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A N-H functionalized perylene diimide with strong red-light absorption for green solvent processed organic electronics

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1. Materials and Methods

Materials: All reagents and solvents were purchased from Millipore-Sigma and used without further purification.

Nuclear Magnetic Resonance (NMR): ^{1}H and ^{13}C NMR spectroscopy experiments were recorded using a Bruker Avance III 500 MHz spectrometer. All experiments were performed in chloroform-d ($CDCl_3$). Chemical shifts (referenced to residual solvent) were reported in parts per million (ppm). Multiplicities were reported as follows: singlet (s), doublet of doublets (dd), and multiplets (m).

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

CHN Elemental Analysis: Elemental analyses were performed by Johnson Li in the Chemical Instrumentation Facility at the University of Calgary (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).

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 using 2 mm quartz cuvettes. Stock solutions (1.0 mg/mL) of each compound were prepared in $CHCl_3$, serially diluted to concentrations between 10^{-5} - 10^{-6} M, and then used to construct calibration curves for determining molar absorptivity. Neat films were prepared from $CHCl_3$ solutions by spin-coating from a 1 % wt/v solution onto clean Corning glass micro slides. Alcohol processed thin films were cast from 40 µL of a 5 mg/mL solution of **X1** in 1:1 *n*-propanol:*n*-butylamine. Alcohol processed solution optical absorbance measurements were recorded for 10^{-5} M solutions of **X1** in 1:1 *n*-propanol:*n*-butylamine. Prior to use, glass slides were cleaned with acetone and isopropanol, followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

Cyclic Voltammetry (CV): Electrochemical measurements were performed using a CH Instruments Inc. Model 1200B Series Handheld Potentiostat. A standard 3-electrode setup was utilized, consisting of a freshly polished glassy carbon disk working electrode (WE), Pt-wire counter electrode (CE), and Ag-wire pseudo-reference electrode (RE). All measurements were referenced to ferrocene (Fc+/0) as internal standard. All cyclic voltammetry experiments were performed at a scan rate of 100 mV/s. Sample solutions, with 1 mM compound and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) supporting electrolyte, were prepared in anhydrous dichloromethane. All electrochemical solutions were sparged with dry gas (either N_2 or argon) for 5 minutes to deoxygenate the system prior to measurements.

Single Crystal XRD: Single crystals of $C_{55}H_{49}N_3O_4$, **X1**, were grown from *o*-xylene (1 mL) and hexanes (1 mL) at 298K. A suitable crystal was selected and mounted on a glass loop using Paratone oil. Diffraction experiments were performed on a Bruker Smart diffractometer equipped with an Incoatec Microfocus (Cu Kα, λ = 1.54178 Å) and an APEX II CCD detector. The crystal was kept at 173 K during data collection. Diffractions spots were integrated and scaled with SAINT [3] and the space group was determined with XPREP[4]. Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimisation.

Organic Field Effect Transistors

Fabrication:

Si/SiO_2 substrates with patterned Au contacts (bottom-gate bottom-contact) were purchased from Fraunhofer IPMS, having channel lengths from 2.5 to 20 µm, channel width of 2000 µm and dielectric thickness of 230 nm. The substrates were plasma treated for 10 minutes, then surface-functionalized with octyltrichlorosilane (1% v/v in toluene) for one hour. X1 was dissolved in 1:1 isopropanol/n-butylamine or n-propanol/n-butylamine solutions at 5 mg/mL. These solutions were then spin-coated at 1000 rpm for 60 seconds onto the treated substrates in an inert atmosphere.

Characterization:

Devices were characterized under vacuum (< 0.1 Pa) in a custom oesProbe A10000-P290 system (Element Instrumentation Inc. & Kreus Design Inc.). A Keithley 2614B was used to modulate the gate-source voltage (V_{GS}) and source-drain voltage (V_{DS}) and measure the source-drain current (I_{DS}). A constant V_{DS} of 70 V was used to obtain the saturation field-effect electron mobility and threshold voltage over a V_{GS} range of 0 to 100 V.

Calculation of Electron Mobility:

The relationship between I_{DS} and V_{GS} in the saturation region are given in **Equation 1**:

$$(1)\ I_{DS} = \frac{\mu C_i W}{2L}(V_{GS} - V_T)^2$$

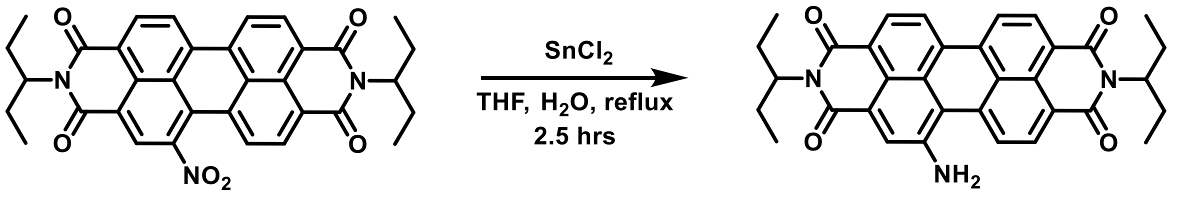
Where C_i is the capacitance of the gate dielectric (1.5×10^{-4} F m^{-2}), µ is the field-effect electron mobility of the material, V_T is the threshold voltage, W is the width of the channel, and L is the length of the channel.

To find the mobility, the equation can be rearranged by taking the square root, giving **Equation 2**:

$$(2)\ \sqrt{I_{DS}} = \sqrt{\frac{\mu C_i W}{2L}}(V_{GS} - V_T)$$

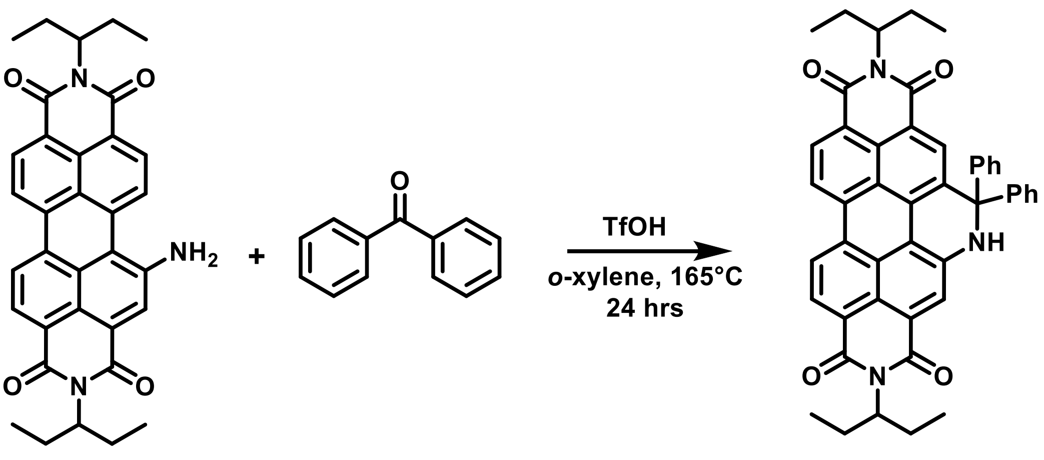
This gives a linear relationship between $\sqrt{I_{DS}}$ and V_{GS}. The slope of linear region of the $\sqrt{I_{DS}}$ vs V_{GS} curve gives $\sqrt{\frac{\mu C_i W}{2L}}$, which all constants are known except µ, for which we can solve. V_T is simply the x-intercept of this line.

2. Synthetic Procedures



1

PDI-NO_2 (2.4 g, 4.2 mmol, 1 eq) and anhydrous $SnCl_2$ (8 grams, 42 mmol, 10 eq) were added to a 125 mL round bottom flask (excess of $SnCl_2$ was shown to improve the yield when compared to similar literature reaction[1]). 50 mL of THF was added, followed by 3 mL of H_2O (H_2O is needed in order to drive the equilibrium towards **1**). The flask was equipped with a reflux condenser and the reaction was refluxed. The reaction mixture changed from red to blue when heating commenced. After TLC indicated the reaction was complete, the solvent was removed *in vacuo*, the product was slurried in H_2O and poured into a 500 L beaker. 300 mL of H_2O was added to the beaker and it was stirred overnight to dissolve Sn-based residues. The resulting H_2O slurry was vacuum filtered to isolate the blue solid. The solid was washed with an additional 2 L of H_2O to ensure Sn-based residues were removed. Compound **1** (PDI-NH_2) was obtained in 53% yield (0.76 g, 0.14 mmol). ^{1}H-NMR data matches the literature for this compound.[2]



X1

Benzophenone (29 mg, 0.16 mmol, 1.6 eq.) was added to a 10 mL pressure tube equipped with a stir bar. *o*-Xylene (2 mL) was added, followed by trifluoromethanesulfonic acid (7.8 µL, 0.09 mmol, 0.9 eq.), and the mixture was stirred for 5 minutes. Compound **1** (54 mg, 0.10 mmol, 1.0 eq.) was added, the vial was sealed, and the reaction was heated at 165 ºC for 24 hrs. During the reaction the solution changed from a dark red colour to dark green. The reaction mixture was poured into a 250 mL separatory funnel and diluted with 35 mL of ethyl acetate. The organic layer was washed twice with saturated $NaHCO_3$(aq) to neutralize residual acid and once with brine. The organic layer was collected, dried with anhydrous $MgSO_4$, and gravity filtered into a 250 mL round bottom flask. The solvent was removed *in vacuo* and the resulting crude solid was dissolved in 30 mL of dichloromethane and passed through a Silica plug eluting with dichloromethane to separate the product from excess benzophenone. The green band was collected, and the solvent was removed *in vacuo*. The resulting dark green solid was precipitated with a 1:3 MeOH:H_2O solution (the product was found to be partially soluble in 100% MeOH) and collected via vacuum filtration. Compound **X1** was obtained in 84% yield (59 mg, 0.084 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 8.55 (m, 1H, Ha), 8.57 (dd, J = 8.0 Hz, 2H, Hb), 8.41 (m, 1H, Hc), 8.09 (m, J = 8.3 Hz, 1H, Hd), 7.37 (m, J , 8H, He), 7.32 (m, 2H, Hf), 5.69 (s, 1H, Hg), 5.01 (s, 1H, Hh), 2.22 (m, 4H, Hi), 1.90 (m, 4H, Hj), 0.89 (m, 12H, Hk).

^{13}C NMR (151 MHz, $CDCl_3$, 27 ºC): δ 144.83 (Q), 140.82 (Q), 135.42 (Q), 131.57 (Q), 130.46 (Q), 128.68 (ar-CH), 128.33 (Q), 127.96 (Ph), 127.95 (Ph), 127.58 (ar-CH), 125.61 (Q), 124.62 (ar-CH), 123.18 (Q), 122.90 (ar-CH), 121.34 (ar-CH), 112.57 (Q), 67.92 (Q), 57.06 (CH), 56.96 (CH), 24.47 (CH_2), 24.44, (CH_2), 10.87 (CH_3), 10.73 (CH_3).

HRMS ([M-2H]+H^+) calculated for $C_{47}H_{38}N_3O_4$: 708.2857; detected [M-2H]+H^+: 708.2861

UV-Vis λ (M^{-1} cm^{-1}): 433 nm (18629), 651 nm (28469)

CHN theoretical (%) C: 79.53, H: 5.54, N: 5.92; found (%) C: 78.83; H: 5.75; N: 5.92

3. NMR Spectra

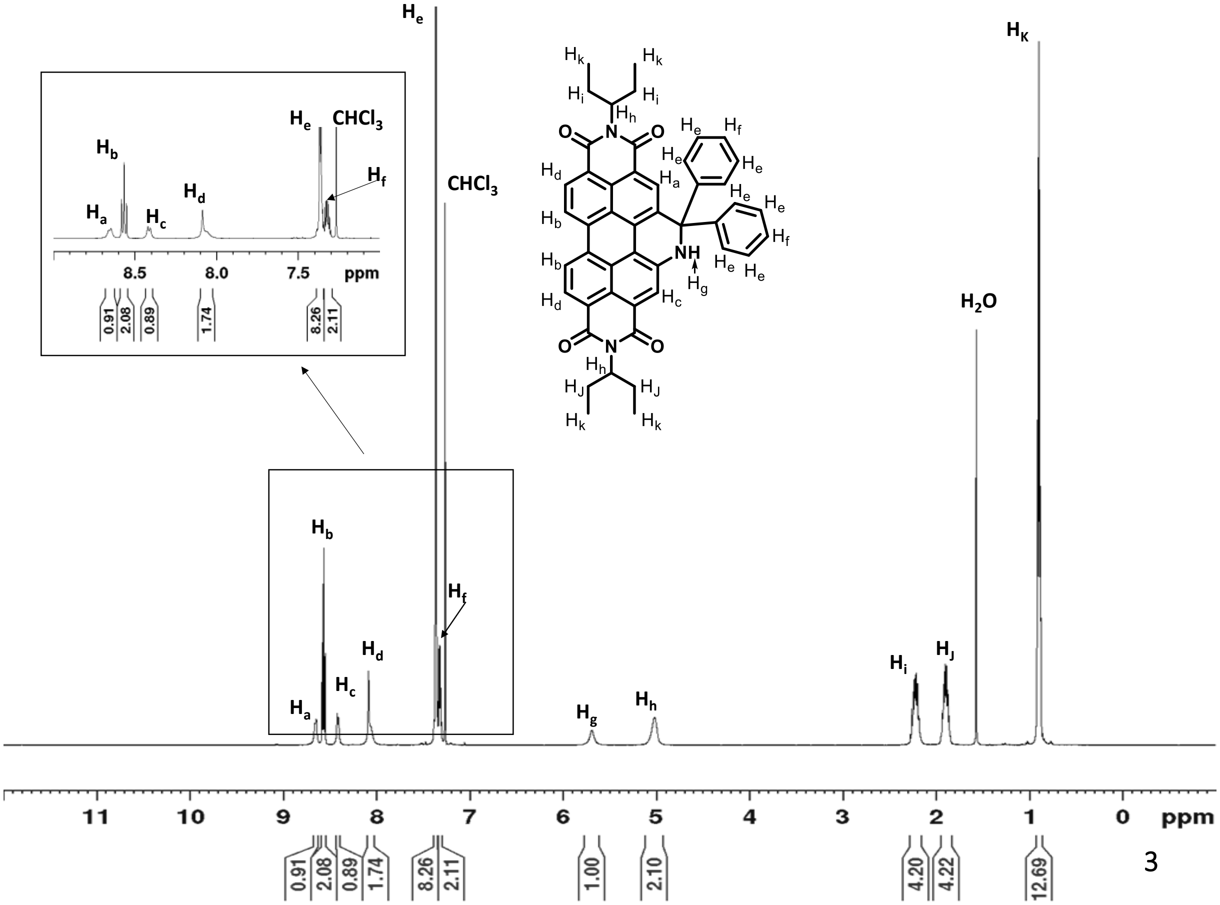


Figure S1: ^{1}H-NMR spectrum of **X1** (500 MHz, CDCl$_3$).

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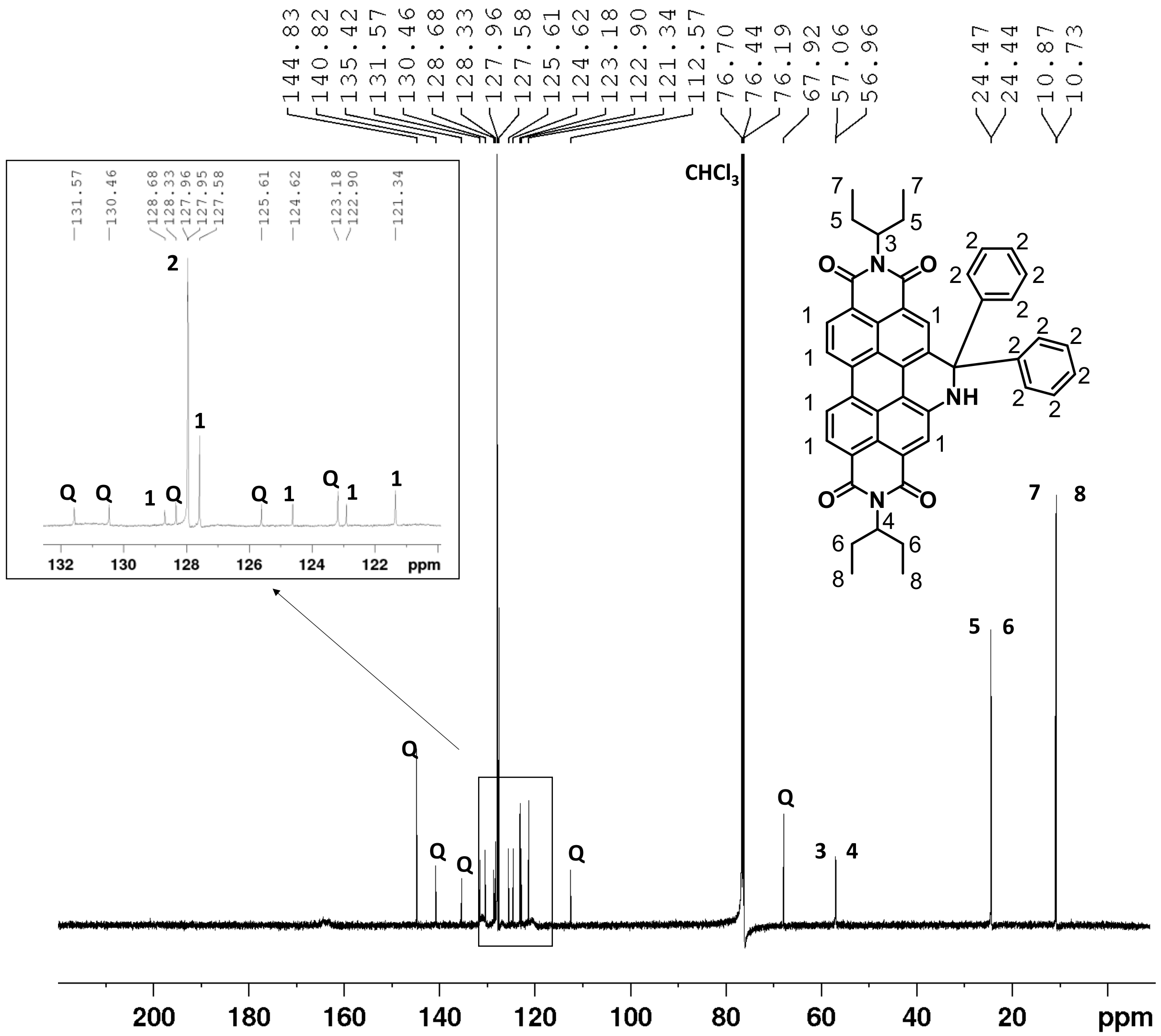


Figure S2: ^{13}C-NMR spectrum of **X1** (126 MHz, CDCl$_3$). Q = quaternary carbon. 9 of the quaternary carbons do not appear in the spectrum or have resonances with very low resolution.

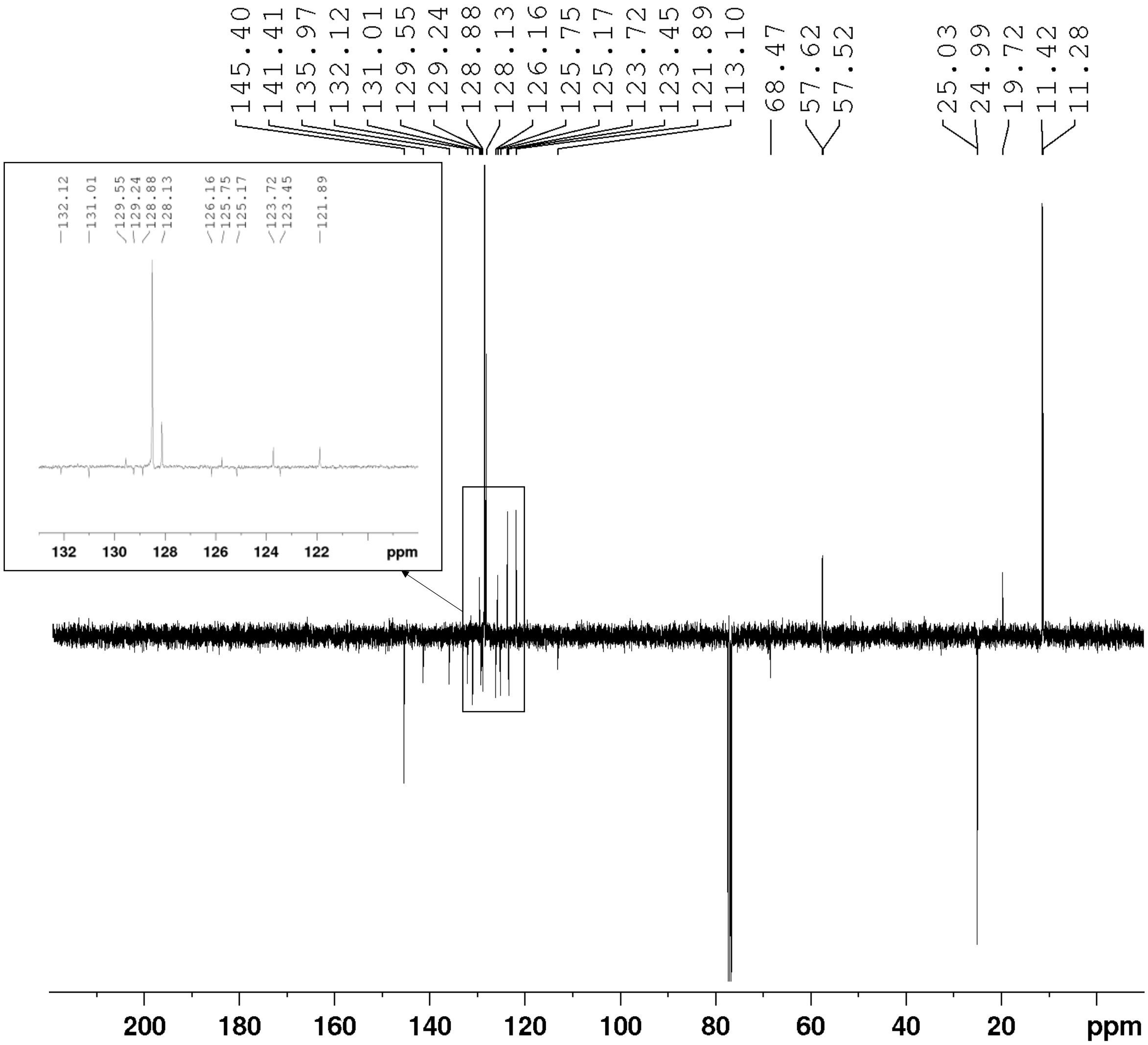
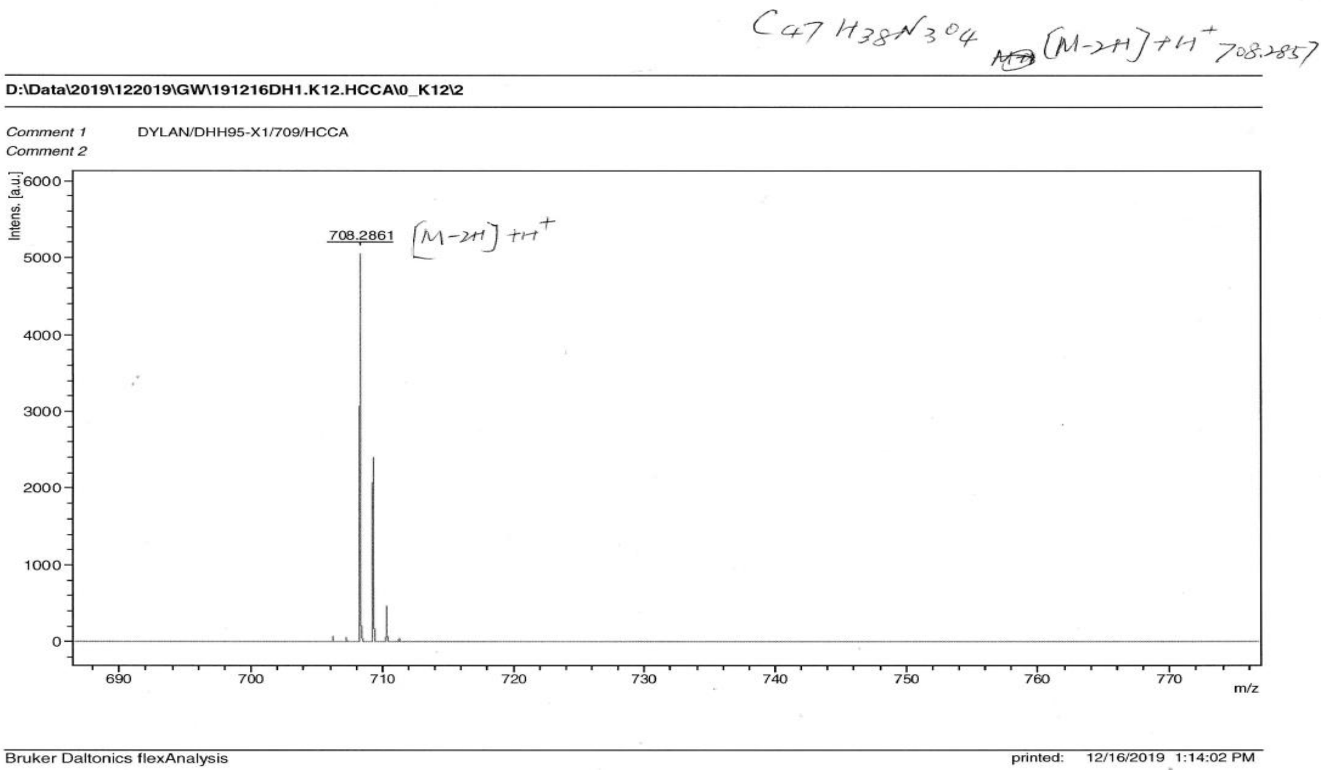


Figure S3: DEPTQ-^{13}C-NMR spectrum of **X1** used for resonance assignment.

4. Mass Spectra



$C_{47}H_{38}N_3O_4$ ~~M+H~~ $[M-2H]+H^+$ 708.2857

D:\Data\2019\122019\GW\191216DH1.K12.HCCA\0_K12\2

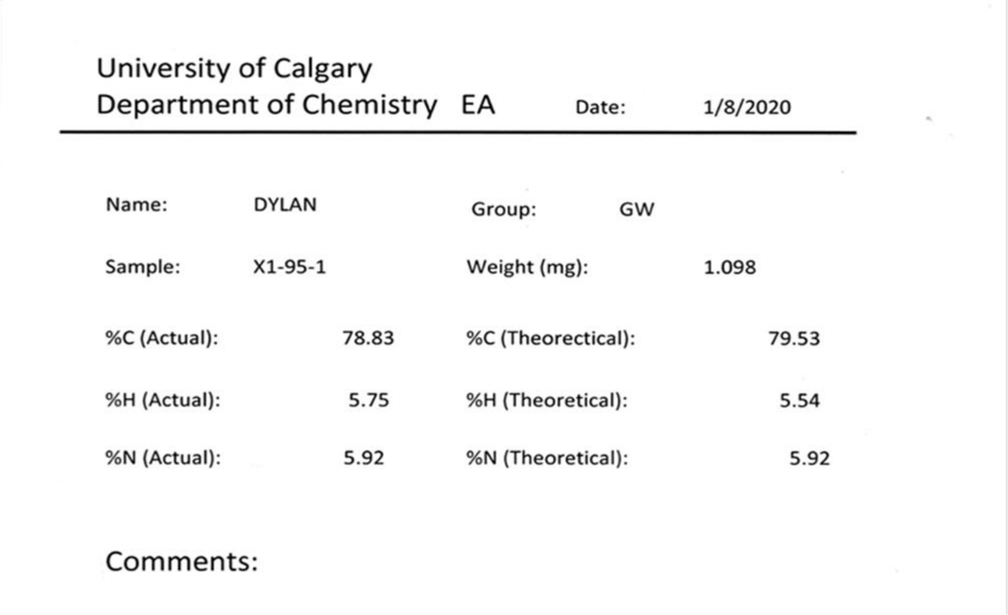
Comment 1 DYLAN/DHH95-X1/709/HCCA

Comment 2

Bruker Daltonics flexAnalysis printed: 12/16/2019 1:14:02 PM

Figure S4: HR-MALDI-TOF-MS Spectrum of **X1**.

5. Elemental Analysis



University of Calgary
Department of Chemistry EA Date: 1/8/2020

Name:	DYLAN	Group:	GW
Sample:	X1-95-1	Weight (mg):	1.098
%C (Actual):	78.83	%C (Theorectical):	79.53
%H (Actual):	5.75	%H (Theoretical):	5.54
%N (Actual):	5.92	%N (Theoretical):	5.92

Comments:

Figure S5: CHN elemental analysis data sheet for **X1.**

6. Thermal Analysis

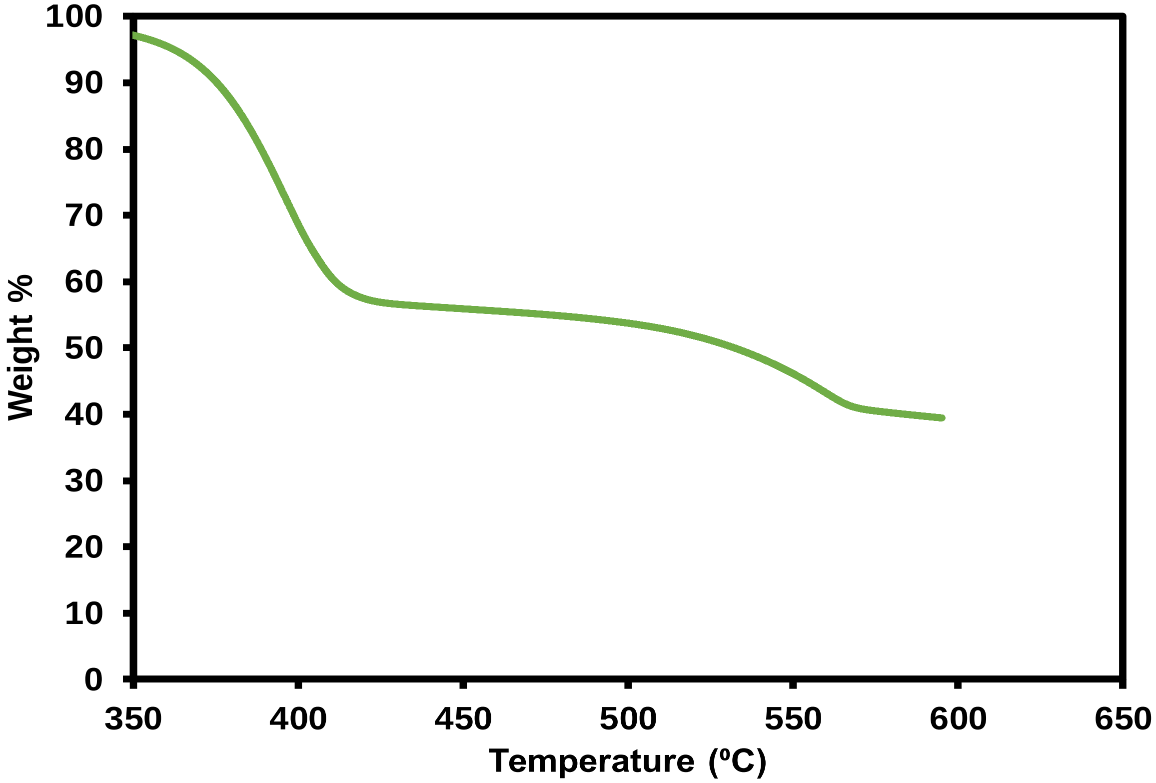


Figure S6: Thermogravimetric Analysis of **X1**.

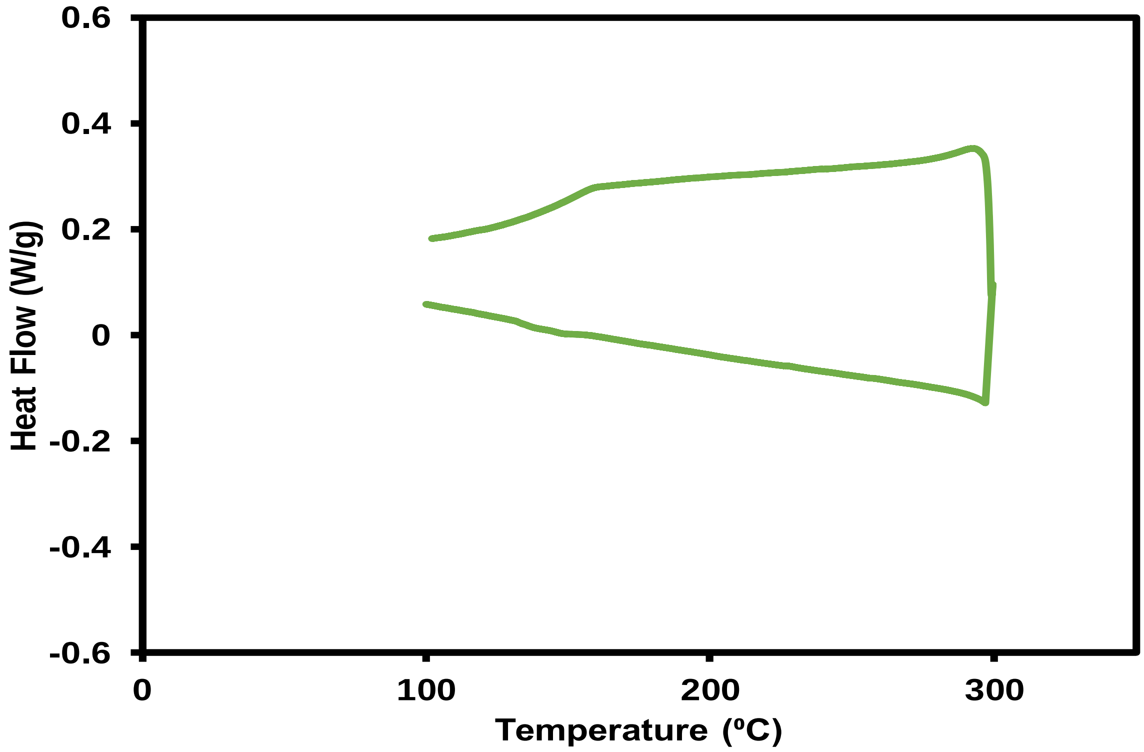


Figure S7: Differential Scanning Calorimetry of **X1**.

7. SC-XRD

Table S1: Crystal data and structure refinement for **X1**

Identification code	X1
Empirical formula	$C_{55}H_{49}N_3O_4$
Formula weight	815.97
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.2115(4)
b/Å	21.6669(5)
c/Å	14.3552(3)
α/°	90
β/°	104.079(2)
γ/°	90
Volume/Å^3	4287.46(18)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.626
F(000)	1728.0
Crystal size/mm^3	0.306 × 0.157 × 0.071
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.546 to 130.29
Index ranges	$-16 \le h \le 16$, $-25 \le k \le 25$, $-15 \le l \le 16$
Reflections collected	26955
Independent reflections	7146 [$R_{int} = 0.0234$, $R_{sigma} = 0.0203$]
Data/restraints/parameters	7146/419/658
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	$R_1 = 0.0485$, $wR_2 = 0.1374$
Final R indexes [all data]	$R_1 = 0.0570$, $wR_2 = 0.1462$
Largest diff. peak/hole / e Å^{-3}	0.81/-0.28

8. Electrochemical Analysis

Table S2: Tabulated Electrochemical Data for **X1**.

Ox E_{on} (V)[a]	Ox $E_{1/2}$ (V)[b]	Red E_{on} (V)[c]	Red $E_{1/2}$ (V)[d]	IP (eV)[e]	EA (eV)[e]	E_g (eV)
0.5 V	0.62	-1.1	-1.22, -1.43	5.4	3.6	1.8

[a] Onset of oxidation

[b] Oxidation half potential

[c] Reduction onset

[d] Reduction half potential

[e] Energy values were calculated by ($E_{1/2}$ + 4.8 eV) where Fc HOMO = 4.8 eV.[8]

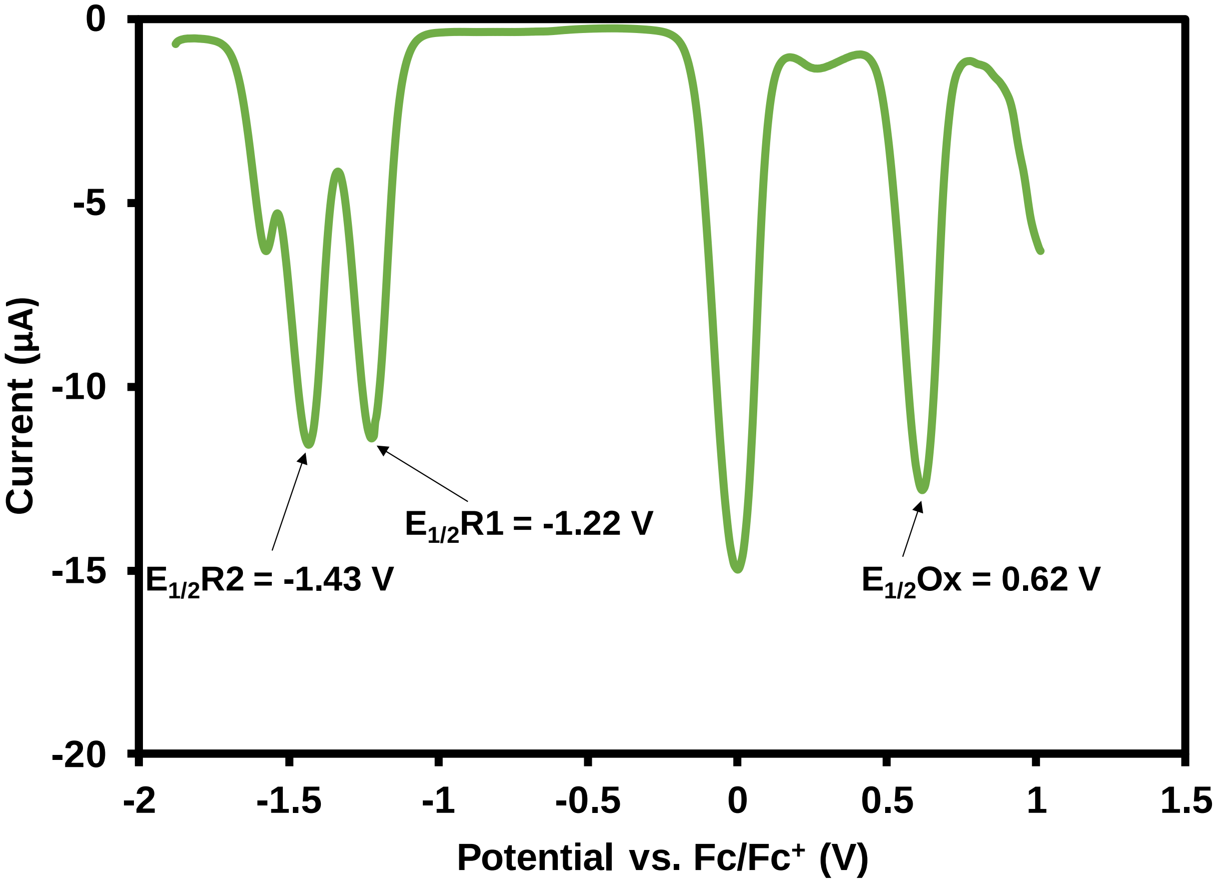


Figure S8: Differential Pulse Voltammogram of **X1** (≈1 mM) in CH_2Cl_2, recorded at 100 mV/s.

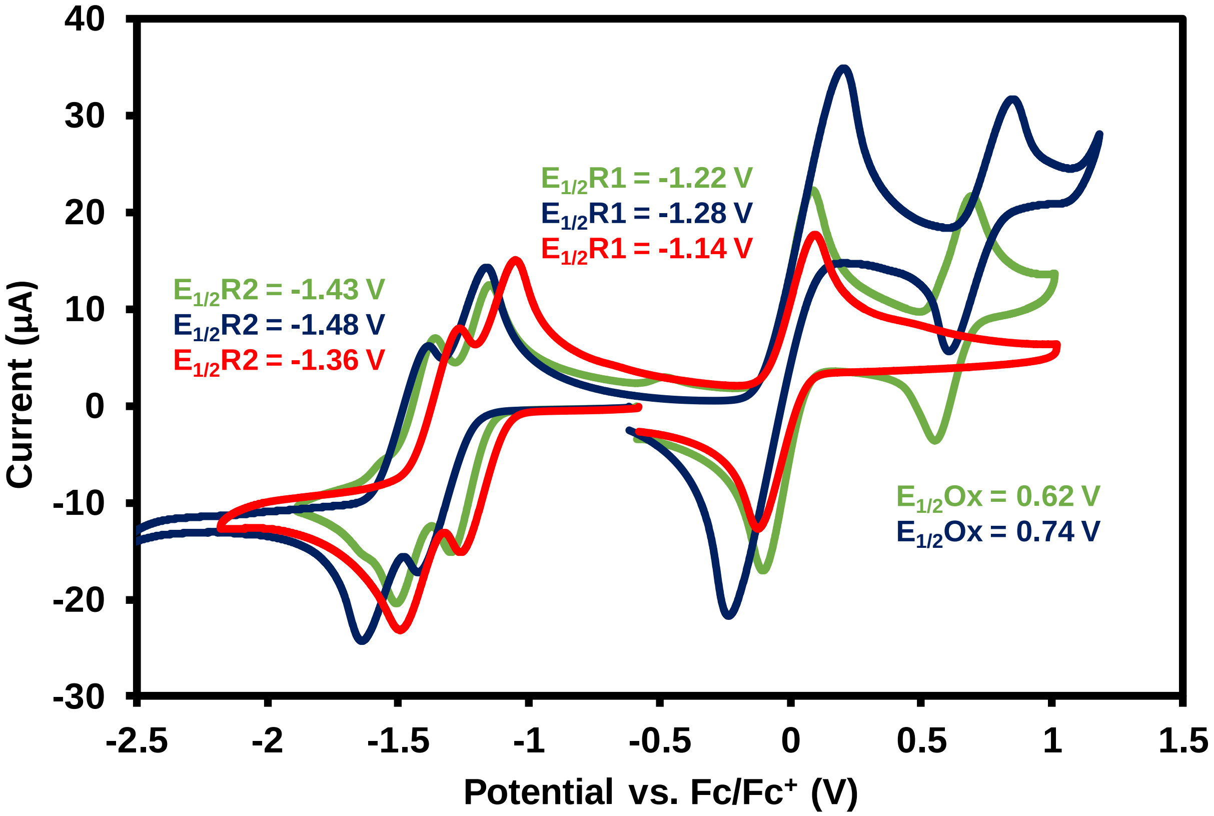
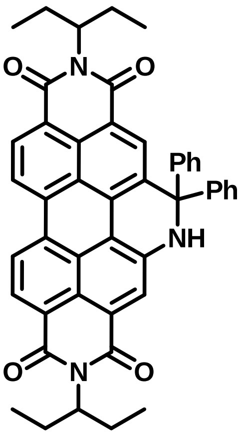
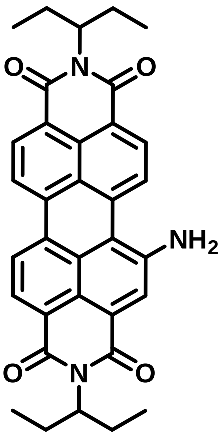


Figure S9: Cyclic Voltammogram of **X1** (green, ≈1 mM), **1** (blue, ≈1 mM), and **PDI** (red, ≈1 mM), in CH_2Cl_2, recorded at 100 mV/s. Half potentials listed. Fc/Fc$^+$ couple shown (0V, internal standard)



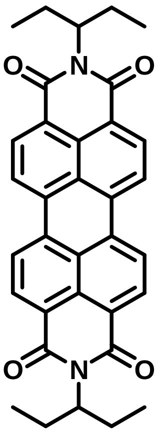
X1

green



1

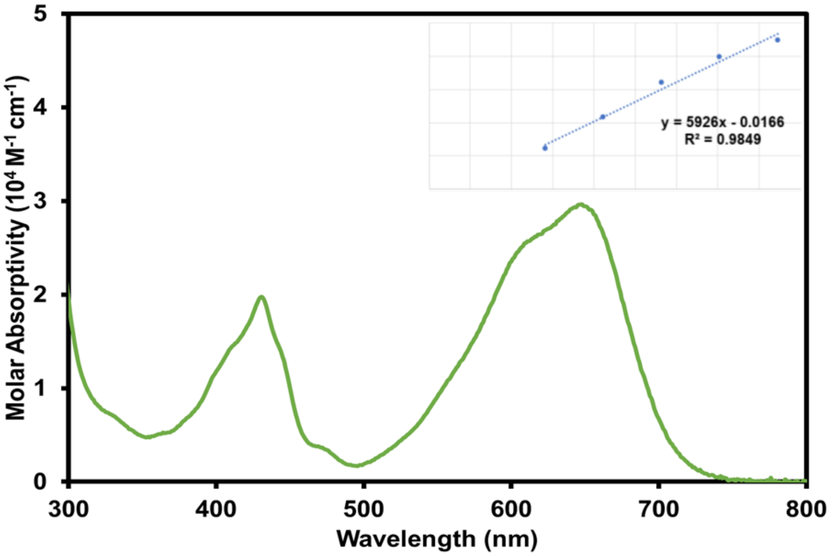
blue



PDI

red

9. Optical Analysis



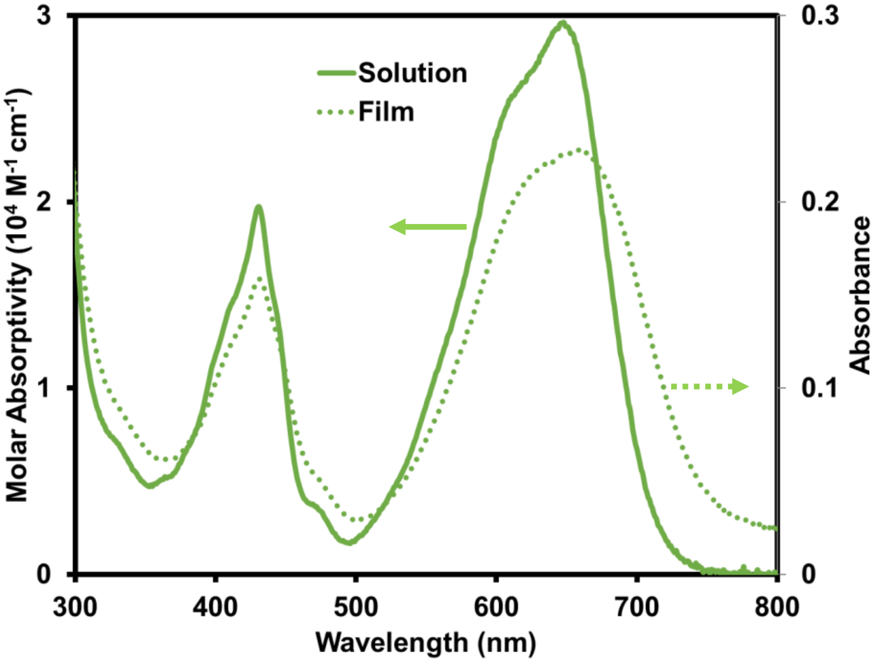


Figure S10: (TOP) Solution optical absorption spectrum of **X1 i**n $CHCl_3$, with calibration curve inset. (BOTTOM) Comparison of solution ($CHCl_3$) and film (spin-cast from $CHCl_3$) spectra of **X1**.

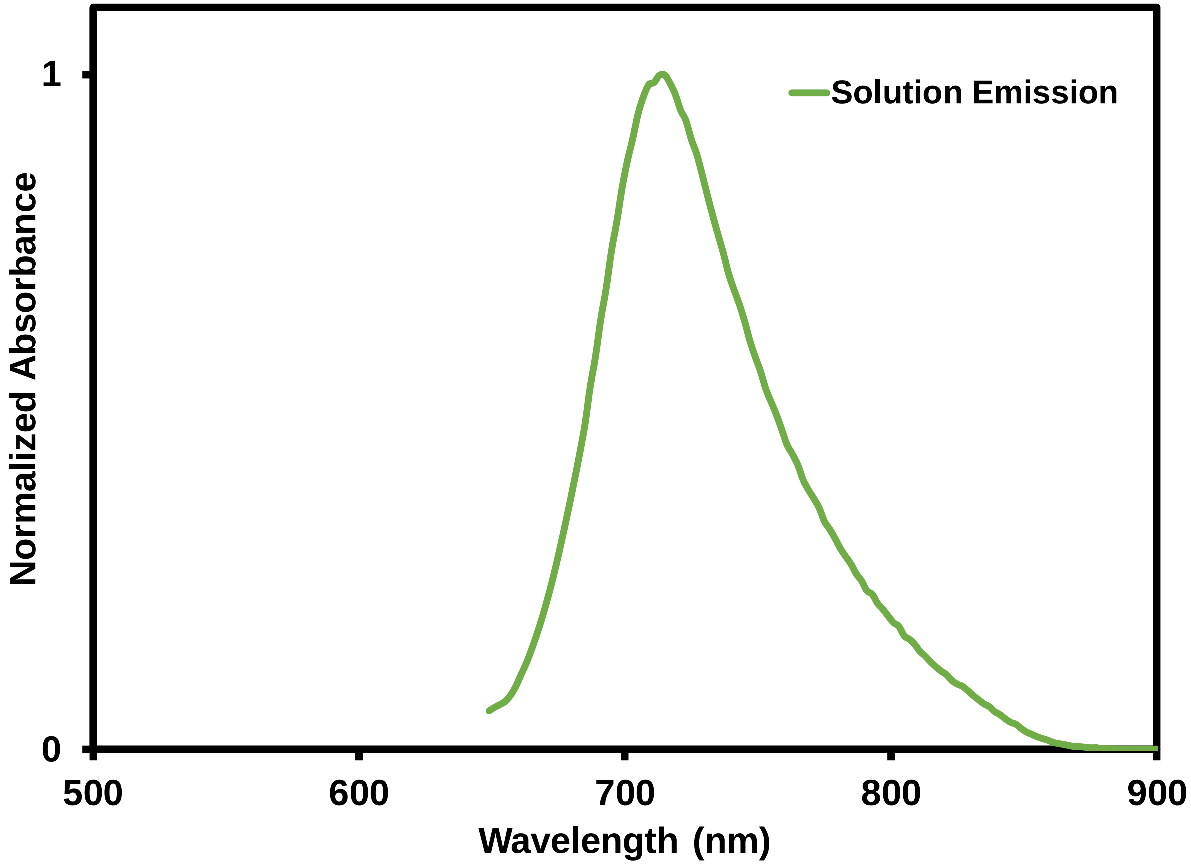


Figure S11: Photoluminescence emission spectra for **X1** in $CHCl_3$ solution.

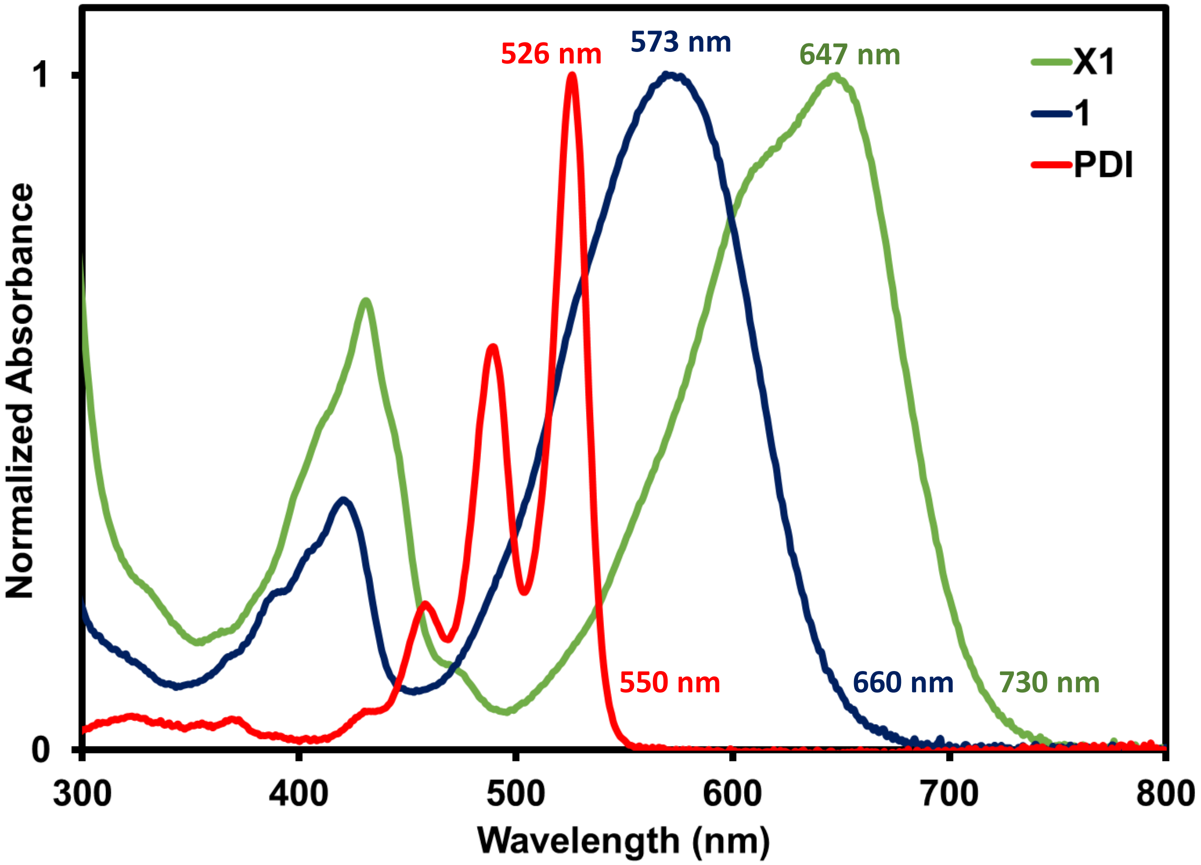
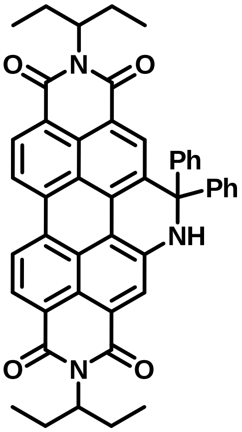
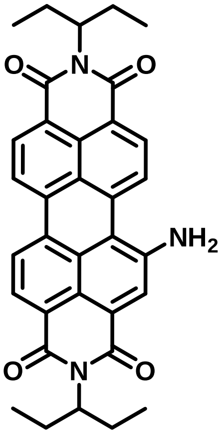


Figure S12: Comparison of the optical absorption spectra of **X1** (green), **1** (blue), and **PDI** (red) in $CHCl_3$.



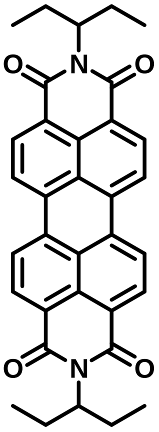
X1

green



1

blue



PDI

red

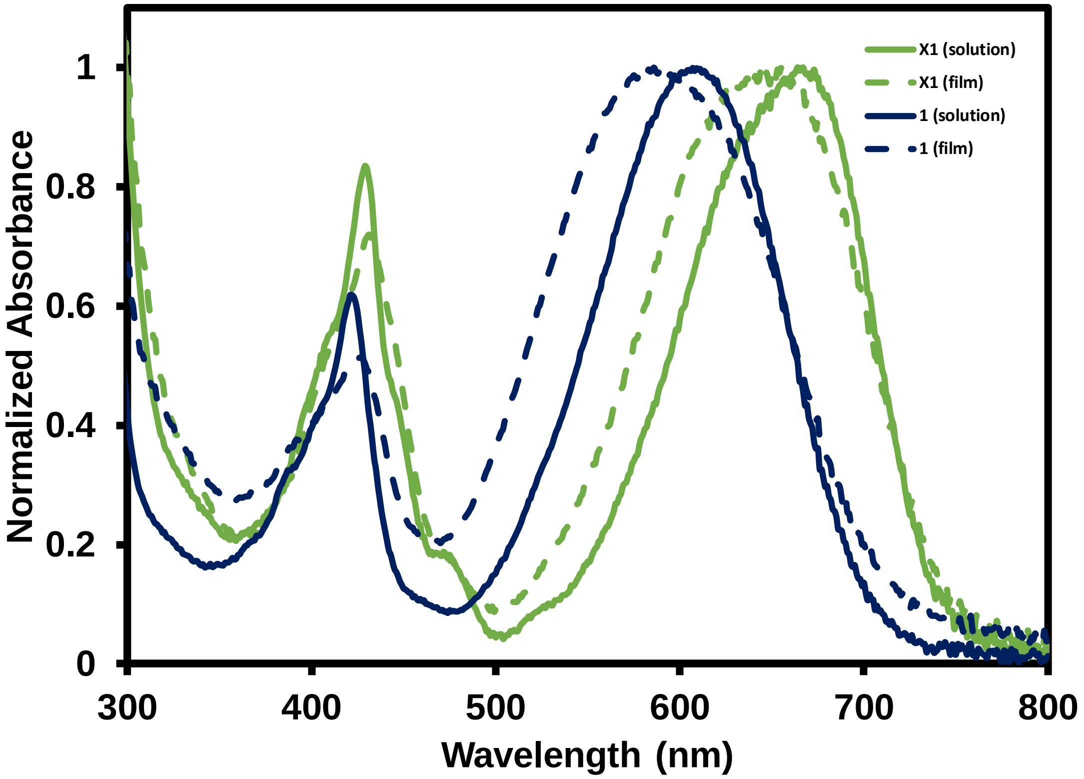
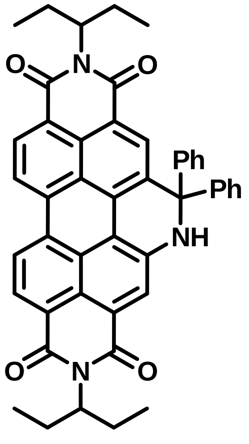
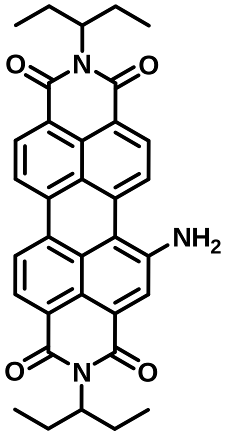


Figure S13: Comparison of the optical absorption spectra of **X1** (green) and **1** (blue). Solutions were diluted from 5 mg/mL in *n*-propanol / butylamine (1:1 v/v) stock solutions. Films were spin-cast from 5 mg/mL in *n*-propanol / butylamine (1:1 v/v) stock solutions. Note: compound **1** = PDI-NH_2. Solid lines (solution spectra) and dashed lines (film spectra).



X1



1

10. Photos

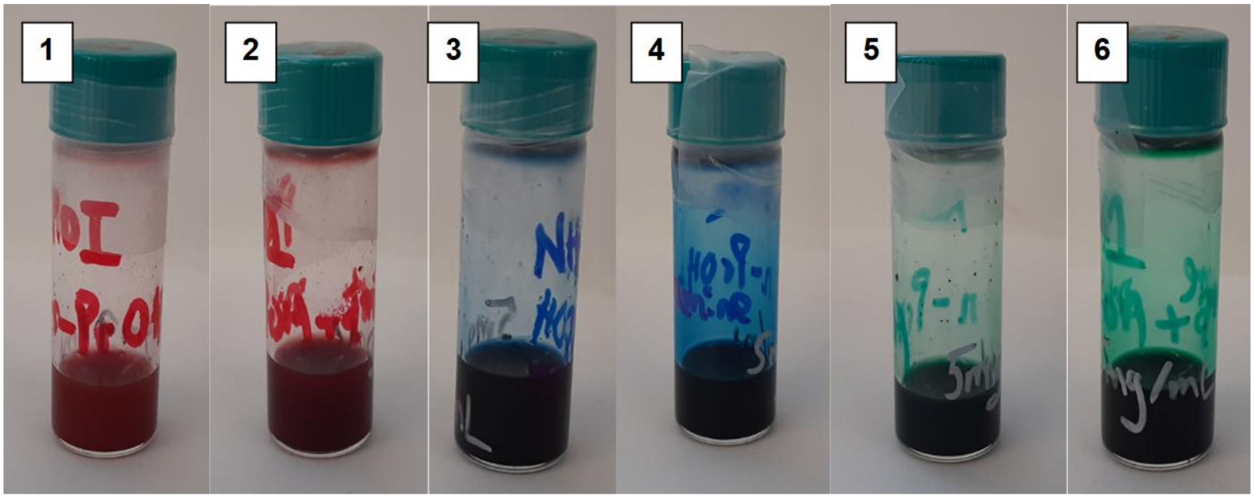


Figure S14: Pictures of 5 mg/mL solutions of: **PDI** (1) *n*-propanol and (2) *n*-propanol / butylamine (1/1 v/v). **1** (3) *n*-propanol and (4) *n*-propanol / butylamine (1:1 v/v). **X1** (5) n-propanol and (6) *n*-propanol / butylamine (1/1 v/v). All compounds could not be fully dissolved (up to 5 mg/mL) in *n*-propanol alone as seen with the particles on the vial sides. Note: compound **1** = PDI-NH_2.

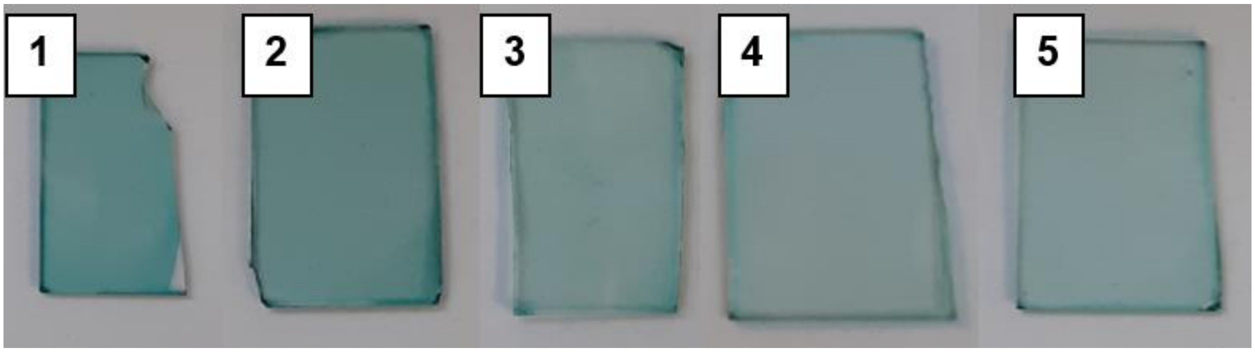


Figure S15: Pictures of thin-films of **X1** spin-cast from 5 mg/mL solutions. (1) $CHCl_3$; (2) 2-Methyl THF; (3) *o*-xylene (4) EtOAc; (5) *n*-PrOH / *n*-butylamine (1:1 v/v).

11. Example OFET Plots

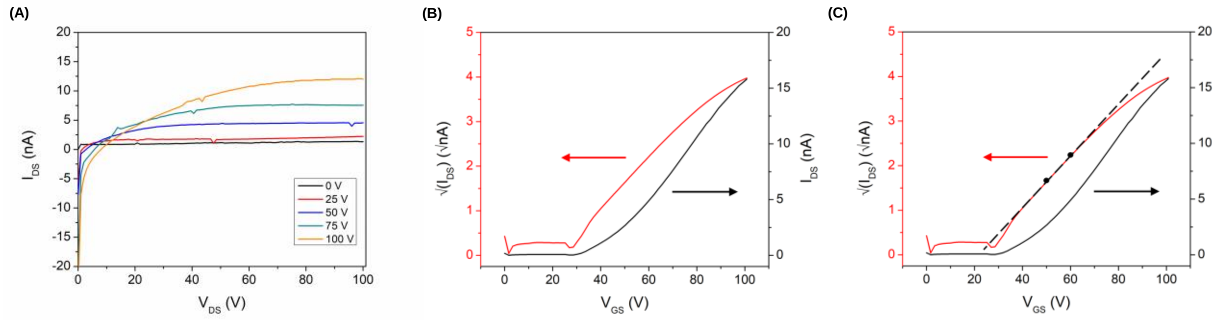


Figure S16: Example OFET output plots (a), transfer plots (b), and transfer plots showing linear region (c) for devices based on films of **X1** processed from *n*-propanol:*n*-butylamine (1:1) solutions and annealed at 200°C.

12. References

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