

Supporting Information

Cyclic Secondary Amine Functionalized Perylene Diimide Polymers for Solution Processed Electrochromic Devices

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1. Materials and Methods

Materials: All reagents and solvents were purchased from Millipore-Sigma and used without further purification. Toluene solvent was dried by storing over 3 Å molecular sieves and purged with N₂ gas before use. **PDI-NH₂**, **X1**, and **Br₂-X1** were synthesized as previously reported.¹⁻³

Microwave Reactions: All microwave reactions were carried out using a Biotage[®] Initiator + microwave reactor. The operational power range 0-400 W from magnetron at 2.45 GHz.

Nuclear Magnetic Resonance (NMR): ¹H, ¹³C and 2D NMR spectroscopy experiments were recorded using a Bruker Avance - 500 MHz, or 400 MHz spectrometer at 300 K. All experiments were performed in chloroform-d (CDCl₃). 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 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. 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).

Single Crystal XRD: SC-XRD was done by Benjamin S. Gelfand from the University of Calgary. Single crystals of C₄₈H₃₈Cl₃N₃O₄, **F1**, were grown by slow evaporation in chloroform at 298 K. A suitable crystal was selected and mounted on a glass loop using Paratone. Diffraction experiments were performed on a Bruker Smart diffractometer equipped with an Incoatec Microfocus (Cu K α , $\lambda = 1.54178$ 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,⁴ and the space group was determined with XPREP.⁵ 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. CCDC #2284202

UV-Visible Spectroscopy (UV-Vis): Optical absorption measurements were performed using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution experiments were run in CHCl₃ using 2 mm quartz cuvettes. Films were spin-cast from 40 μ L of 10 mg/mL solution of compounds onto quartz glass substrate that 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 (0.071 cm^2), Pt-wire counter electrode, and Ag-wire pseudo-reference electrode (for solution CV) or Ag/Ag^+ non-aqueous reference electrode (for film CV, filled with 10 mM silver nitrate (AgNO_3) and 0.1 M lithium perchlorate (LiClO_4) in acetonitrile). All measurements were referenced to ferrocene ($\text{Fc}^+/0$) as external standard. For the solution CV, 1 mM compound and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) supporting electrolyte, were prepared in anhydrous dichloromethane. For the film CV, 0.1 M LiClO_4 supporting electrolyte was prepared in anhydrous acetonitrile. All electrochemical solutions were sparged with dry gas (N_2) for 15 minutes to deoxygenate the system prior to measurements.

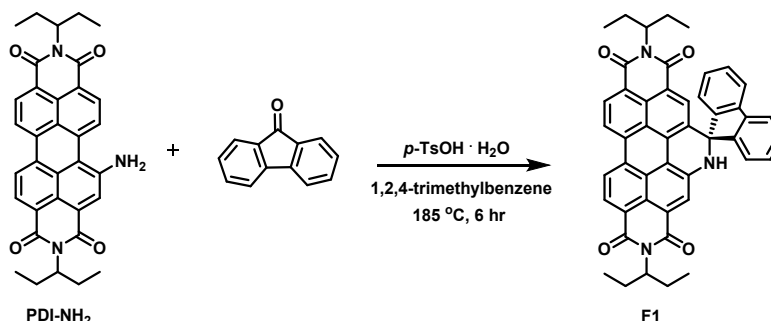
Size-exclusion Chromatography (SEC): Size-exclusion chromatography (SEC) was done by Catherine Beaumont from the Université Laval. SEC was used to obtain the number-average (M_n) and the weight-average (M_w) of the polymers. The Tosoh EcoSEC HLC-8321GPC/HT apparatus equipped with an RI detector was used. The column consists of a TSKgel GMHhr-H(20) HT2, 20 μm , mixed bed, 7.8 mm ID x 30 cm column and a TSKgel GMHhr-H guard column (30 μm , 7.5 mm ID x 7.5). BHT (0.0125 % w/v) was added to 1,2,4-Trichlorobenzene (TCB). This TCB mixture was used as the eluent with a flow rate of 1 mL min^{-1} and the temperature of the system was set to $130 \text{ }^\circ\text{C}$. Samples were prepared by dissolving the polymers in TCB with a concentration of 1 mg mL^{-1} . Prior to the analysis, the samples were stirred overnight at $110 \text{ }^\circ\text{C}$ to ensure complete dissolution. The calibration was performed using polystyrene narrow standards dissolved in TCB.

Device Fabrication: Electrochromic devices (ECDs) were fabricated using a structure ITO/polymer film/ gel electrolyte/ ITO, as shown in Figure S31. The ITO glass was cleaned via sonication with water, acetone, and isopropyl alcohol, for 15 min each, and dried with N_2 . The gel electrolyte was prepared by dissolving poly (methyl methacrylate) (PMMA, $M_w \sim 120,000$) in a 1 M lithium perchlorate (LiClO_4) in propylene carbonate (PC) solution at a ratio of 30 wt% and placed in an oven at $90 \text{ }^\circ\text{C}$ until a clear gel has formed.⁹ Then, devices were assembled with two ITO/glass substrates (one with the polymer film), together with the gel electrolyte in contact. Double sided scotch tape was used as a spacer ($\sim 80 \mu\text{m}$) between the ITO pieces. The ECDs have an active area of 3 cm^2 (3 cm x 1 cm). The working electrode is the ITO with the polymer film, whereas the counter electrode is the ITO glass only. External potentials of - 3.6 V and + 1.2 V were applied to the ECDs to achieve the switchable color changes by using an EC Epsilon Eclipse Potentiostat, whereas the change in absorption was measured with an Agilent Technologies Cary 60 UV-Vis spectrometer.

Atomic Force Microscopy: All AFM images were measured using a TT-2 AFM (AFM workshop) with tapping mode. The images were processed using Gwyddion. The films were spin-coated on ITO glass (20 mm x 15 mm) using 100 μL of 20 mg mL^{-1} solution in chlorobenzene at 2000 rpm for 60 seconds. The ITO glass was cleaned via sonication with water, acetone, and isopropyl alcohol, for 15 min each, and dried with N_2 .

X-Ray Diffraction: XRD experiments were performed on a PROTO AXRD Benchtop Diffractometer using coupled $2\theta/\theta$ scans and $\text{CuK}\text{-}\alpha$ radiation source with wavelength of 0.15418 nm. The X9 and F9 films were spin-coated on glass substrates (20 mm x 15 mm) using 100 μL of 20 mg mL^{-1} solution in chlorobenzene at 2000 rpm for 60 seconds.

2. Synthetic Procedure



Synthesis of **F1**

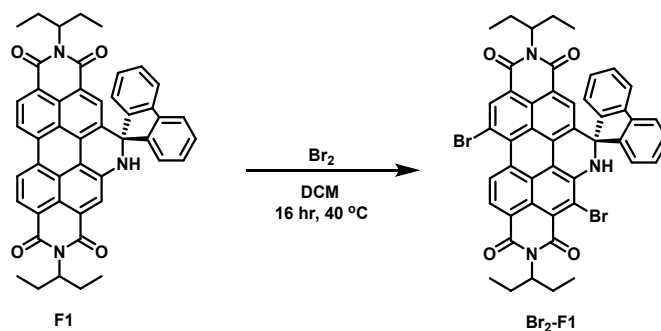
To a 150 mL pressure vial equipped with a stir bar, **PDI-NH₂** (332 mg, 0.608 mmol, 1.0 eq.), fluoren-9-one (149 mg, 0.827 mmol, 1.4 eq.), *p*-toluenesulfonic acid monohydrate (350 mg, 1.840 mmol, 3.0 eq.) and 1,2,4-trimethylbenzene (9 mL) were added. The reaction mixture was purged with N₂ for 10 minutes and capped under N₂ before being placed on heat at 185 °C for 6 hours. The reaction mixture turned from purple to dark blue to green. Then, the reaction mixture was cooled to room temperature, before being transferred to a separatory funnel, which was diluted with dichloromethane (DCM), then washed with water (3 x 50 mL), then once with brine. Collected organic phase was dried over Na₂SO₄, then the solvent was removed *in vacuo*. The resulting crude solid was subjected to silica column chromatography using toluene (1% ethyl acetate) as eluent to collect green band. Then, solvent was removed *in vacuo*. The resulting solid was slurried in water:methanol (1:1, v:v) and the solid flakes were collected *via* vacuum filtration to obtain pure **F1** as a dark green solid (287.8 mg, 67%).

¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.56 (ov, 2H, H_A and H_B), 8.54 (d, J = 8.2 Hz, 1H, H_C), 8.42 (d, J = 7.7 Hz, 1H, H_D), 7.88 (s, 1H, H_E), 7.78 (dd, J = 7.7, 0.9 Hz, 2H, H_F), 7.63 (dd, J = 7.6, 0.9 Hz, 2H, H_G), 7.50 – 7.43 (ov, 3H, H_H and H_I), 7.28 (td, J = 7.5, 1.1 Hz, 2H, H_J), 5.17 (s, 1H, H_K), 4.99 (s, 2H, H_L), 2.28 – 2.06 (m, 4H, H_M), 1.85 (m, 4H, H_M), 0.88 (t, J = 7.4 Hz, 6H, H_N), 0.81 (t, J = 7.5 Hz, 6H, H_N).

¹³C NMR (126 MHz, CDCl₃) δ 154.5, 142.9, 137.3, 136.0, 132.4, 130.5, 130.4 (1), 129.9, 129.4, 129.2 (2), 127.3 (3), 126.6, 125.9, 125.7 (4), 123.9 (5), 123.5, 121.9 (6), 120.9 (7), 111.7, 69.7, 60.5, 57.8 (8), 57.5 (8), 25.2 (9), 25.1 (9), 21.2, 14.4, 11.5 (10), 11.4 (10).

MALDI-TOF Mass Spectrometry: Calculated (M-2H)+H⁺ for C₄₇H₃₇N₃O₄: 706.2700; detected (M-2H)+H⁺: 706.2695.

CHN Elemental Analysis: Theoretical (%) C: 79.75, H: 5.27, N: 5.94; Found (%) C: 79.69, H: 5.29, N: 5.79.



Synthesis of **Br2-F1**

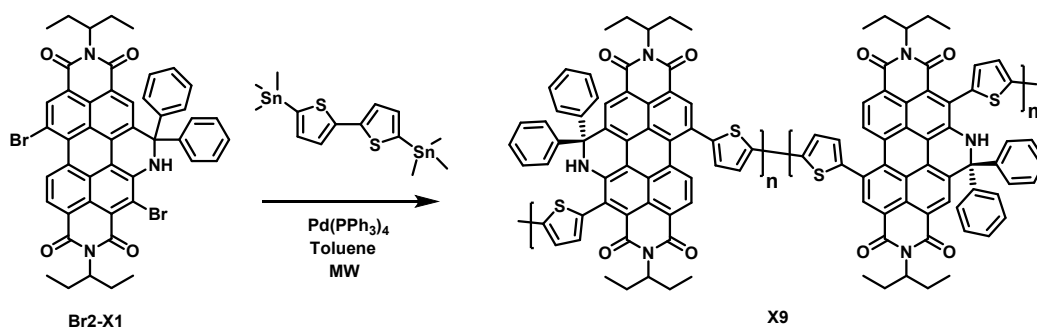
To a 20 mL pressure vial equipped with a stir bar, **F1** (194 mg, 0.274 mmol, 1.0 eq.) and 15 mL of dichloromethane (DCM) were added. To this mixture was added liquid bromine (0.3 mL, 5.482 mmol, 20 eq.). The pressure vial was capped and stirred at 40 °C for 16 hours. Then, excess bromine in the reaction mixture was fully quenched with saturated $\text{Na}_2\text{S}_2\text{O}_5$ aqueous solution. The reaction mixture was transferred into a 250 mL separatory funnel and diluted with DCM. The organic phase was washed with water twice and once with brine. The collected organic phase was dried with anhydrous Na_2SO_4 , then gravity filtered. The solvent was removed *in vacuo*. The resulting crude product was redissolved in DCM and wet loaded and subjected to silica gel column chromatography using DCM (20% hexane) as eluent. The second green-band fraction was collected, and the solvent was removed *in vacuo*. The resulting solid was slurried in methanol and subjected to vacuum filtration to obtain pure **Br2-F1** as a black solid (206 mg, 87%).

^1H NMR (500 MHz, CDCl_3) δ 9.91 (d, $J = 8.4$ Hz, 1H, H_A), 8.88 (s, 1H, H_B), 8.54 (d, $J = 8.4$ Hz, 1H, H_C), 7.80 (dt, $J = 7.6, 0.9$ Hz, 2H, H_D), 7.54 (dt, $J = 7.6, 0.9$ Hz, 2H, H_E), 7.50 (s, 1H, H_F), 7.50 – 7.47 (dt, $J = 7.6, 1.1$ Hz, 2H, H_G), 7.28 (dt, $J = 7.6, 1.1$ Hz, 2H, H_H), 6.22 (s, 1H, H_I), 5.11 – 5.02 (m, 1H, H_J), 4.89 (m, 1H, H_J), 2.24 (m, 2H, H_K), 2.09 (m, 2H, H_K), 1.95 (m, 2H, H_K), 1.81 (m, 2H, H_K), 0.93 (t, $J = 7.5$ Hz, 6H, H_L), 0.80 (t, $J = 7.4$ Hz, 6H, H_L).

^{13}C NMR (126 MHz, CDCl_3) δ 154.1, 141.1, 139.2 (1) 137.4, 134.5, 131.6, 131.5, 130.6 (2), 129.3 (3), 128.8 (4), 128.6, 128.2, 127.9, 127.1 (5), 126.1, 125.7 (6), 123.9, 121.0 (7), 119.6, 111.9, 77.4, 69.7, 58.4 (8), 57.8 (8), 25.1 (9), 25.0 (9), 11.5 (10), 11.4 (10).

MALDI-TOF Mass Spectrometry: Calculated $(\text{M}-2\text{H})+\text{H}^+$ for $\text{C}_{47}\text{H}_{35}\text{Br}_2\text{N}_3\text{O}_4$: 862.0911; detected $(\text{M}-2\text{H})+\text{H}^+$: 862.0938.

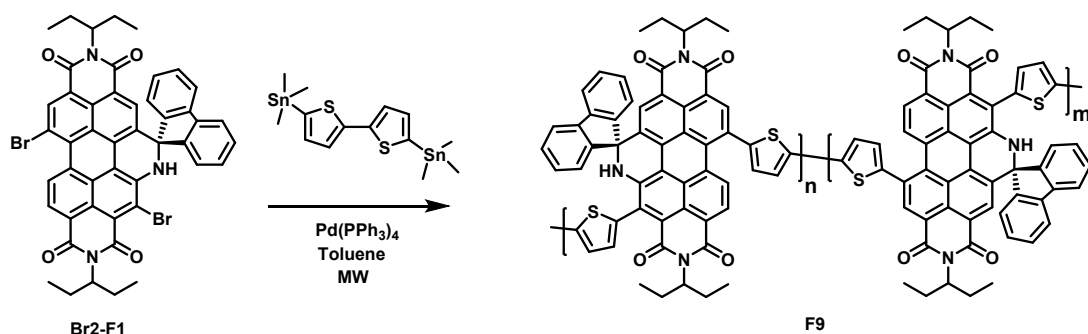
CHN Elemental Analysis: Theoretical (%) C: 65.22, H: 4.08, N: 4.85; Found (%) C: 65.51, H: 4.10, N: 4.70.



Synthesis of **X9** (Microwave Assisted)

In a 0.2-0.5 mL microwave vial equipped with a stir-bar, **Br2-X1** (102 mg, 0.12 mmol, 1.0 eq.) was added. Under a nitrogen atmosphere, 2,5-bis(trimethylstannyl)thiophene (57.8 mg, 0.12 mmol, 1.0 eq.) and Pd(PPh₃)₄ (2.9 mg, 0.002 mmol, 0.02 eq.) were added, then sealed with a Teflon[®] cap. Then, dry toluene (3 mL) was added with a syringe under nitrogen. The polymerization reaction mixture was subjected to multistep heating condition at 80 °C (10 minutes), 110 °C (10 minutes), 140 °C (3 hours), and at 150 °C (1 hour) in a microwave reactor. After the reaction mixture was cooled down, the polymer was end-capped by adding 2-tributylstannylthiophene (0.060 mmol) *via* syringe, and the mixture was further subjected to microwave reaction at 80 °C (5 minutes), 110 °C (5 minutes), and at 140 °C (15 minutes). The reaction mixture was again cooled down, then 2-bromothiophene (0.120 mmol) was added *via* syringe, and was subjected to microwave reaction at 80 °C (5 minutes), 110 °C (5 minutes), and at 140 °C (15 minutes). After the reaction, the reaction mixture was precipitated out by pouring into the methanol. The resulting precipitate was subjected to Soxhlet extraction for purification using methanol, acetone, hexane, and chloroform, sequentially. The extracted **X9** solution in chloroform was reduced in volume upto ~ 5 mL *in vacuo*. which was precipitated into methanol. The resulting precipitate was subjected to vacuum filtration to obtain **X9** as a black solid (87.6 mg, 83%). $M_n = 21.4$ kDa; $M_w = 62.3$ kDa; PDI = 2.92

¹H NMR (500 MHz, CDCl₃) δ 8.69 - 8.66 (m, 1H, H_A), 8.44 - 8.42 (m, 1H, H_B), 8.21 - 8.19 (m, 1H, H_C), 7.98 (s, 1H, H_D), 7.38 - 7.35 (m, 6H, H_E), 7.33 - 7.32 (m, 2H, H_F), 7.31 - 7.30 (m, 1H, H_G), 7.23 - 7.22 (m, 4H, H_H), 6.99 - 6.96 (m, 1H, H_I), 5.92 - 5.89 (m, 1H, H_J), 5.02 - 4.89 (m, 2H, H_K), 2.21 - 1.82 (m, 8H, H_L), 0.92 - 0.85 (m, 12H, H_M).



Synthesis of **F9** (Microwave Assisted)

In a 0.2-0.5 mL microwave vial equipped with a stir-bar, **Br2-F1** (104 mg, 0.120 mmol, 1.0 eq.) was added. Under a nitrogen atmosphere, 2,5-bis(trimethylstannyl)thiophene (59.1 mg, 0.120 mmol, 1.0 eq.) and Pd(PPh₃)₄ (2.8 mg, 0.002 mmol, 0.02 eq.) were added, then sealed with a Teflon[®] cap. Then, dry toluene (3 mL) was added with a syringe under nitrogen. The polymerization reaction mixture was subjected to multistep heating condition at 80 °C (10 minutes), 110 °C (10 minutes), 140 °C (3 hours), and at 150 °C (1 hour) in a microwave reactor. After the reaction mixture was cooled down, the polymer was end-capped by adding 2-tributylstannylthiophene (0.060 mmol) *via* syringe, and the mixture was further subjected to microwave reaction at 80 °C (5 minutes), 110 °C (5 minutes), and at 140 °C (15 minutes). The reaction mixture was again cooled down, then 2-bromothiophene (0.120 mmol) was added *via* syringe, and was subjected to microwave reaction at 80 °C (5 minutes), 110 °C (5 minutes), and at 140 °C (15 minutes). After the reaction, the reaction mixture was precipitated out by pouring into the methanol. The resulting precipitate was subjected to Soxhlet extraction for purification using methanol, acetone, hexane, and chloroform, sequentially. The extracted **F9** solution in chloroform was reduced in volume upto ~ 5 mL *in vacuo*. which was precipitated into methanol. The resulting precipitate was subjected to vacuum filtration to obtain **F9** as a green solid (98.7 mg, 91%). $M_n = 29.7$ kDa; $M_w = 122.6$ kDa; PDI = 4.59

¹H NMR (500 MHz, CDCl₃) δ 8.63, 8.52 (s, 1H, H_A), 8.46 - 8.33 (m, 1H, H_B), 8.24 - 8.10 (m, 1H, H_C), 7.79-7.74 (m, 2H, H_D), 7.67 - 7.56 (m, 2H, H_E), 7.49 - 7.40 (ov, 2H, H_F and H_G), 7.33 - 7.18 (ov, 4H, H_H and H_I), 7.13 - 6.99 (m, 1H, H_J), 6.80 - 6.65 (m, 1H, H_I), 5.27 - 4.48 (m, 8H, H_L), 0.95 - 0.78 (m, 12H, H_M).

3. ^1H NMR Spectroscopy

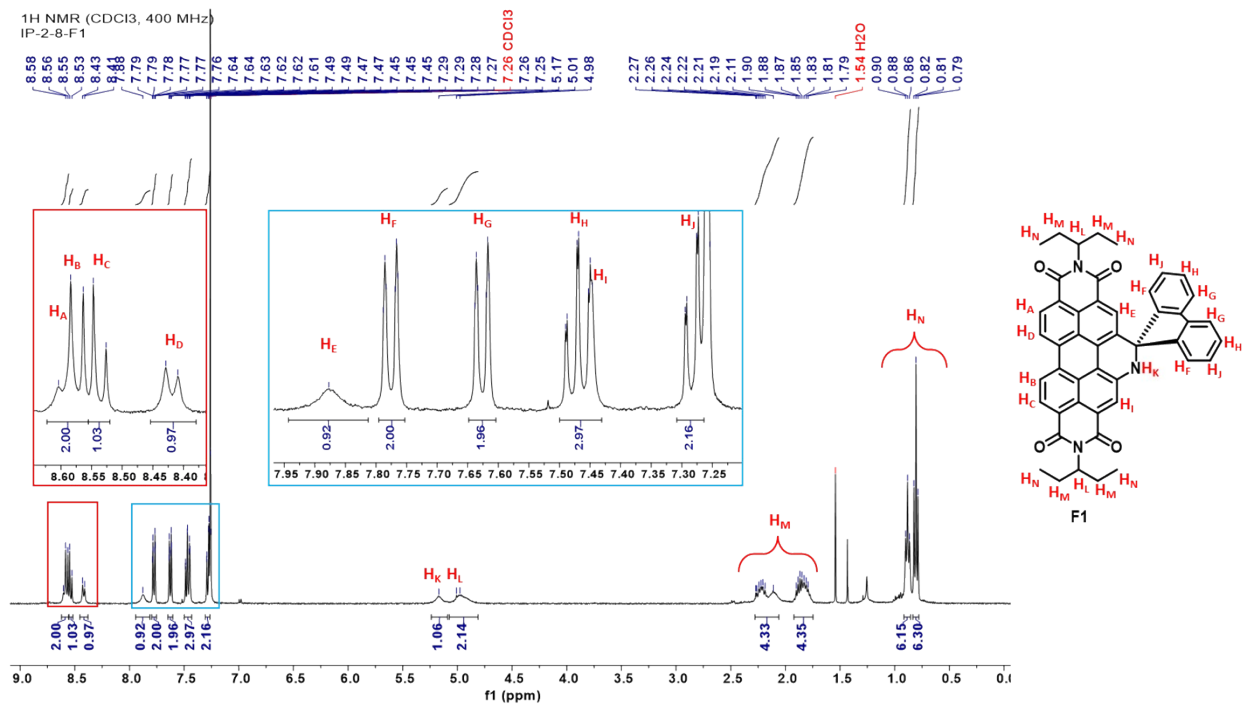


Figure S1. ^1H NMR spectrum of F1 (400 MHz, CDCl₃)

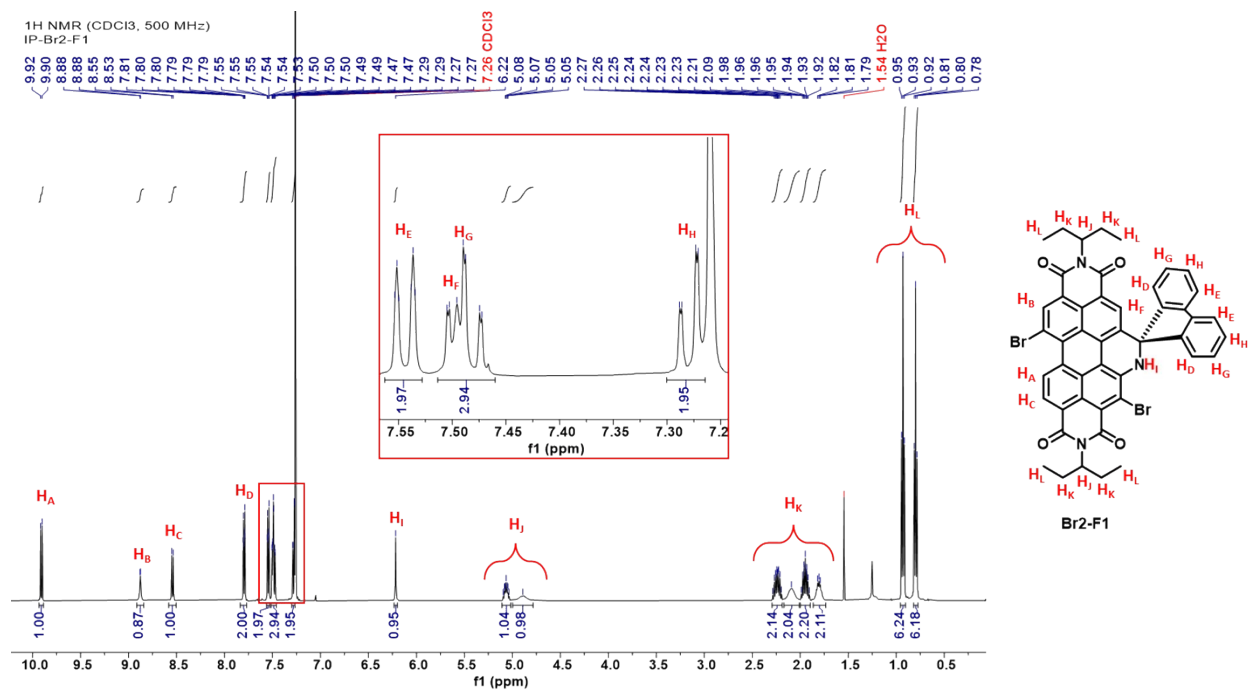


Figure S2. ¹H NMR spectrum of Br2-F1 (500 MHz, CDCl₃).

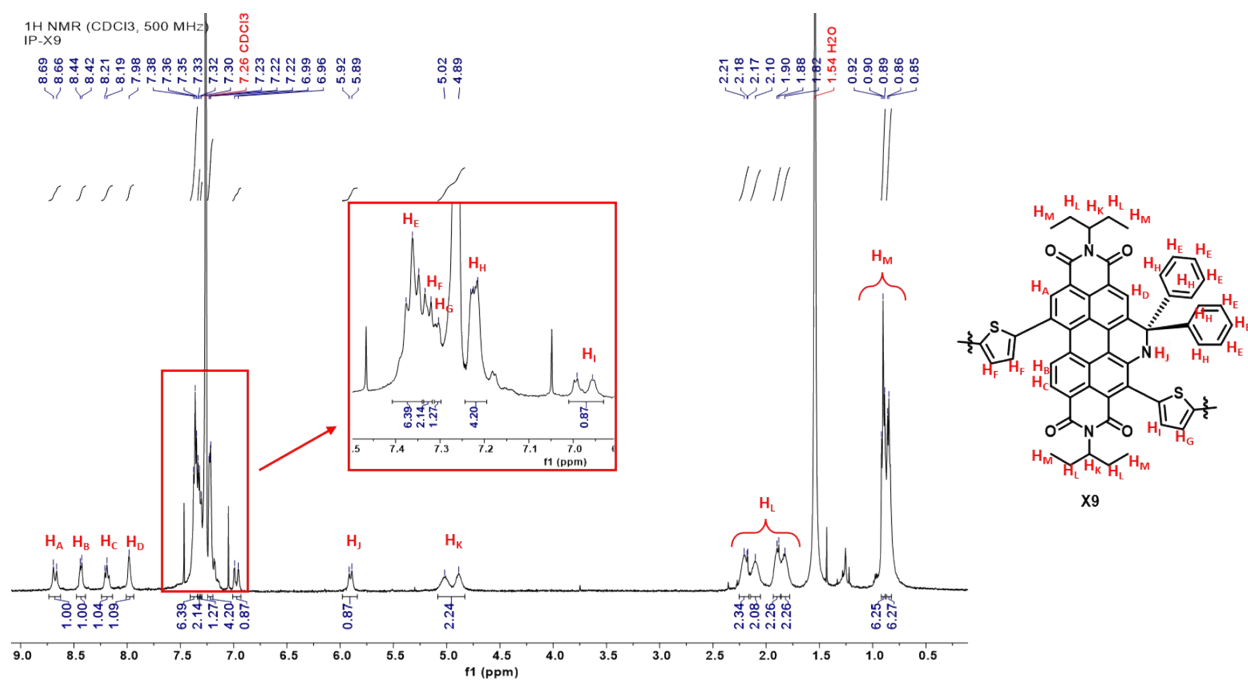


Figure S3. ¹H NMR spectrum of X9 (500 MHz, CDCl₃).

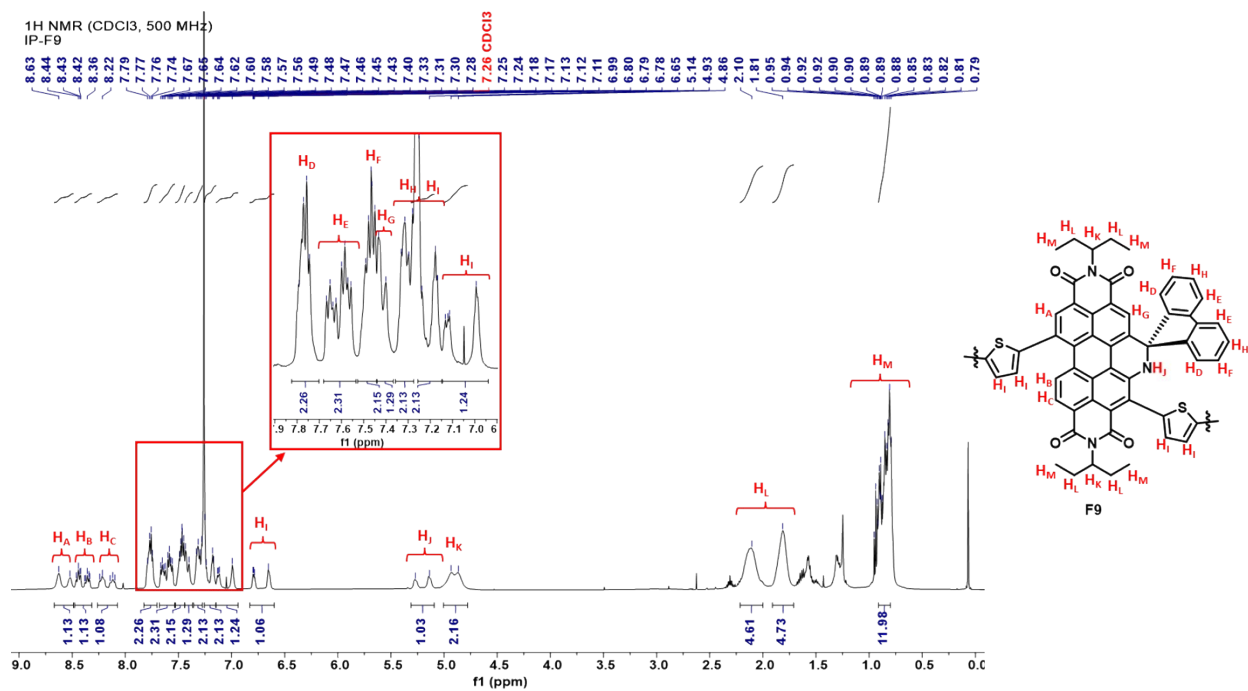


Figure S4. ¹H NMR spectrum of F9 in (500 MHz, CDCl₃).

4. ^{13}C NMR Spectroscopy

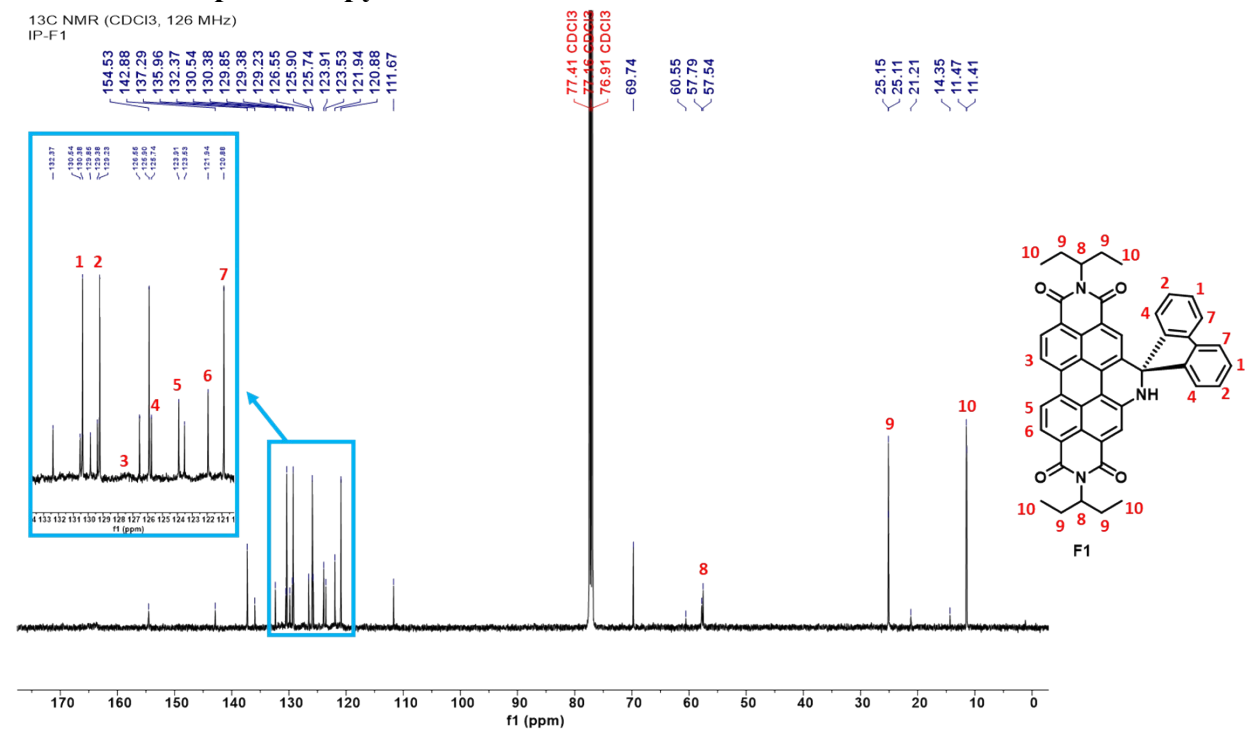


Figure S5. ^{13}C NMR spectrum of **F1** (126 MHz, CDCl₃)

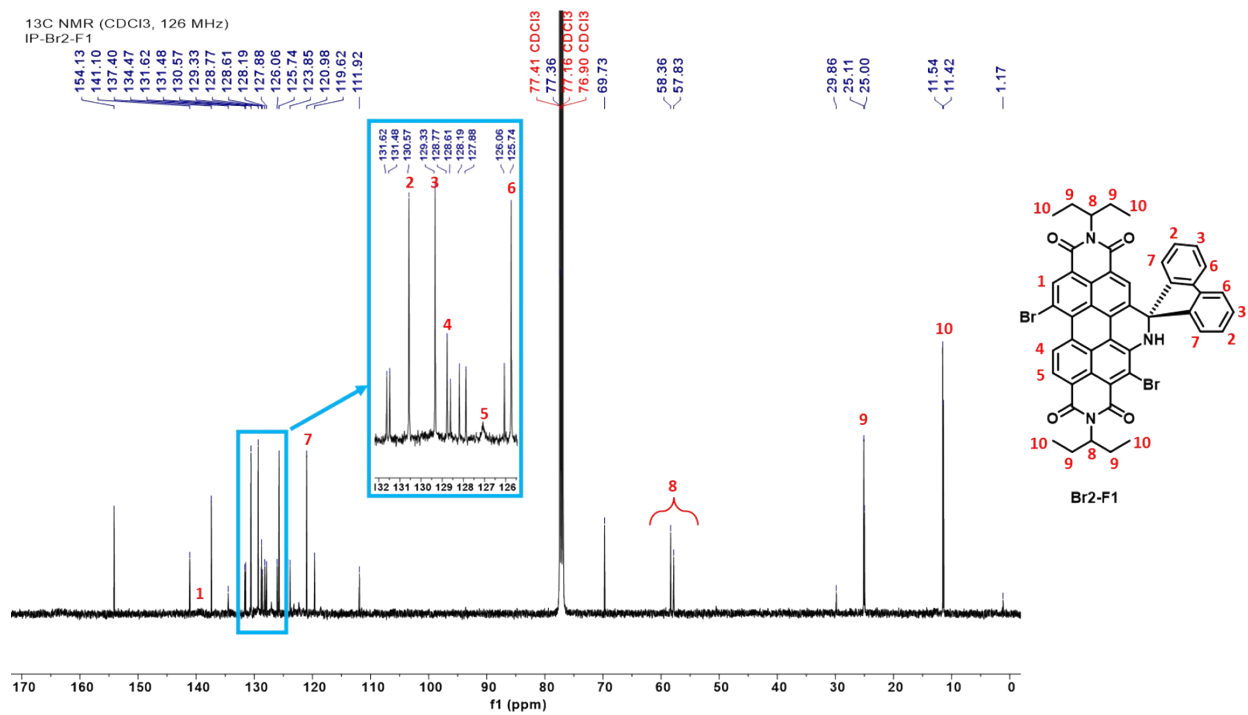


Figure S6. ¹³C NMR spectrum of **Br2-F1** (126 MHz, CDCl₃)

5. 2D NMR Spectroscopy

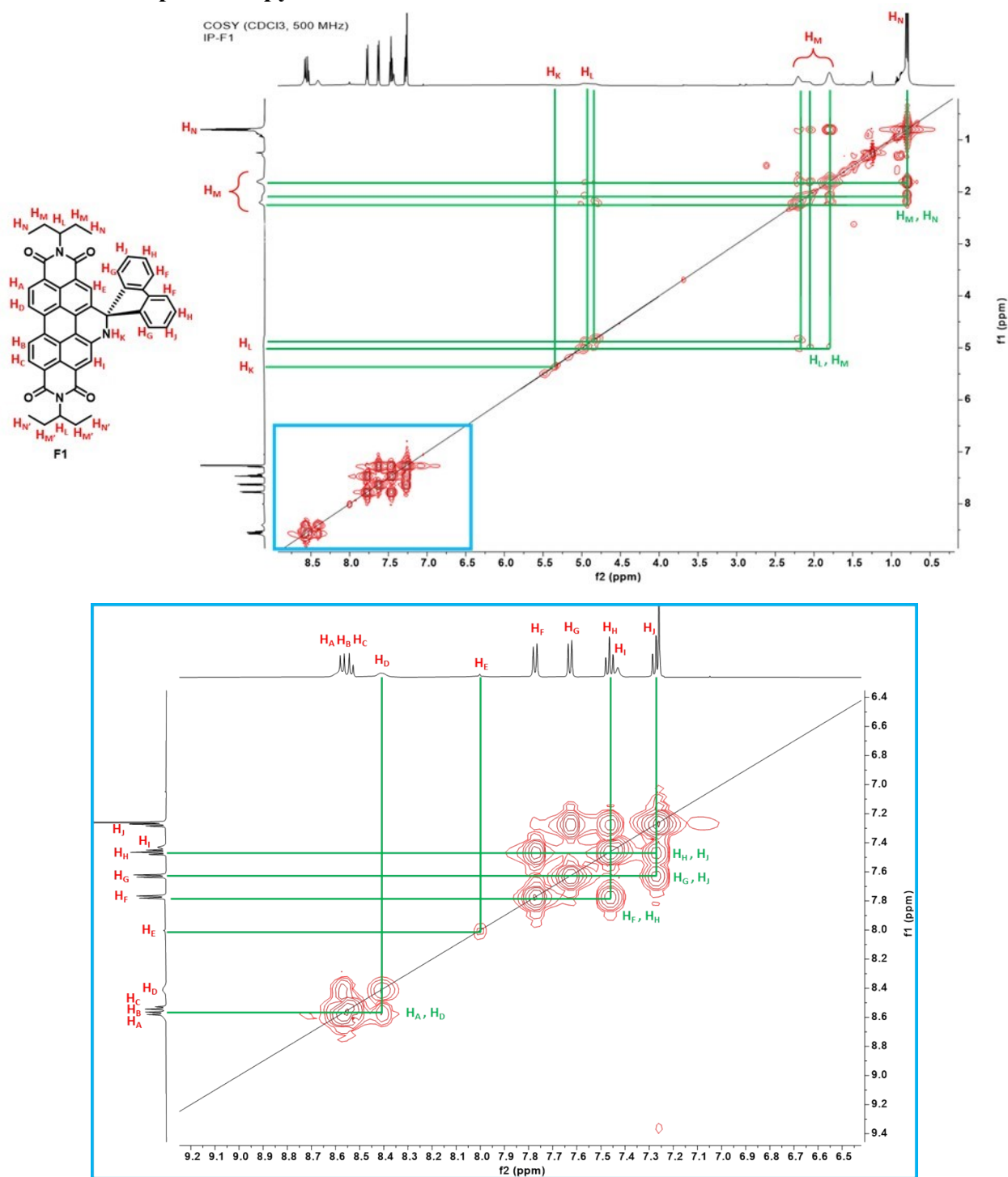


Figure S7. ¹H-¹H correlation spectroscopy (COSY) spectrum of **F1** (500 MHz, CDCl₃).

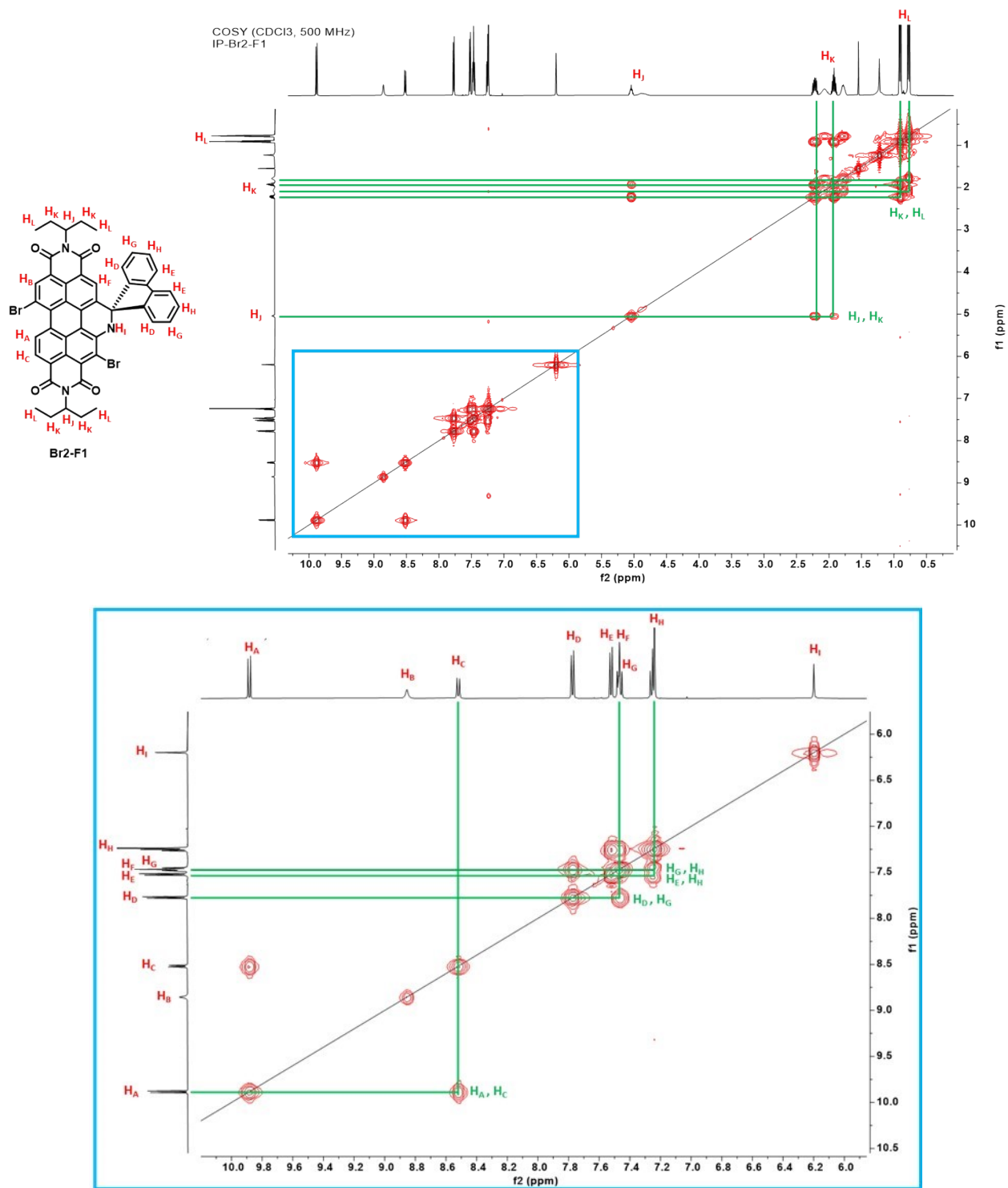


Figure S8. ¹H-¹H correlation spectroscopy (COSY) spectrum of **Br2-F1** (500 MHz, CDCl₃).

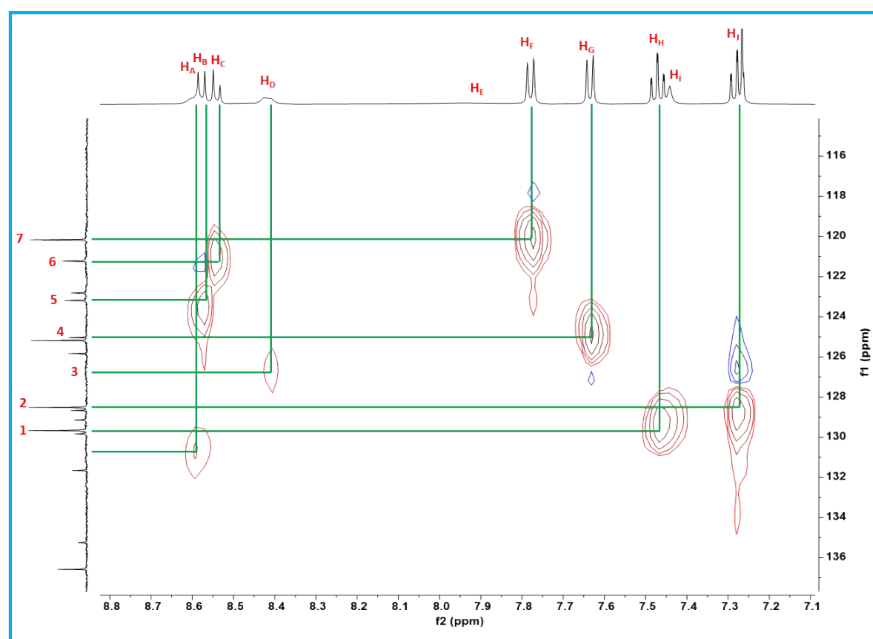
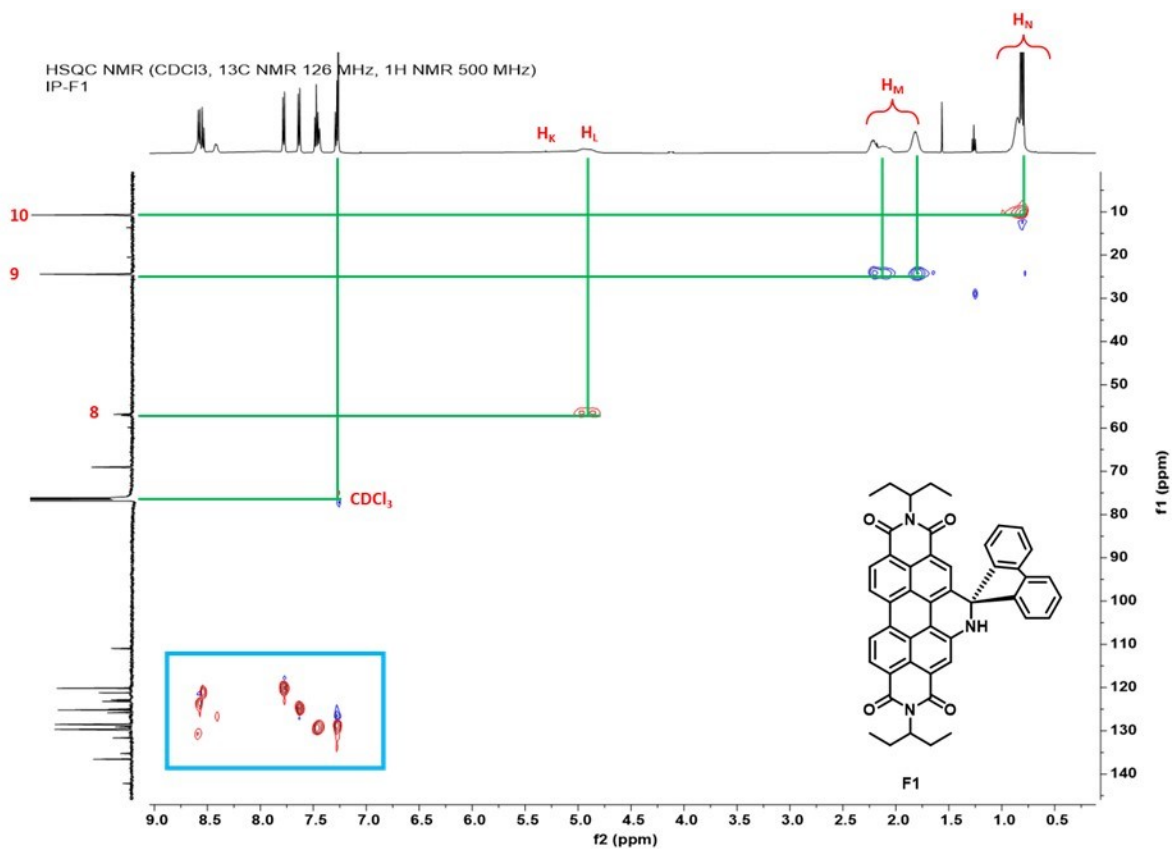


Figure S9. ¹³C-¹H heteronuclear single quantum coherence (HSQC) spectrum of **F1** (500 MHz, CDCl₃).

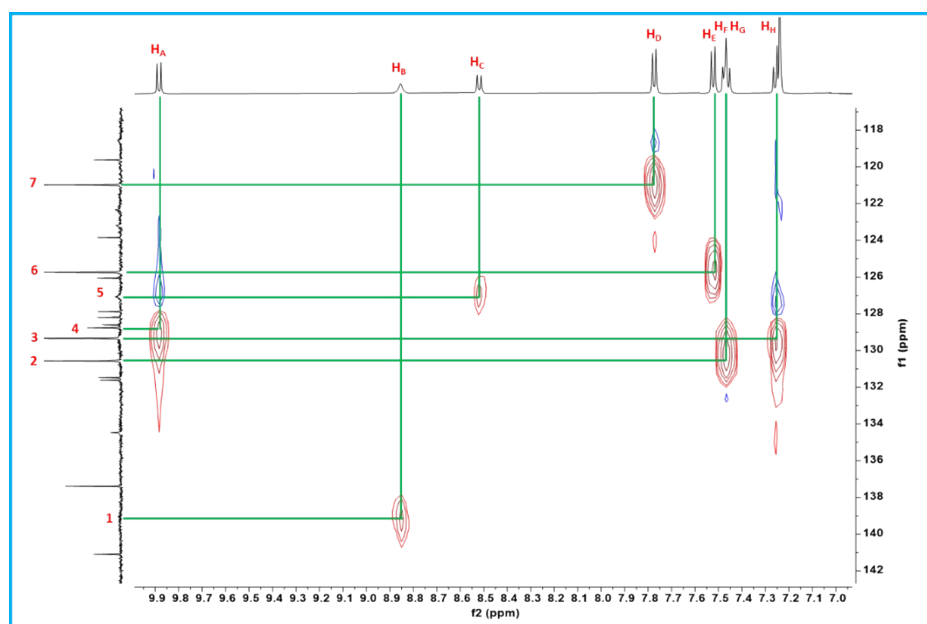
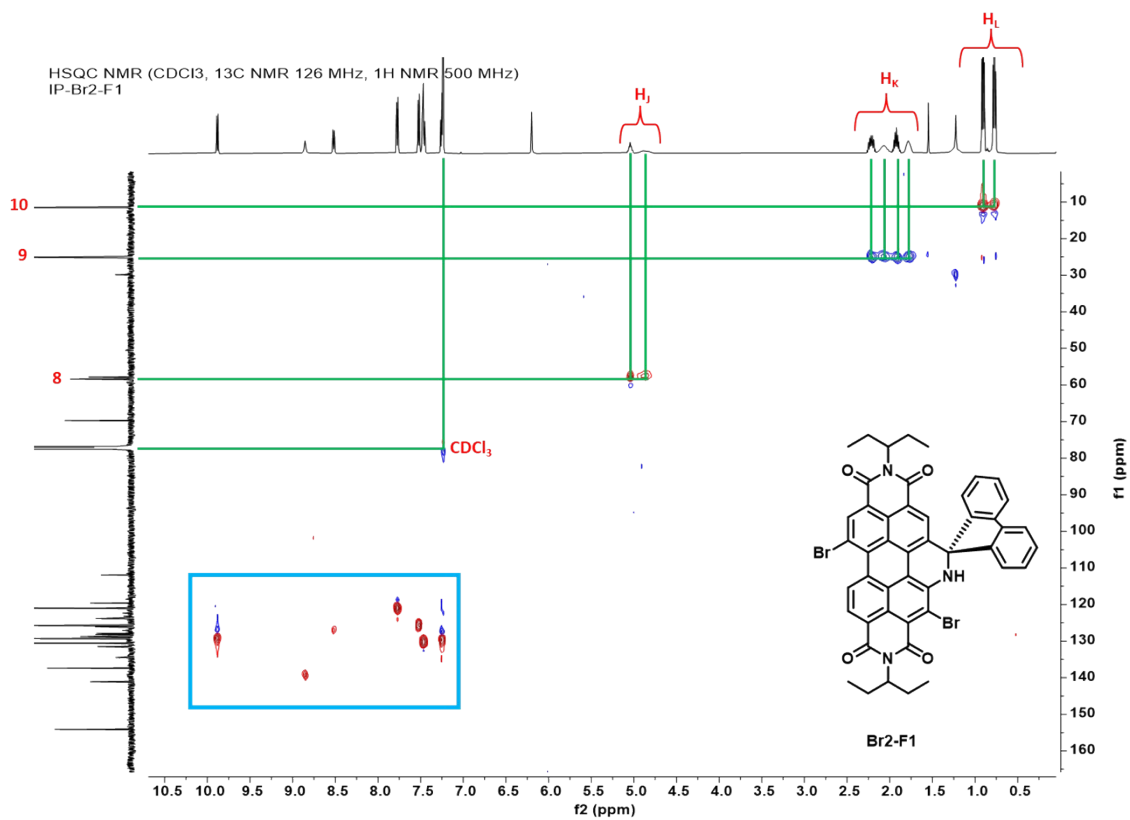


Figure S10. ¹³C-¹H heteronuclear single quantum coherence (HSQC) spectrum of **Br2-F1** (500 MHz, CDCl₃).

6. MALDI-TOF Mass Spectrometry

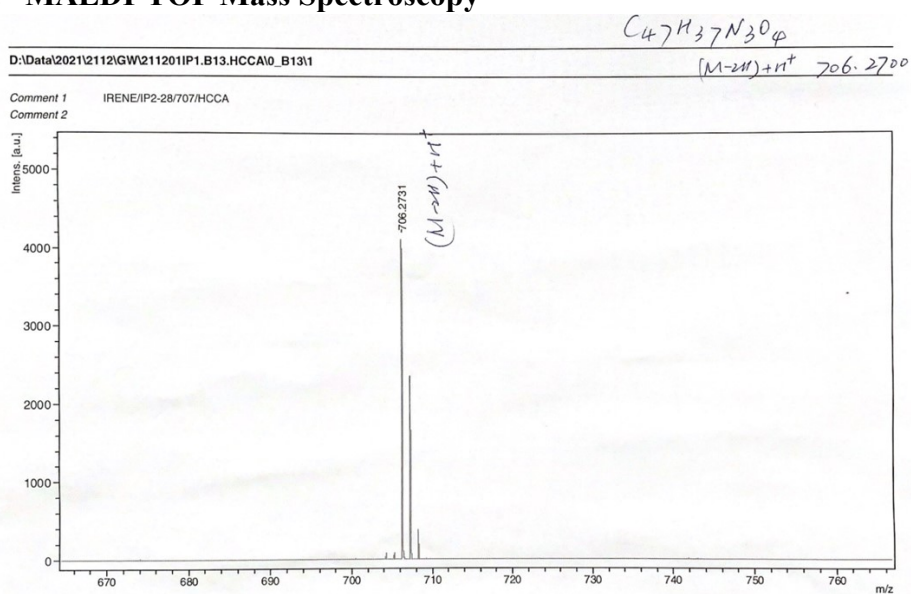
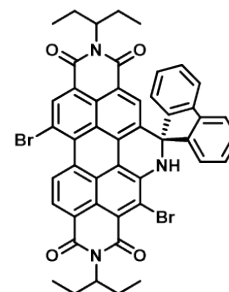
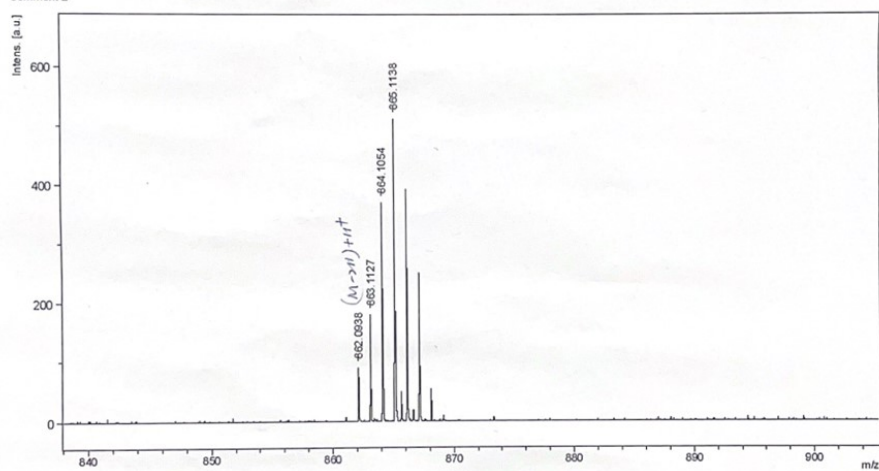


Figure S11. MALDI mass spectrometry of **F1**: Calculated $(M-2H)+H^+$ for $C_{47}H_{37}N_3O_4$: 706.2700; detected $(M-2H)+H^+$: 706.2695.

$C_{47}H_{35}Br_2N_3O_4$
 $(M-2H)^+H^+$ 862.0911

D:\Data\2023\2301\GW230123\IP1.H12.HCCA10_H1211

Comment 1 IRENE/IP316/665/HCCA
Comment 2



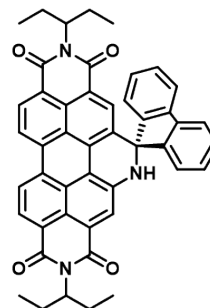
Br₂-F1

Chemical Formula: $C_{47}H_{35}Br_2N_3O_4$
Exact Mass: 863.10

Figure S12. MALDI mass spectrometry of **Br₂-F1**: Calculated $(M-2H)^+H^+$ for $C_{47}H_{35}Br_2N_3O_4$: 862.0911; detected $(M-2H)^+H^+$: 862.0938.

7. Elemental Analysis

University of Calgary			
Department of Chemistry EA		Date:	6-1-2022
Name:	IRENE	Group:	GW
Sample:	IP271-2	Weight (mg):	2.139
%C (Actual):	79.69	%C (Theoretical):	79.75
%H (Actual):	5.29	%H (Theoretical):	5.27
%N (Actual):	5.79	%N (Theoretical):	5.94
%S (Actual):	0.07	%S (Theoretical):	



F1

Chemical Formula: $C_{47}H_{37}N_3O_4$

Exact Mass: 707.28

Elemental Analysis: C, 79.75; H, 5.27; N, 5.94; O, 9.04

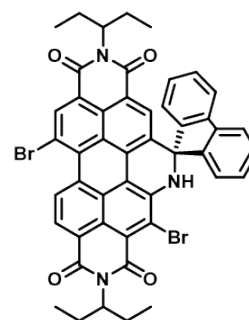
Figure S13. CHN elemental analysis **F1**. Theoretical (%) C: 79.75, H: 5.27, N: 5.94; Found (%) C: 79.69, H: 5.29, N: 5.79.

University of Calgary

Department of Chemistry EA

Date: 1-25-2023

Name:	IRENE	Group:	GW
Sample:	IP316-2	Weight (mg):	1.566
%C (Actual):	65.51	%C (Theoretical):	65.22
%H (Actual):	4.10	%H (Theoretical):	4.08
%N (Actual):	4.70	%N (Theoretical):	4.85
%S (Actual):	0.00	%S (Theoretical):	



Br₂-F1

Chemical Formula: C₄₇H₃₅Br₂N₃O₄

Exact Mass: 863.10

Elemental Analysis: C, 65.22; H, 4.08; Br, 18.46; N, 4.85; O, 7.39

Figure S14. CHN elemental analysis **Br₂-F1**. Theoretical (%) C: 65.22, H: 4.08, N: 4.85; Found (%) C: 65.51, H: 4.10, N: 4.70.

8. Size-Exclusion Chromatography

Chromatogram report

Header

Title		Data acquisition date and time	2023-06-20 09:41:23
Sample name	X9	Calculation date and time	2023-06-20 10:34:50
Database name	Catherine	Acquisition time [min]	0.000 - 25.000
Data name	RSLT0001	Sampling interval [ms]	100
Method name	TCB_JUIN_2023	Cup number	1
Channel	RI	Calculation type	Molecular Mass

[mV]

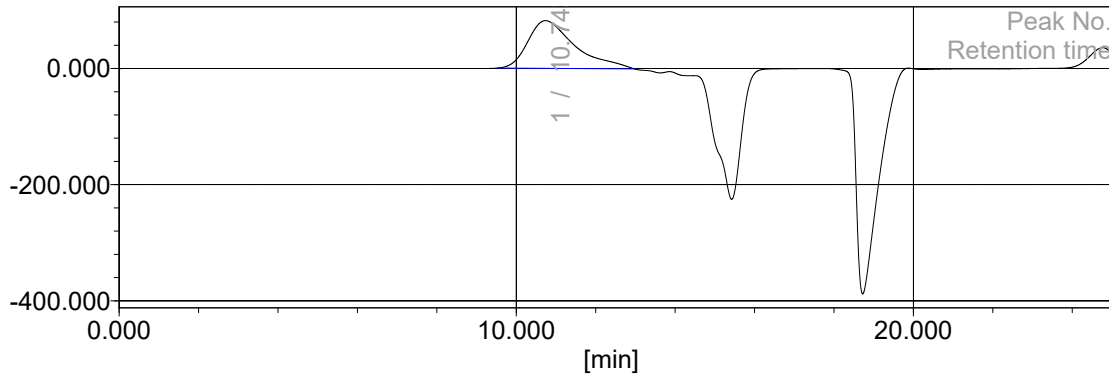


Figure S15. GPC traces of X9

Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	9.523	0.703	600,467	Mn	21,383
Peak top	10.743	82.439	63,635	Mw	62,339
Peak end	12.975	-0.704	964	Mz	111,297
				Mz+1	168,964
				Mv	62,339
Height [mV]			82.233	Mp	61,695
Area [mV*s]			6749.374	Mz/Mw	1.785
Area% [%]			100.000	Mw/Mn	2.915
[eta]			62338.66405	Mz+1/Mw	2.710

Molecular mass calculation result (RI)

Total

	[min]	[mV]	[mol]		
Peak start	9.523	0.703	600,467	Mn	21,383
Peak top	10.743	82.439	63,635	Mw	62,339
Peak end	12.975	-0.704	964	Mz	111,297
				Mz+1	168,964
				Mv	62,339
Height [mV]			82.233	Mp	61,695
Area [mV*s]			6749.374	Mz/Mw	1.785
Area% [%]			100.000	Mw/Mn	2.915
[eta]			62338.66405	Mz+1/Mw	2.710

Chromatogram report

Header

Title		Data acquisition date and time	2023-06-20 10:06:25
Sample name	F9	Calculation date and time	2023-06-20 10:28:23
Database name	Catherine	Acquisition time [min]	0.000 - 25.000
Data name	RSLT0002	Sampling interval [ms]	100
Method name	TCB_JUIN_2023	Cup number	2
Channel	RI	Calculation type	Molecular Mass

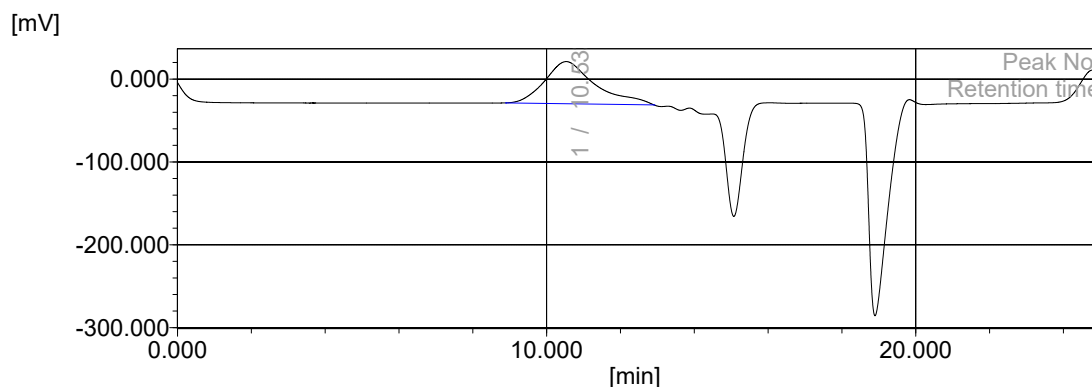


Figure S16. GPC traces of F9

Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.890	-28.692	3,239,906	Mn	26,734
Peak top	10.533	21.159	88,609	Mw	122,634
Peak end	12.908	-31.145	1,156	Mz	365,031
				Mz+1	816,935
				Mv	122,634
Height [mV]			50.854	Mp	82,453
Area [mV*s]			4830.308	Mz/Mw	2.977
Area% [%]			100.000	Mw/Mn	4.587
[eta]			122633.70073	Mz+1/Mw	6.662

Molecular mass calculation result (RI)

Total

	[min]	[mV]	[mol]		
Peak start	8.890	-28.692	3,239,906	Mn	26,734
Peak top	10.533	21.159	88,609	Mw	122,634
Peak end	12.908	-31.145	1,156	Mz	365,031
				Mz+1	816,935
				Mv	122,634
Height [mV]			50.854	Mp	82,453
Area [mV*s]			4830.308	Mz/Mw	2.977
Area% [%]			100.000	Mw/Mn	4.587
[eta]			122633.70073	Mz+1/Mw	6.662

9. Single Crystal X-Ray Diffraction

Table S1. Crystal data and structure refinement for **F1**. CCDC #2284202

Identification code	F1
Empirical formula	C ₄₈ H ₃₈ Cl ₃ N ₃ O ₄
Formula weight	827.16
Temperature/K	173.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	12.1058(3)
b/Å	17.1587(4)
c/Å	20.0948(5)
α/°	90
β/°	106.5645(11)
γ/°	90
Volume/Å ³	4000.86(17)
Z	4
ρ _{calc} /cm ³	1.373
μ/mm ⁻¹	2.479
F(000)	1720.0
Crystal size/mm ³	0.466 × 0.168 × 0.134
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.9 to 136.796
Index ranges	-13 ≤ h ≤ 14, -19 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	33525
Independent reflections	7181 [R _{int} = 0.0295, R _{sigma} = 0.0235]
Data/restraints/parameters	7181/138/564
Goodness-of-fit on F ²	1.035
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0541, wR ₂ = 0.1513
Final R indexes [all data]	R ₁ = 0.0628, wR ₂ = 0.1621
Largest diff. peak/hole / e Å ⁻³	0.72/-0.56

10. Electrochemical Analysis

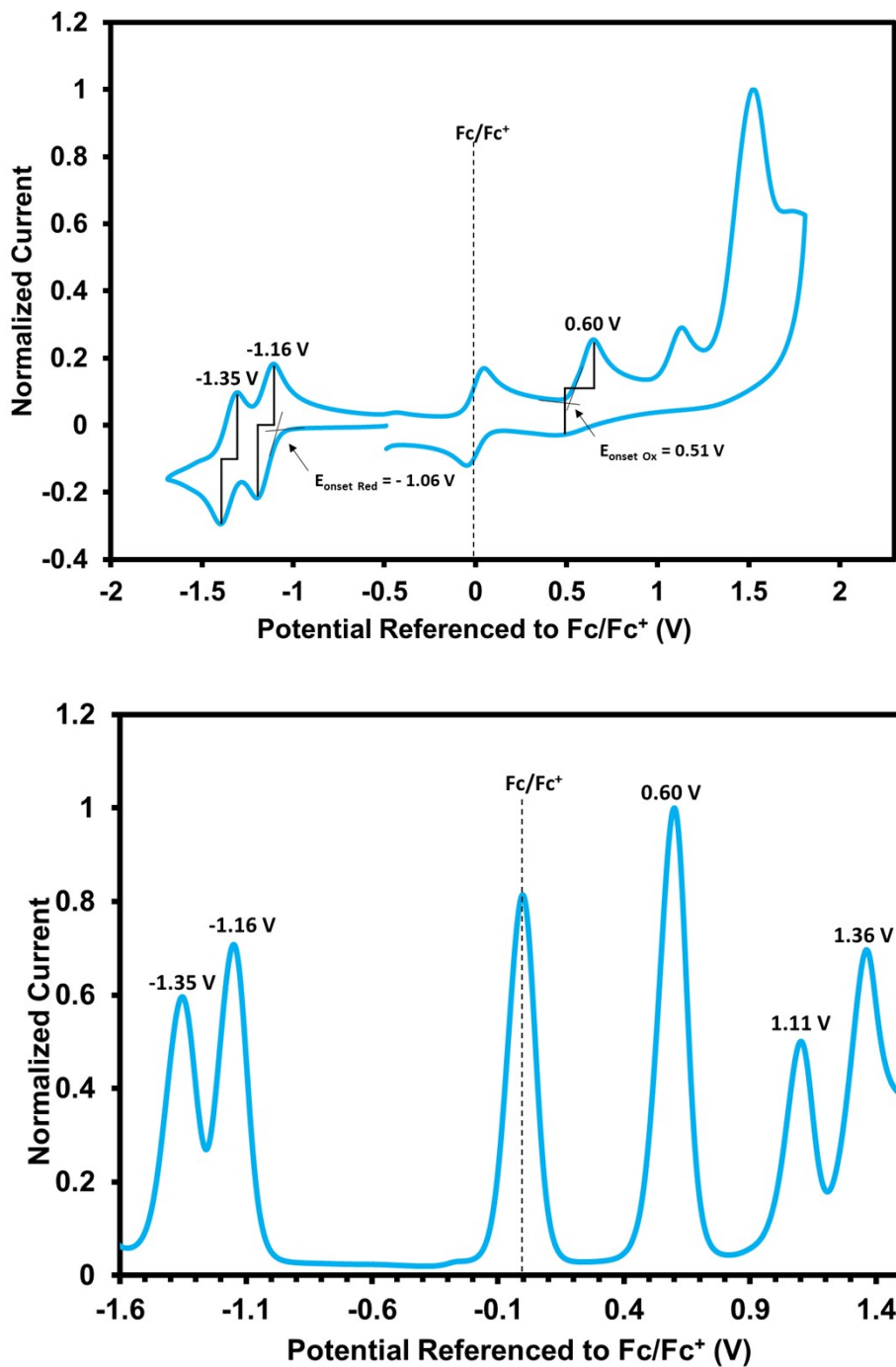


Figure S17. (Top) Cyclic Voltammogram of **F1** (Bottom) Differential pulse voltammogram of **F1**. Measured in CH₂Cl₂, recorded at 100 mV/s. Fc/Fc⁺ couple shown (Fc: ferrocene).

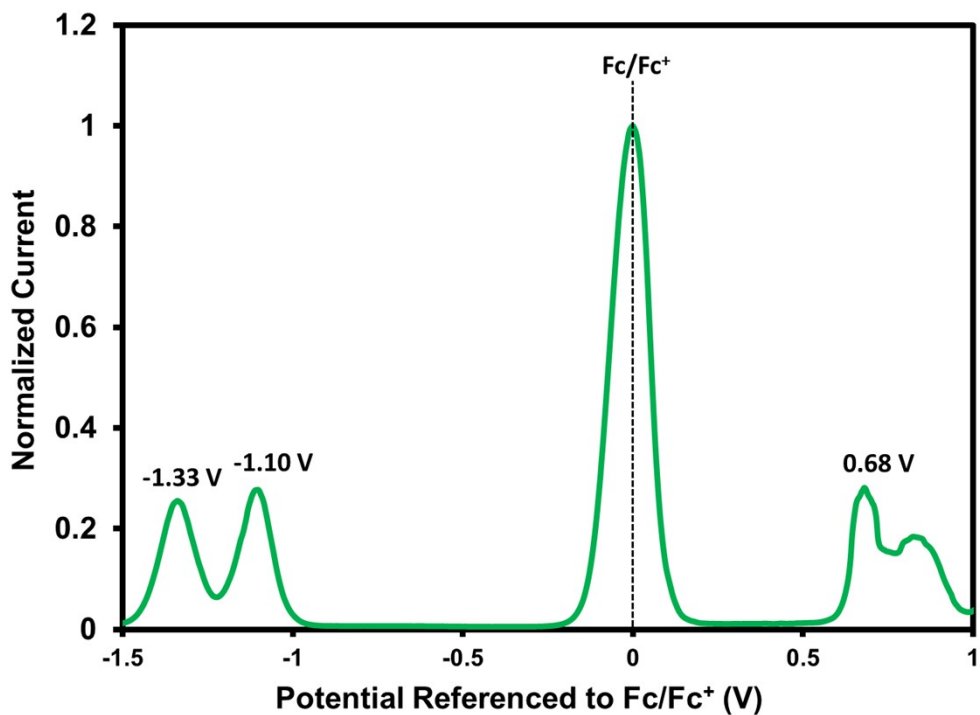
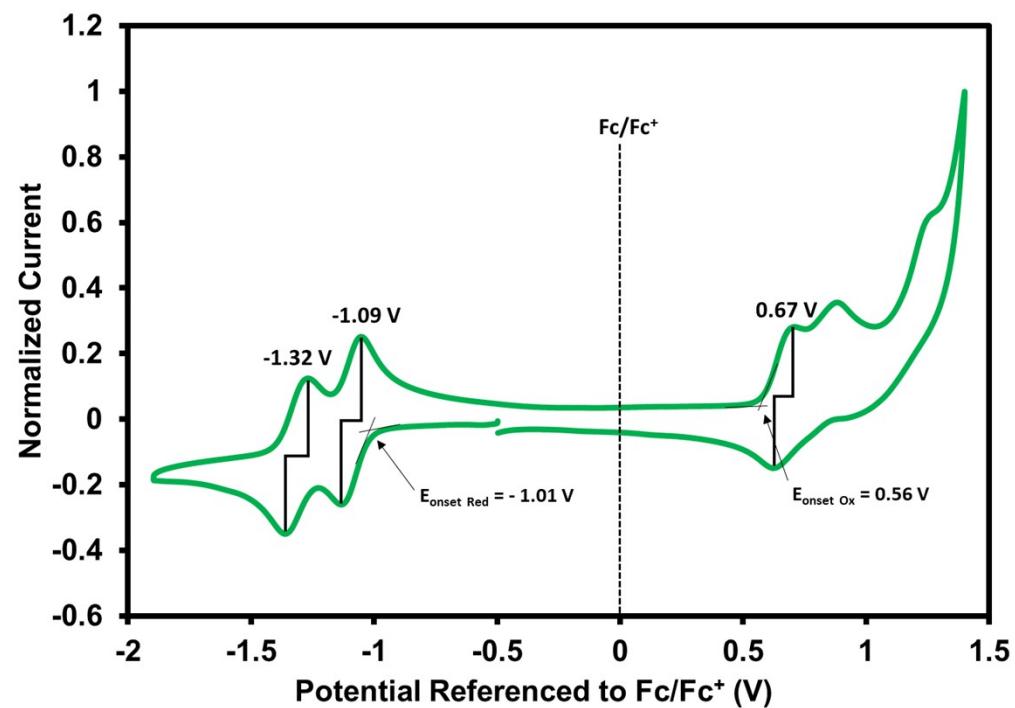


Figure S18. (Top) Cyclic Voltammogram of **X9** (Bottom) Differential pulse voltammogram of **X9**. Measured in CH₂Cl₂, recorded at 100 mV/s. Fc/Fc⁺ couple shown (Fc: ferrocene).

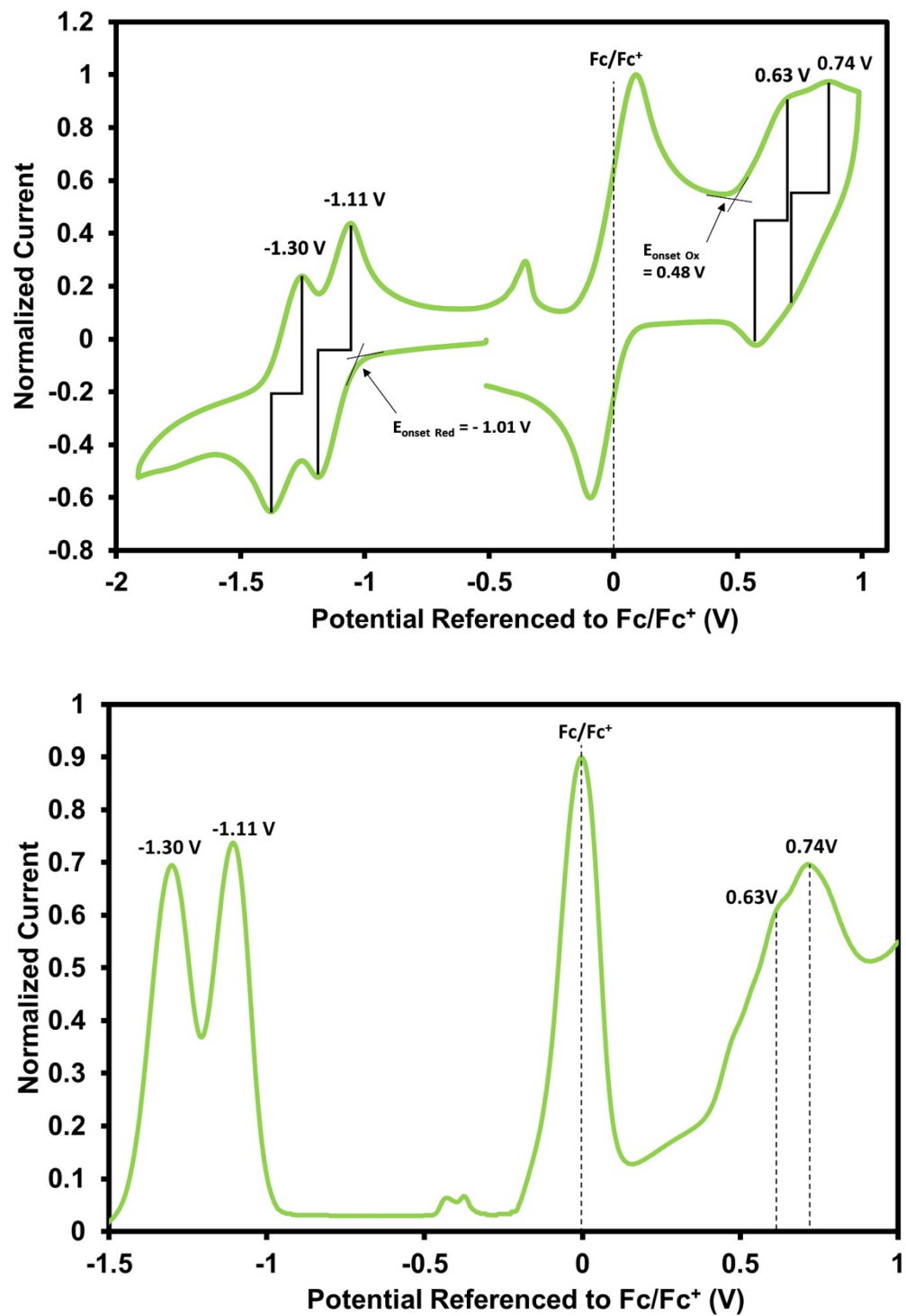


Figure S19. (Top) Cyclic Voltammogram of **F9** (Bottom) Differential pulse voltammogram of **F9**. Measured in CH₂Cl₂, recorded at 100 mV/s. Fc/Fc⁺ couple shown (Fc: ferrocene).

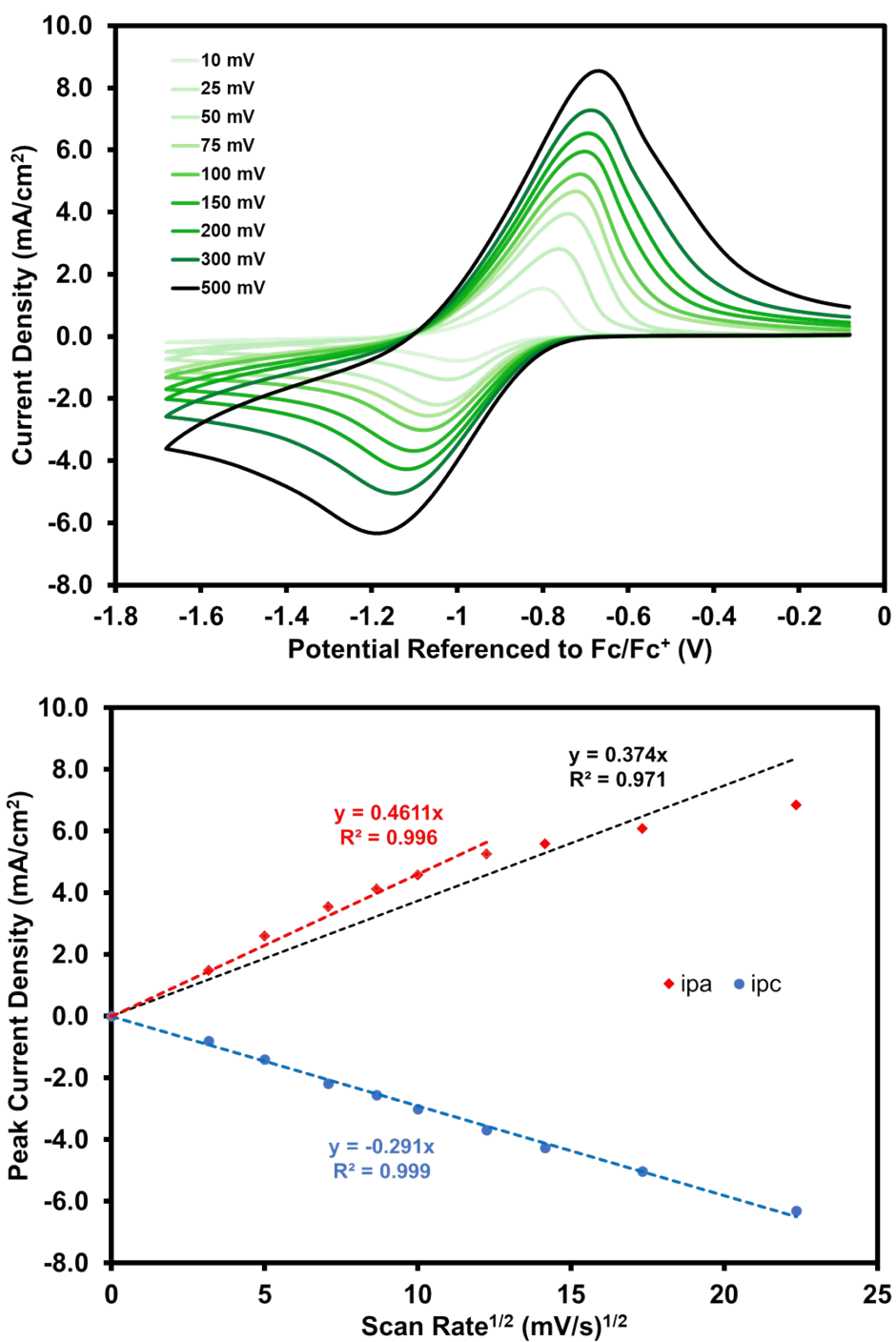


Figure S20. (Top) Cyclic voltammogram of electrochemically conditioned (10 initial cycles at 50 mV s⁻¹) X9 film at different scan rates of 10, 25, 50, 75, 100, 150, 200, 300 and 500 mV s⁻¹. The film CV measurement was done in the supporting electrolyte (0.1 M LiClO₄ in ACN), referenced to the Fc/Fc⁺ couple (Fc: ferrocene). (Bottom) Peak current density as a function of square root of scan rates.

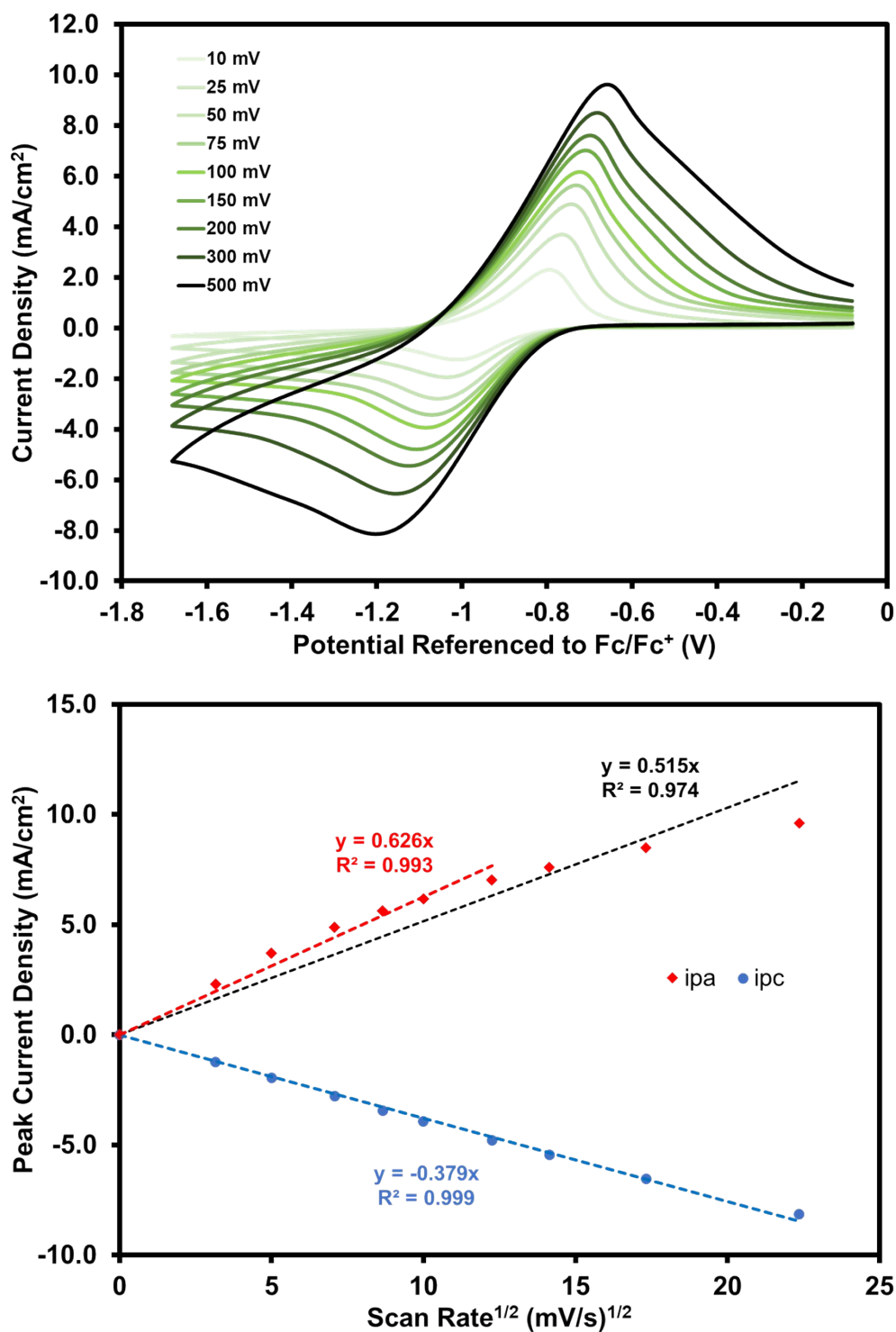


Figure S21. (Top) Cyclic voltammogram of electrochemically conditioned (10 initial cycles at 50 mV s⁻¹) F9 film at different scan rates of 10, 25, 50, 75, 100, 150, 200, 300 and 500 mV s⁻¹. The film CV measurement was done in the supporting electrolyte (0.1 M LiClO₄ in ACN), referenced to the Fc/Fc⁺ couple (Fc: ferrocene). (Bottom) Peak current density as a function of square root of scan rates.

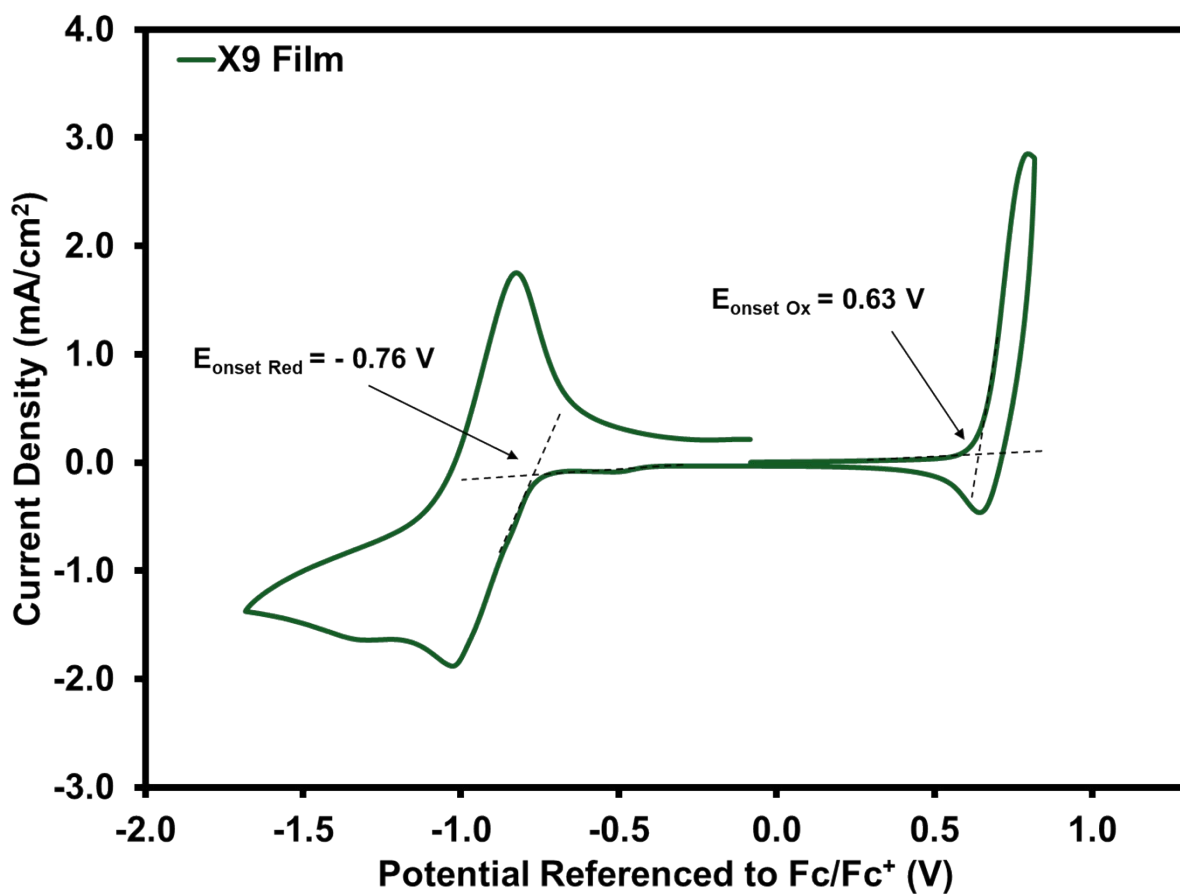


Figure S22. Cyclic voltammogram of a full redox cycle of X9 film (not electrochemically conditioned). The film CV measurement was done in the supporting electrolyte (0.1 M LiClO₄ in ACN), referenced to the Fc/Fc⁺ couple (Fc: ferrocene), at a scan rate of 50 mV s⁻¹. The reduction onset and oxidation onsets are -0.76 V and 0.63 V, respectively.

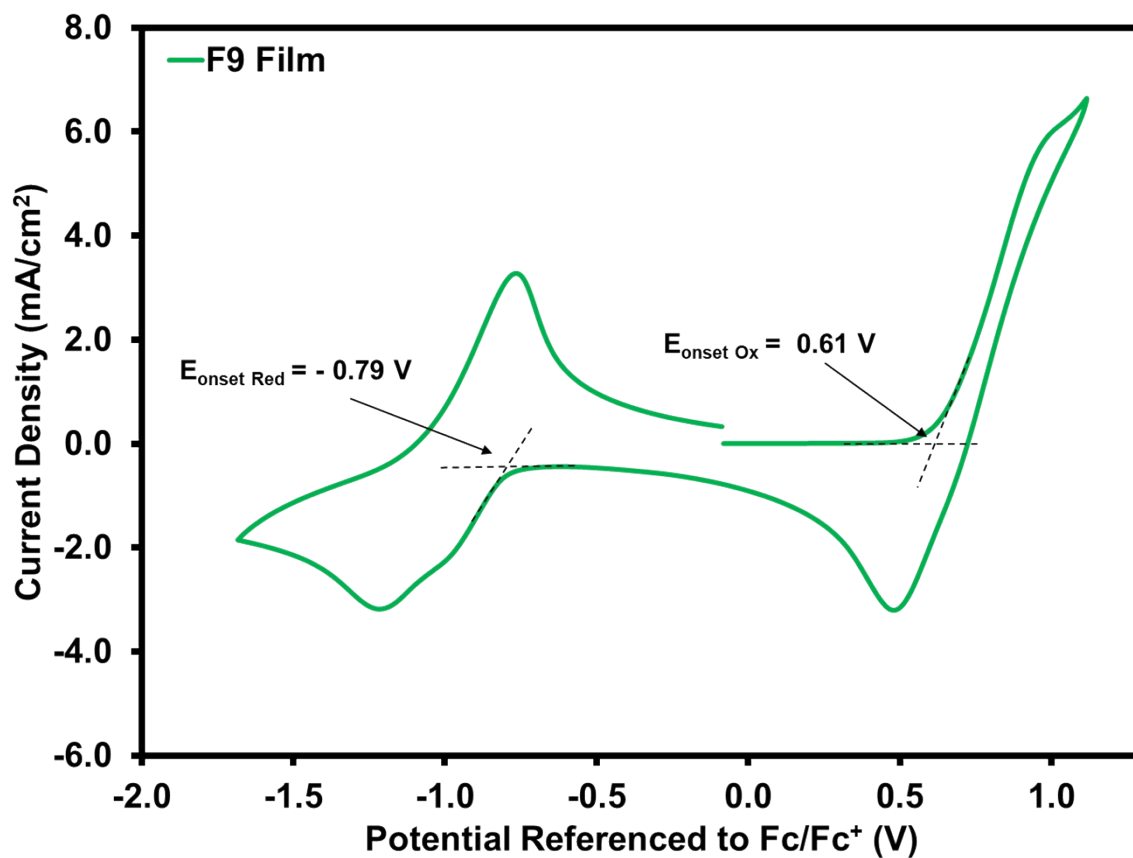


Figure S23. Cyclic voltammogram of a full redox cycle of **F9** film (not electrochemically conditioned). The film CV measurement was done in the supporting electrolyte (0.1 M LiClO₄ in ACN), referenced to the Fc/Fc⁺ couple (Fc: ferrocene), at a scan rate of 50 mV s⁻¹. The reduction onset and oxidation onsets are -0.79 V and 0.61 V, respectively.

11. Optical Absorption and Photoluminescence Spectra

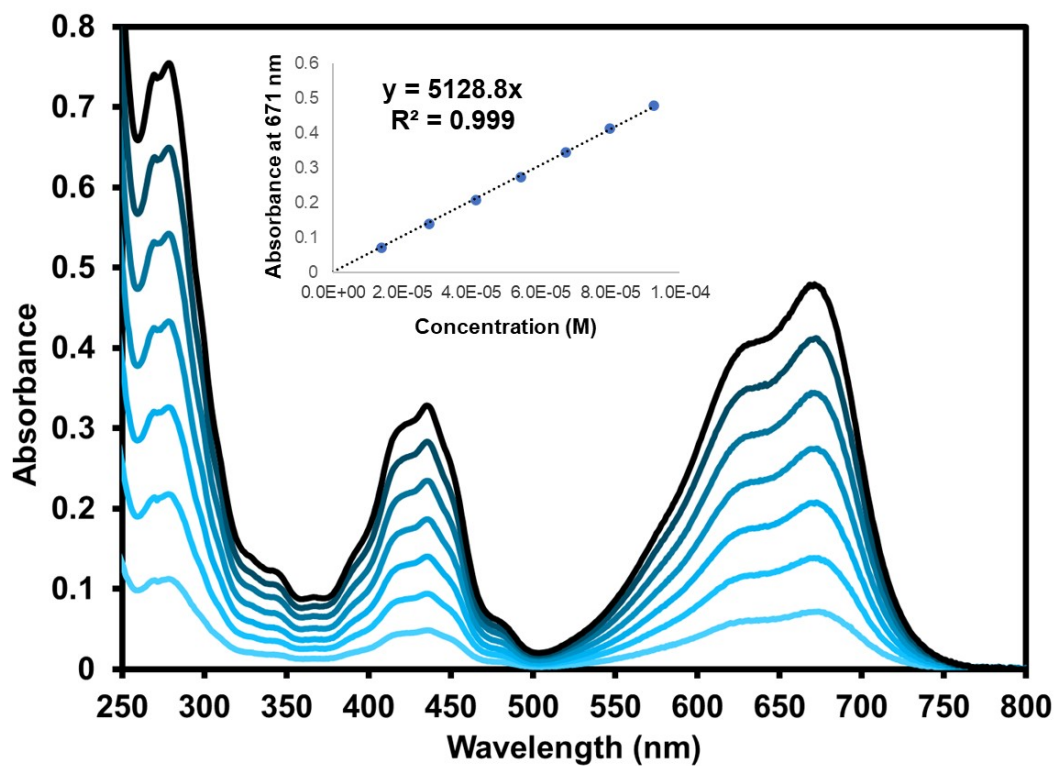


Figure S24. Absorbance calibration curve of F1 in CHCl_3 ($\epsilon_{671} = 25,900 \text{ M}^{-1}\text{cm}^{-1}$).

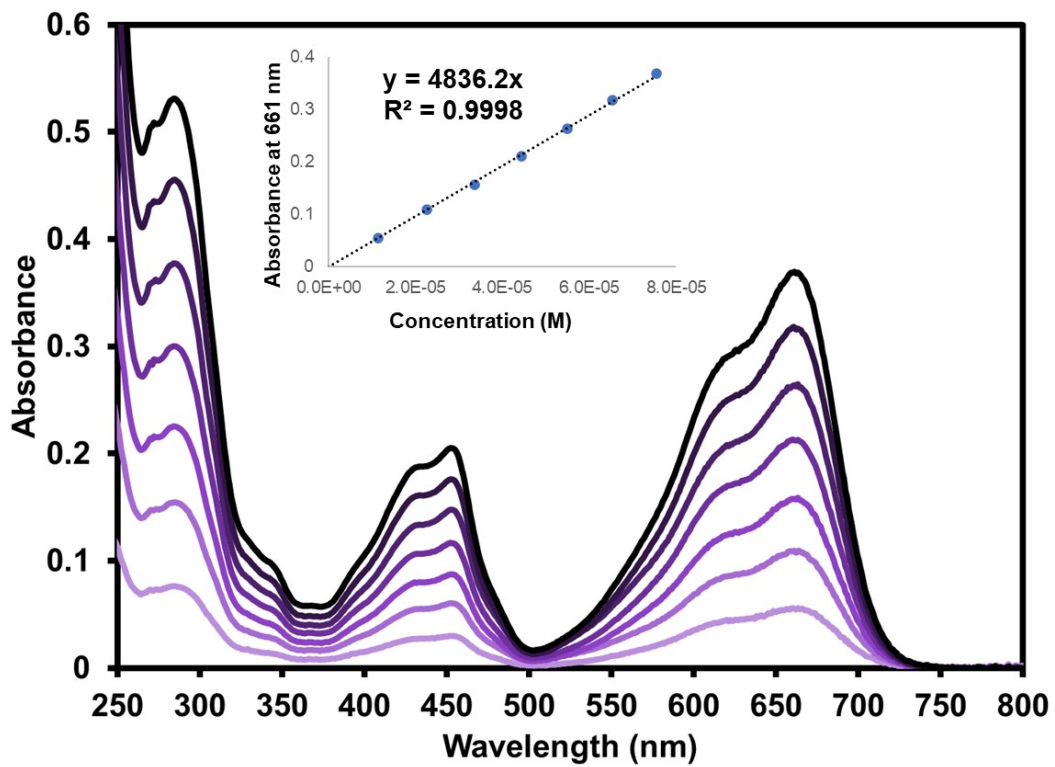


Figure S25. Absorbance calibration curve of **Br₂-F1** in CHCl₃ ($\epsilon_{661} = 24,397 \text{ M}^{-1}\text{cm}^{-1}$).

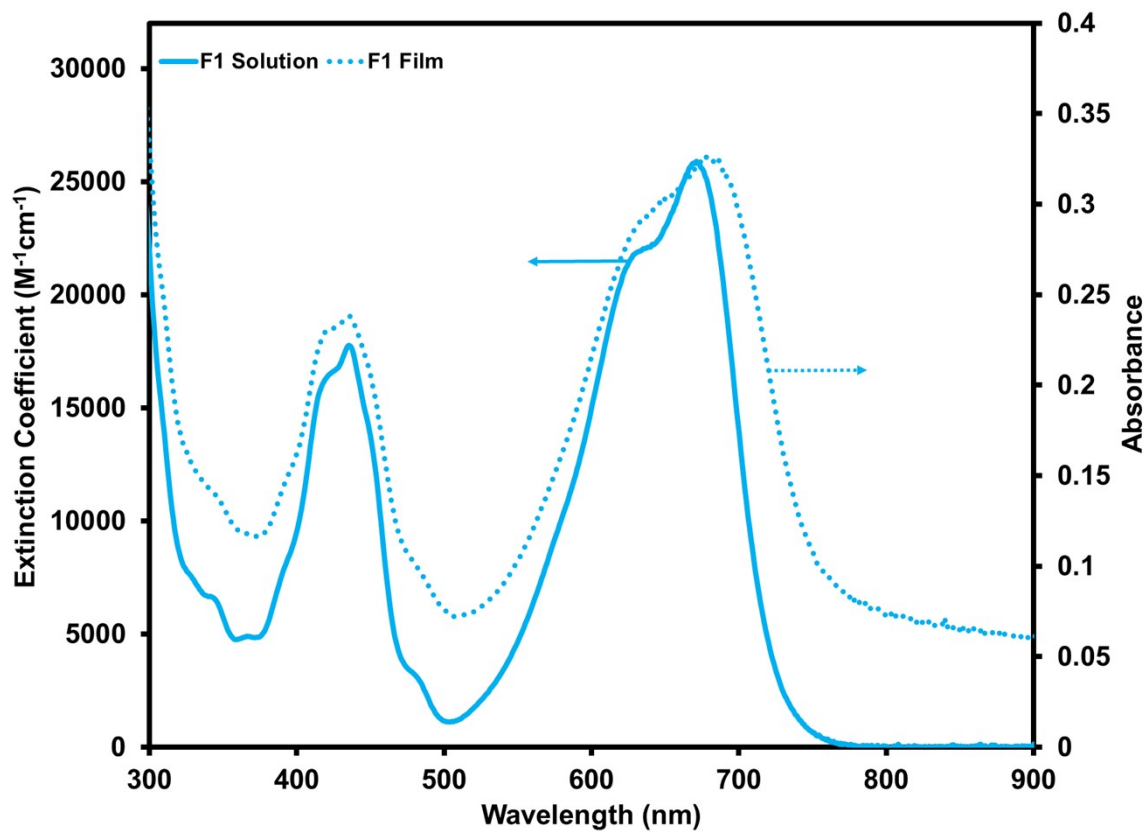


Figure S26. Comparison of the normalized optical absorption spectra of F1 solution (CHCl_3) and film (spin-casted from 40 μL of 10 mg/mL in CHCl_3 at 1000 rpm for 60 seconds).

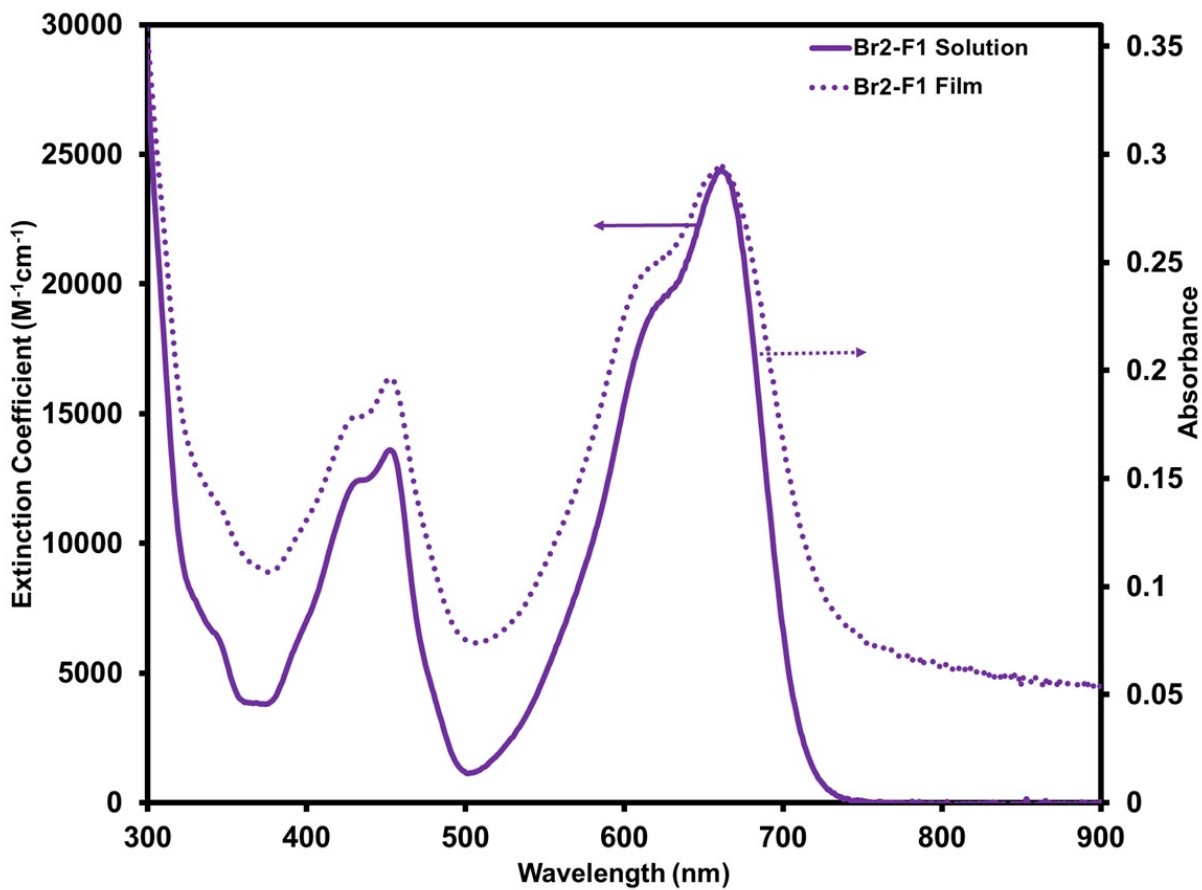


Figure S27. Comparison of the normalized optical absorption spectra of **Br2-F1** solution (CHCl_3) and film (spin-casted from 40 μL of 10 mg/mL in CHCl_3 at 1000 rpm for 60 seconds).

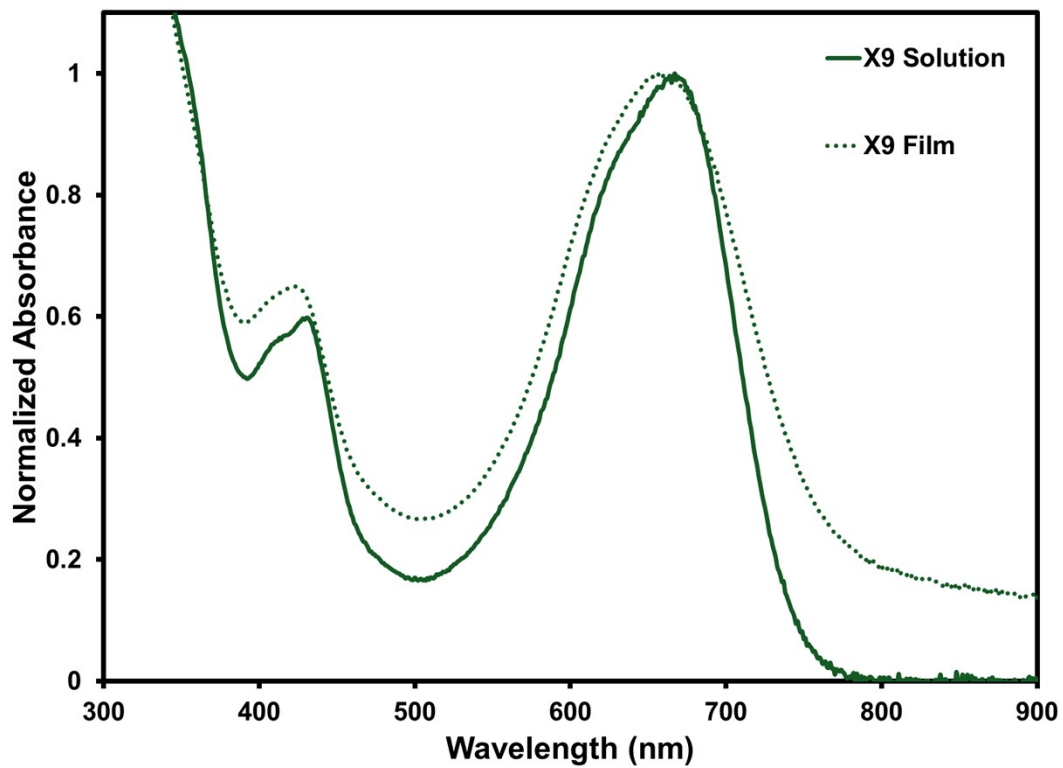


Figure S28. Comparison of the normalized optical absorption spectra of **X9** solution (CHCl_3) and film (spin-casted from 40 μL of 10 mg/mL in CHCl_3 at 1000 rpm for 60 seconds).

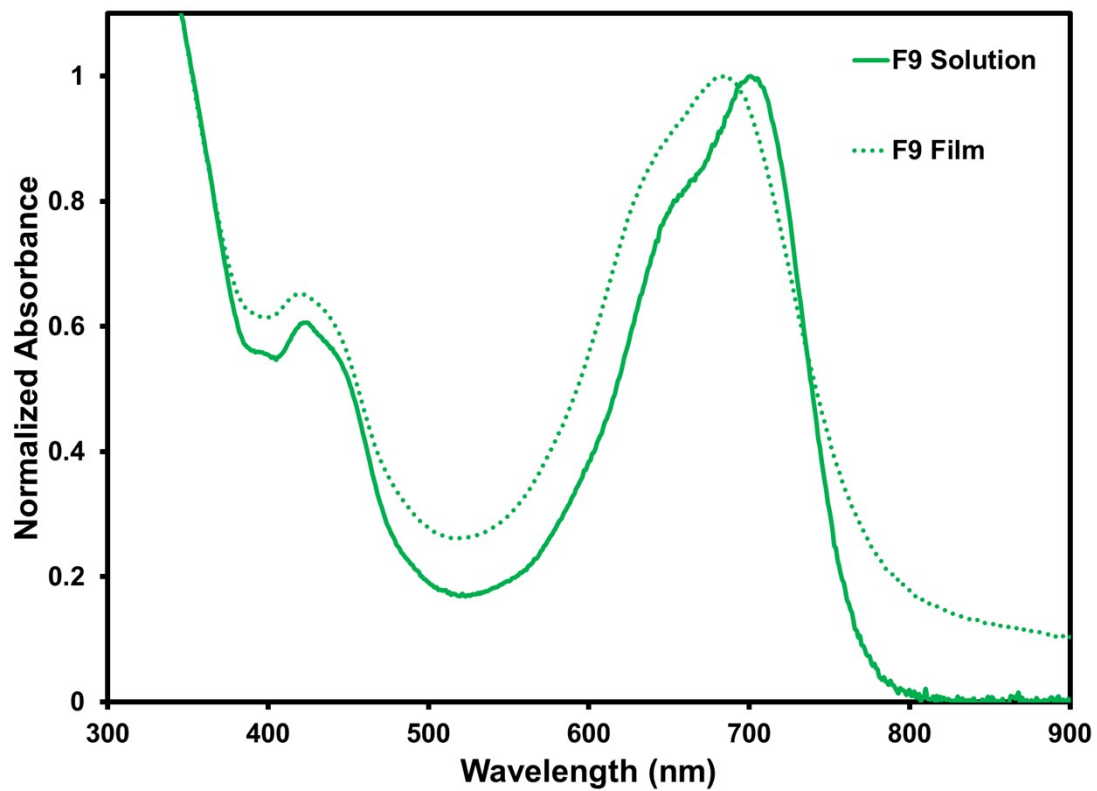


Figure S29. Comparison of the normalized optical absorption spectra of **F9** solution (CHCl_3) and film (spin-casted from 40 μL of 10 mg/mL in CHCl_3 at 1000 rpm for 60 seconds).

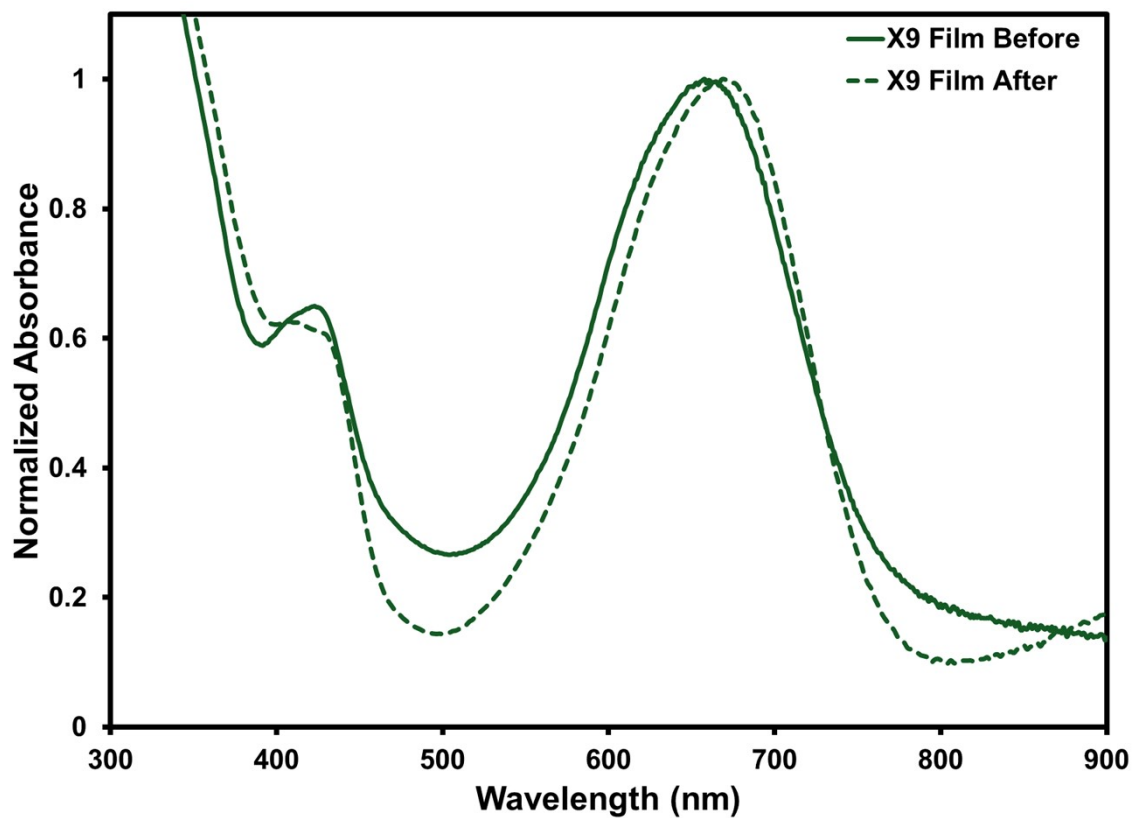


Figure S30. Normalized optical absorption spectra of X9 based ECD before and after the electrochemical conditioning (10 cycles).

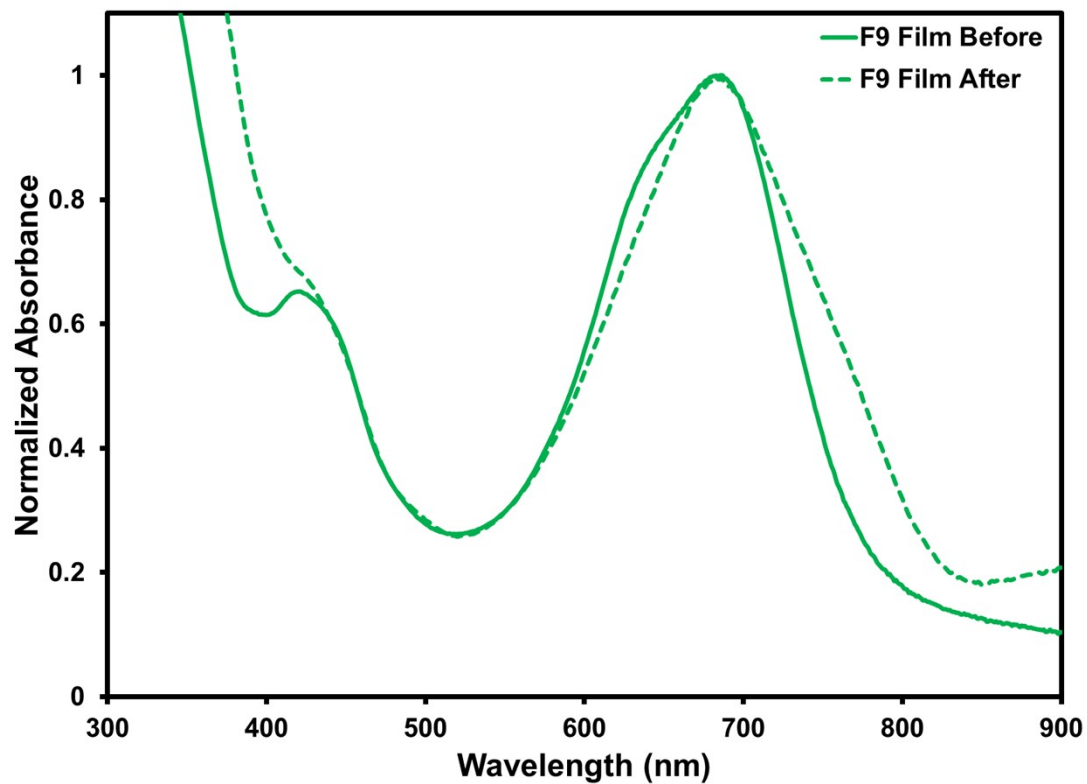


Figure S31. Normalized optical absorption spectra of **F9** based ECD before and after the electrochemical conditioning (10 cycles).

12. Electrochromic Devices

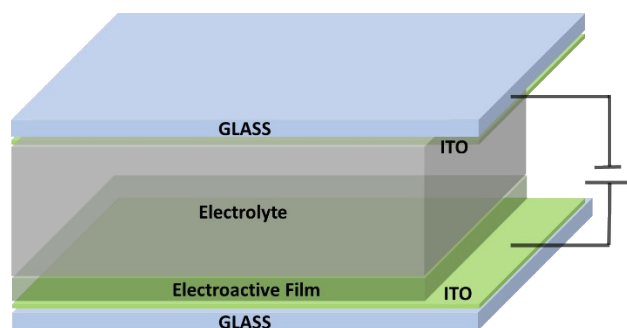


Figure S32. Schematic structure of the ECD fabricated with **X9** or **F9** polymer film as electrochromic active film.

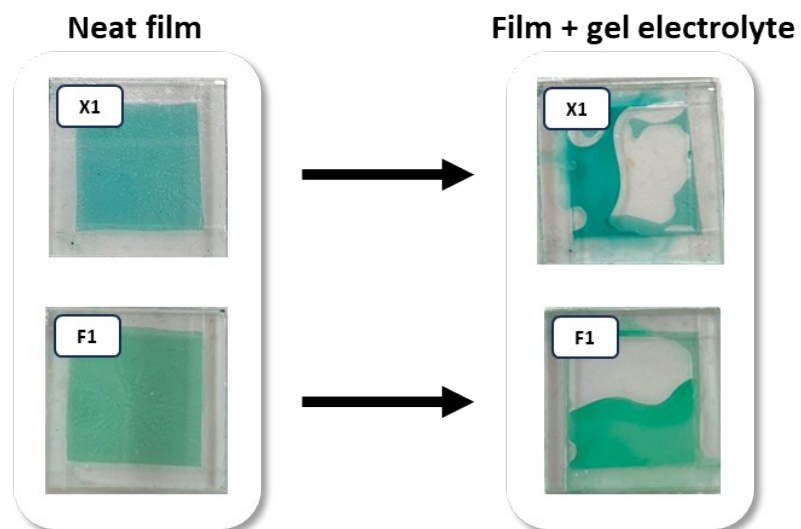


Figure S33. X1 and F1 spin-casted films (10 mg/mL in chloroform) showing no solvent resistance to the gel electrolyte used ($\text{LiClO}_4\text{-PC-PMMA}$).

13. Atomic Force Microscopy Images

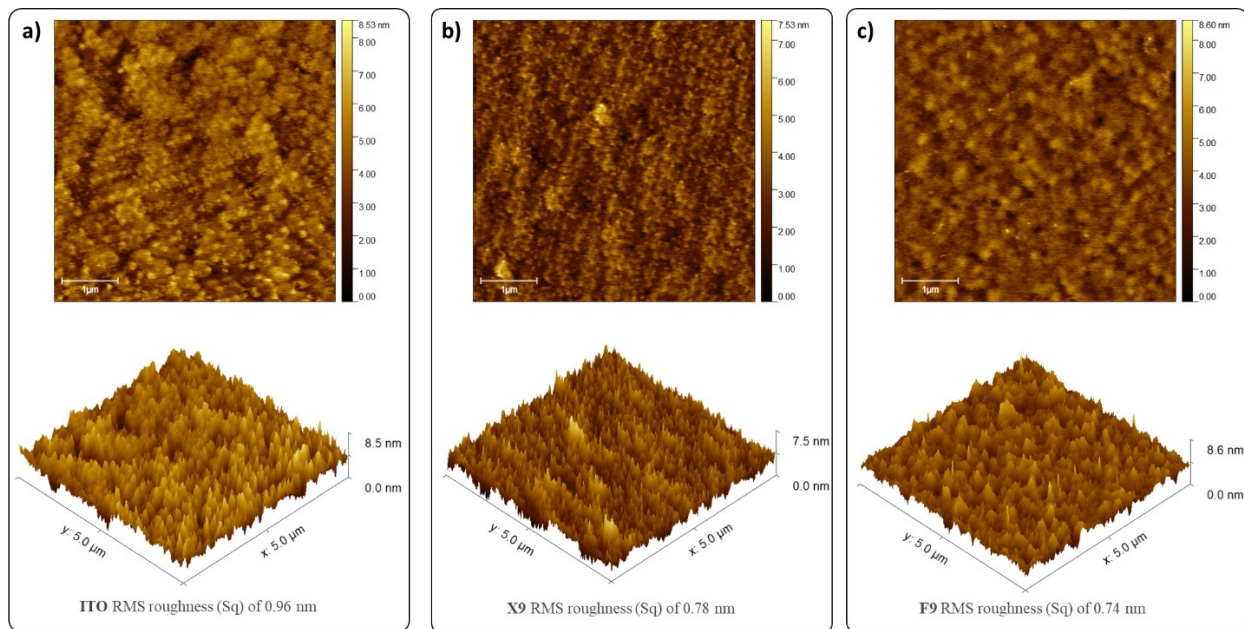


Figure S34. AFM images of **a)** ITO glass substrate as a reference **b)** X9 film spin coated onto ITO glass substrate and **c)** F9 film spin coated onto ITO glass substrate. The films were spin-coated on ITO glass (20 mm x 15 mm) using 100 μL of 20 mg mL⁻¹ solution in chlorobenzene at 2000 rpm for 60 seconds.

14. X-Ray Diffraction Images

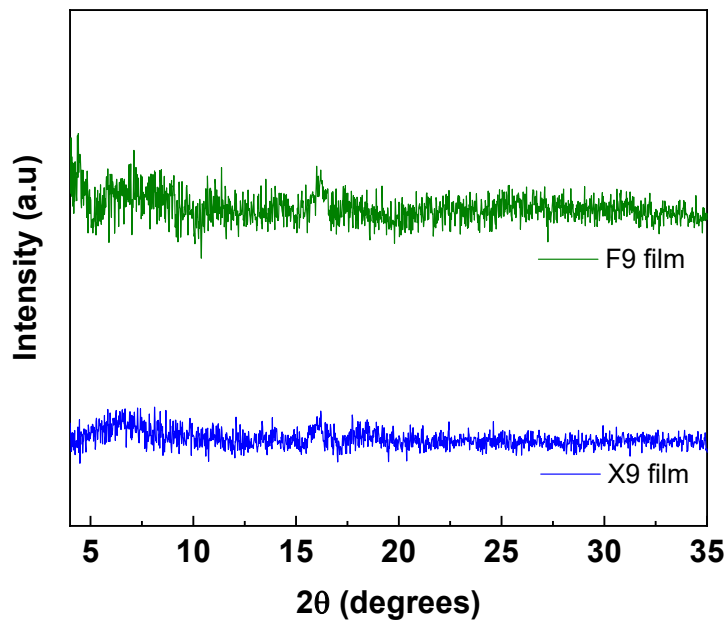


Figure S35. XRD images of **X9** and **F9** films spin coated onto glass substrates. The films were spin-coated on glass substrate (20 mm x 15 mm) using 100 μL of 20 mg mL^{-1} solution in chlorobenzene at 2000 rpm for 60 seconds.

15. References

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