Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Synthesis, Self-Assembly, and Air-Stable Radical Anions of Unconventional 6,7-*Bis*-nitrated, N-Annulated Perylene Diimides

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Materials and Methods

Materials: All reactants and reagents were purchased from Millipore-Sigma. PDIN-H was synthesized as previously reported.[1]

CHN Elemental Analysis: Performed by Johnson Li in the Chemical Instrumentation Facility at the UofC. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data, using ~1.5 mg of sample (with particle sizes ranging between 0.2 and 0.5 mm in diameter).

Nuclear Magnetic Resonance (NMR): ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy spectra were recorded on a Bruker Avance-500 MHz spectrometer at 300 K or a Bruker Fourier-300 MHz spectrometer.

High-resolution Mass Spectrometry (HRMS): High-resolution MALDI mass spectrometry measurements were performed courtesy of Johnson Li in the Chemical Instrumentation Facility at the UofC. A Bruker Autoflex III Smartbeam MALDI-TOF (Na:YAG laser, 355nm), setting in positive reflective mode, was used to acquire spectra.

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 ~0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at scan rate 100 mV/s. All electrochemical solutions were purged with dry N_2 for 5 minutes to deoxygenate the system. Solution CV measurements were carried out with a small molecule concentration of ~0.5 mg/mL in dichloromethane. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the onsets of oxidation and reduction ($E_{ox}Fc/Fc+$, $E_{red}Fc/Fc+$) referenced to a ferrocene internal standard to that of the ionization potential of ferrocene using a conversion value of 4.8.[2]

UV-Visible-nearIR Spectroscopy (UV-Vis-nearIR): All measurements were recorded using an Agilent Technologies Cary 60 spectrometer at room temperature. All solution experiments were run in $CHCl_3$ or DMSO using 2 mm quartz cuvettes. Films were spin-cast onto Corning glass micro slides.

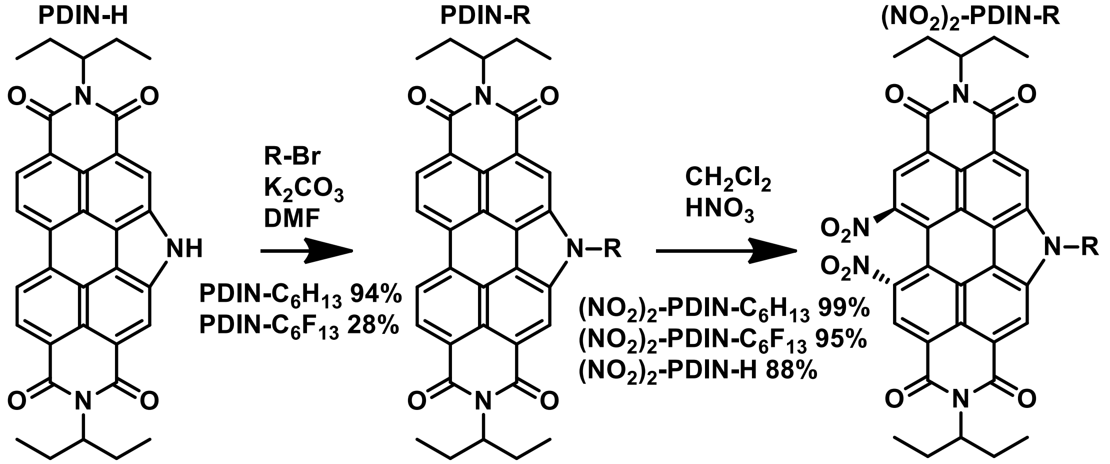
SpectroElectroChemistry: Measurements were recorded using an Agilent Technologies Cary 60 spectrometer at room temperature and a BASi Epsilon Eclipse potientostat. The cell was a 1 mm path length cell with a platinum mesh working electrode, platinum wire auxiliary electrode and a non-aqueous Ag/Ag^{+} reference electrode. All measurements were done in CH_2Cl_2 with 0.1 M $TBAPF_6$.

Crystal Structure Determinations: Single crystals of **1** were grown by evaporation of an acetonitrile solution. Single crystals of **2** were grown by evaporation of an acetonitrile solution. Single crystals of **3** were grown by diffusion of methanol into an acetonitrile solution. A suitable crystal of each compound was selected and mounted on a glass loop using Paratone. For **1**, Nonius Kappa diffractometer equipped with a Siemens Fine Focus Ceramic Tube (graphite monochromated Mo Kα, λ = 0.71069 Å) and an APEX II CCD detector. For **2** and **3**, diffraction experiments were performed on a Bruker Smart diffractometer equipped with an Incoatec Microfocus (graphite monochromated Cu Kα, λ = 1.54178 Å) and an APEX II CCD detector. All samples were kept at 173 K during data collection. For each compound, diffractions spots were integrated and scaled with SAINT[1] and the space group was determined with XPREP.[2] Using Olex2,[3] the structure was solved with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimisation. In order to obtain stable and physically reasonable models, geometric restraints were used to model the disorder in the imide alkyl chains, in all three compounds, and for the hexyl and perfluorohexyl in **1** and **2**, respectively. In **2**, electron density contributions from solvent molecules, speculated to be acetonitrile, were modelled using the SQUEEZE routine in PLATON,[6] owing to its diffuse nature and the large number of free variables used to model the disorder in the molecule of interest.

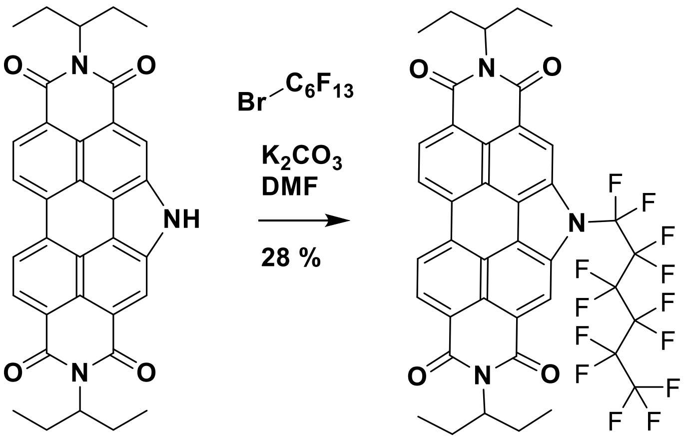
Table S1. Crystallographic data for compounds **1**, **2**, and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{40}H_{39}N_5O_8$	$C_{40}H_{26}F_{13}N_5O_8$	$C_{49}H_{42}N_5O_8$
Formula weight	717.76	951.66	828.87
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1$	P-1	I2/a
a / Å	11.1189(7)	14.2289(6)	19.5153(4)
b / Å	18.9403(9)	16.6846(8)	11.3613(2)
c / Å	16.6209(10)	18.0479(8)	38.0505(8)
α / °	90	94.134(4)	90
β / °	96.749(3)	96.411(3)	103.5490(10)
γ / °	90	100.484(3)	90
Volume / $Å^3$	3476.0(3)	4168.0(3)	8201.7(3)
Z	4	4	8
ρ_{calc} / g/cm^3	1.372	1.517	1.343
μ / mm^{-1}	0.097	1.284	0.754
Reflns. collected	46992	33648	23392
Unique reflns.	16546	12782	7266
R_{int}, R_{sigma}	0.0316, 0.0375	0.0474, 0.0617	0.0199, 0.0187
GoF on F^2	1.028	1.037	1.029
R_1, wR_2 ($I>=2\sigma$ [I])	0.0481, 0.1164	0.0742, 0.2056	0.404, 0.1085
R_1, wR_2 (all data)	0.0618, 0.1262	0.0879, 0.2224	0.0450, 0.1134
$\Delta\rho_{min/max}$ / e/ $Å^3$	0.42/-0.34	0.53/-0.55	0.34/-0.32
Flack parameter	0.1(9)	–	–

Synthetic Details/Experimental Procedures



Scheme S1: General synthetic scheme for **$(NO_2)_2$-PDIN-C_6H_{13}** (**1**), **$(NO_2)_2$-PDIN-C_6F_{13}** (**2**), and **$(NO_2)_2$-PDIN-H** (**3**) as synthesized from previously reported materials **PDIN-H** and **PDIN-C_6H_{13}**.[1]

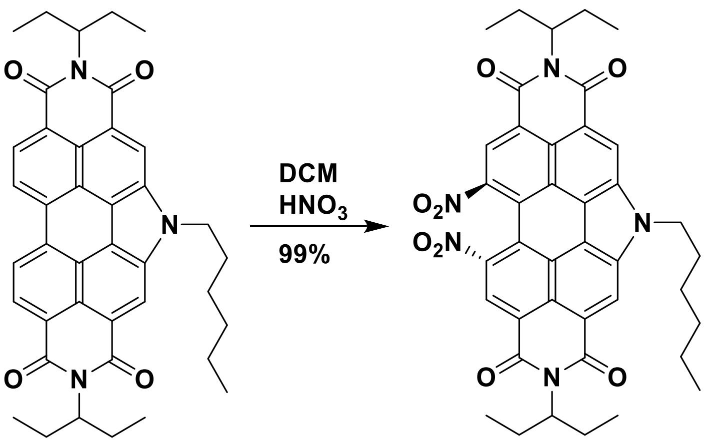


PDI-NC$_6$F$_{13}$: To a 20 mL pressure vial with a stir bar was added **PDIN-H** (1.0 g, 1.8 mmol) and potassium carbonate (386 mg, 2.8 mmol). Next, 15 mL of a previously degassed dimethylformamide was cannula transferred to the reaction vial. Perfluorohexylbromide (0.6 mL, 1.1 g, 2.8 mmol) was added via syringe. The vial was capped and purged with nitrogen for 10 minutes before heating to 100 °C for three days until TLC (DCM eluent) showed no remaining **PDIN-H**. The reaction mixture was cooled and diluted to 200 mL with methanol to precipitate PDIN-R materials. 50 mL of conc sodium hydroxide in water (50%) was added to re-dissolve unreacted **PDIN-H**. The mixture was filtered and washed with sodium hydroxide/methanol solutions until the filtrate ran clear to remove any possible unreacted **PDIN-H**. The solid was dried in air *in vacuo*. The orange crude product was redissolved in DCM and filtered through silica to further remove residual **PDIN-H**. The filtrate was mixed 1:1 with methanol. DCM was removed on a rotatory evaporator to precipitate the crude product into the remaining methanol. The suspension was filtered to give crude **PDIN-C$_6$F$_{13}$** (480 mg, 30%). Crude **PDIN-C$_6$F$_{13}$** was further purified by silica gel column chromatography using a DCM to acetone gradient (up to 3% acetone). The first fraction was found to be pure **PDI-NC$_6$F$_{13}$** (440 mg, 28%).

MALDI: Calculated M-2H + H^+ = 860.1788 Found: 860.1815

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 2H), 9.00 (d, J = 7.9 Hz, 2H), 8.93 (d, J = 7.9 Hz, 2H), 5.20 (m, 2H), 2.34 (m, 4H), 2.00 (m, 4H), 0.97 (t, J = 7. Hz, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 132.96, 132.87, 125.25, 124.28, 121.39, 121.21, 57.47, 24.62, 10.84



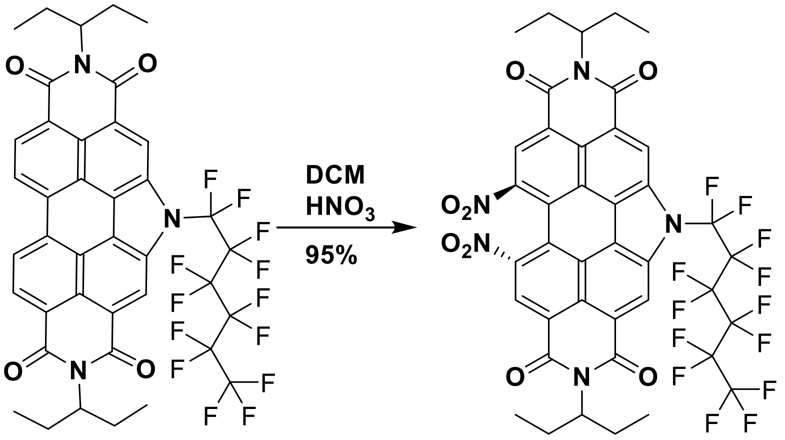
$(NO_2)_2$-PDIN-C_6H_{13} (1): To a 250 mL round bottom flask with a stir bar was added **PDIN-C_6H_{13}** (1.0 g, 1.16 mmol) and 100 mL DCM. To this mixture was added ~1.5 mL (36 mmol, 31 eq) fuming nitric acid (large excess). The reaction mixture was stirred for 15 minutes during which the colour changed from red to purple. When TLC (DCM eluent) showed only a single purple spot, the reaction was quenched with 100 mL water. The mixture was then washed 3 times with water. The organic phase was dried with $MgSO_4$ and filtered through silica gel. The filtrate was mixed 1:1 with methanol. DCM was removed on a rotatory evaporator to precipitate the crude product into the remaining methanol. The suspension was filtered to give crude pure **$(NO_2)_2$-PDIN-C_6H_{13} (1)** was obtained as a purple solid (1.29 g, > 95%).

CHN Elemental Analysis: Theoretical C: 66.93 %, H: 5.48 %, N: 9.76 %. Found: C: 66.99 %, H: 5.30 %, N: 9.76 %.

MALDI: Theoretical: M + Na^+ 740.2691 Found: 740.2676

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38 (s, 2H), 9.24 (s, 2H), 5.23 – 5.15 (m, 2H), 5.06 (t, *J* = 7.3 Hz, 2H), 2.37 – 2.24 (m, 6H), 2.06 – 1.95 (m, 4H), 1.51 (dt, *J* = 15.1, 7.3 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.33 (dt, *J* = 14.7, 7.2 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 12H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.36, 164.55, 163.18, 162.19, 148.91, 135.23, 126.91, 124.18, 123.83, 123.71, 123.11, 122.45, 121.39, 118.80, 58.45, 47.51, 31.75, 31.27, 26.87, 25.06, 22.42, 13.88, 11.30.



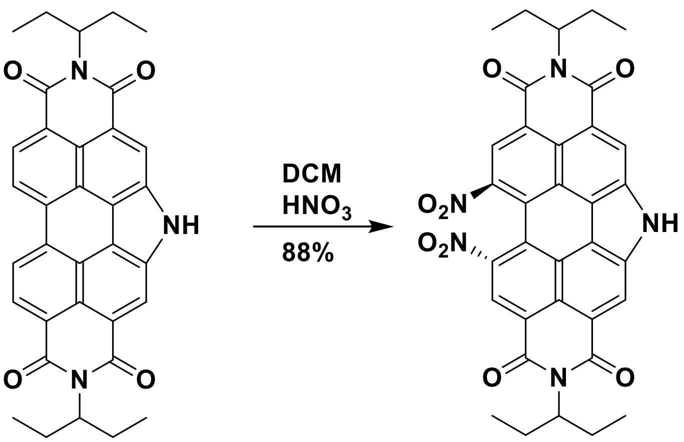
(NO$_2$)$_2$-PDIN-C$_6$F$_{13}$ (2): To a 250 mL round bottom flask with a stir bar was added **PDIN-C$_6$F$_{13}$** (400 mg, 0.464 mmol) and 50 mL DCM. To this mixture was added ~0.75 mL (18 mmol, 38 eq) fuming nitric acid. The reaction mixture was stirred for 60 minutes during which the colour changed from red to purple. When TLC (DCM eluent) showed only a single purple spot, the reaction was quenched with 100 mL water. The mixture was then washed 3 times with water. The organic phase was dried with MgSO$_4$ and filtered through silica gel. The filtrate was mixed 1:1 with methanol. DCM was removed on a rotatory evaporator to precipitate the crude product into the remaining methanol. The suspension was filtered to give crude pure **(NO$_2$)$_2$-PDIN-C$_6$F$_{13}$ (2)** (418 mg, 95%).

CHN Elemental Analysis: Theoretical C: 50.48 %, H: 2.75 %, N: 7.36 %. Found: C: 50.44 %, H: 2.61 %, N: 7.10 %.

MALDI: Calculated M-2H + H$^+$ = 950.149 Found: 950.1497

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.42 (s, 2H), 9.22 (s, 2H), 5.21 – 5.14 (m, 2H), 2.38 – 2.26 (m, 4H), 2.06 – 1.94 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 149.00, 133.24, 126.79, 125.10, 123.08, 122.93, 121.90, 120.19, 58.23, 24.47, 10.76



$(NO_2)_2$-PDIN-H (3): To a 500 mL round bottom flask with a stir bar was added **PDIN-H** (1.0 g, 1.8 mmol) and 250 mL DCM. This reaction required more DCM to better solubilize the less soluble **PDIN-H**. To this mixture was added 8 mL (192 mmol, 107 mmol) fuming nitric acid. The reaction mixture was stirred for 60 minutes, to ensure complete consumption of **PDIN-H,** during which the colour changed from red to purple. When TLC (DCM eluent) showed only a single purple spot, the reaction was quenched with 100 mL water. The mixture was then washed 3 times with water. The organic phase was dried with $MgSO_4$ and filtered. The filtrate was mixed 1:1 with methanol. DCM was removed on a rotatory evaporator to precipitate the crude product into the remaining methanol. The suspension was filtered to give crude pure **$(NO_2)_2$-PDIN-H (3)** was obtained as a purple solid (974 mg, 84%).

CHN Elemental Analysis: Theoretical C: 64.45 %, H: 4.30 %, N: 11.05 %. Found: C: 64.53 %, H: 4.13 %, N: 10.84 %.

MALDI: Calculated M + Na = 656.17521 Found: M + Na = 656.1721

^{1}H NMR (600 MHz, $CDCl_3$) 10.67 (s, 1H), 9.43 (s, 2H), 9.31 (s, 2H), 5.19 (m, 2H), 2.32 (m, 4H), 2.01 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.44, 133.40, 126.43, 123.23, 122.34, 118.92, 57.96, 24.51, 10.80.

NMR Spectra

^{1}H NMR Spectra

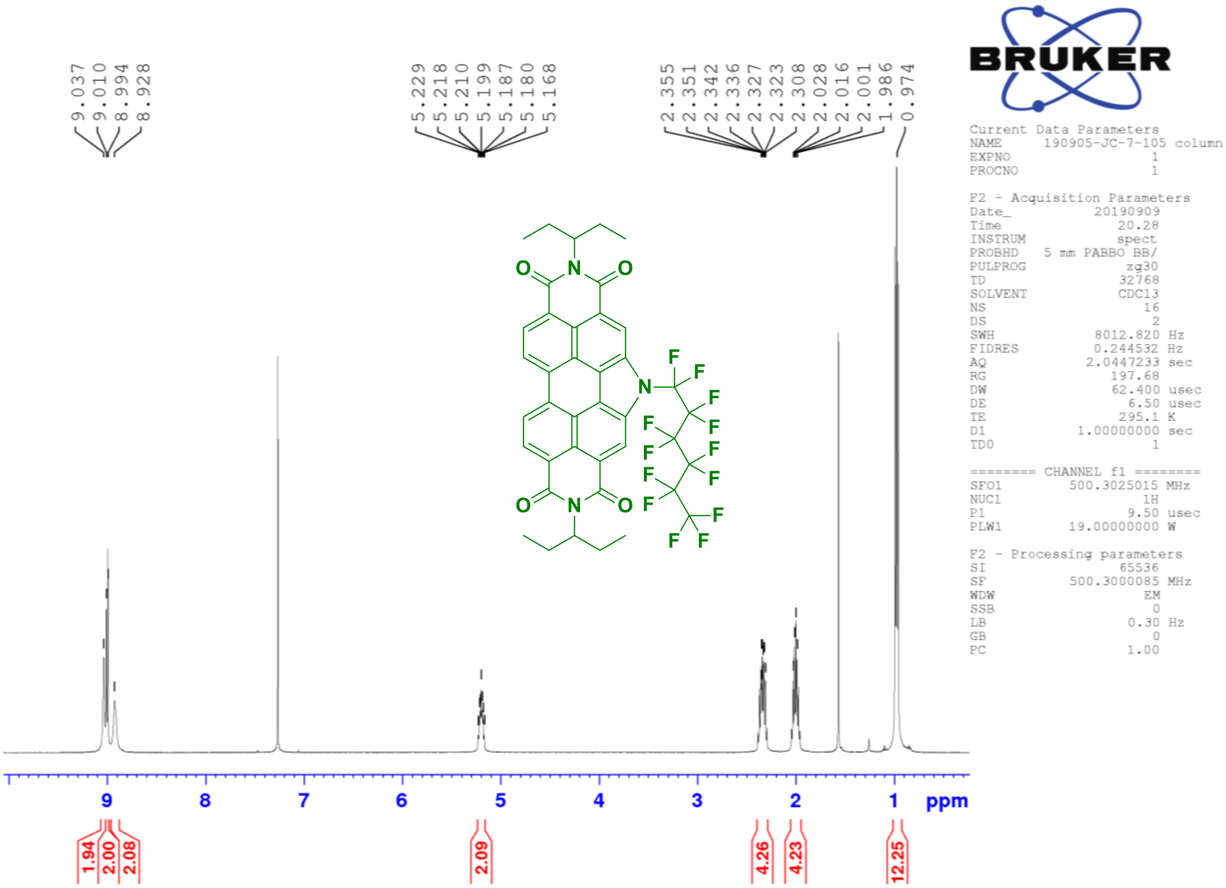


Fig S1: **PDIN-C_6F_{13}** ^{1}H NMR spectrum (500 MHz, CDCl3) δ 9.04 (s, 2H), 9.00 (d, J = 7.9 Hz, 2H), 8.93 (d, J = 7.9 Hz, 2H), 5.20 (m, 2H), 2.34 (m, 4H), 2.00 (m, 4H), 0.97 (t, J = 7. Hz, 12H).

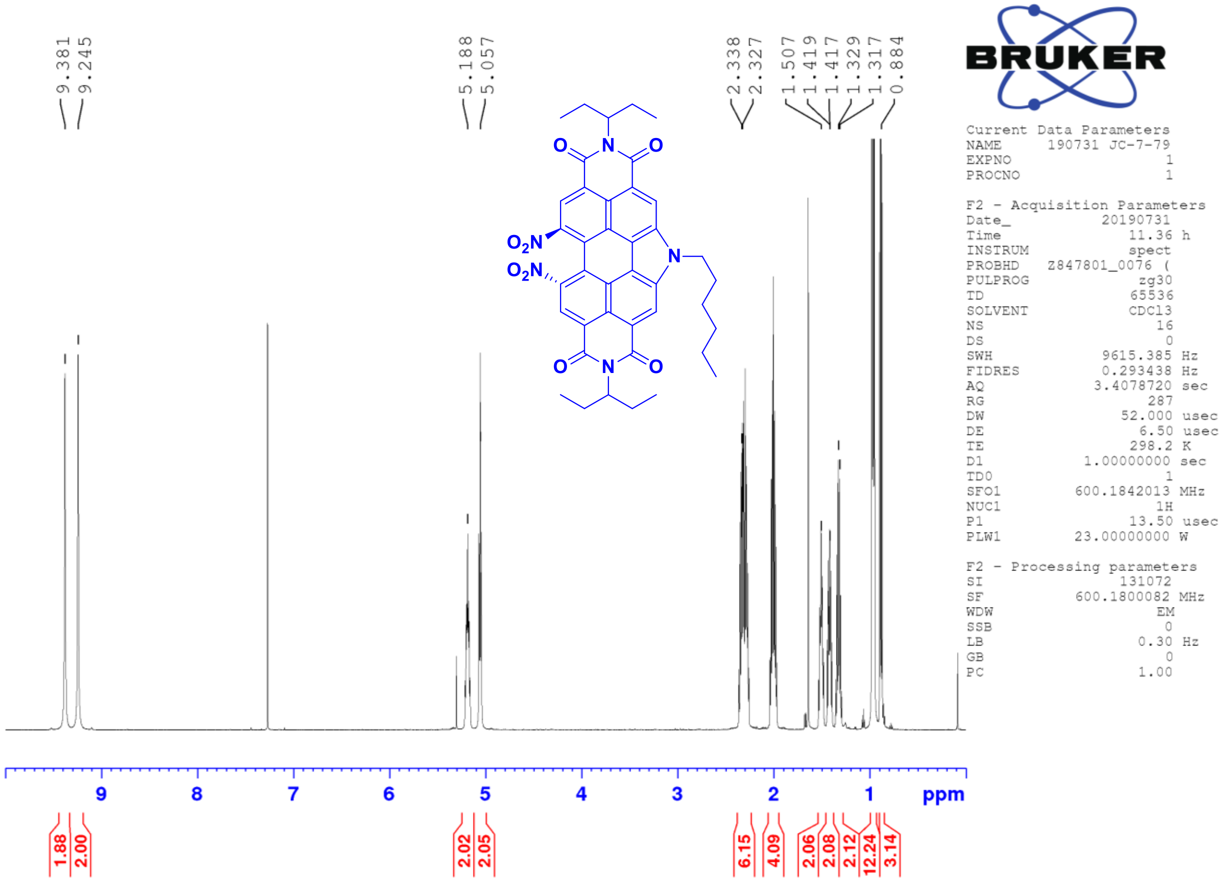


Fig S2: **$(NO_2)_2$-PDIN-C_6H_{13}** ^1H NMR spectrum (600 MHz, $CDCl_3$) δ 9.38 (s, 2H), 9.24 (s, 2H), 5.23 – 5.15 (m, 2H), 5.06 (t, *J* = 7.3 Hz, 2H), 2.37 – 2.24 (m, 6H), 2.06 – 1.95 (m, 4H), 1.51 (dt, *J* = 15.1, 7.3 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.33 (dt, *J* = 14.7, 7.2 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 12H), 0.88 (t, *J* = 7.3 Hz, 3H).

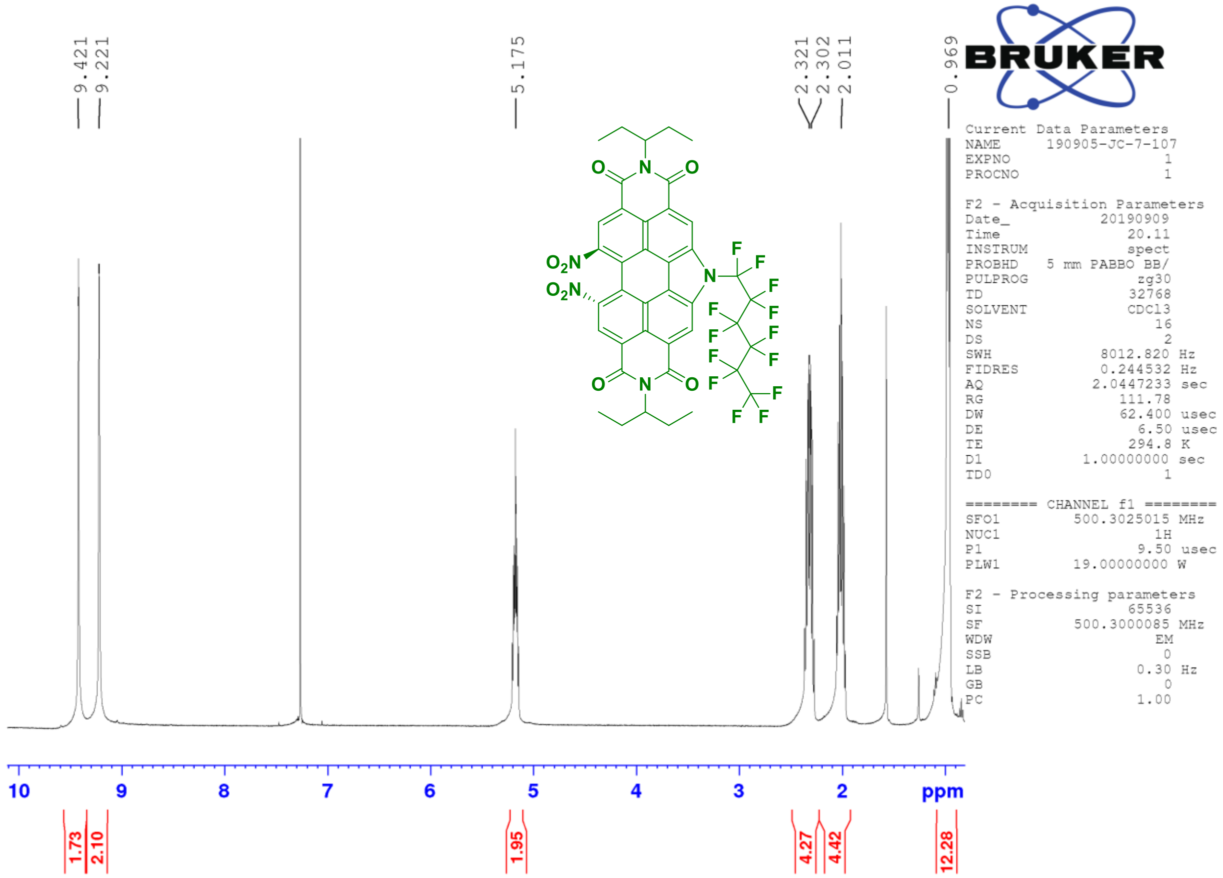


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Fig S3: **$(NO_2)_2$-PDIN-C_6F_{13}** ^1H NMR spectrum (500 MHz, $CDCl_3$) δ 9.42 (s, 2H), 9.22 (s, 2H), 5.21 – 5.14 (m, 2H), 2.38 – 2.26 (m, 4H), 2.06 – 1.94 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 12H).

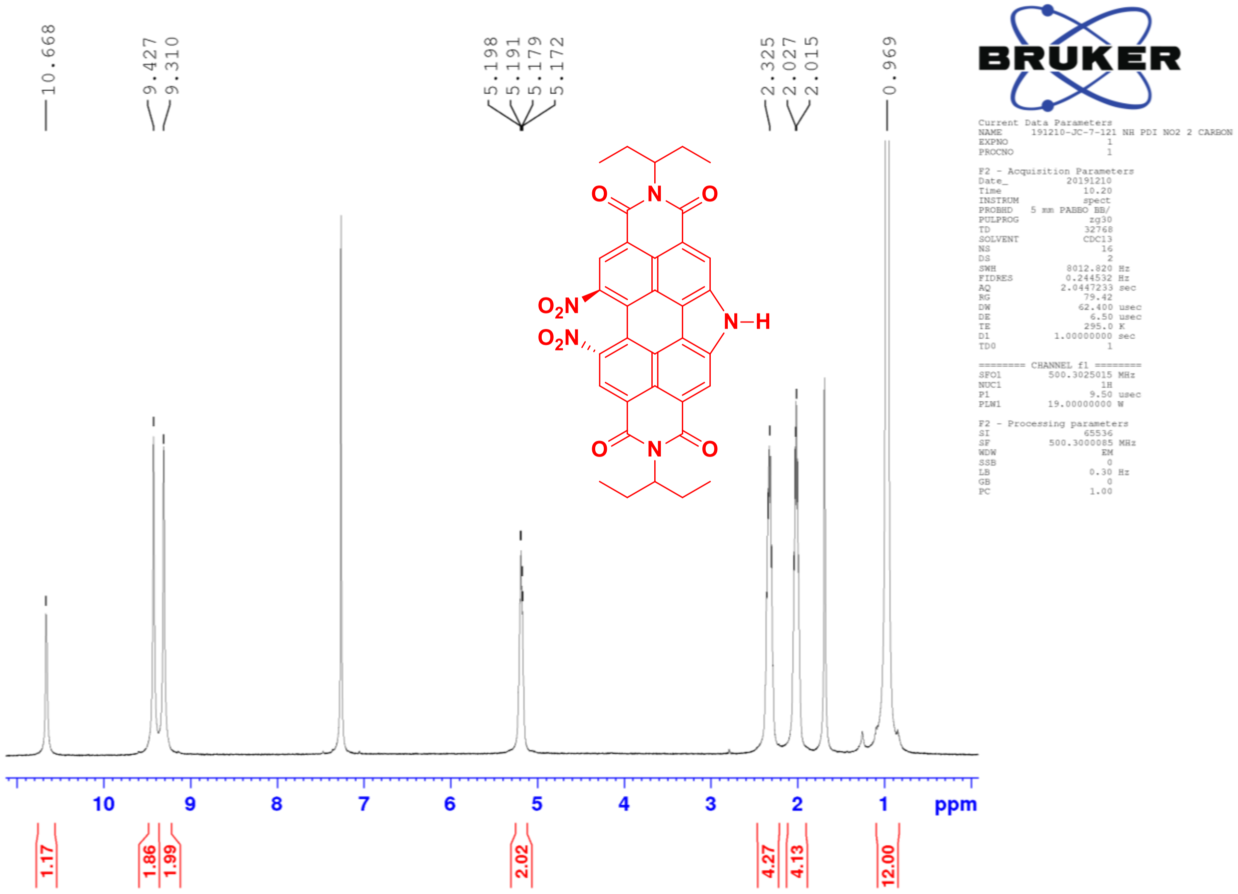

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Fig S4: **$(NO_2)_2$-PDIN-H** ^{1}H NMR spectrum (600 MHz, $CDCl_3$) δ 10.67 (s, 1H), 9.43 (s, 2H), 9.31 (s, 2H), 5.19 (m, 2H), 2.32 (m, 4H), 2.01 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR Spectra

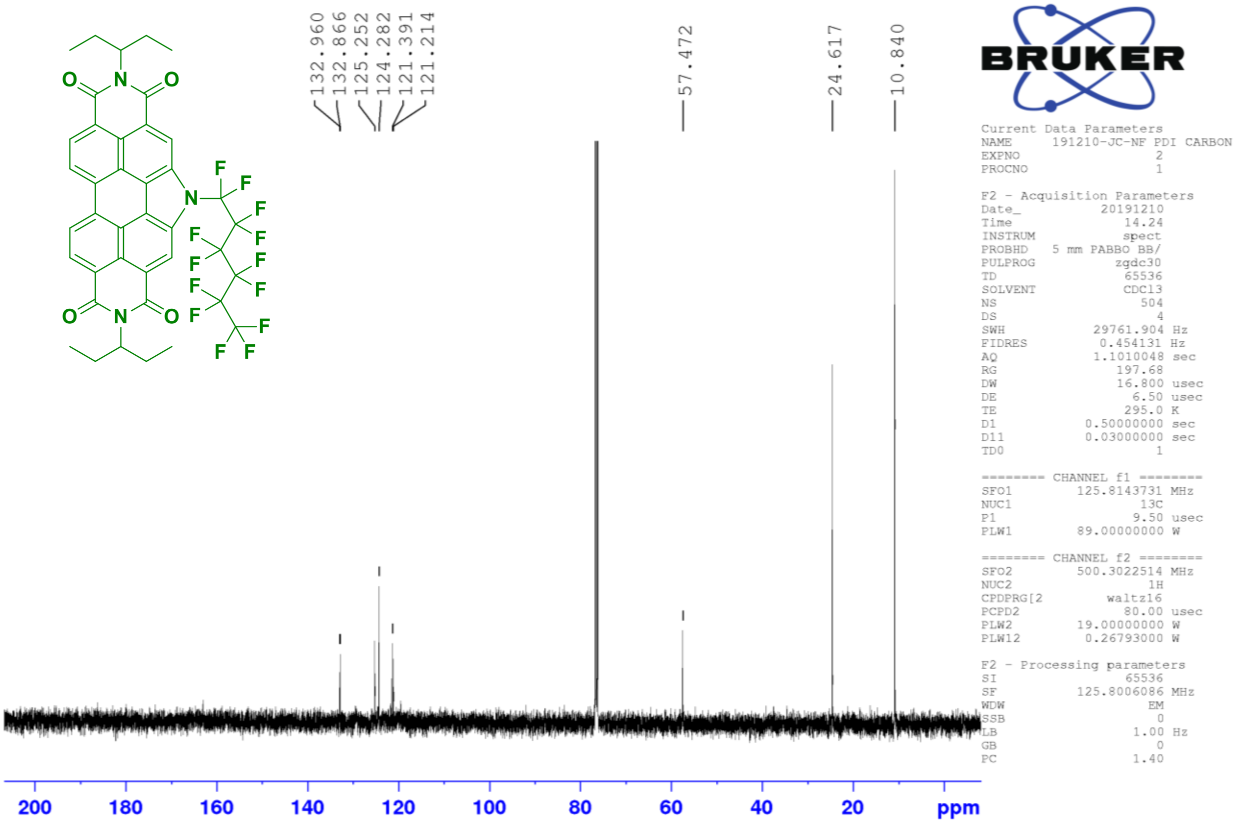

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Fig S5: **PDIN-C_6F_{13}** ^{13}C NMR spectrum (75 MHz, $CDCl_3$) δ 132.96, 132.87, 125.25, 124.28, 121.39, 121.21, 57.47, 24.62, 10.84

Carbons corresponding to fluoroalkyl chain are not visible due to C-F coupling

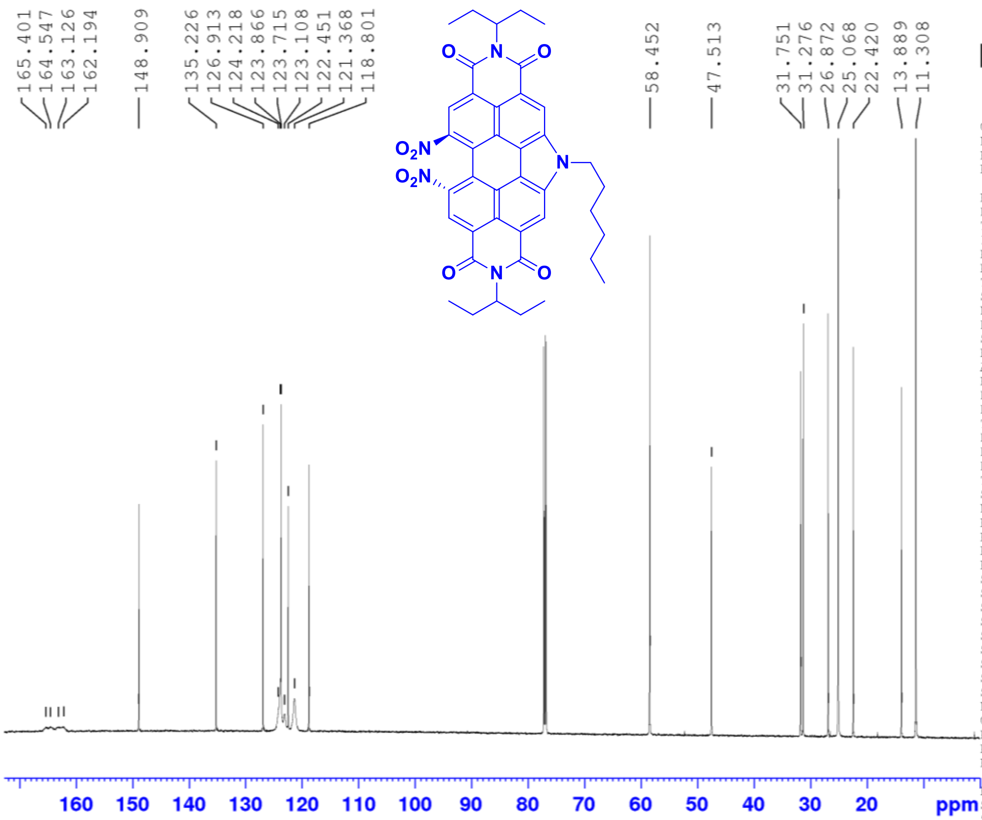

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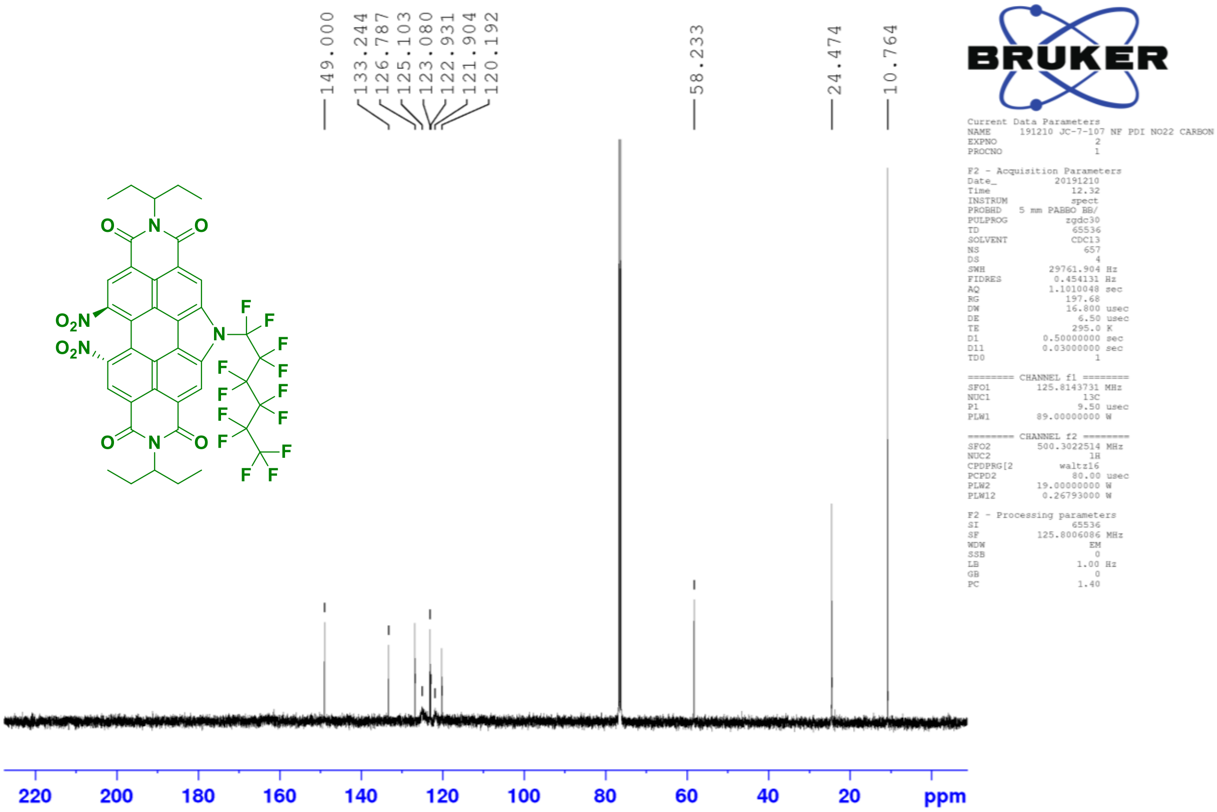
Fig S6: **$(NO_2)_2$-PDIN-C_6H_{13}** ^{13}C NMR spectrum (151 MHz, $CDCl_3$) δ 165.36, 164.55, 163.18, 162.19, 148.91, 135.23, 126.91, 124.18, 123.83, 123.71, 123.11, 122.45, 121.39, 118.80, 58.45, 47.51, 31.75, 31.27, 26.87, 25.06, 22.42, 13.88, 11.30.

Note: this spectrum was run in conjunction with the NOESY and HMBC spectra (**S21**, **S22**). Since the goal was to observe the carbonyl carbon to aryl proton coupling, this necessitated an extremely high concentration and higher number of scans than previous experiments. The higher signal to noise ratio revealed that several of the resonances are extremely broad and poorly resolved.



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PLW1         89.00000000 W

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PLW12         0.26793000 W

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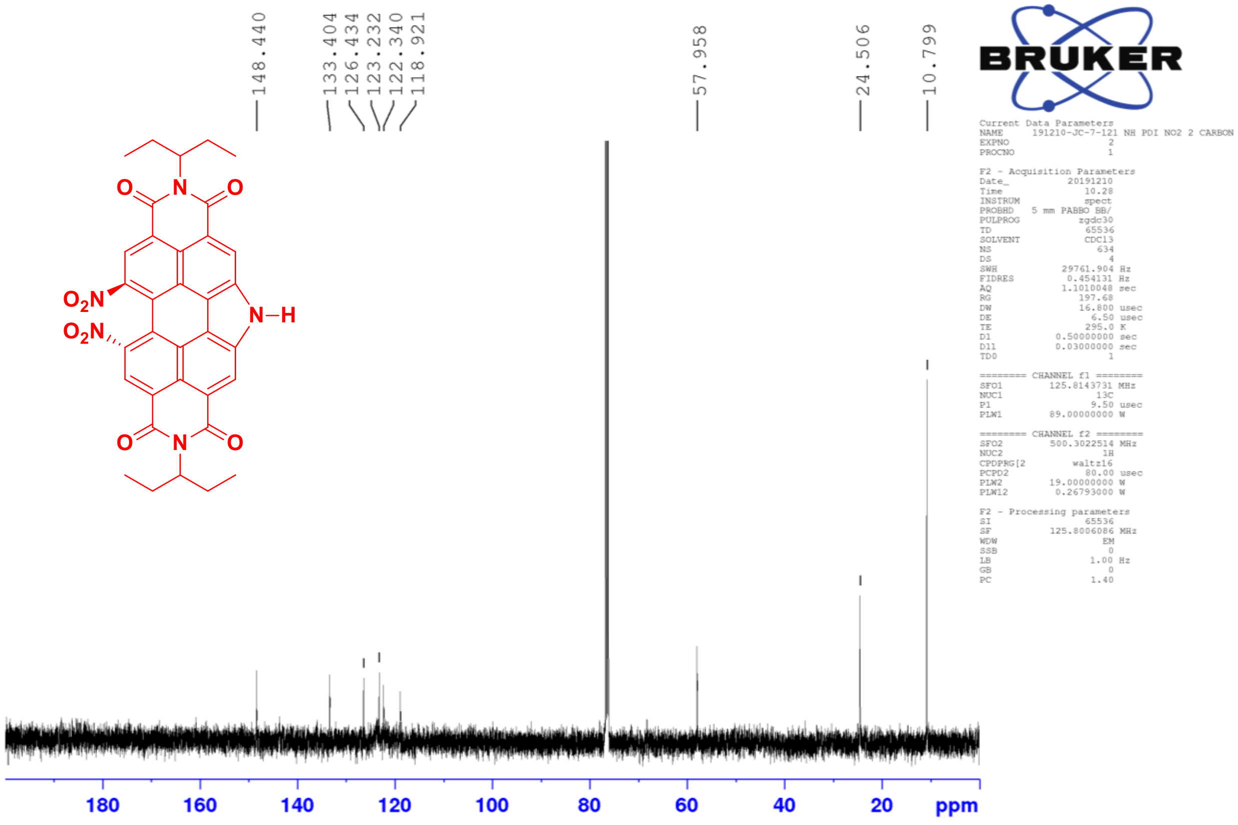
Fig S7: **$(NO_2)_2$-PDIN-C_6F_{13}** ^{13}C NMR spectrum (125 MHz, $CDCl_3$) δ 149.00, 133.24, 126.79, 125.10, 123.08, 122.93, 121.90, 120.19, 58.23, 24.47, 10.76

Note: Carbons corresponding to fluoroalkyl chains are not visible due to C-F coupling. No attempt to resolve resonances analogous to the broad resonances observed in **$(NO_2)_2$-PDIN-C_6H_{13}** was made.



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EXPNO                    2
PROCNO                   1

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Time                 10.28
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PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     634
DS                       4
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FIDRES            0.454131 Hz
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DE                    6.50 usec
TE                   295.0 K
D1              0.50000000 sec
D11             0.03000000 sec
TD0                      1

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SFO1           125.8143731 MHz
NUC1                   13C
P1                    9.50 usec
PLW1           89.00000000 W

======== CHANNEL f2 ========
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NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.26793000 W

F2 - Processing parameters
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SF             125.8006086 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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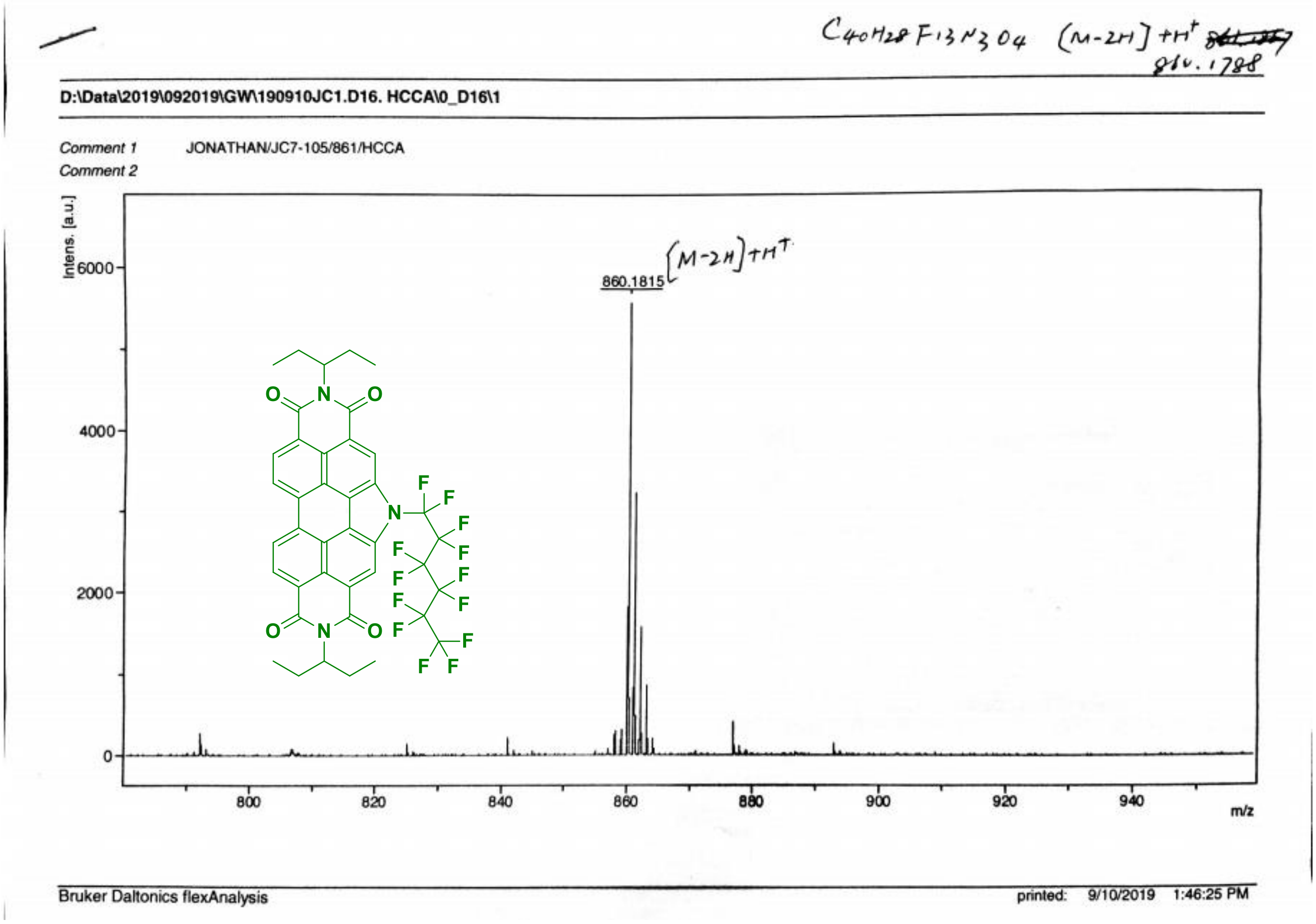
Fig S11: **$(NO_2)_2$-PDIN-H** ^{13}C NMR spectrum (125 MHz, $CDCl_3$) δ 148.44, 133.40, 126.43, 123.23, 122.34, 118.92, 57.96, 24.51, 10.80.

Note: No attempt to resolve resonances analogous to the broad resonances observed in **$(NO_2)_2$-PDIN-C_6H_{13}** was made.

Mass Spectrometry - MALDI



$C_{40}H_{28}F_{13}N_3O_4$ (M-2H] +H$^+$
860.1788

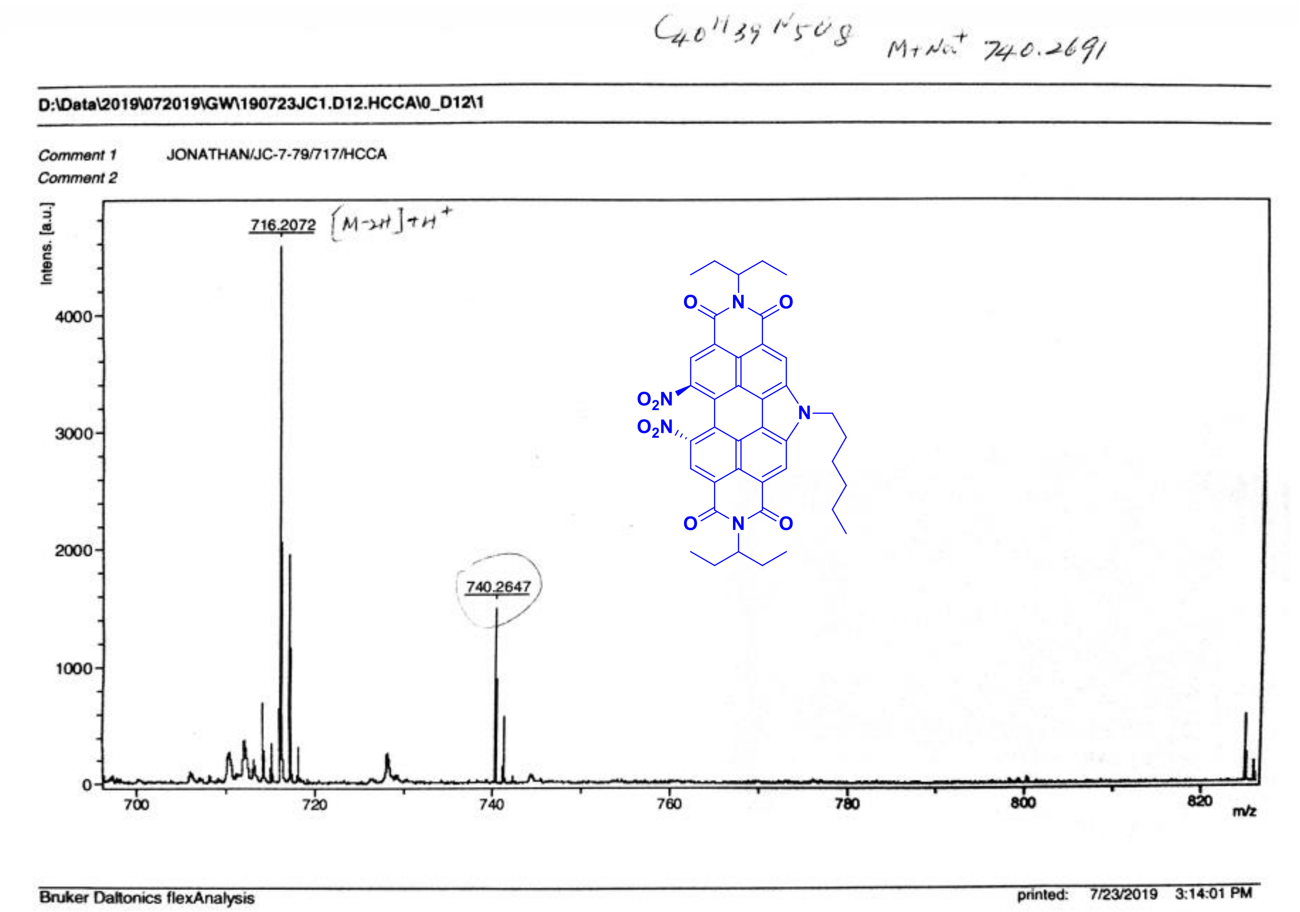
D:\Data\2019\092019\GW\190910JC1.D16. HCCA\0_D16\1

Comment 1 JONATHAN/JC7-105/861/HCCA
Comment 2

Bruker Daltonics flexAnalysis

printed: 9/10/2019 1:46:25 PM

Fig S12: **PDIN-C_6F_{13}** MALDI MS: Calculated M-2H + H$^+$ = 860.1788 Found: 860.1815.



$C_{40}H_{39}N_5O_8$ $M+Na^+$ 740.2691

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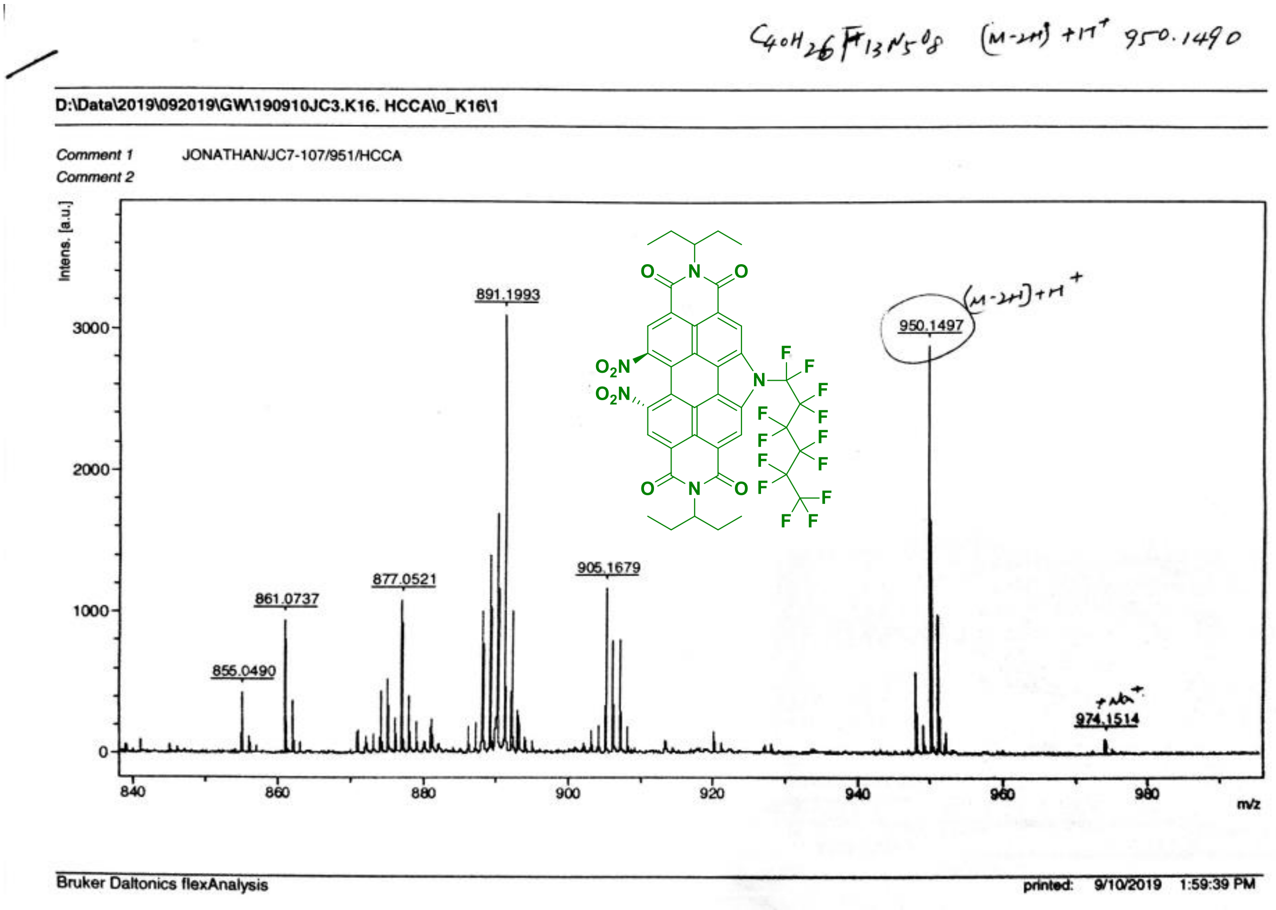
Comment 1 JONATHAN/JC-7-79/717/HCCA

Comment 2

Bruker Daltonics flexAnalysis printed: 7/23/2019 3:14:01 PM

Fig S13: **$(NO_2)_2$-PDIN-C_6H_{13}** MALDI MS: Calculated M + Na^+ = 740.2691 Found: 740.2676.



$C_{40}H_{26}F_{13}N_5O_8$ $(M-2H)+H^+$ 950.1490

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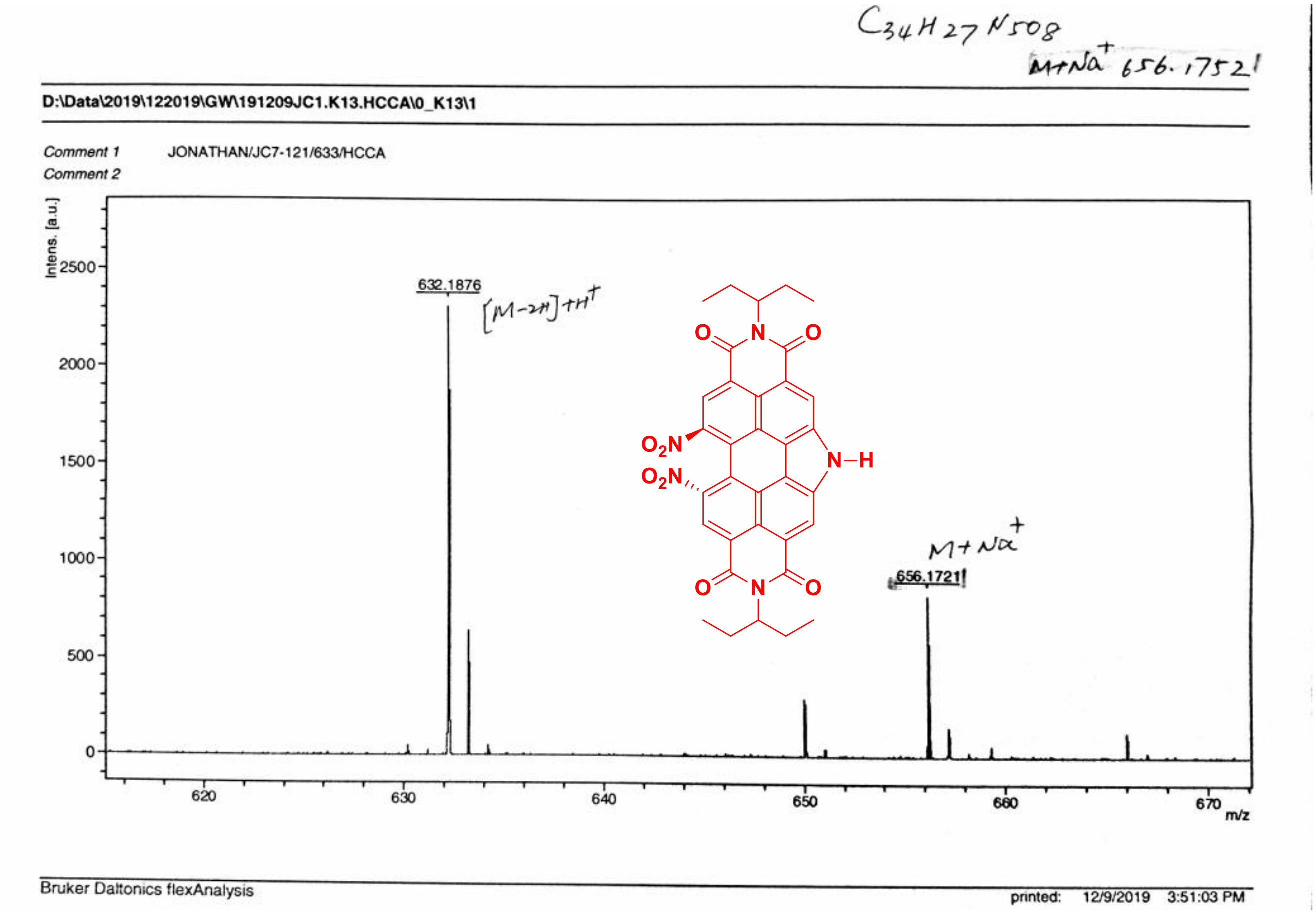
Comment 1 JONATHAN/JC7-107/951/HCCA

Comment 2

Bruker Daltonics flexAnalysis

printed: 9/10/2019 1:59:39 PM

Fig S14: **$(NO_2)_2$-PDIN-C_6F_{13}** MALDI MS: Calculated M-2H + H^+ = 950.149 Found: 950.1497


$C_{34}H_{27}N_5O_8$

$M+Na^+$ 656.17521

D:\Data\2019\122019\GW\191209JC1.K13.HCCA\0_K13\1

Comment 1 JONATHAN/JC7-121/633/HCCA

Comment 2

Bruker Daltonics flexAnalysis

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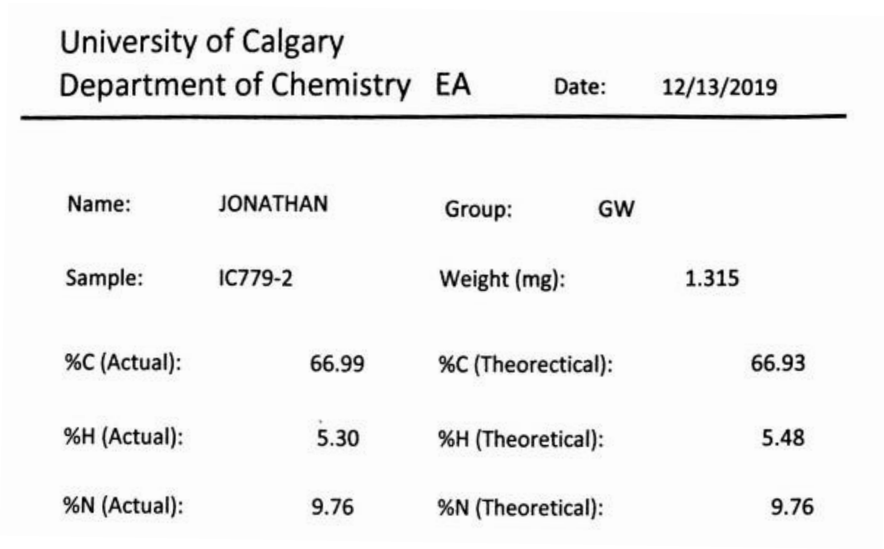
Fig S15: **$(NO_2)_2$-PDIN-H** MALDI MS: Calculated M + Na = 656.17521 Found: M + Na = 656.1721

CHN Elemental Analysis



University of Calgary
Department of Chemistry EA Date: 12/13/2019

Name:	JONATHAN	Group:	GW
Sample:	IC779-2	Weight (mg):	1.315
%C (Actual):	66.99	%C (Theorectical):	66.93
%H (Actual):	5.30	%H (Theoretical):	5.48
%N (Actual):	9.76	%N (Theoretical):	9.76

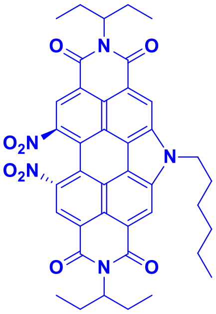
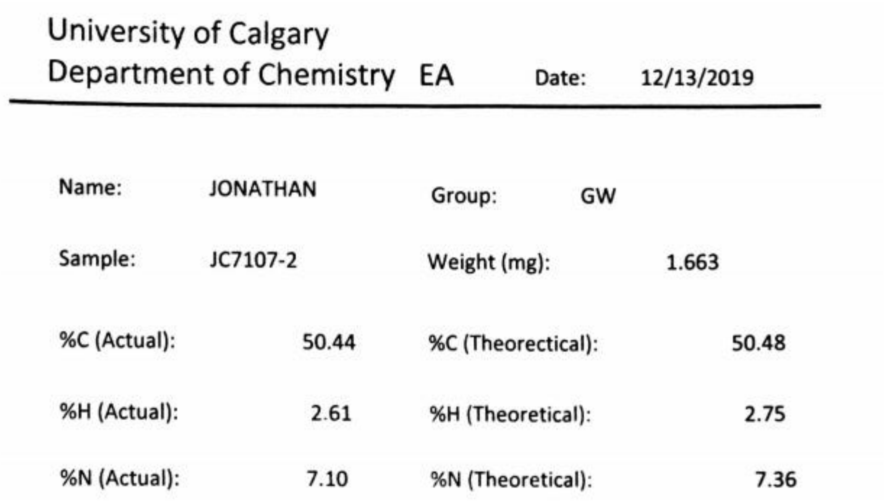


Fig S16: **$(NO_2)_2$-PDIN-C_6H_{13}** elemental analysis.



University of Calgary
Department of Chemistry EA Date: 12/13/2019

Name:	JONATHAN	Group:	GW
Sample:	JC7107-2	Weight (mg):	1.663
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%H (Actual):	2.61	%H (Theoretical):	2.75
%N (Actual):	7.10	%N (Theoretical):	7.36

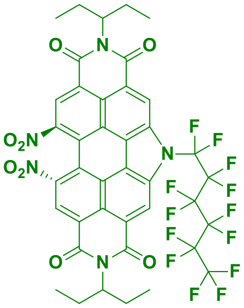
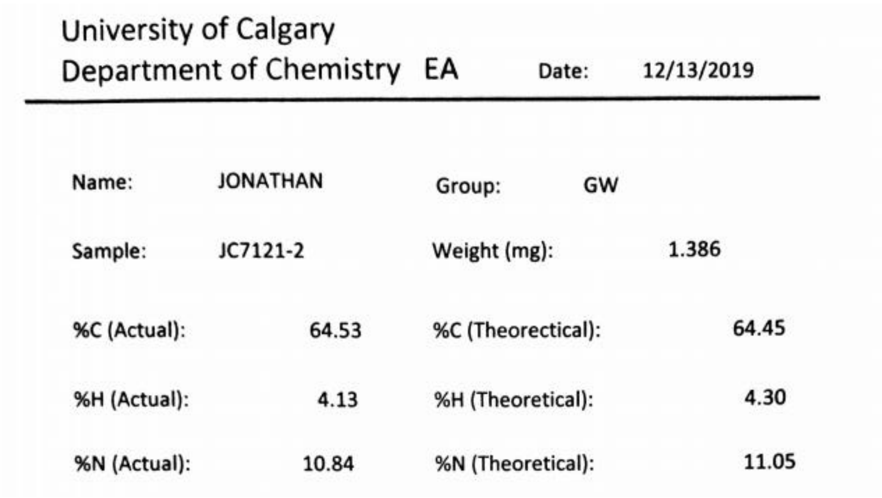


Fig S17: **$(NO_2)_2$-PDIN-C_6F_{13}** elemental analysis.



University of Calgary
Department of Chemistry EA Date: 12/13/2019

Name:	JONATHAN	Group:	GW
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%H (Actual):	4.13	%H (Theoretical):	4.30
%N (Actual):	10.84	%N (Theoretical):	11.05

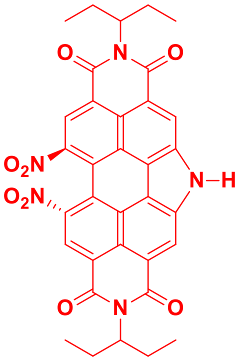
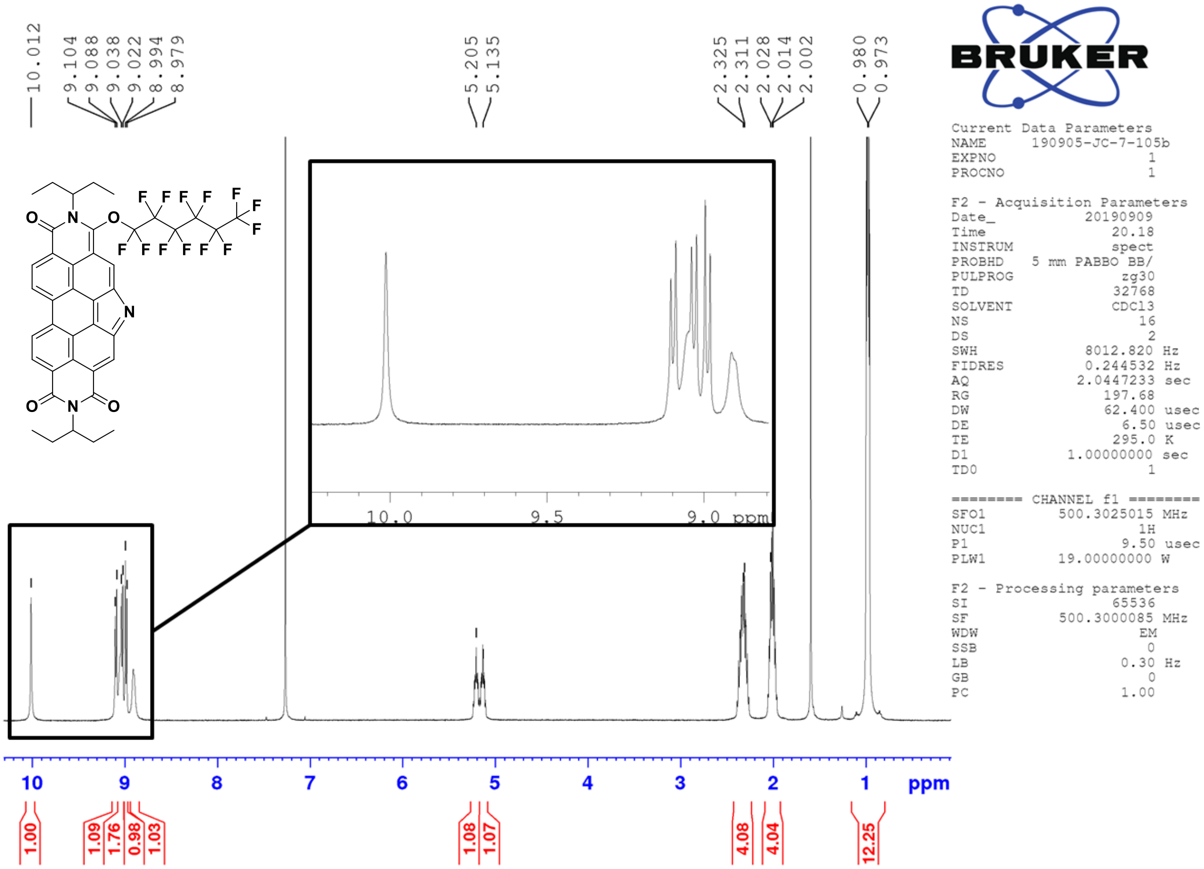


Fig S18: **(NO$_2$)$_2$-PDIN-H** elemental analysis.

Supplementary Figures



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TE                   295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                  1H
P1                  9.50 usec
PLW1         19.00000000 W

F2 - Processing parameters
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WDW                     EM
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LB                    0.30 Hz
GB                       0
PC                    1.00
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Fig S19: ^{1}H NMR spectra of the major impurity found during the formation of **PDIN-C$_6$F$_{13}$**. Note the total of six inequivalent aromatic resonances consisting of four doublets and two singlets. Additionally, the imide NCH peaks are split into two resonances at 5 ppm. We believe that this spectrum is most consistent with an O-alkylated PDIN, shown inset.

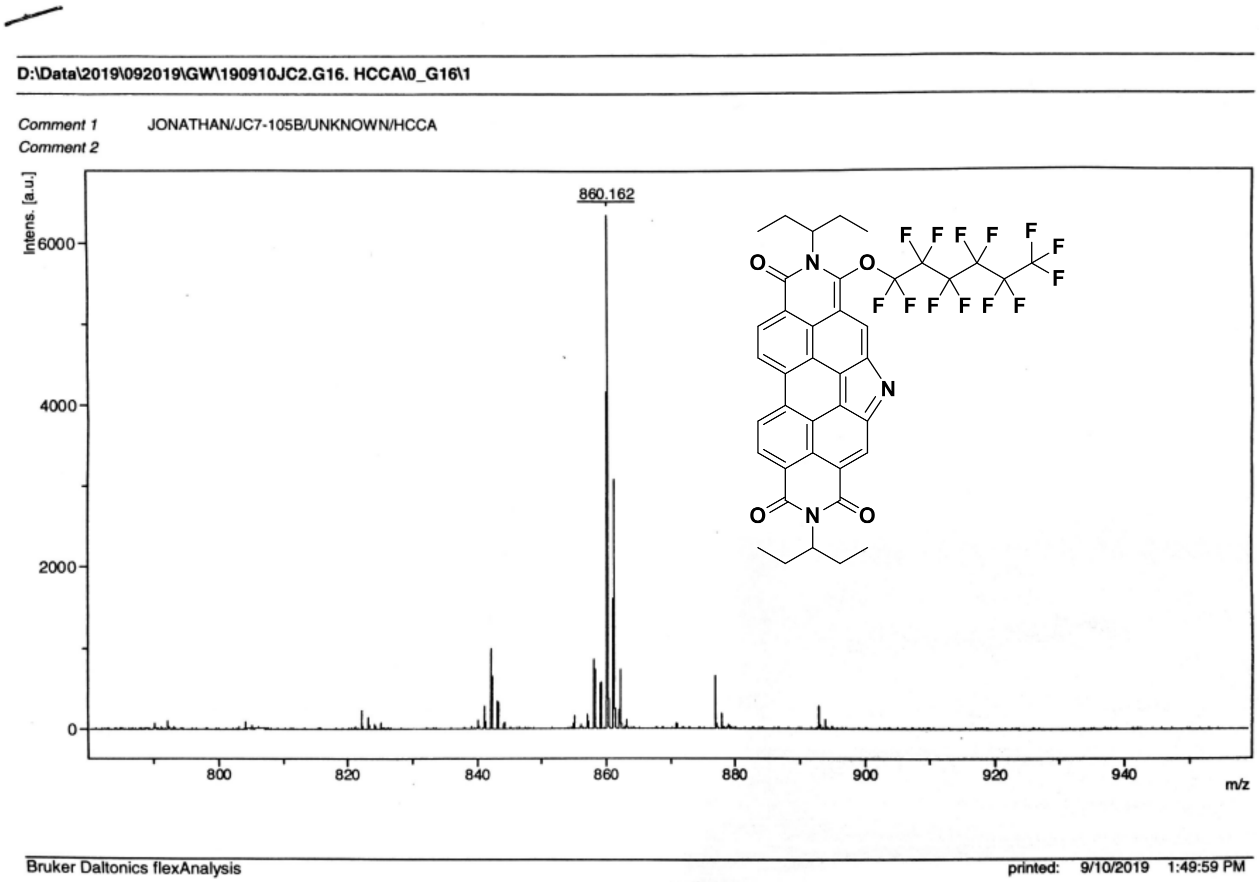

Fig S20: MALDI MS of the major impurity found during the formation of **PDIN-C_6F_{13}**: Calculated M-2H + H^+ = 860.1788 Found: 860.162. This spectrum further reinforces that the impurity is the O-alkylated product.

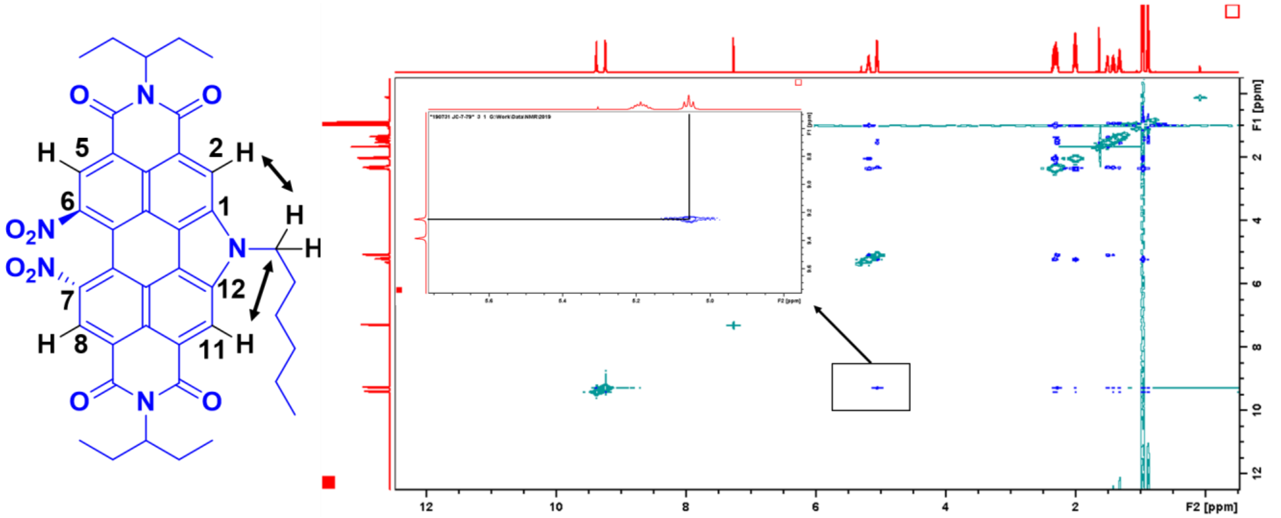

Fig S21: NOESY NMR spectra of **1** showing correlation between pyrrole N-CH2 (5.06 ppm) and 2,11 aromatic protons (9.24 ppm).

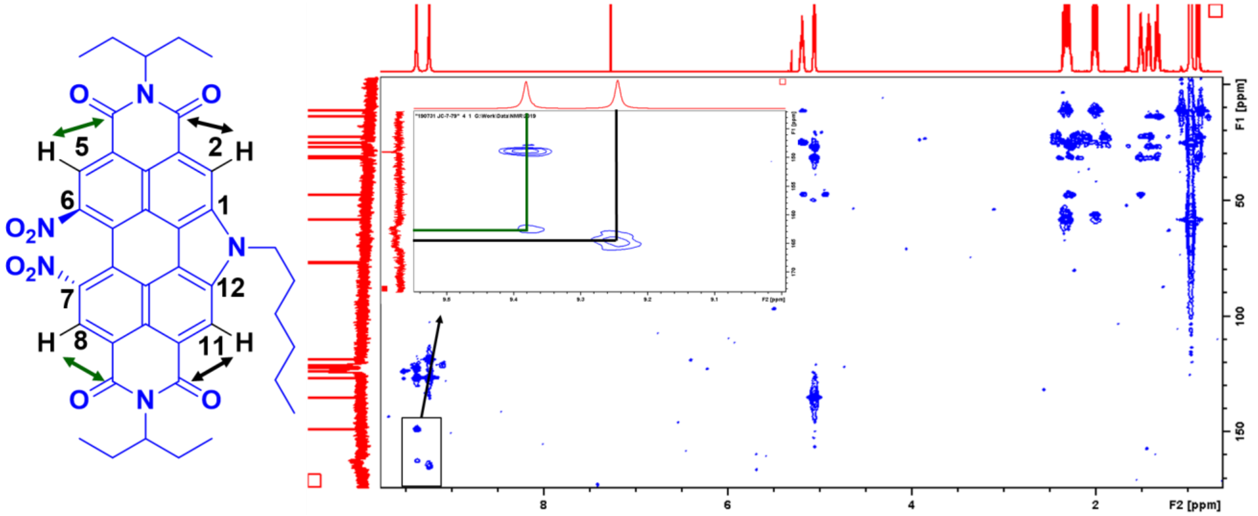

Fig S22: HMBC NMR spectra of **1** showing correlation between aromatic protons and imide carbonyls. As per **Figure S21** above, the aromatic resonance at 9.24 ppm was assigned as the 2, 11 protons (correlation highlighted in black). Therefore, the correlation (highlighted in green) with the resonance at 9.38 ppm is attributed to the 5, 8 protons. The expected correlation between the 5, 8 protons and the imide carbonyl is present. However, the intensity is between that of noise and the confirmed correlation between the 2, 11 protons. We believe that this is inconclusive and potentially consistent with either bay (6, 7; shown) or headland (5, 8) nitro substitution.

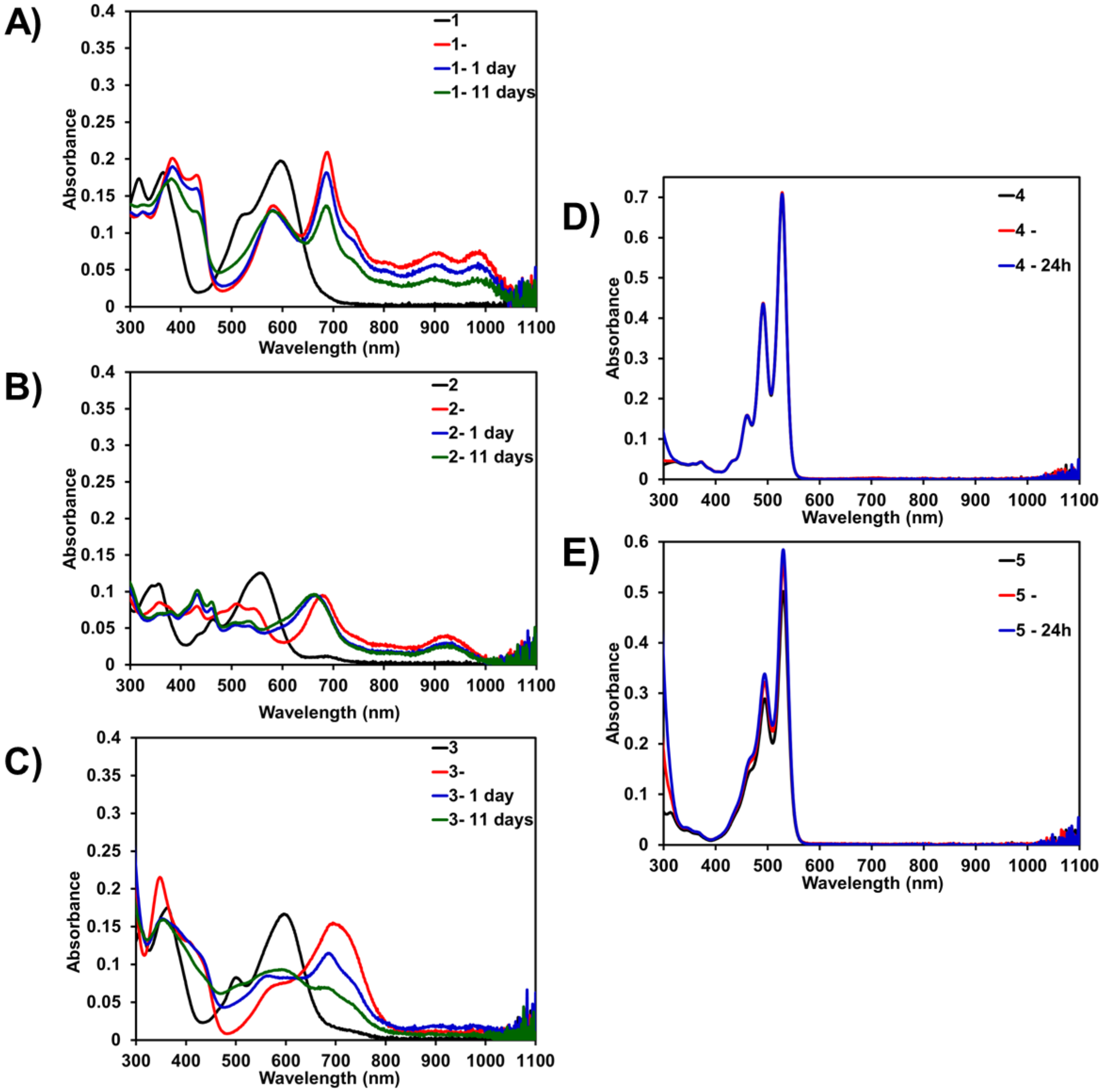

Fig S23: UV-Vis-nearIR absorption spectra of **A**) **1**, **B**) **2**, **C**) **3**, **D**) **4** (ethyl-propyl perylene diimide, **PDI**), and **E**) **5** (**PDIN-C_6H_{13}**) in dilute DMSO solution without (black trace) sodium thiosulfate, with one equivalent sodium thiosulfate (red trace), 24 h after sodium thiosulfate addition (blue trace), and 11 days after sodium thiosulfate addition (green trace). We would like to note that the evolution of each of **1**-**3** show isosbestic points indicating a single molecule to single molecule transition. However, the evolved species is inconsistent the neutral molecule. We believe that this decomposition is the in-situ formation of the dianion which only further shows the resistance of the radical anion to oxygen. See **Fig S24** for chemical structures.

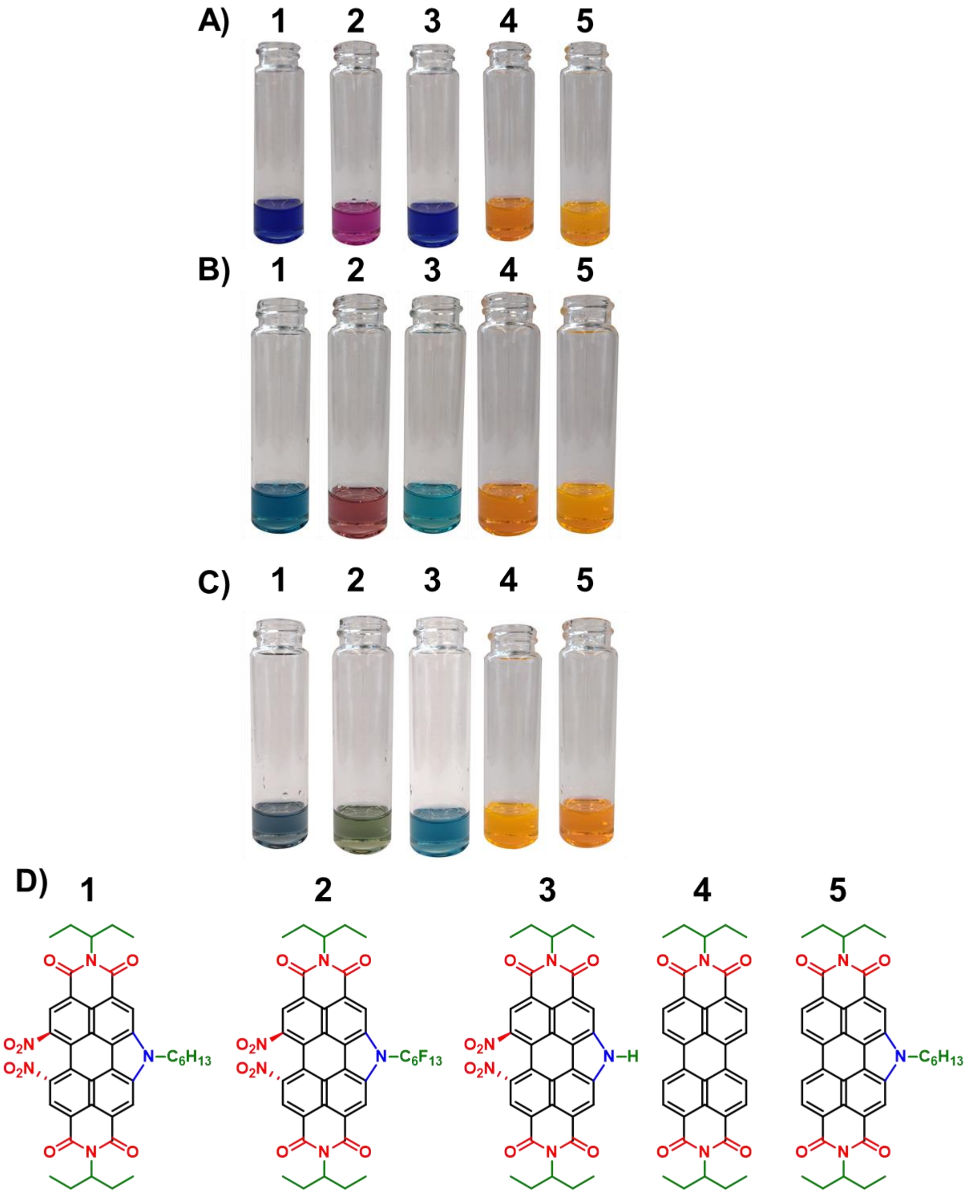

Fig S24: Photographs of **1**, **2**, **3**, **4** (ethyl-propyl perylene diimide, **PDI**), and **5** (**PDIN-C$_6$H$_{13}$**) in dilute DMSO solution without (**A**) sodium thiosulfate, with one equivalent sodium thiosulfate (**B**), and 24 h after sodium thiosulfate addition (**C**). Chemical structures of **1-5** (**D**).

References

1. Bruker-AXS. SAINT; Madison, Wisconsin, USA, 2017.
2. Bruker-AXS. XPREP; Madison, Wisconsin, USA, 2017
3. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
4. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
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6. Spek, A.L. (2015). Acta Cryst. C71, 9-18.