

## **Supporting Information**

### **ProDOT-Assisted Isomerically Pure Indophenines**

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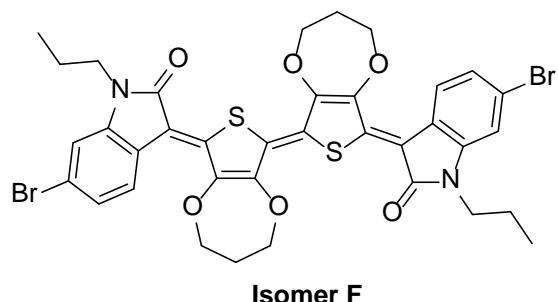
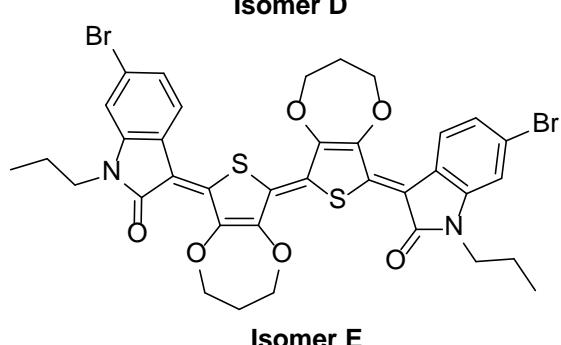
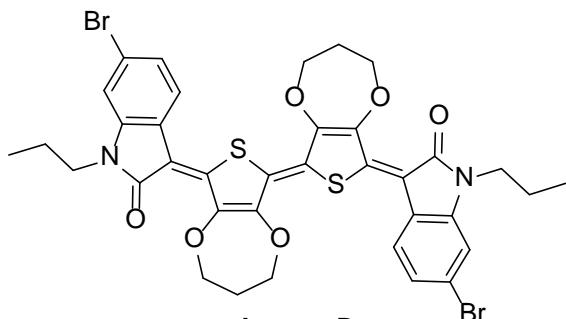
TGA traces for molecules **1-3** (p. S14)

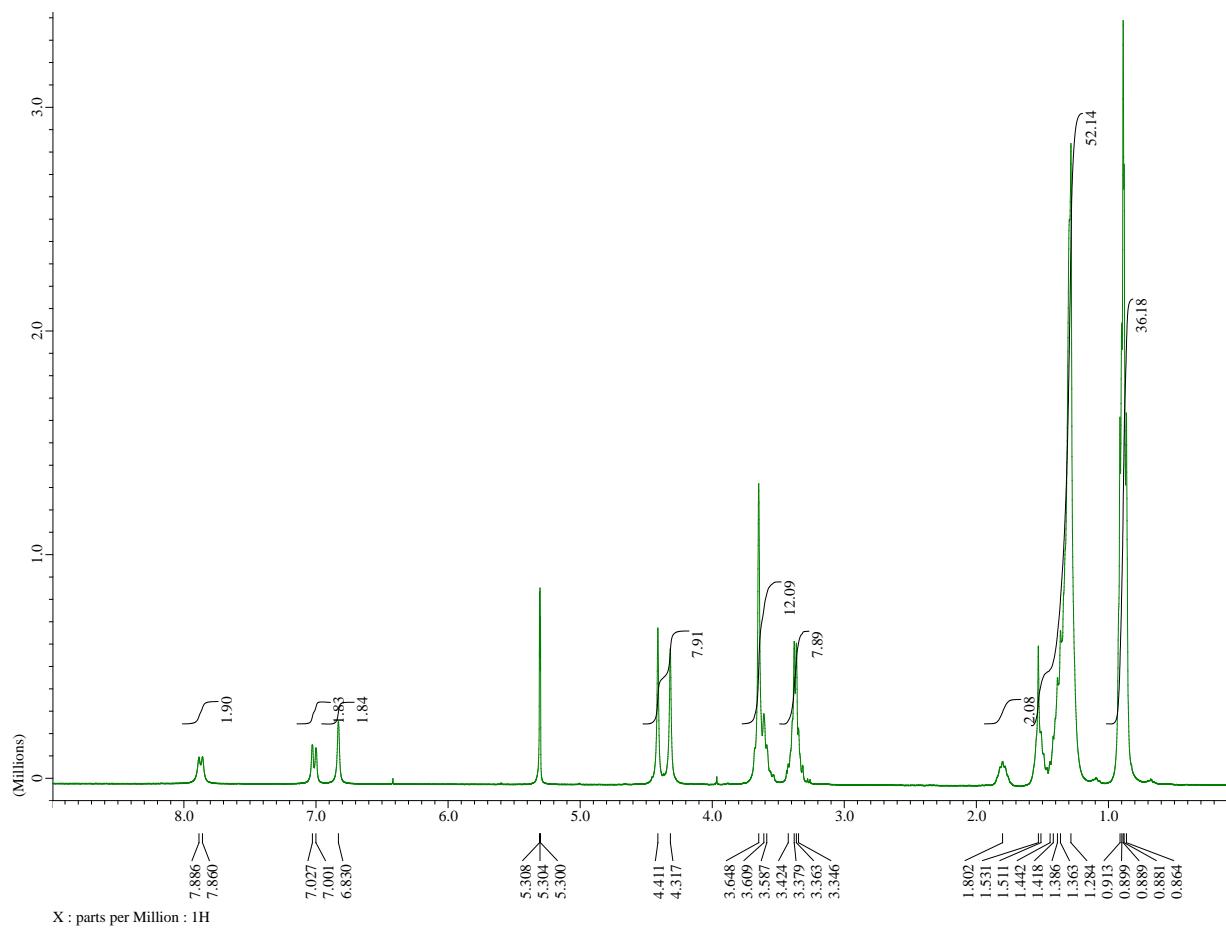
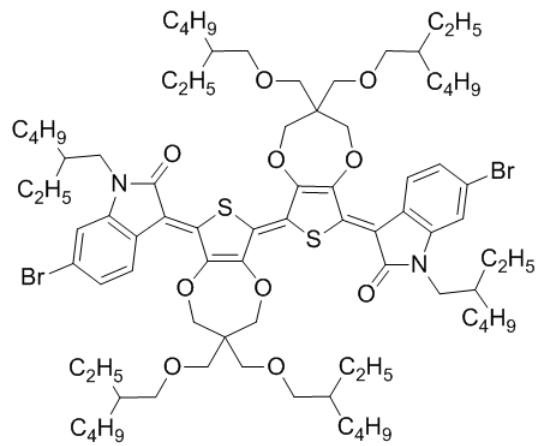
Cyclic voltammograms for molecules **1** and **3** (p. S15)

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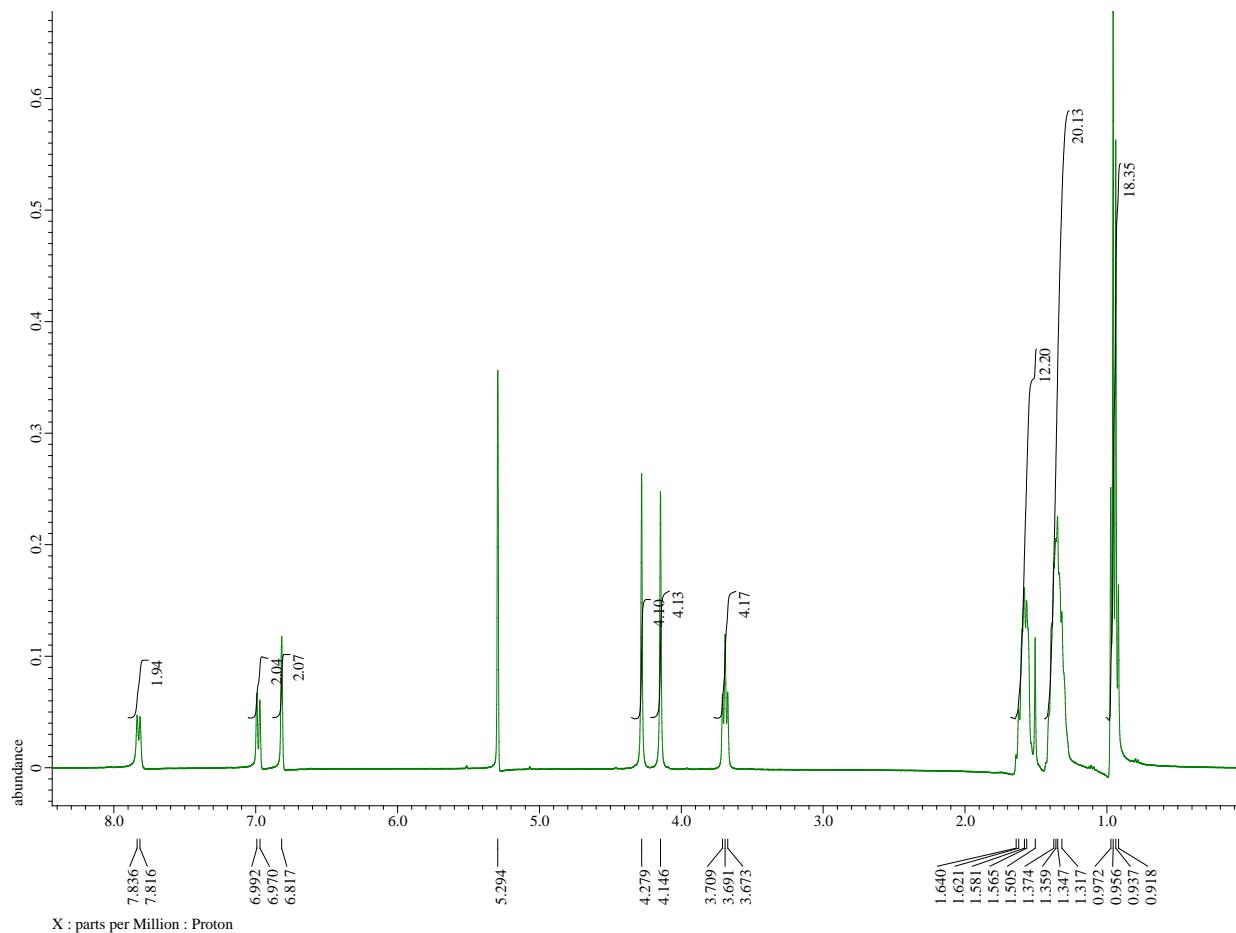
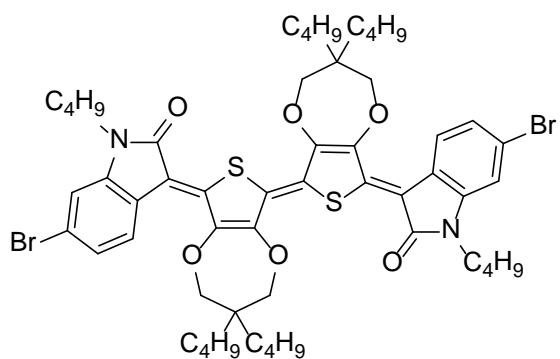
**Table S1.** Absolute and relative energies of indophenine isomers via B3LYP/6-31G(d,p) calculations.

Isomer	Total energy (Hartrees)	Relative energy (kcal/mol)
<b>D</b>	-7891.77210110	7.6
<b>E</b>	-7891.77811172	3.8
<b>F</b>	-7891.78423100	0

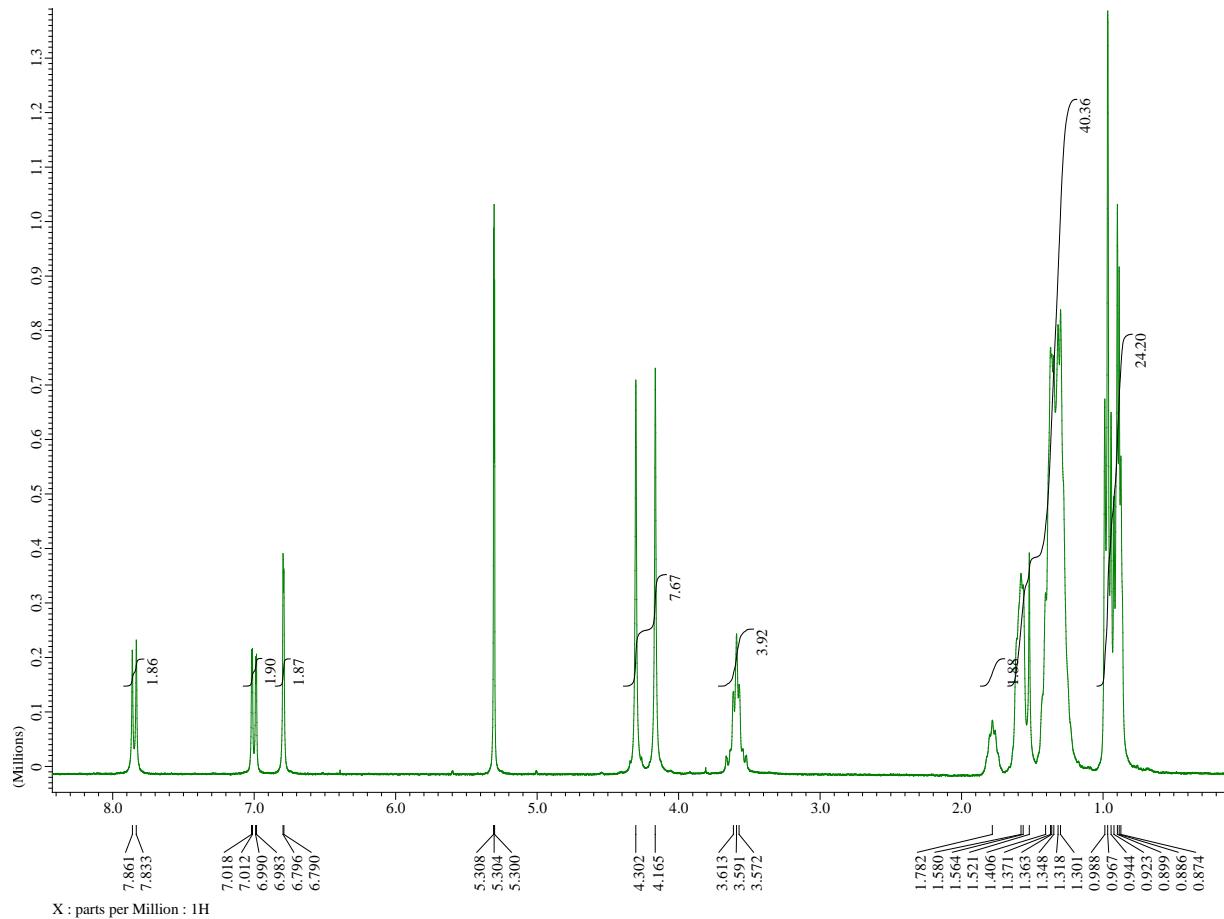
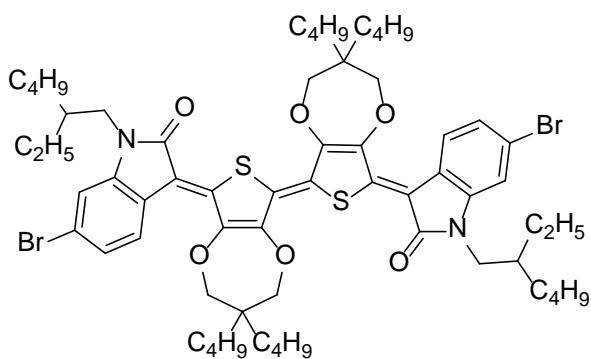




**Figure S1.**  $^1\text{H}$  NMR spectrum of molecule **1** in  $\text{CD}_2\text{Cl}_2$  (300 MHz).



**Figure S2.**  $^1\text{H}$  NMR spectrum of molecule **2** in  $\text{CD}_2\text{Cl}_2$  (400 MHz).



**Figure S3.**  $^1\text{H}$  NMR spectrum of molecule **3** in  $\text{CD}_2\text{Cl}_2$  (300 MHz).

## Details for Single Crystal X-ray Diffraction Data Collection and Refinement of **3**

A green crystal of **3**, grown from chloroform:acetonitrile was used for the data collection.

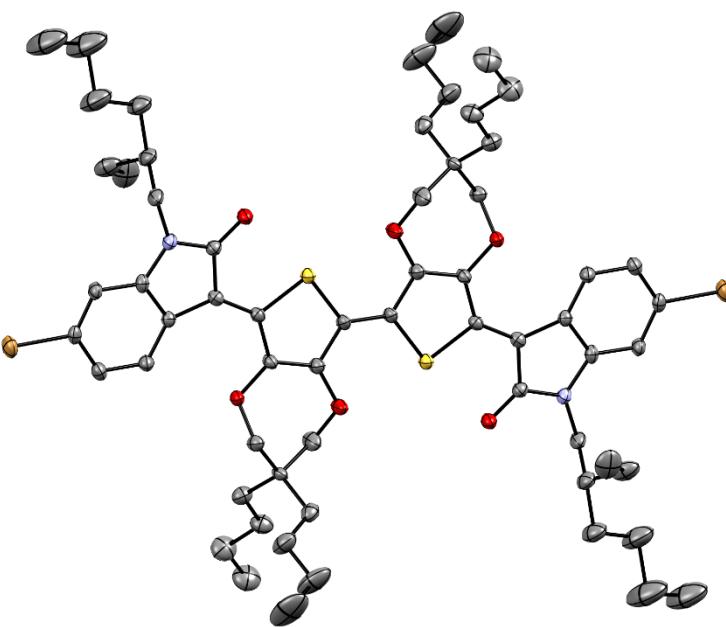
Table S2 contains crystal data, collection parameters, and refinement criteria for the crystal structure of **3**. A crystal was placed on the tip of a Mitigen micromount and X-ray intensity data were measured at low temperature (173(2) K, Oxford Cryosystems desktop cooler) with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku XtaLAB mini diffractometer.

The intensity data were corrected for absorption and decay (CrystalClear). Final cell constants were calculated from the xyz centroids of 10580 strong reflections from the actual data collection after integration (CrystalClear). The structure was solved and refined using SHELXL-2013. A direct-methods solution was calculated that provided most of the non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining nonhydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the non-hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

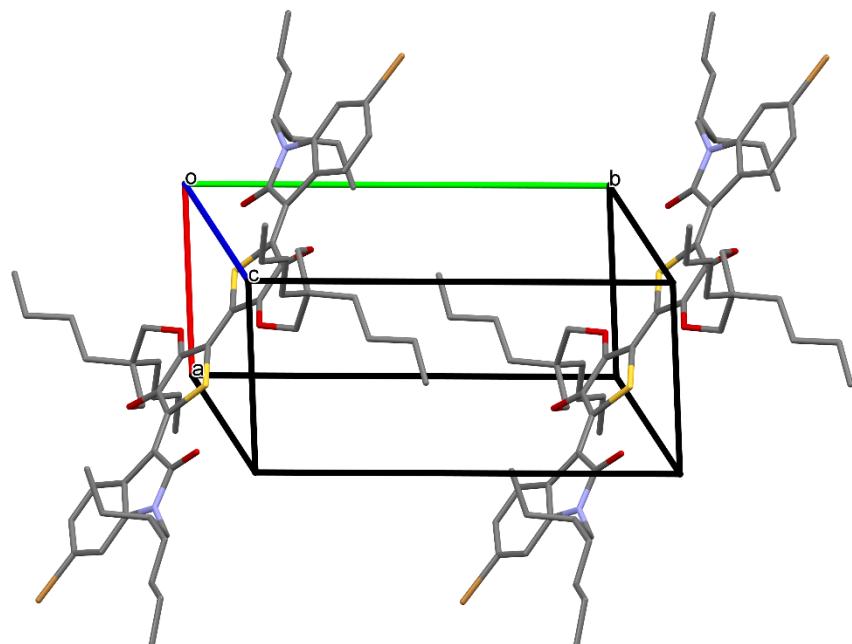
The asymmetric unit of **3** is composed of one half of the molecule. No solvent is present in the structure. Positional disorder was modeled in the 2-ethylhexyl group (atoms C13-C20) over two unique conformations. Appropriate pairwise thermal parameter constraints and positional restraints were employed. The occupancies of the two disorder conformations were freely refined, with a final model occupancy ratio of 75/25.

**Table S2.** Data Collection and Refinement Details for **3**

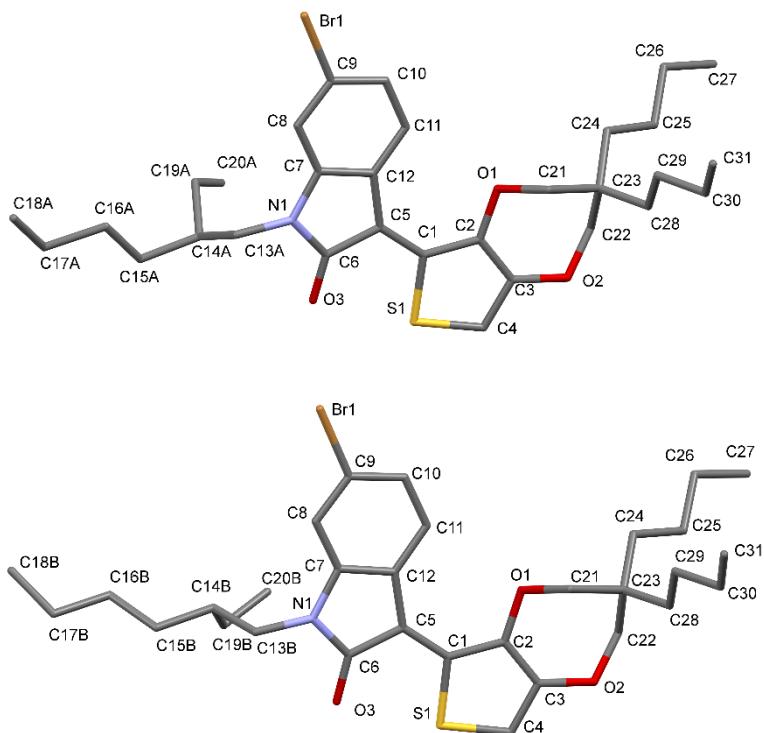
Chemical Formula	C <sub>62</sub> H <sub>84</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
Molar Mass	1177.28
Crystal color, habit	green, rod
Crystal System	triclinic
Crystal dimensions (mm)	0.61, 0.10, 0.03
Space Group	<i>P</i> -1
<i>a,b,c</i> (Å)	6.2227(12), 13.638(3), 17.947(4)
$\alpha, \beta, \gamma$ (°)	78.429(6), 89.290(6), 88.540(6)
<i>V</i> (Å <sup>3</sup> )	1491.6(5)
<i>Z, Z'</i>	1, 0.5
$\mu$ (mm <sup>-1</sup> )	1.483
Density (g cm <sup>-3</sup> )	1.311
Absorption correction	multi-scan (REQAB)
No. of measured, independent, observed [F <sup>2</sup> > 2.0σ(F <sup>2</sup> )] reflections	14270, 6087, 3451
<i>R</i> <sub>int</sub>	0.089
R[F <sup>2</sup> > 2.0(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.076, 0.186, 1.028
Number of unique Reflections	6087
Number of Parameters	355
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.58, -0.39



**Figure S4.** Thermal ellipsoid plot of **3** (30% probability ellipsoids; hydrogens omitted for clarity).



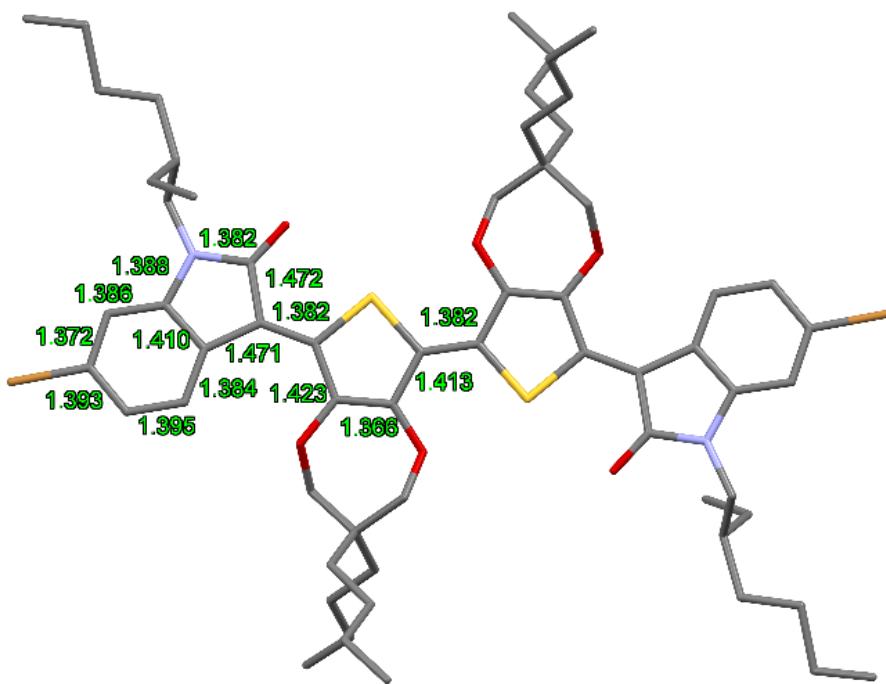
**Figure S5.** Unit cell diagram of **3**.



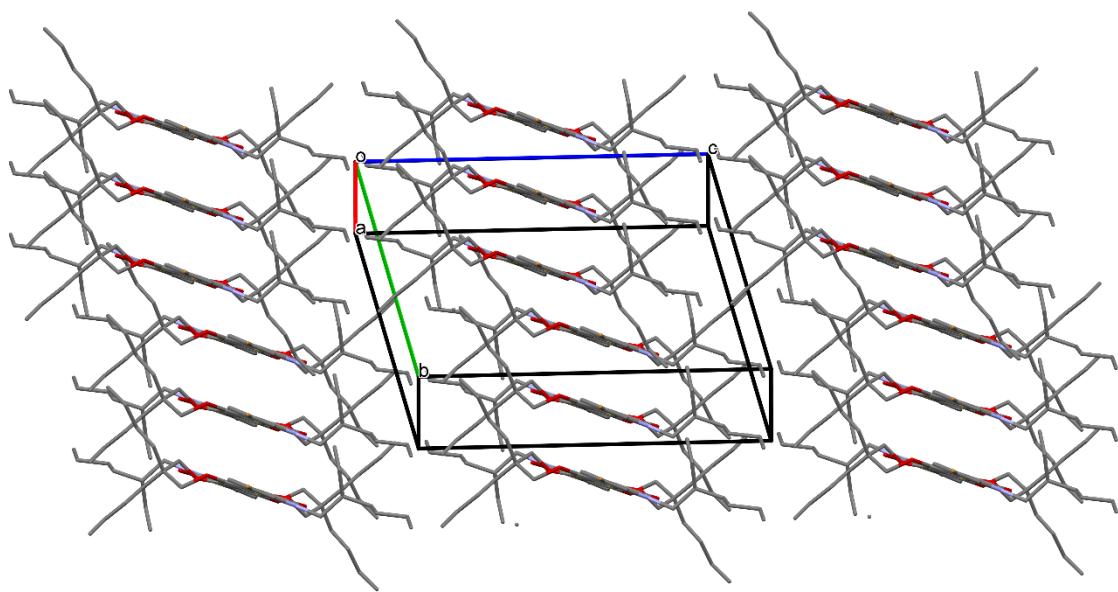
**Figure S6.** Numbered asymmetric unit of structure **3**.  
Major disorder component shown above, minor disorder component below.

**Table S3.** Selected Bond Lengths of **3**

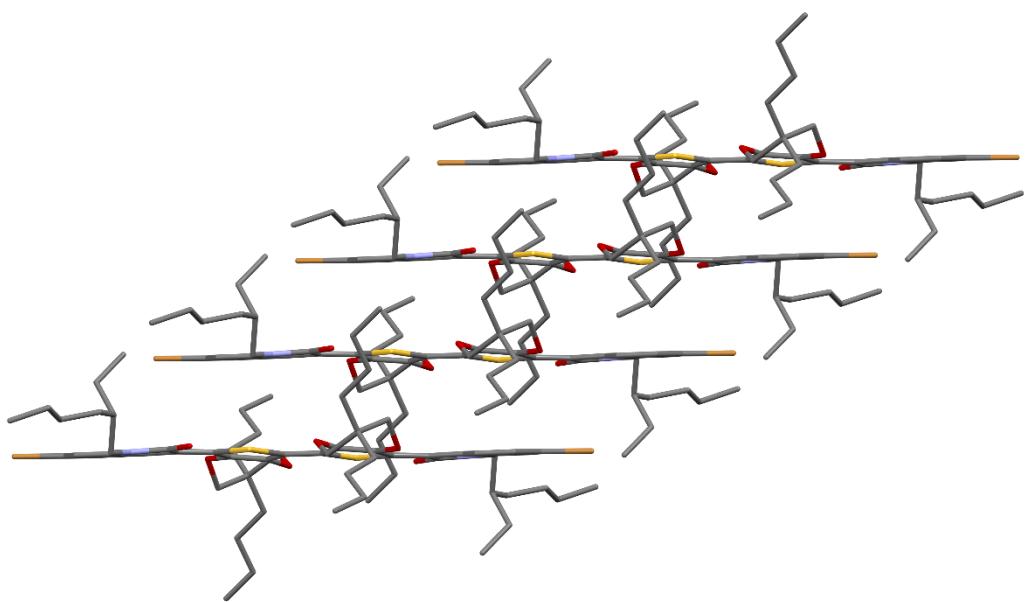
Atom 1	Atom 2	Length (Å)
C9	C10	1.393(8)
C10	C11	1.395(7)
C11	C12	1.384(8)
C12	C5	1.471(7)
C12	C7	1.410(7)
C7	C8	1.386(7)
C8	C9	1.372(8)
C5	C6	1.472(8)
C6	N1	1.382(6)
N1	C7	1.388(7)
C5	C1	1.382(7)
C1	C2	1.423(8)
C2	C3	1.366(7)
C3	C4	1.413(8)
C4	C4 (-x,-y,-z)	1.382(7)



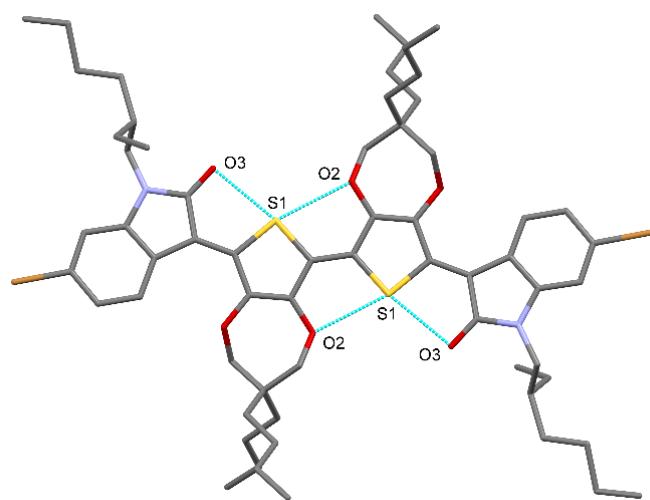
**Figure S7.** Select bond distances in the indophenine core of **3** (units of Å).



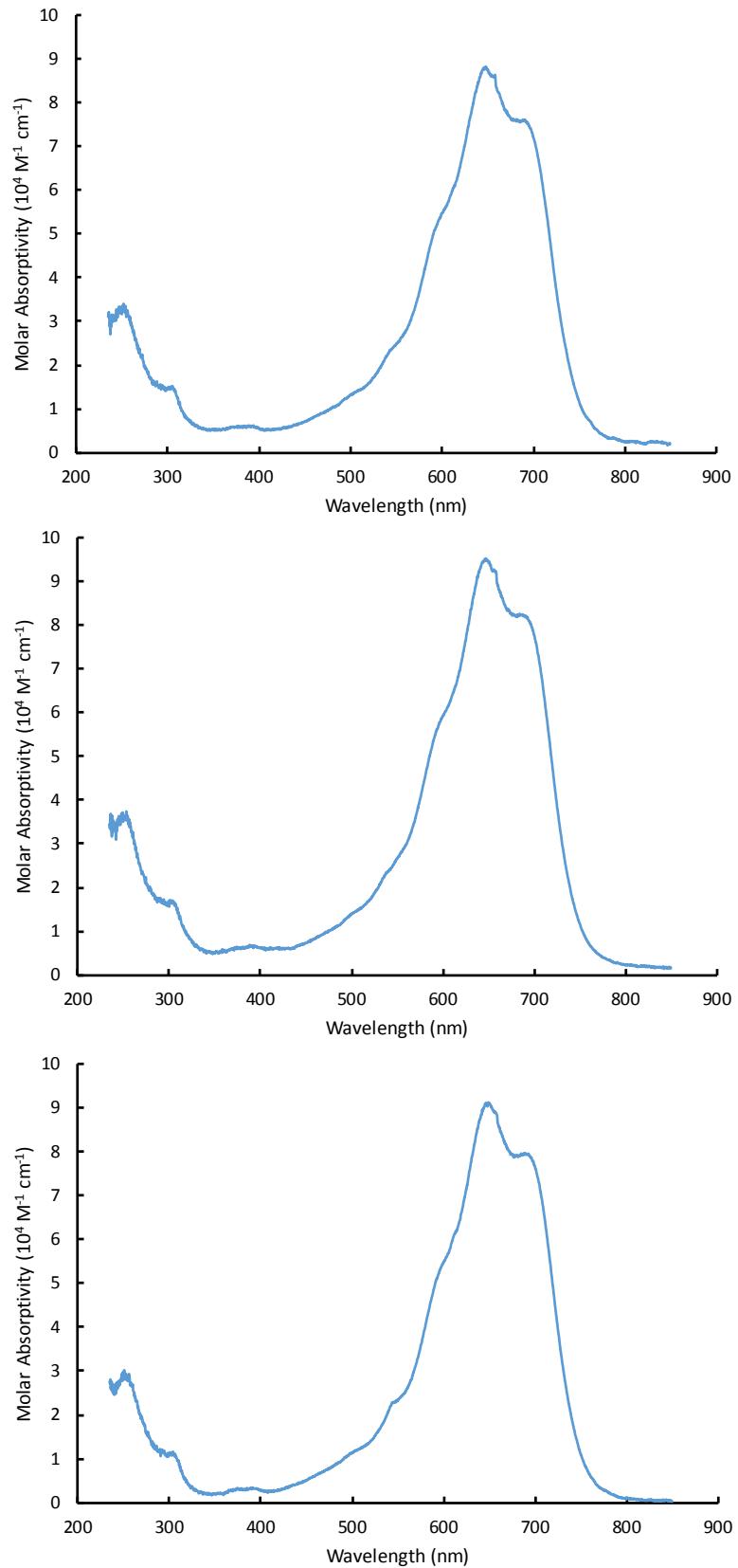
**Figure S8.** Packing diagram of **3** showing discrete  $\pi$ -stacking and aliphatic regions.



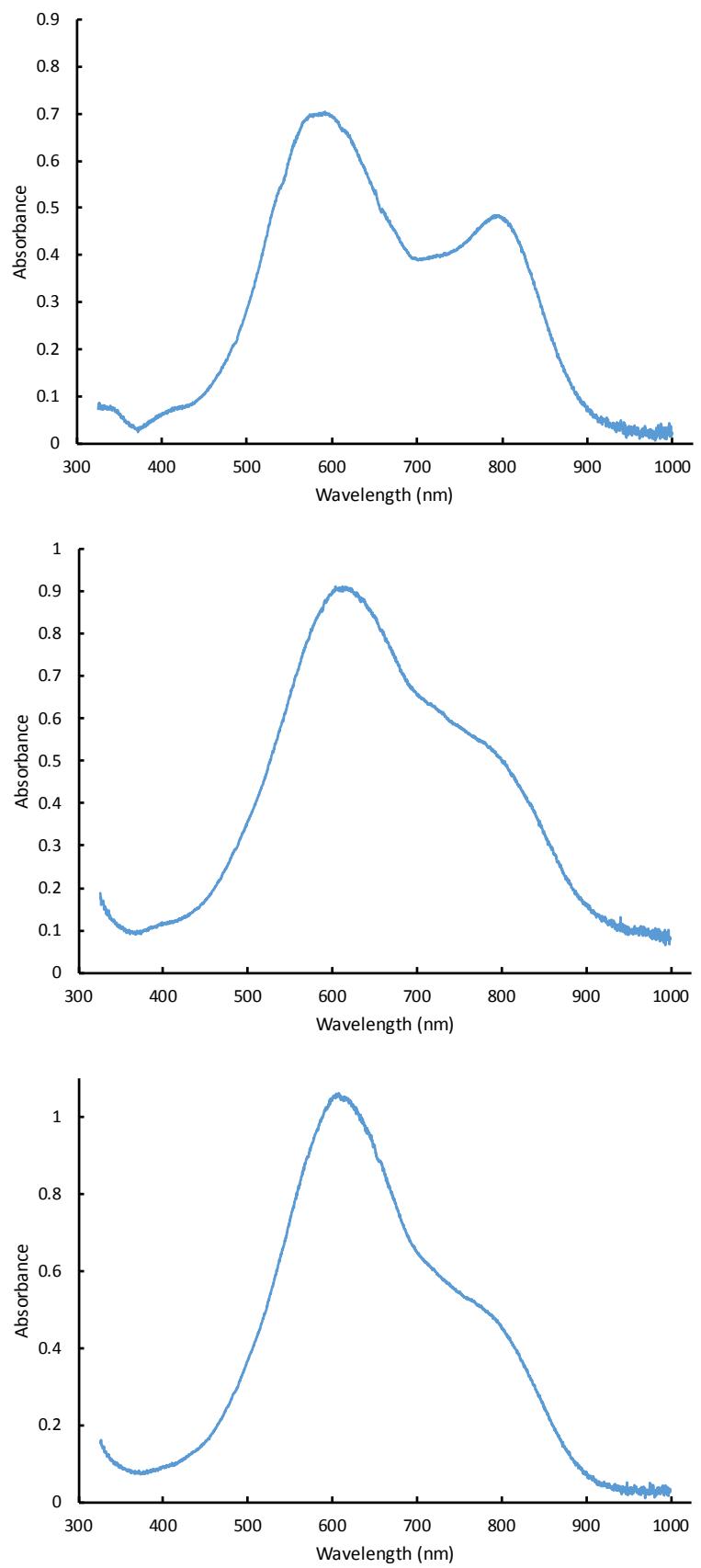
**Figure S9.** Packing diagram of **3** showing infinite  $\pi$ -stacking arrangement.



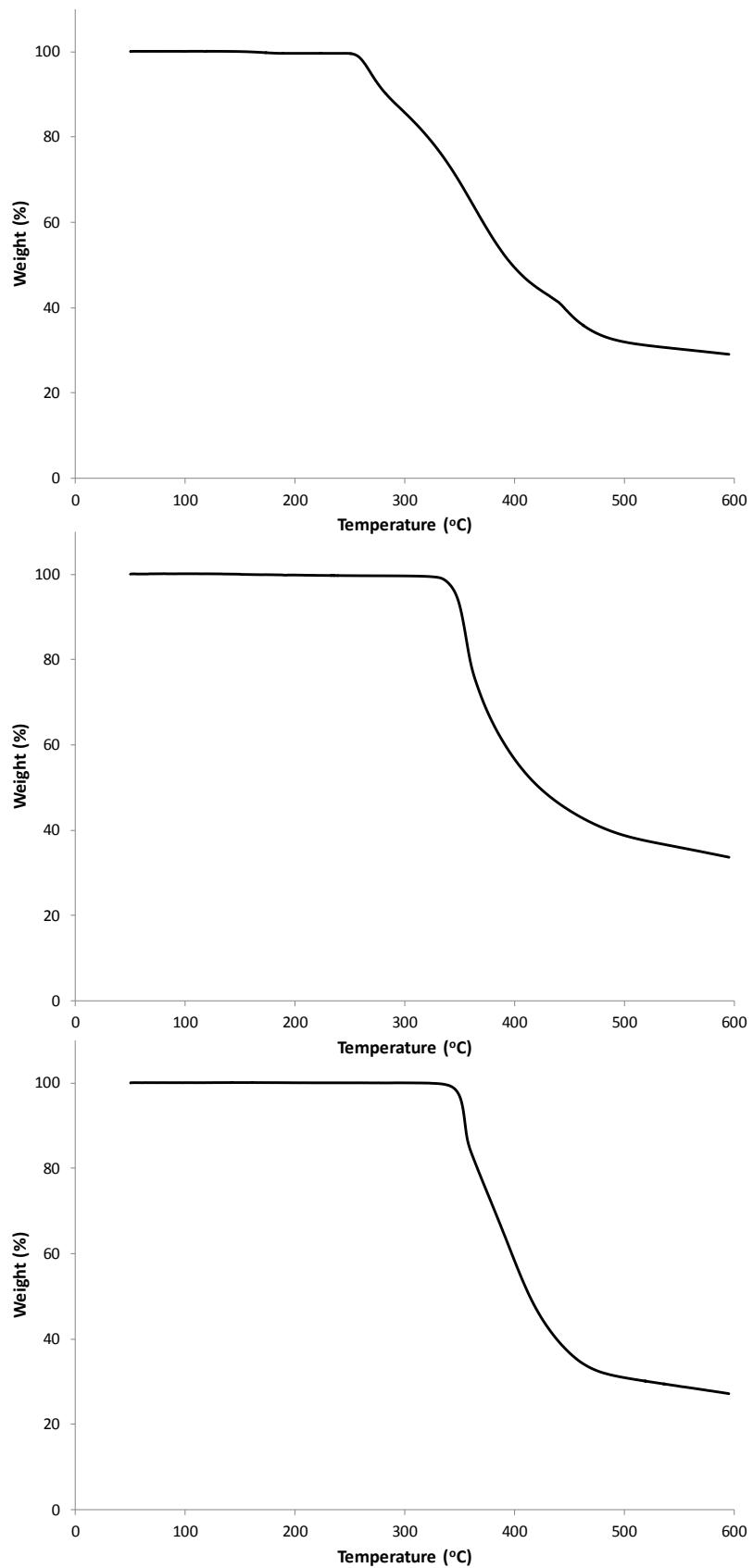
**Figure S10.** Short S...O contacts in the structure of **3**.



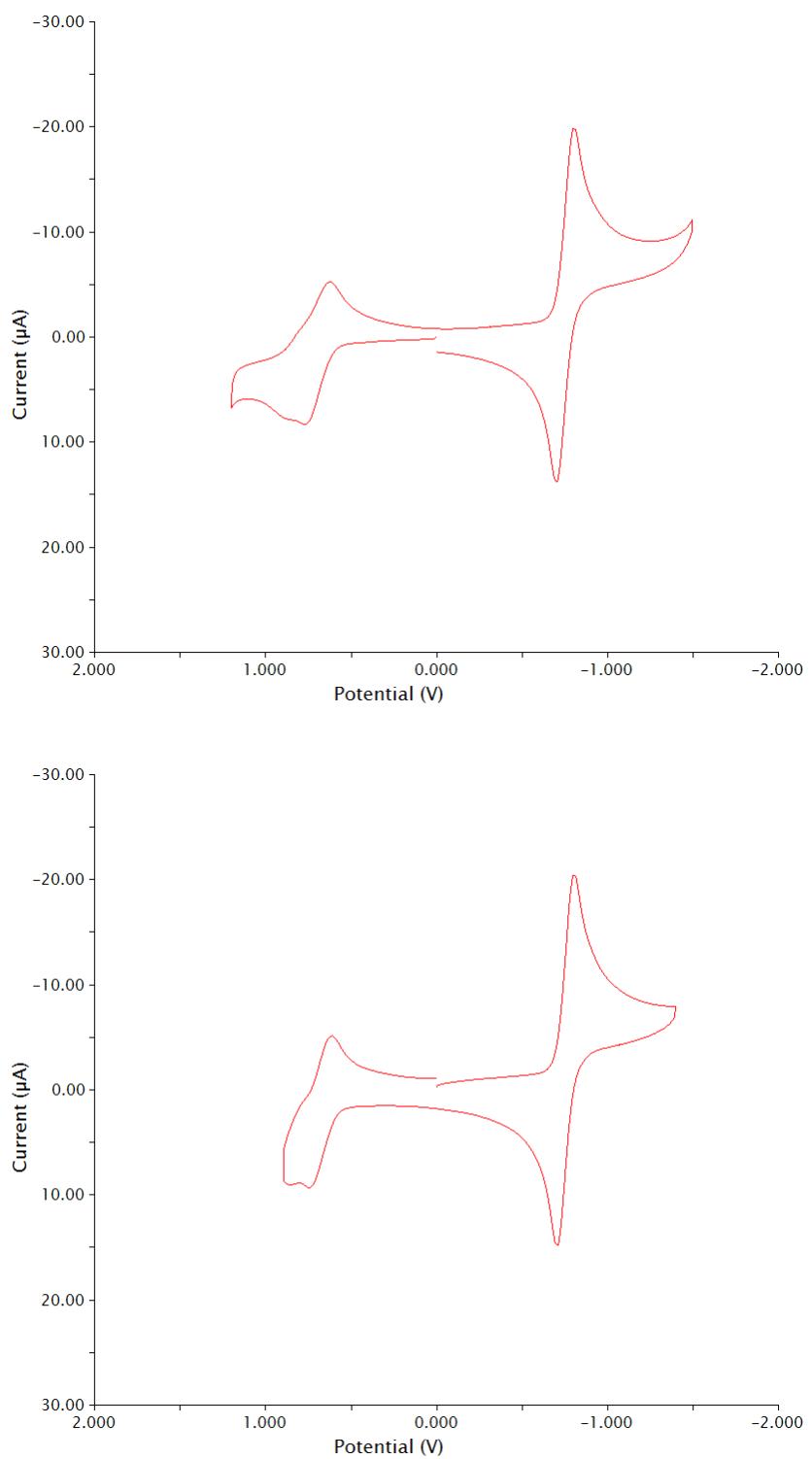
**Figure S11.** Electronic spectra of **1** (top), **2** (middle), and **3** (bottom) in dichloromethane.



**Figure S12.** Thin-film electronic spectra of **1** (top), **2** (middle), and **3** (bottom).



**Figure S13.** TGA traces for **1** (top), **2** (middle), and **3** (bottom).



**Figure S14.** Cyclic voltammograms of **1** (top) and **3** (bottom)  
in 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> ( $v = 100$  mV/s)

Computational details and Cartesian coordinates for  
calculated geometry of indophenine **Isomer D**

# opt=tight freq b3lyp/6-31g(d,p) geom=connectivity int=ultrafine  
Imaginary frequencies=0; Total energy= -7891.77210110

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Center #	Atomic #	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	6.417210	2.295147	-0.750240
2	6	0	5.287302	1.480760	-0.633188
3	6	0	5.408615	0.180968	-0.130883
4	6	0	6.701347	-0.291935	0.224730
5	6	0	7.837922	0.499284	0.112244
6	6	0	7.664186	1.798670	-0.373344
7	6	0	4.474550	-0.912143	0.075621
8	6	0	5.275687	-2.044213	0.645034
9	7	0	6.606291	-1.601194	0.674925
10	35	0	9.200664	2.925904	-0.534012
11	8	0	4.923643	-3.120534	1.110021
12	6	0	7.688806	-2.416493	1.202079
13	6	0	8.519510	-3.109023	0.112636
14	6	0	9.653003	-3.950979	0.704444
15	6	0	2.221521	-2.055991	-0.213770
16	6	0	0.882543	-1.713798	-0.244704
17	6	0	0.617890	-0.306120	-0.220232
18	16	0	2.157935	0.578092	-0.187557
19	6	0	3.102468	-0.925052	-0.090630
20	8	0	2.707161	-3.291905	-0.471430
21	6	0	2.287548	-4.374438	0.372754
22	6	0	0.847378	-4.794138	0.099880
23	6	0	-0.183999	-3.737389	0.477356
24	8	0	-0.157925	-2.575232	-0.378706
25	6	0	-2.221521	2.055988	-0.213768
26	6	0	-0.882543	1.713794	-0.244704
27	6	0	-0.617891	0.306117	-0.220232
28	16	0	-2.157936	-0.578095	-0.187555
29	6	0	-3.102468	0.925049	-0.090628
30	8	0	-2.707160	3.291902	-0.471427
31	6	0	-2.287545	4.374434	0.372758
32	6	0	-0.847376	4.794135	0.099882
33	6	0	0.184002	3.737384	0.477355
34	8	0	0.157925	2.575228	-0.378708
35	6	0	-6.417213	-2.295146	-0.750239
36	6	0	-5.287304	-1.480760	-0.633185
37	6	0	-5.408616	-0.180969	-0.130881
38	6	0	-6.701347	0.291936	0.224732

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39	6	0	-7.837922	-0.499282	0.112246
40	6	0	-7.664188	-1.798668	-0.373343
41	6	0	-4.474550	0.912142	0.075623
42	6	0	-5.275686	2.044213	0.645034
43	7	0	-6.606290	1.601196	0.674925
44	35	0	-9.200667	-2.925900	-0.534012
45	8	0	-4.923641	3.120534	1.110020
46	6	0	-7.688804	2.416495	1.202078
47	6	0	-8.519506	3.109028	0.112634
48	6	0	-9.652998	3.950984	0.704441
49	1	0	6.329163	3.303893	-1.134870
50	1	0	4.327076	1.871440	-0.949374
51	1	0	8.821658	0.136595	0.382273
52	1	0	7.218591	-3.163801	1.847133
53	1	0	8.327886	-1.784260	1.830831
54	1	0	7.850378	-3.740655	-0.482764
55	1	0	8.929031	-2.355580	-0.571131
56	1	0	10.229344	-4.445106	-0.083207
57	1	0	9.263673	-4.729354	1.370023
58	1	0	10.347820	-3.334501	1.286258
59	1	0	2.980591	-5.185191	0.142455
60	1	0	2.438337	-4.091109	1.420534
61	1	0	0.730459	-5.055130	-0.957872
62	1	0	0.631910	-5.697371	0.686468
63	1	0	-1.197889	-4.126752	0.364441
64	1	0	-0.048205	-3.413162	1.517784
65	1	0	-2.980588	5.185188	0.142461
66	1	0	-2.438332	4.091104	1.420537
67	1	0	-0.730458	5.055128	-0.957870
68	1	0	-0.631907	5.697367	0.686471
69	1	0	1.197892	4.126747	0.364438
70	1	0	0.048211	3.413157	1.517782
71	1	0	-6.329166	-3.303892	-1.134869
72	1	0	-4.327078	-1.871442	-0.949371
73	1	0	-8.821659	-0.136593	0.382274
74	1	0	-7.218590	3.163802	1.847133
75	1	0	-8.327887	1.784262	1.830828
76	1	0	-7.850371	3.740659	-0.482764
77	1	0	-8.929027	2.355586	-0.571134
78	1	0	-10.347819	3.334507	1.286251
79	1	0	-9.263668	4.729357	1.370023
80	1	0	-10.229336	4.445115	-0.083210

Computational details and Cartesian coordinates for  
calculated geometry of indophenine **Isomer E**

# opt=tight freq b3lyp/6-31g(d,p) geom=connectivity int=ultrafine  
Imaginary frequencies=0; Total energy= -7891.77811172

Center #	Atomic #	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	7.242112	-2.485891	-0.263801
2	6	0	5.928490	-2.010355	-0.279358
3	6	0	5.671219	-0.636579	-0.207354
4	6	0	6.788780	0.246218	-0.159269
5	6	0	8.102682	-0.205341	-0.138105
6	6	0	8.303362	-1.586246	-0.185270
7	6	0	4.474549	0.201015	-0.229466
8	6	0	4.963495	1.606822	-0.241874
9	7	0	6.350818	1.566509	-0.170901
10	35	0	10.095434	-2.253764	-0.154045
11	8	0	4.301346	2.641924	-0.292987
12	6	0	7.178509	2.762235	-0.151097
13	6	0	7.662728	3.148132	1.253531
14	6	0	8.538763	4.403532	1.232434
15	6	0	2.381451	-1.268301	-0.075145
16	6	0	1.011363	-1.126310	-0.121520
17	6	0	0.562401	0.222939	-0.286301
18	16	0	1.959551	1.319239	-0.400962
19	6	0	3.110677	-0.033529	-0.215934
20	8	0	3.030534	-2.457930	0.063996
21	6	0	2.670254	-3.287800	1.181203
22	6	0	1.330225	-3.989237	0.994785
23	6	0	0.139095	-3.041506	1.039395
24	8	0	0.098499	-2.136362	-0.079559
25	6	0	-2.588197	2.143613	-0.480356
26	6	0	-1.213893	1.992024	-0.502389
27	6	0	-0.750365	0.646679	-0.328977
28	16	0	-2.150931	-0.436441	-0.172833
29	6	0	-3.298771	0.920708	-0.220058
30	8	0	-3.246954	3.262005	-0.861263
31	6	0	-2.974608	4.483324	-0.157227
32	6	0	-1.611804	5.065634	-0.515347
33	6	0	-0.436732	4.217039	-0.044205
34	8	0	-0.308372	2.967513	-0.754784
35	6	0	-6.132114	-2.780710	-0.483795
36	6	0	-5.127302	-1.808994	-0.473187
37	6	0	-5.426988	-0.494198	-0.102143
38	6	0	-6.771194	-0.171826	0.230537
39	6	0	-7.785799	-1.121183	0.222354

40	6	0	-7.433966	-2.426692	-0.132861
41	6	0	-4.654540	0.733671	-0.026151
42	6	0	-5.602660	1.795761	0.441565
43	7	0	-6.858129	1.177125	0.543857
44	35	0	-8.797665	-3.767971	-0.146142
45	8	0	-5.402934	2.952985	0.787300
46	6	0	-8.041182	1.884605	1.006245
47	6	0	-8.965614	2.339681	-0.131733
48	6	0	-10.202677	3.073277	0.393021
49	1	0	7.438037	-3.550095	-0.318027
50	1	0	5.109263	-2.708452	-0.365409
51	1	0	8.943197	0.475703	-0.094002
52	1	0	6.563396	3.563933	-0.568791
53	1	0	8.030474	2.608392	-0.824720
54	1	0	6.784669	3.310356	1.889065
55	1	0	8.217664	2.310383	1.692893
56	1	0	8.868461	4.670517	2.240753
57	1	0	7.993983	5.261153	0.822528
58	1	0	9.434904	4.255826	0.619000
59	1	0	3.479964	-4.018203	1.252297
60	1	0	2.670223	-2.681304	2.097187
61	1	0	1.332060	-4.536434	0.045764
62	1	0	1.211672	-4.725900	1.800456
63	1	0	-0.800071	-3.594777	0.974923
64	1	0	0.136392	-2.461130	1.971991
65	1	0	-3.778641	5.156766	-0.458605
66	1	0	-3.071522	4.304975	0.919777
67	1	0	-1.543805	5.212285	-1.599070
68	1	0	-1.522027	6.053820	-0.044345
69	1	0	0.512004	4.723673	-0.230553
70	1	0	-0.514922	4.005420	1.030635
71	1	0	-5.905601	-3.801449	-0.766813
72	1	0	-4.123604	-2.091751	-0.768815
73	1	0	-8.809060	-0.873214	0.474695
74	1	0	-7.676686	2.752323	1.562977
75	1	0	-8.582915	1.238359	1.707995
76	1	0	-8.393868	2.993038	-0.800610
77	1	0	-9.269139	1.470430	-0.727724
78	1	0	-10.802065	2.429916	1.047375
79	1	0	-9.922544	3.962333	0.968826
80	1	0	-10.845967	3.399305	-0.429559

Computational details and Cartesian coordinates for  
calculated geometry of indophenine **Isomer F**

# opt=tight freq b3lyp/6-31g(d,p) geom=connectivity int=ultrafine  
Imaginary frequencies=0; Total energy= -7891.78423100

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Center #	Atomic #	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-8.218763	-0.320137	0.076948
2	6	0	-8.581457	1.016153	-0.102004
3	6	0	-7.634316	2.021467	-0.286116
4	6	0	-6.273684	1.704248	-0.273357
5	6	0	-5.855397	0.384656	-0.067857
6	6	0	-6.860671	-0.613928	0.082835
7	6	0	-4.567382	-0.303178	-0.014129
8	6	0	-4.886388	-1.749843	0.129273
9	7	0	-6.268466	-1.865262	0.218953
10	8	0	-4.108161	-2.701037	0.182738
11	6	0	-6.947169	-3.145734	0.342805
12	6	0	-7.437063	-3.712861	-0.997121
13	6	0	-8.153028	-5.054910	-0.823587
14	35	0	-10.440177	1.468180	-0.113028
15	6	0	-3.241104	0.092496	-0.037052
16	6	0	-2.663213	1.412383	-0.039888
17	6	0	-1.285444	1.428982	-0.082598
18	6	0	-0.677819	0.131841	-0.096648
19	16	0	-1.936805	-1.126551	-0.081708
20	8	0	-3.448707	2.525494	-0.032838
21	6	0	-3.187893	3.522227	0.970352
22	6	0	-1.941461	4.349821	0.680691
23	6	0	-0.645891	3.563094	0.826490
24	8	0	-0.499607	2.534833	-0.169886
25	6	0	3.241105	-0.092498	-0.037051
26	6	0	2.663214	-1.412385	-0.039888
27	6	0	1.285445	-1.428985	-0.082598
28	6	0	0.677820	-0.131844	-0.096648
29	16	0	1.936806	1.126549	-0.081707
30	8	0	3.448707	-2.525496	-0.032838
31	6	0	3.187893	-3.522229	0.970353
32	6	0	1.941461	-4.349824	0.680692
33	6	0	0.645891	-3.563096	0.826490
34	8	0	0.499608	-2.534835	-0.169887
35	6	0	8.218763	0.320138	0.076946
36	6	0	8.581459	-1.016151	-0.102005
37	6	0	7.634320	-2.021465	-0.286118
38	6	0	6.273687	-1.704249	-0.273358
39	6	0	5.855398	-0.384658	-0.067856

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40	6	0	6.860671	0.613928	0.082834
41	6	0	4.567382	0.303175	-0.014129
42	6	0	4.886387	1.749841	0.129273
43	7	0	6.268464	1.865261	0.218953
44	8	0	4.108160	2.701034	0.182738
45	6	0	6.947166	3.145734	0.342807
46	6	0	7.437054	3.712865	-0.997120
47	6	0	8.153018	5.054914	-0.823586
48	35	0	10.440180	-1.468175	-0.113028
49	1	0	-8.972733	-1.087981	0.196254
50	1	0	-7.954821	3.044174	-0.444918
51	1	0	-5.542661	2.481260	-0.439497
52	1	0	-7.782946	-3.029435	1.043203
53	1	0	-6.224993	-3.830344	0.796037
54	1	0	-8.106105	-2.989414	-1.478260
55	1	0	-6.571292	-3.829046	-1.658782
56	1	0	-8.487159	-5.450007	-1.787388
57	1	0	-9.035863	-4.957778	-0.181303
58	1	0	-7.492586	-5.801720	-0.369122
59	1	0	-4.079438	4.154248	0.965549
60	1	0	-3.114386	3.035539	1.952582
61	1	0	-2.007569	4.770766	-0.328515
62	1	0	-1.913784	5.189777	1.387536
63	1	0	0.223300	4.206631	0.678557
64	1	0	-0.575508	3.109266	1.824365
65	1	0	4.079437	-4.154250	0.965549
66	1	0	3.114385	-3.035541	1.952582
67	1	0	2.007569	-4.770769	-0.328514
68	1	0	1.913784	-5.189779	1.387538
69	1	0	-0.223300	-4.206632	0.678557
70	1	0	0.575508	-3.109267	1.824365
71	1	0	8.972732	1.087984	0.196252
72	1	0	7.954825	-3.044172	-0.444921
73	1	0	5.542667	-2.481262	-0.439499
74	1	0	7.782946	3.029434	1.043201
75	1	0	6.224991	3.830341	0.796043
76	1	0	8.106095	2.989419	-1.478263
77	1	0	6.571280	3.829051	-1.658777
78	1	0	7.492578	5.801722	-0.369115
79	1	0	9.035857	4.957782	-0.181307
80	1	0	8.487144	5.450014	-1.787387