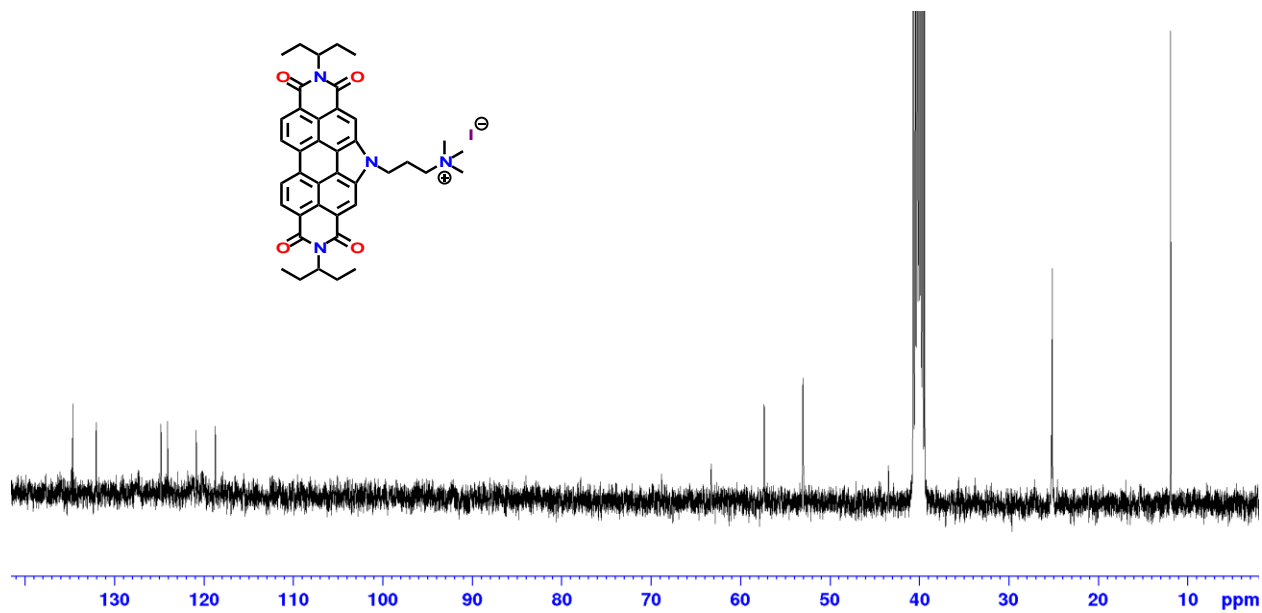




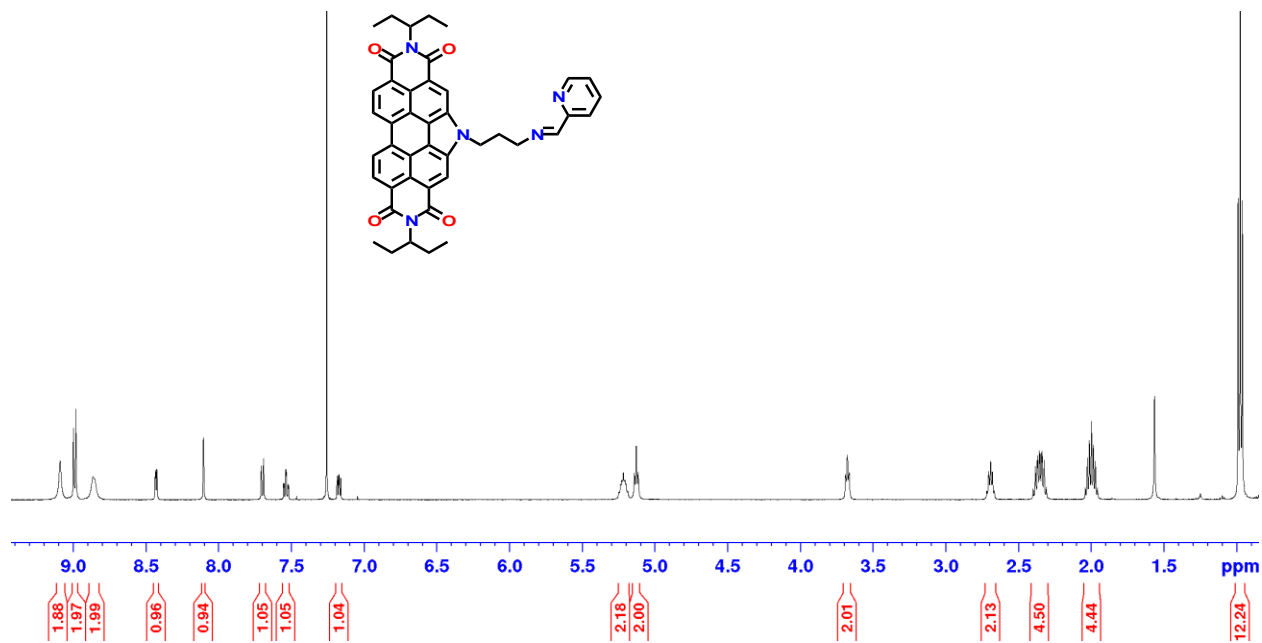
**Figure S5:** <sup>13</sup>C-NMR spectrum of compound **2** in CDCl<sub>3</sub>



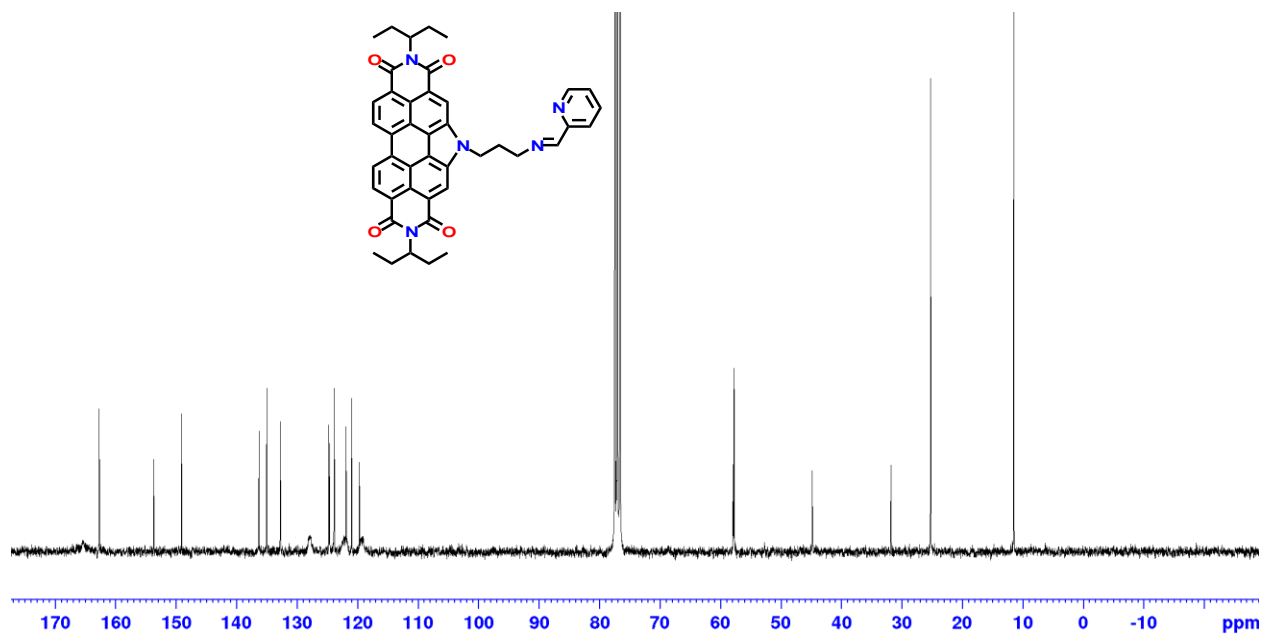
**Figure S6:** <sup>1</sup>H-NMR spectrum of compound **3** in DMSO-D<sub>6</sub>



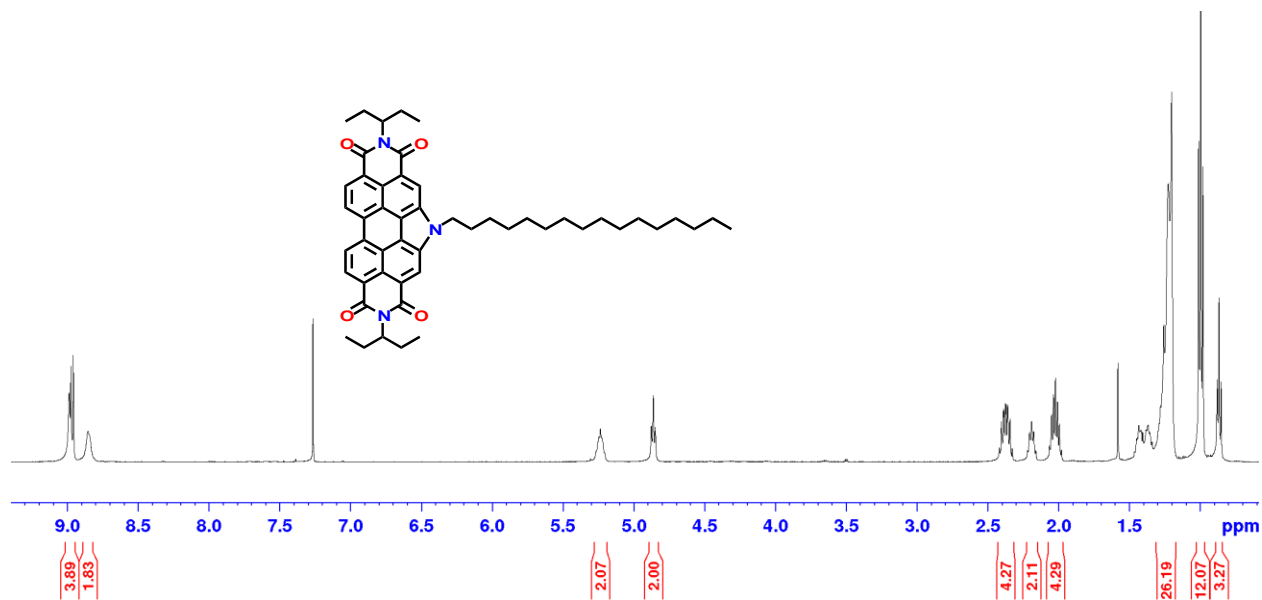
**Figure S7:**  $^{13}\text{C}$ -NMR spectrum of compound 3 in DMSO- $\text{D}_6$



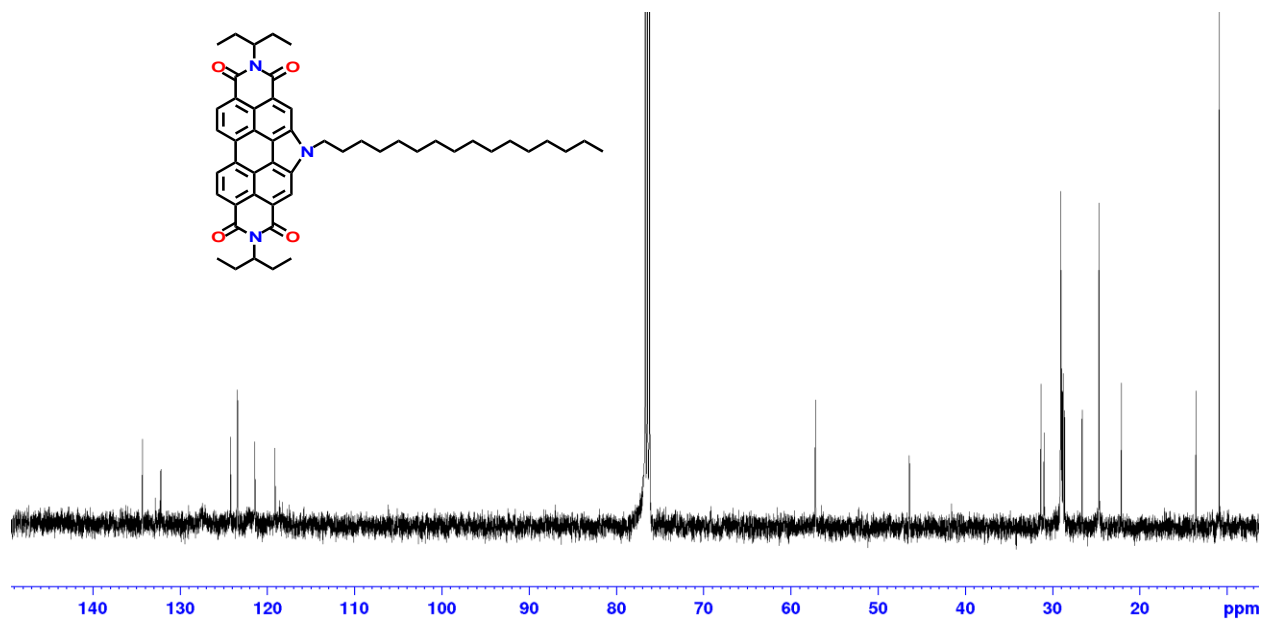
**Figure S8:** <sup>1</sup>H-NMR spectrum of compound **4** in CDCl<sub>3</sub>



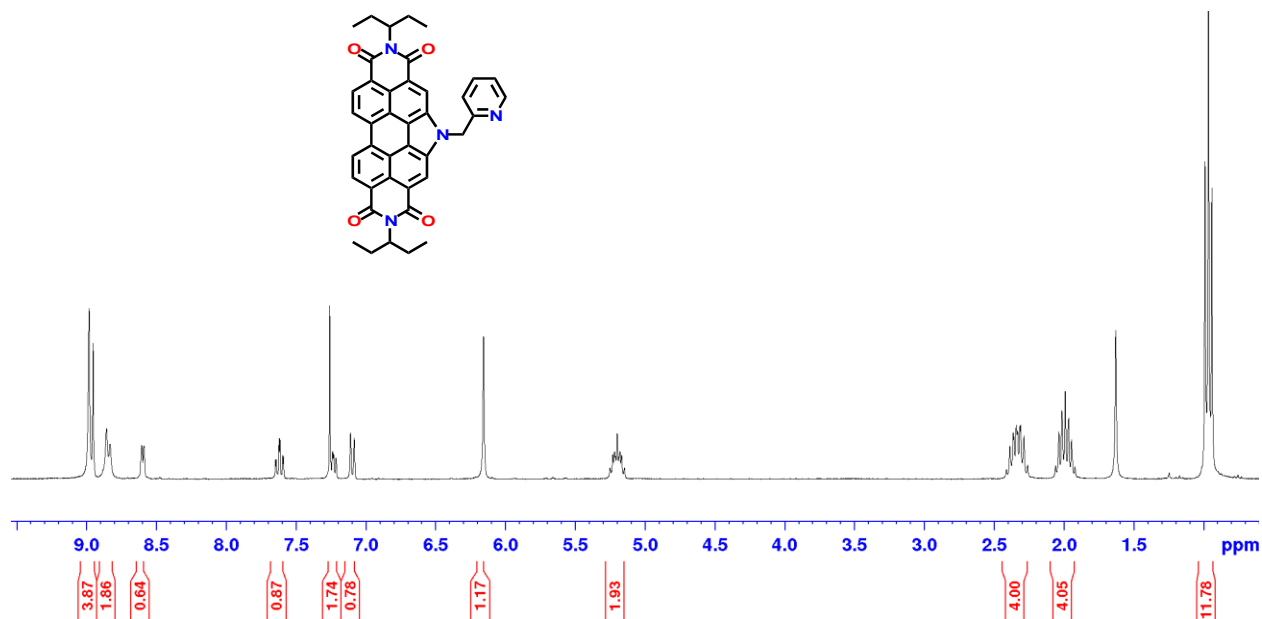
**Figure S9:**  $^{13}\text{C}$ -NMR spectrum of compound **4** in  $\text{CDCl}_3$



**Figure S10:** <sup>1</sup>H-NMR spectrum of compound 5 in CDCl<sub>3</sub>

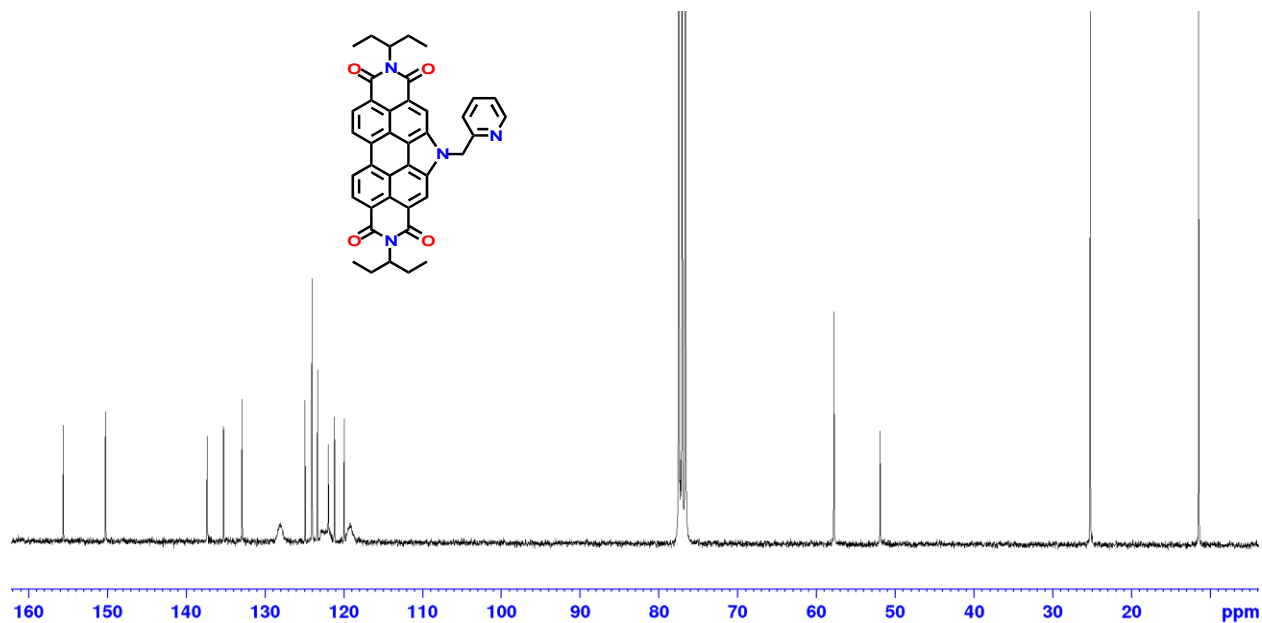


**Figure S11:**  $^{13}\text{C}$ -NMR spectrum of compound 5 in  $\text{CDCl}_3$

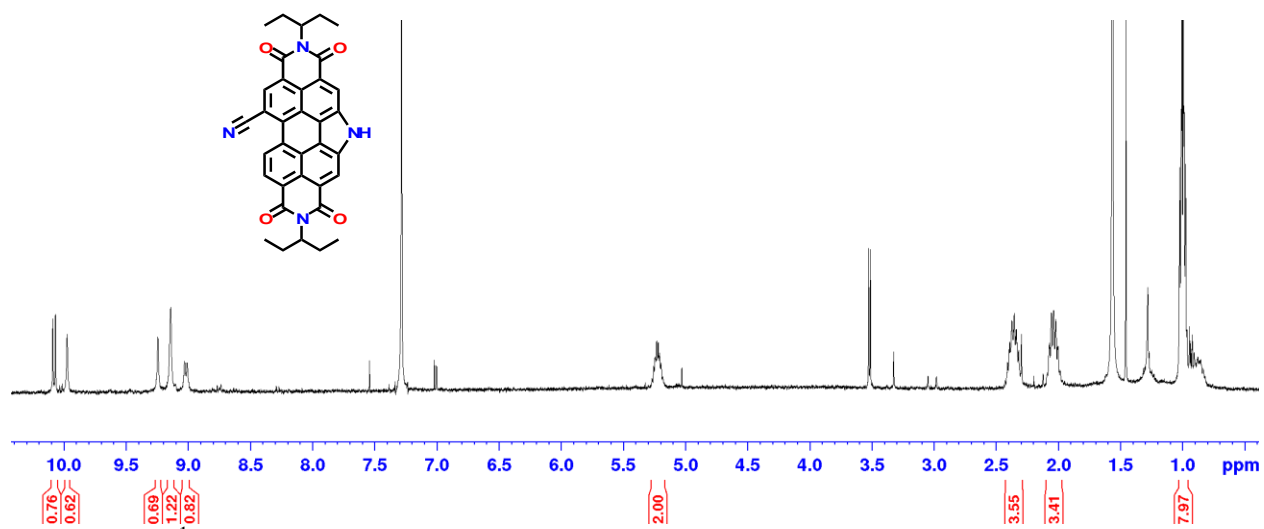


**Figure S12:** <sup>1</sup>H-NMR spectrum of compound **6** in CDCl<sub>3</sub>

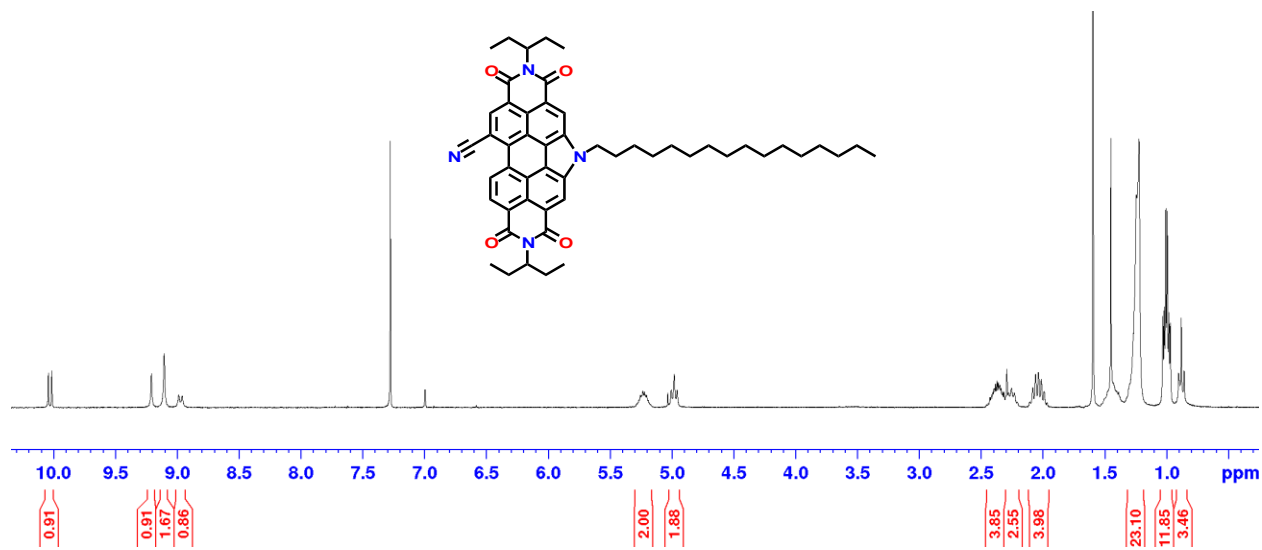




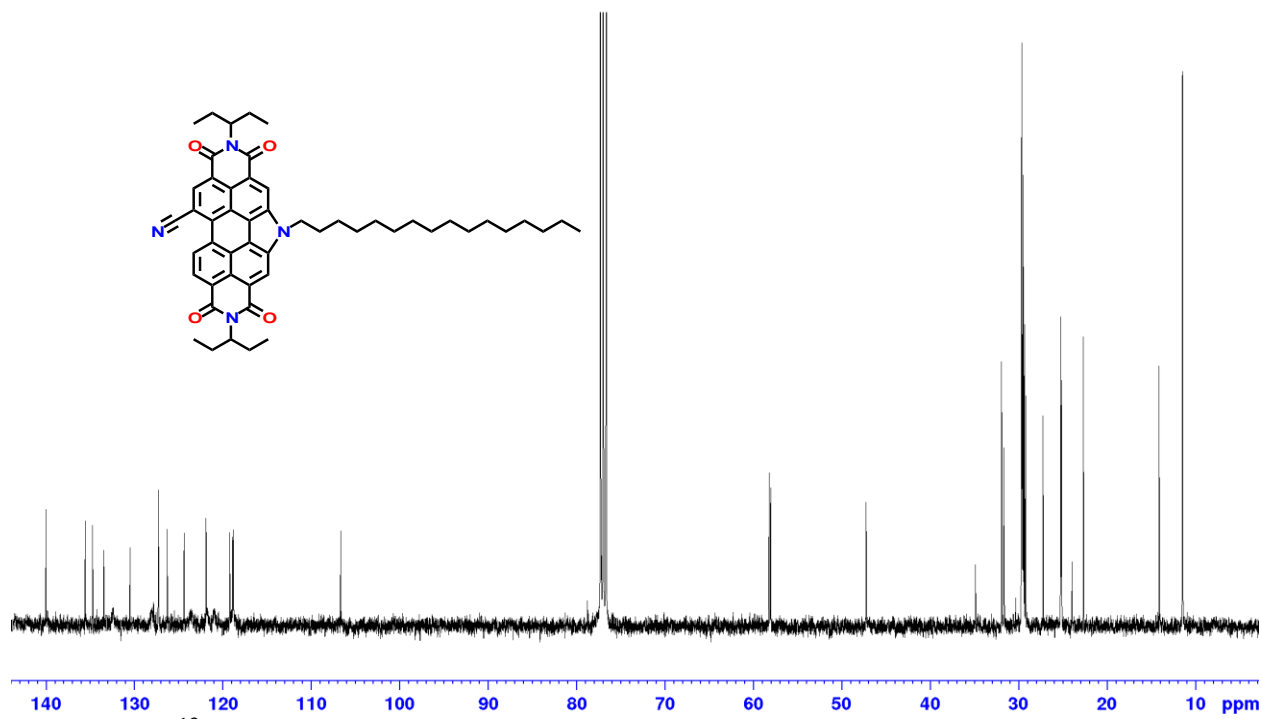
**Figure S13:** <sup>13</sup>C-NMR spectrum of compound **6** in CDCl<sub>3</sub>



**Figure S14:** <sup>1</sup>H-NMR spectrum of compound H-N-PDI-CN in CDCl<sub>3</sub>

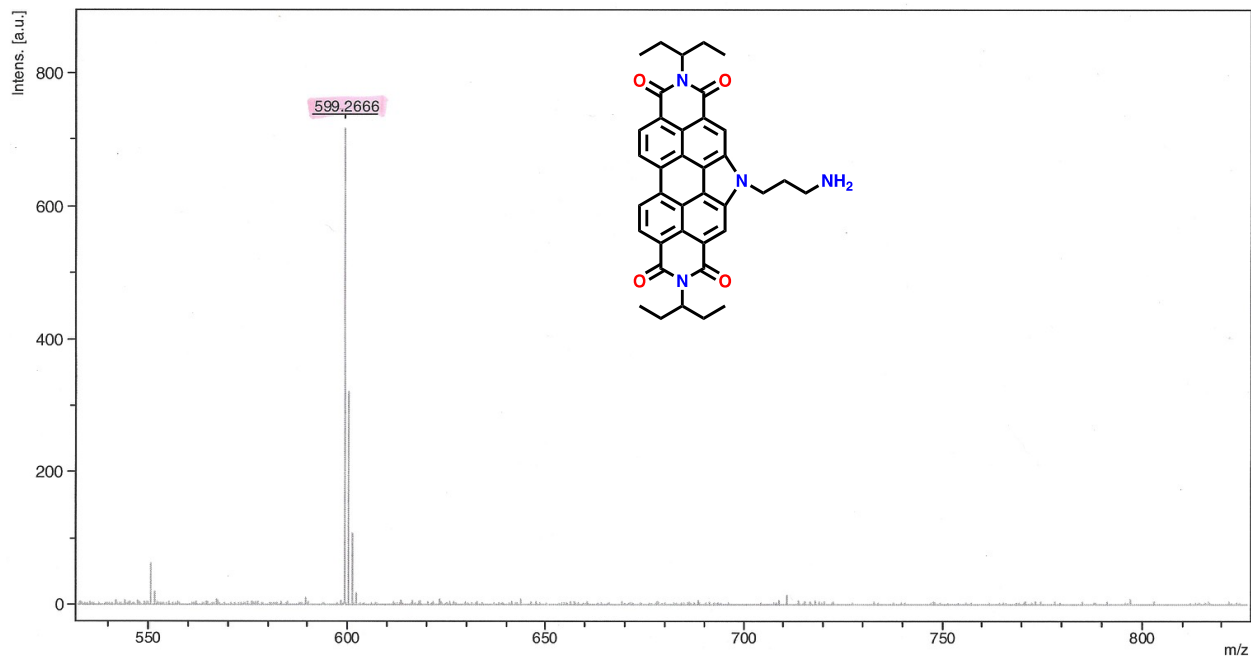


**Figure S15:** <sup>1</sup>H-NMR spectrum of compound 7 in CDCl<sub>3</sub>

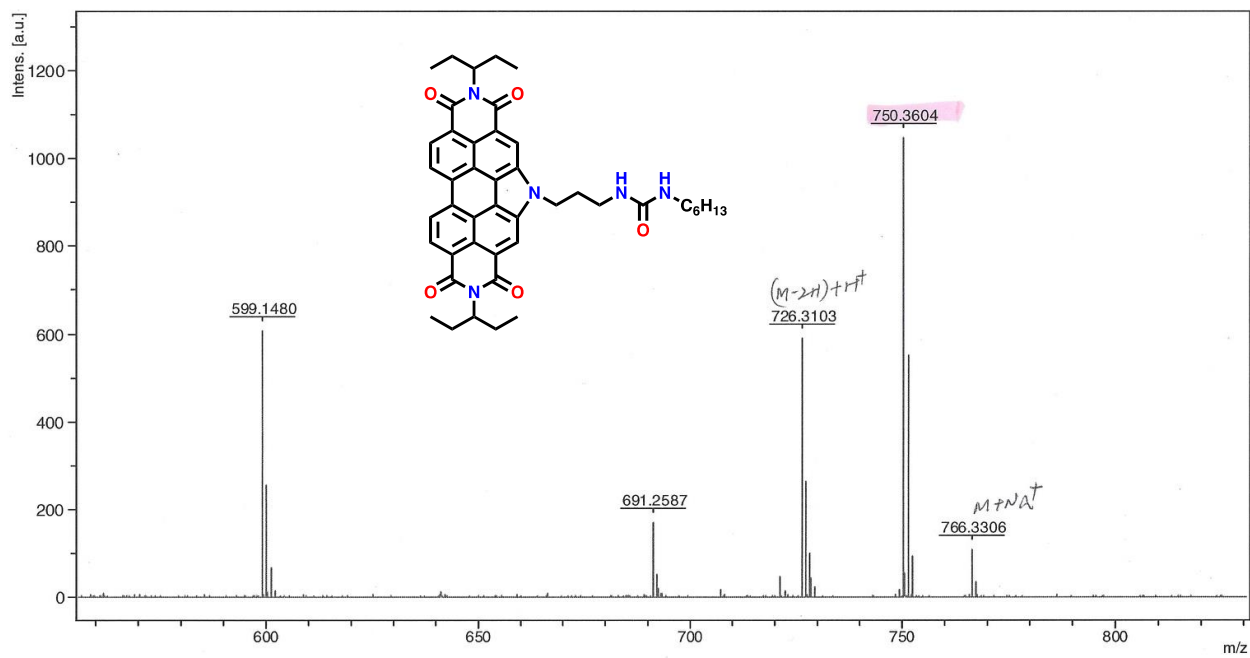


**Figure S16:**  $^{13}\text{C}$ -NMR spectrum of compound 7 in  $\text{CDCl}_3$

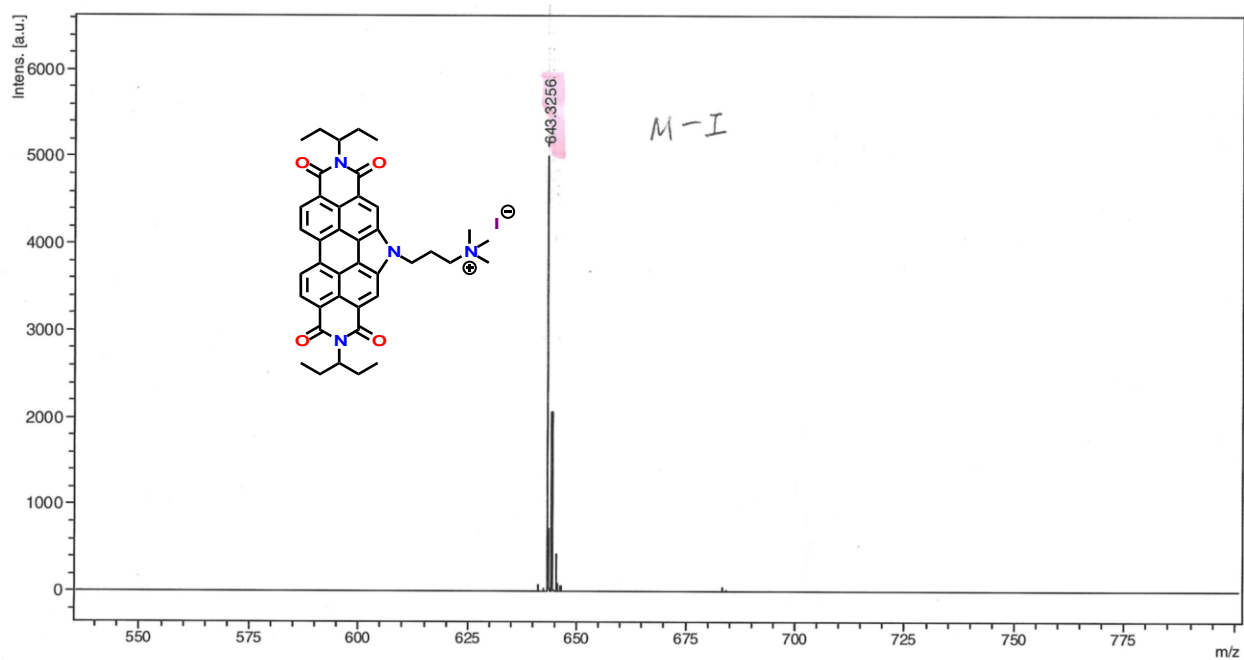
## S.4 Mass Spectrometry



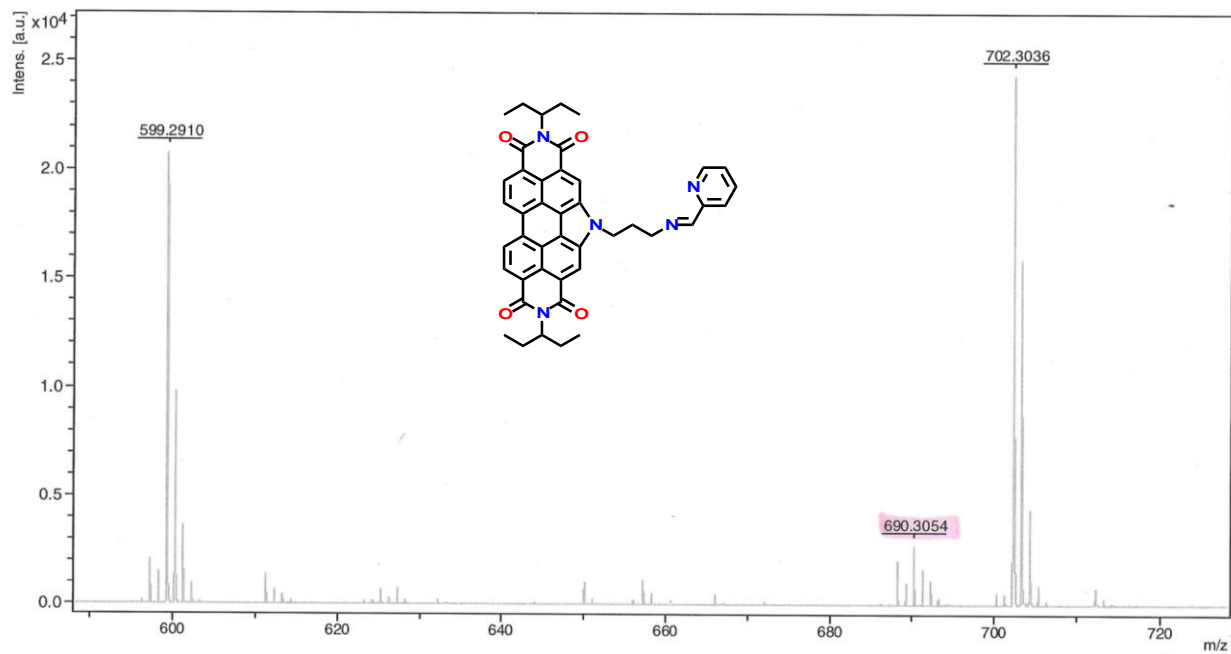
**Figure S17:** MALDI-TOF spectrum of compound 1



**Figure S18:** MALDI-TOF spectrum of compound 2

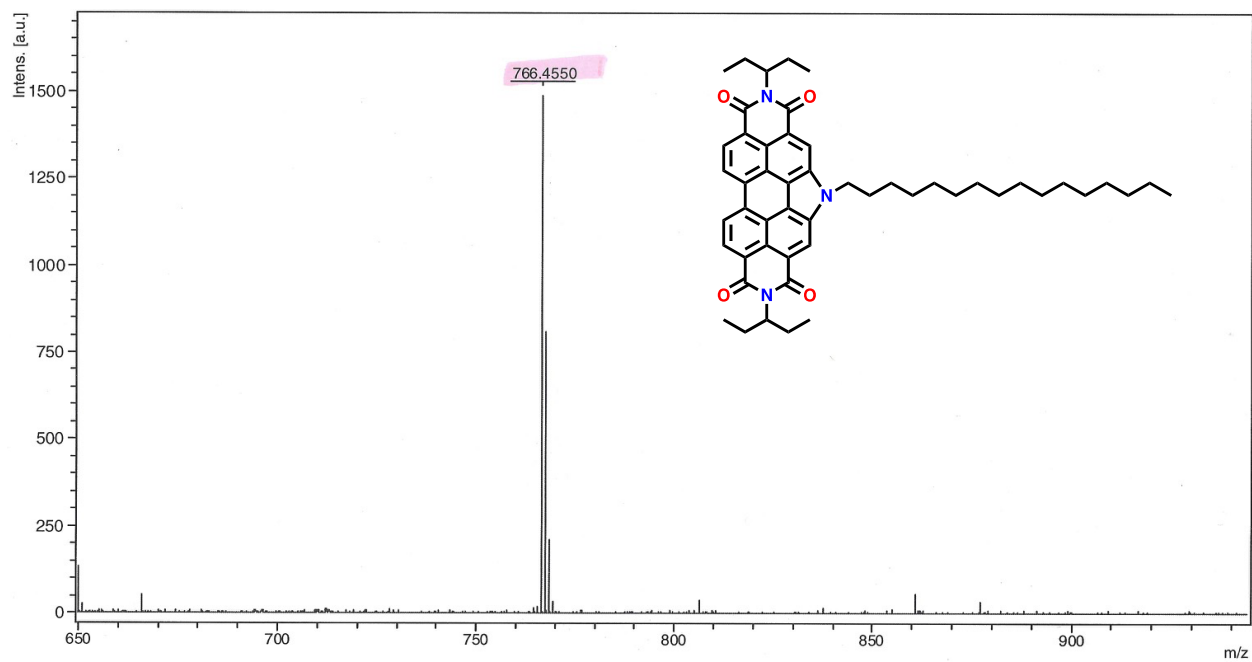


**Figure S19:** MALDI-TOF spectrum of compound **3**

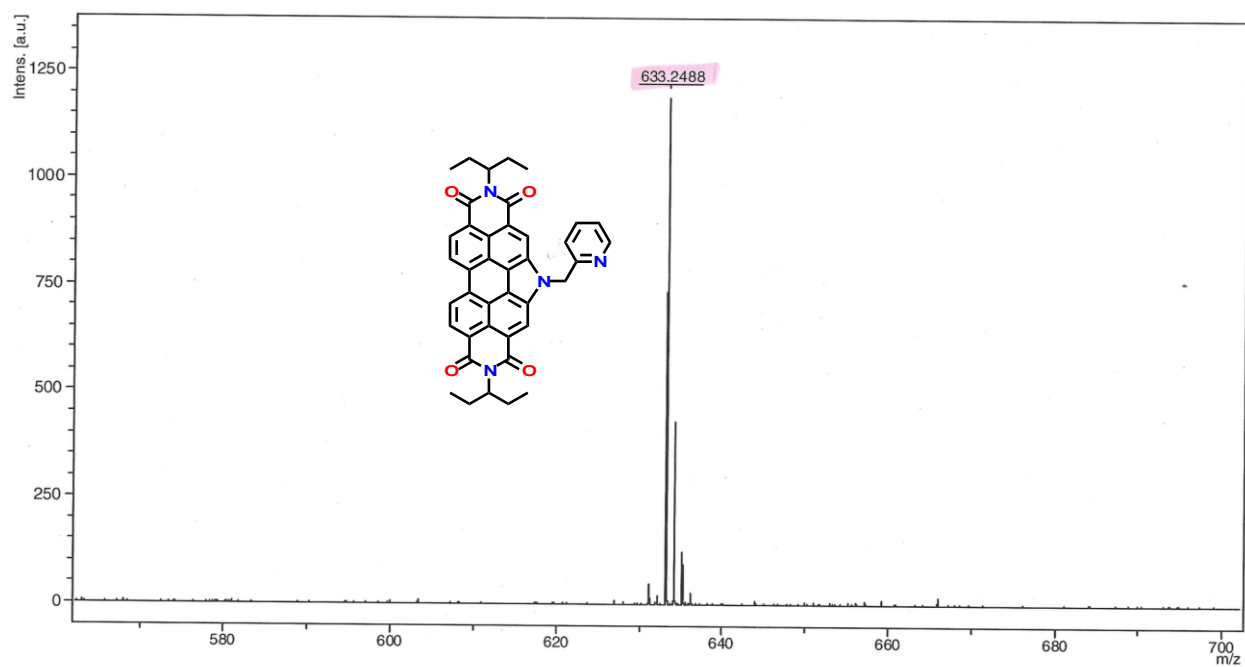


**Figure S20:** MALDI-TOF spectrum of compound **4**

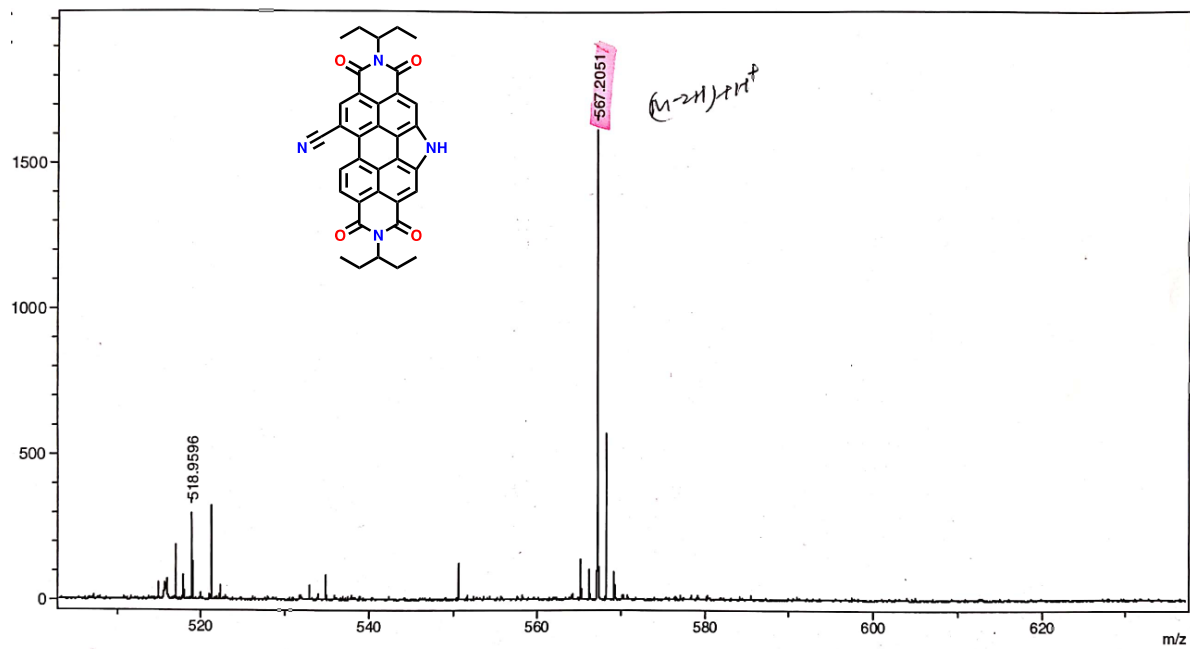




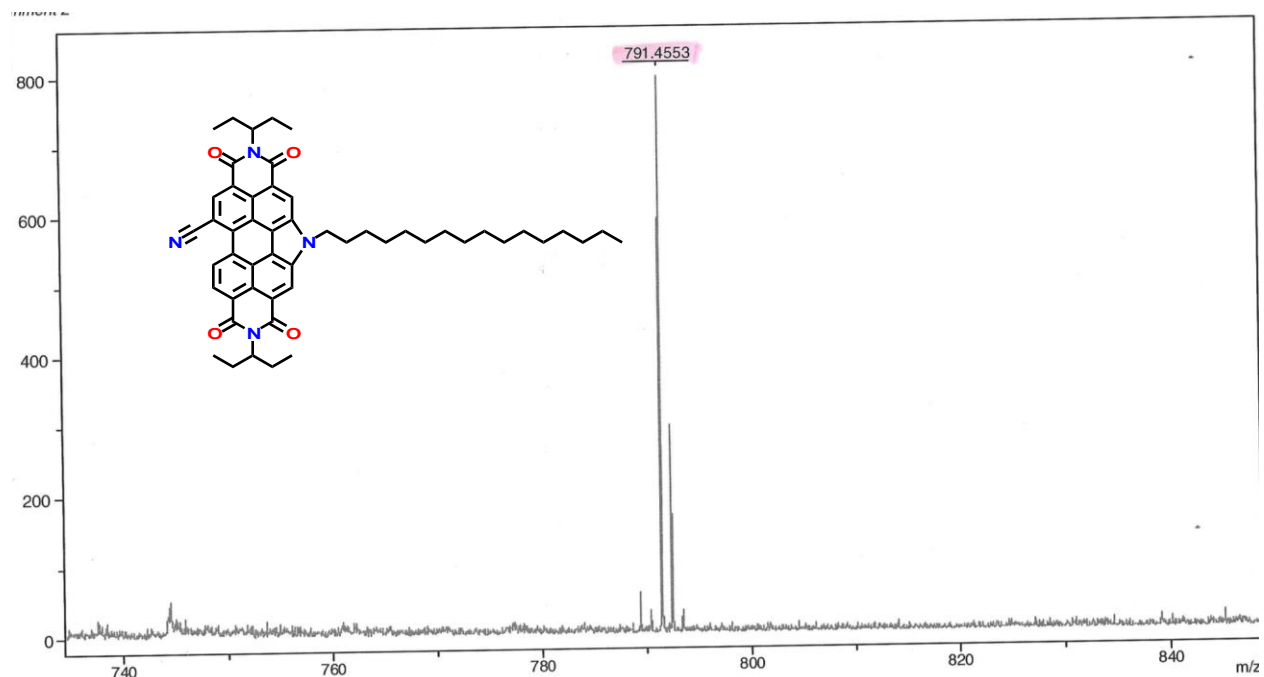
**Figure S21:** MALDI-TOF spectrum of compound **5**



**Figure S22:** MALDI-TOF spectrum of compound 6



**Figure S23:** MALDI-TOF spectrum of compound H-N-PDI-CN



**Figure S24:** MALDI-TOF spectrum of compound **7**

## S.5 CHN Elemental Analysis

University of Calgary

Department of Chemistry EA

Date: 3/17/2020

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Name:	MARK	Group:	GW
Sample:	MM337-1	Weight (mg):	1.512
%C (Actual):	73.27	%C (Theoretical):	73.98
%H (Actual):	5.77	%H (Theoretical):	6.04
%N (Actual):	8.92	%N (Theoretical):	9.33

**Figure S25:** CHN elemental analysis of compound **1**

University of Calgary

Department of Chemistry EA

Date: 3/17/2020

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Name:	MARK	Group:	GW
Sample:	MM333-1	Weight (mg):	1.652
%C (Actual):	72.51	%C (Theoretical):	72.60
%H (Actual):	6.80	%H (Theoretical):	6.79
%N (Actual):	9.09	%N (Theoretical):	9.62

**Figure S26:** CHN elemental analysis of compound **2**

University of Calgary

Department of Chemistry EA

Date: 3-10-2021

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Name:	MARK	Group:	GW
Sample:	MM3-129-1	Weight (mg):	1.525
%C (Actual):	60.37	%C (Theoretical):	74.62
%H (Actual):	5.64	%H (Theoretical):	6.73
%N (Actual):	7.03	%N (Theoretical):	8.76

**Figure S27:** CHN elemental analysis of compound **3**

University of Calgary

Department of Chemistry EA

Date: 3/17/2020

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Name:	MARK	Group:	GW
Sample:	MM331-2	Weight (mg):	1.91
%C (Actual):	74.77	%C (Theoretical):	74.87
%H (Actual):	5.81	%H (Theoretical):	5.70
%N (Actual):	9.86	%N (Theoretical):	10.15

**Figure S28:** CHN elemental analysis of compound 4



University of Calgary

Department of Chemistry EA

Date: 3/17/2020

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Name:	MARK	Group:	GW
Sample:	MM343-1	Weight (mg):	1.79
%C (Actual):	78.39	%C (Theoretical):	78.19
%H (Actual):	8.55	%H (Theoretical):	8.01
%N (Actual):	5.21	%N (Theoretical):	5.47

**Figure S29:** CHN elemental analysis of compound **5**

University of Calgary

Department of Chemistry EA

Date: 4-7-2021

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Name:	MARK	Group:	GW
Sample:	MM3-45-1	Weight (mg):	0.7
%C (Actual):	74.86	%C (Theoretical):	75.69
%H (Actual):	3.64	%H (Theoretical):	5.40
%N (Actual):	8.77	%N (Theoretical):	8.83

**Figure S30:** CHN elemental analysis of compound **6**

University of Calgary

Department of Chemistry EA

Date: 3-10-2021

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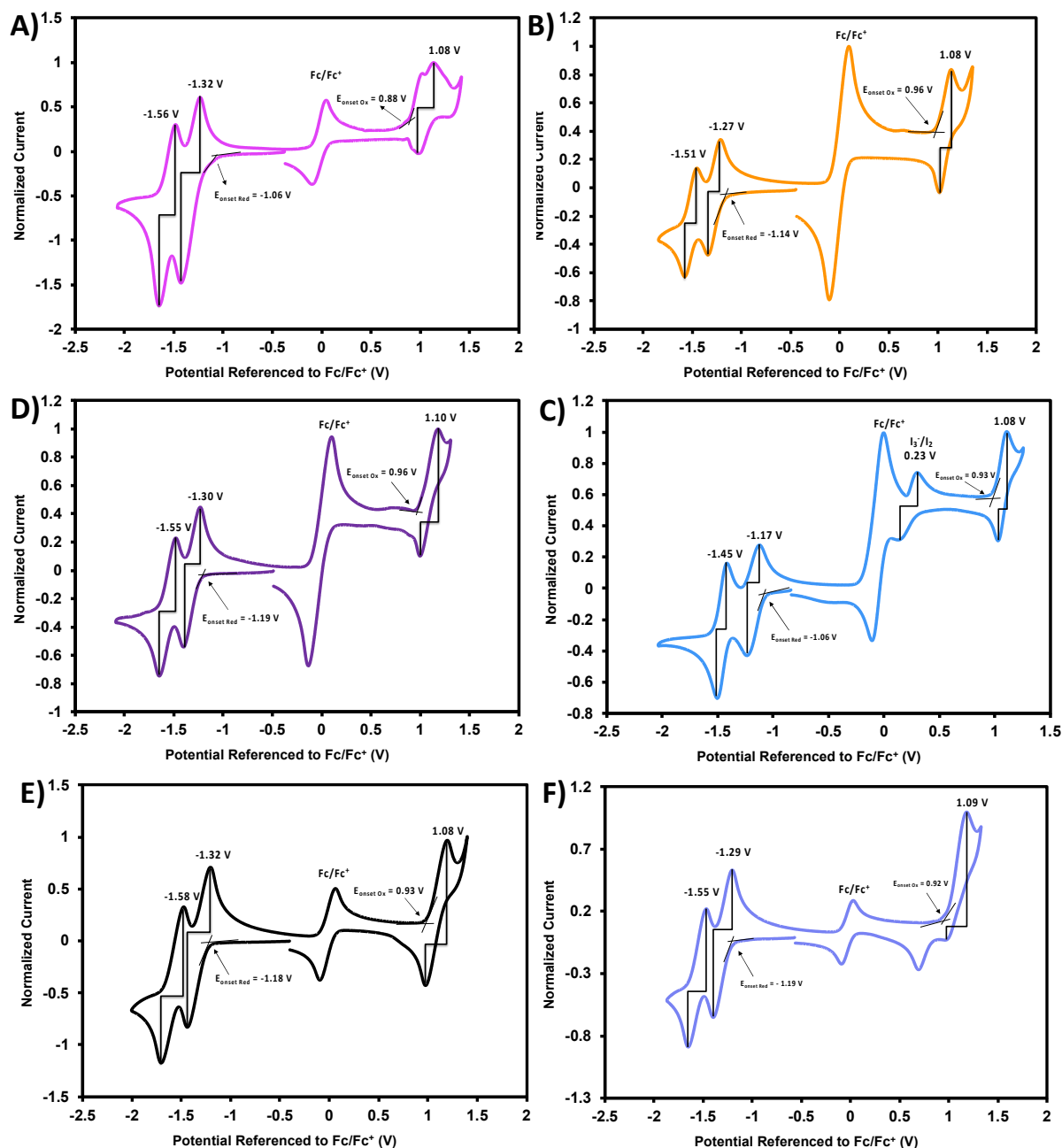
Name:	MARK	Group:	GW
Sample:	MM3-133-1	Weight (mg):	1.608
%C (Actual):	75.72	%C (Theoretical):	77.24
%H (Actual):	7.78	%H (Theoretical):	7.63
%N (Actual):	6.72	%N (Theoretical):	7.06

**Figure S31:** CHN elemental analysis of compound **7**

## S.6 Electrochemical and Optical Data Tables

**Table S1:** Electrochemical and optical data for compounds **1-7**

Compound	$E_{1/2 \text{ red}}$ (V)	$E_{1/2 \text{ ox}}$ (V)	$\epsilon$ Sol ( $\text{M}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{max}}$ Sol/ Film (nm)
<b>1</b>	-1.3, -1.5	1.1	67,825	531/ 499
<b>2</b>	-1.3, -1.5	1.1	82,190	531/ 494
<b>3</b>	-1.2, -1.4	1.1	81,795	524/ 493
<b>4</b>	-1.3, -1.5	1.1	86,705	531/ 499
<b>5</b>	-1.3, -1.5	1.1	84,080	531/ 499
<b>6</b>	-1.3, -1.5	1.1	82,115	528/ 499
<b>7</b>	-1.1, -1.4	-	61,130	541/ 508

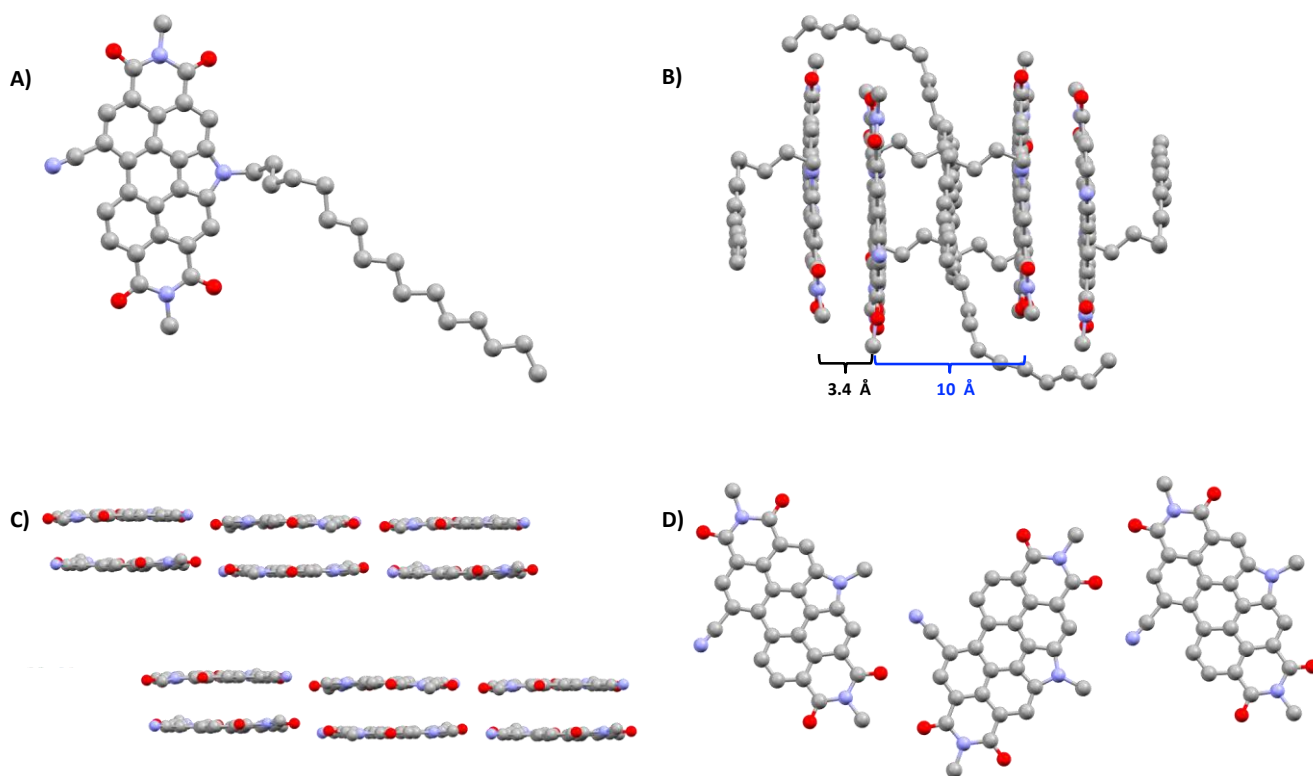


**Figure S32:** Cyclic voltammograms of compounds **1** (A), **2** (B), **3** (C), **4** (D), **5** (E) and **6** (F). All measurements in dichloromethane solution at 100 mV/s, except **5** which was performed in acetonitrile at 100 mV/s. Internal reference to ferrocene/ferrocenium redox couple.  $E_{1/2}$  values listed along with the onset of both oxidation and reduction. Lines show the anodic and cathodic peaks used to determine  $E_{1/2}$ . Notes: Compound **1** has a buried oxidation event at ~1V due to amine oxidation. Compound **6** has a reduction event ~-0.8V upon negative scan to zero which is attributed to the pyridine moiety.

## S.7 X-Ray Crystallographic Data

Table S2: Crystallographic data for **7**. CCDC# 2108930





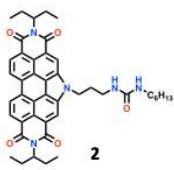







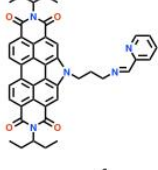
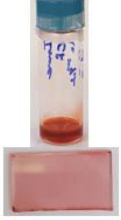


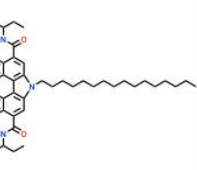



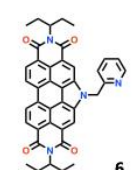


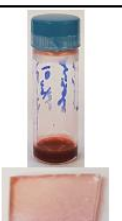
Compound	<b>7</b>
Empirical formula	C <sub>51</sub> H <sub>60</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	793.03
Temperature	173.0
Crystal system	Triclinic
Space group	P-1
a/Å	12.9973(10)
b/Å	19.3514(14)
c/Å	19.6063
α/°	113.984(5)
β/°	94.612(4)
γ/°	91.666(4)
Volume/Å <sup>3</sup>	4480.6(6)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.176
μ/mm <sup>-1</sup>	0.583
Reflections collected	43711
Unique reflections	14701
R <sub>int</sub> , R <sub>sigma</sub>	0.0279,0.0322
Goodness-of-fit on F <sup>2</sup>	0.942
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.1162, wR <sub>2</sub> = 0.2120
Final R indexes [all data]	R <sub>1</sub> = 0.1797, wR <sub>2</sub> = 0.2345
Largest diff. peak/hole / e Å <sup>-3</sup>	0.30/-0.27



**Figure S33:** Structural features of compound **7** in the solid state: **A)** single crystal structure, carbon is light grey, nitrogen is blue, and oxygen is red. **B)** packing arrangement with distances shown between each grouping of molecules **C)** layered packing motif **D)** hydrogen bonding network. Hydrogen atoms have been omitted and imide alkyl chains have been truncated to C<sub>1</sub> for clarity. Pyrrolic alkyl chain has been truncated to C<sub>1</sub> for **C)** and **D)**. **11c** crystallized in the P-1 space group with an R factor of 0.179 and unit cell parameters:  $a = 13.0 \text{ \AA}$ ,  $b = 19.4 \text{ \AA}$ ,  $c = 19.7 \text{ \AA}$ ,  $\alpha = 114.0^\circ$ ,  $\beta = 94.6^\circ$ , and  $\gamma = 91.7^\circ$ . This data was collected and solved by Dr. Benjamin S. Gelfand, University of Calgary, X-Ray Crystallography Facility. CCDC# 2108930

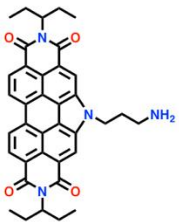











## S.8 Solubility Tables

**Table S3:** Solubility of compounds **1-6** at 10 mg/mL in solutions of chloroform, 2Me-THF and anisole along with their thin-films made on Corning glass substrates *via* spin-casting at room temperature.

	Chloroform	2Me-THF	Anisole
 <b>1</b>		 Sparingly Soluble	
 <b>2</b>	 Sparingly Soluble	 Sparingly Soluble	 Sparingly Soluble
 <b>3</b>	 Sparingly Soluble	 Sparingly Soluble	 Sparingly Soluble
 <b>4</b>	 Sparingly Soluble	 Sparingly Soluble	
 <b>5</b>	 Sparingly Soluble	 Sparingly Soluble	 Sparingly Soluble
 <b>6</b>	 Sparingly Soluble	 Sparingly Soluble	 Sparingly Soluble



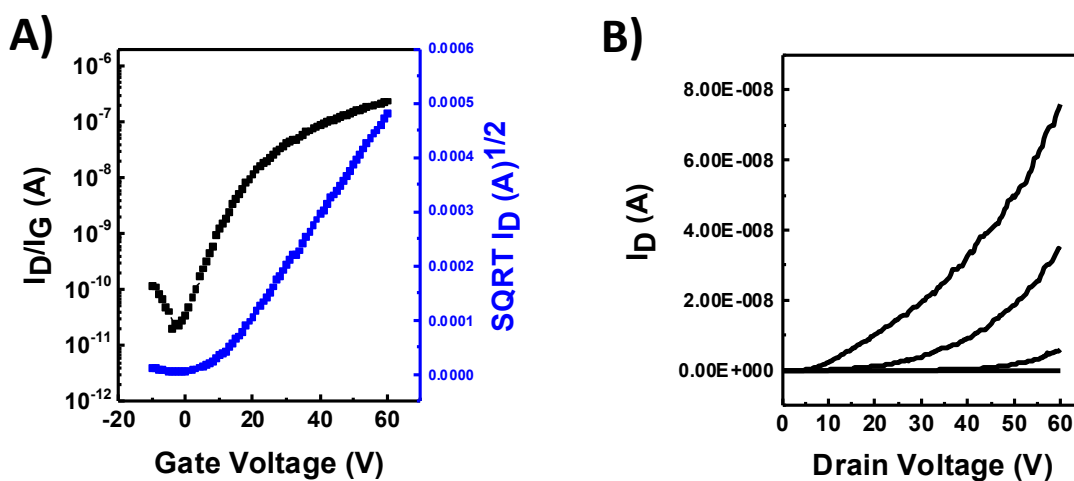
**Table S4:** Solubility of compounds **1** and **3** at 10 mg/mL in methanol, ethanol, *n*-propanol, water and 1:1 v/v ratio of *n*-propanol : acetic acid. All solubilities evaluated at room temperature.

	Methanol	Ethanol	<i>n</i> -Propanol	Water	<i>n</i> -Propanol/acetic acid
 <p><b>1</b></p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>	 <p>Not Soluble</p>	
 <p><b>3</b></p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>	 <p>Sparingly Soluble</p>

## S.9 Organic Field Effect Transistors

**Table S5:** Average and maximum hole mobility ( $\mu_{h\text{ av}}, \mu_{h\text{ max}}$ ), annealing temperatures, threshold voltages ( $V_{th}$ ), and  $I_{on}/I_{off}$  current ratios for OFETs fabricated from compound **7** with 2.5  $\mu\text{m}$  channel length and 10,000  $\mu\text{m}$  channel width. Results are average from 4 devices.

Compound	Annealing Temp ( $^{\circ}\text{C}$ )	$\mu_{\text{ave}}$ ( $\times 10^{-6}$ $\text{cm}^2/\text{Vs}$ )	$\mu_{\text{max}}$ ( $\times 10^{-6}$ $\text{cm}^2/\text{Vs}$ )	$V_{th}$ (V)	$I_{ON/OFF}$
<b>7</b>	As cast	$0.064 \pm 0.048$	0.133	6.89	$10^3$
	100	$4.63 \pm 1.41$	6.47	8.55	$10^4$



**Figure S34:** A) Representative Transfer ( $V_{DS} = 60$  V) and B) output characteristics of compound **7** annealed at 100  $^{\circ}\text{C}$

## S.10 References

1. Bruker-AXS. SAINT; Madison, Wisconsin, USA 2017
2. Bruker-AXS. XPREP; Madison, Wisconsin, USA 2017
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. *J. Appl. Cryst.*, 2009, **42**, 339-341
4. G. M Sheldrick. *Acta Cryst A71.*, 2015, 3-8
5. G. M Sheldrick. *Acta Cryst C71.*, 2015, 3-8
6. Y. Ito, A. Virkar, S. Mannsfeld, J. H. Oh and M. Toney, *J. Am. Chem. Soc.*, 2009, **131**, 9396–9404.