

Electronic Supporting Information For

Modulating High-Energy Visible Light Absorption to Attain Neutral-State Black Electrochromic Polymers

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1 NMR, GPC, TGA of Polymers P1-P3

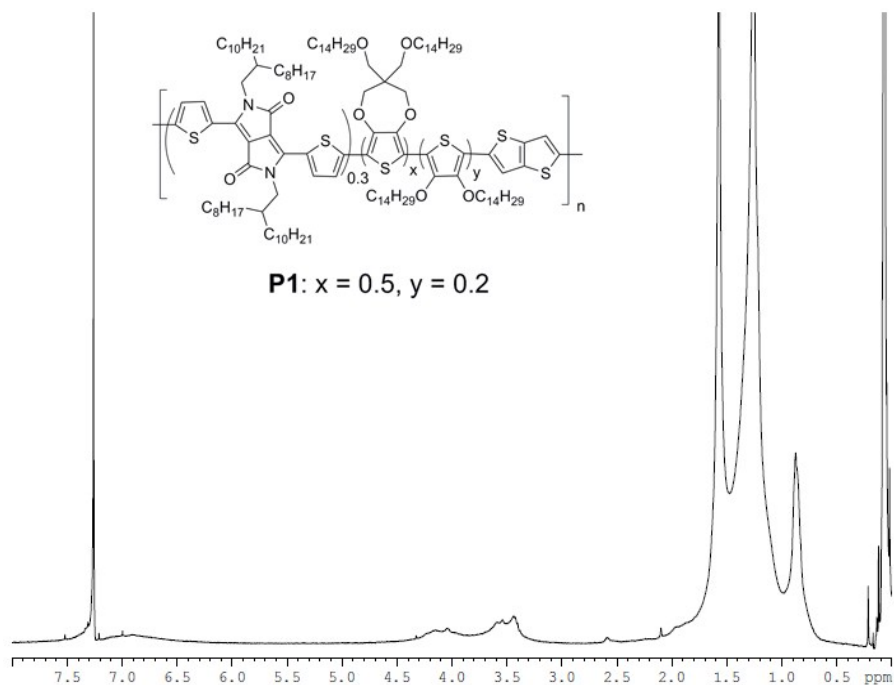


Figure S1 ¹H NMR spectrum of **P1**.

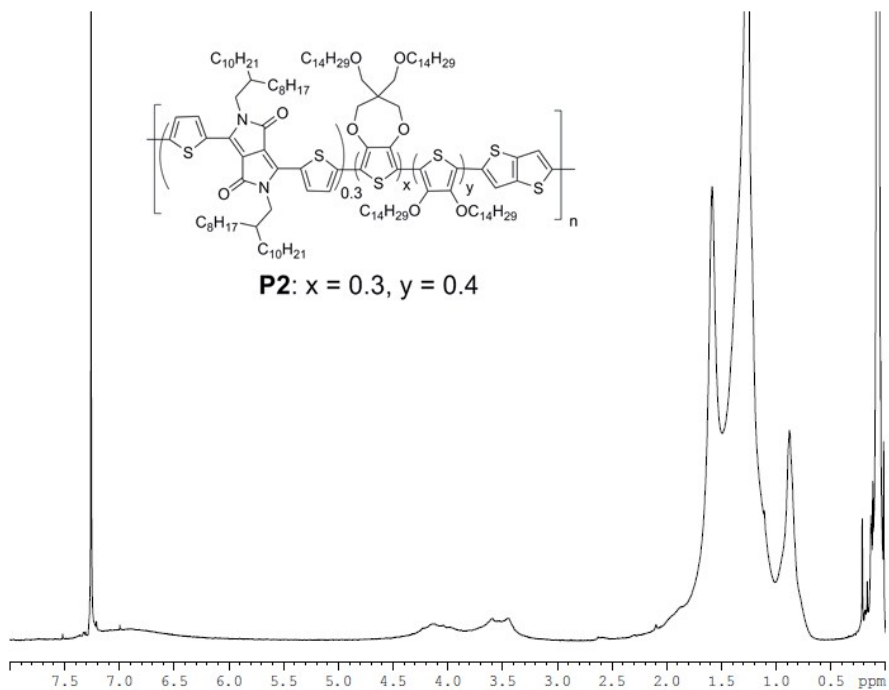
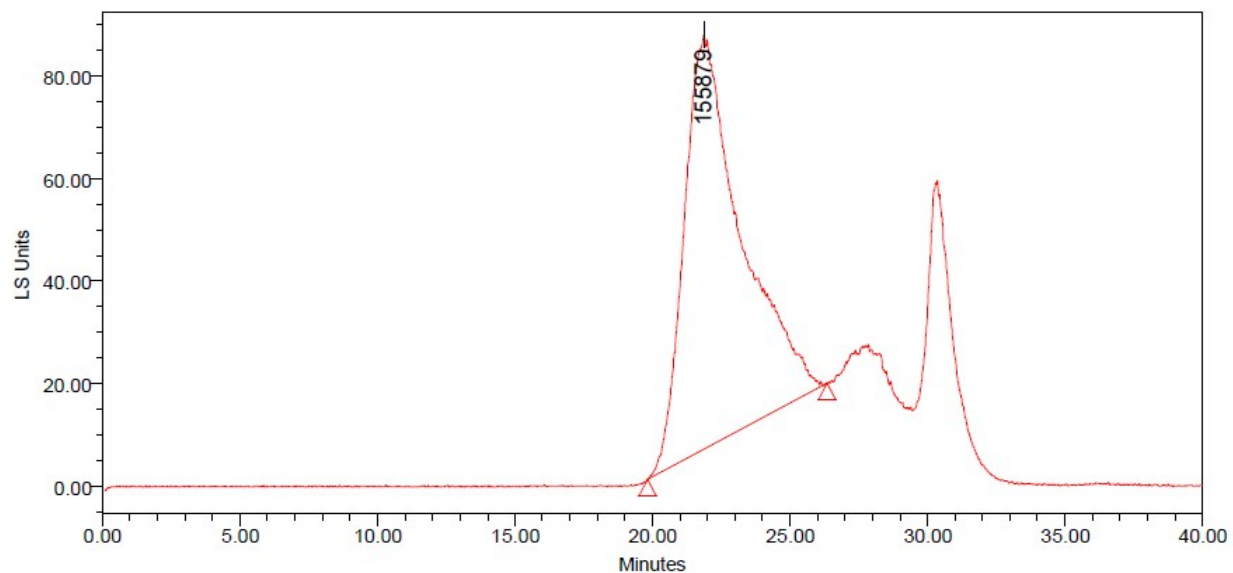
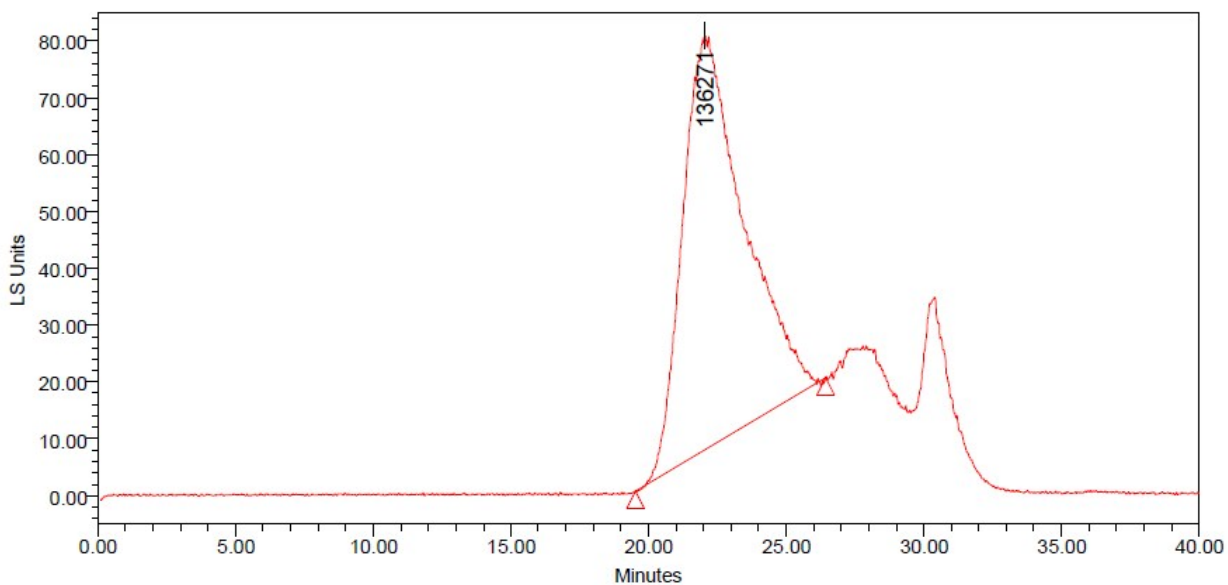


Figure S2 ¹H NMR spectrum of **P2**.



GPC Results										
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		77413	133264	155879	191403	244990		1.721463		

Figure S5 GPC plot of P2.



GPC Results										
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		74451	124956	136271	181866	237310		1.678371		

Figure S6 GPC plot of P3.

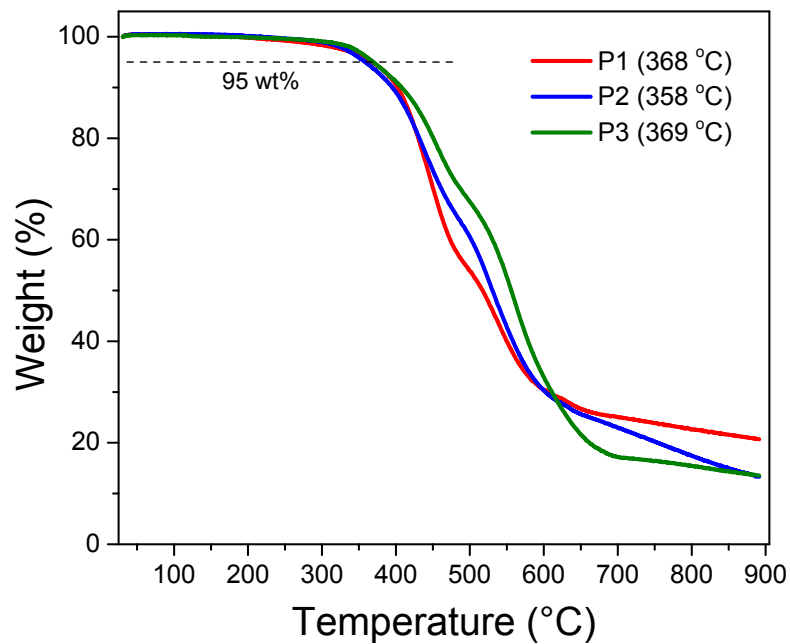


Figure S7 TGA plots of **P1-P3**.

2 UV-visible Spectra of P1-P3 Solutions

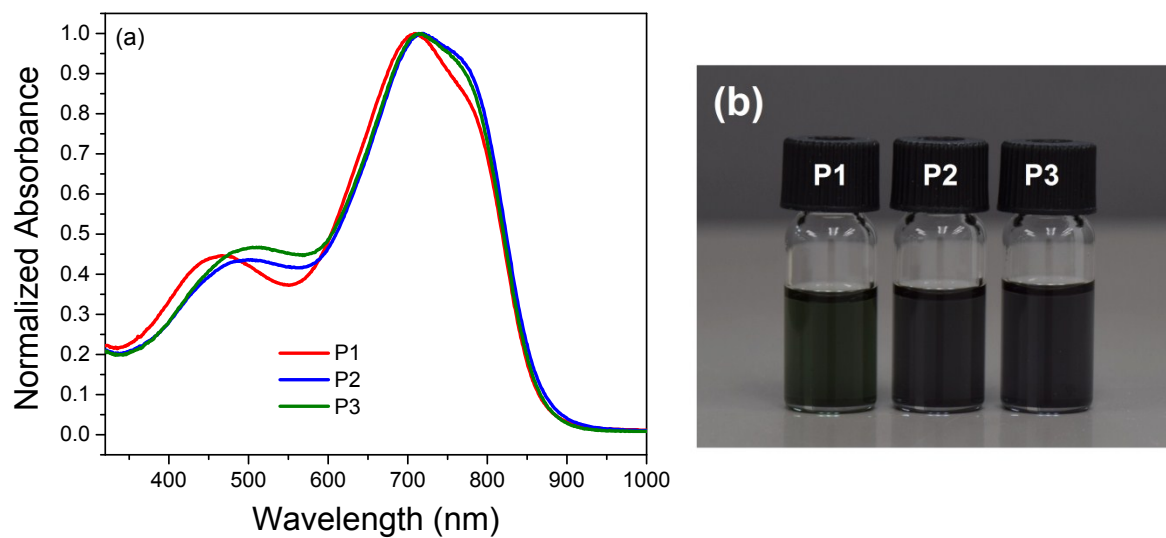


Figure S8 (a) UV-visible spectra and (b) photos of **P1-P3** dilute solutions in chloroform.

3 Cyclic Voltammograms of P1-P3 Thin Films

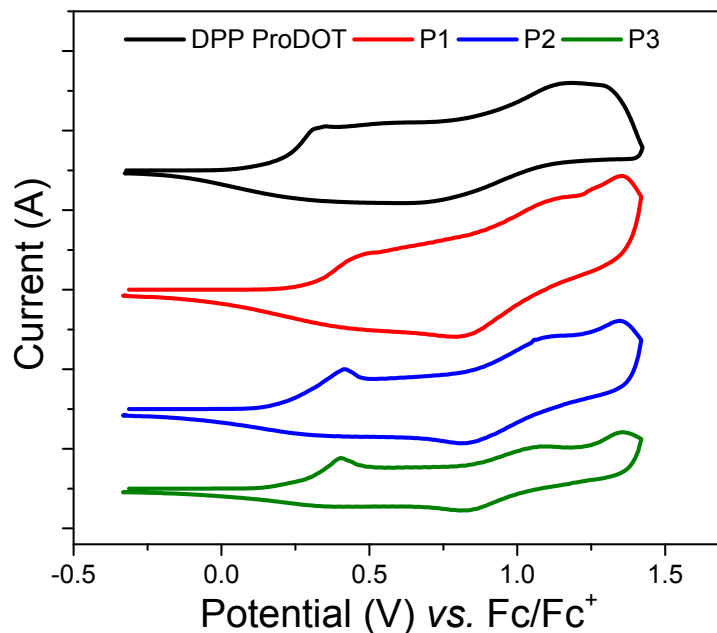


Figure S9 Cyclic voltammograms of **P1-P3** in comparison to DPP ProDOT. Measurements recorded in 0.1M LiClO₄/ACN electrolyte/solvent couple at a scan rate of 50 mV/s calibrated vs. ferrocene/ferrocenium couple.

4 Summary of Optical and Electrochemical Properties of P1-P3

Table S1 Optical and Electrochemical Properties of **P1-P3**.

Polymer	λ_{max} (nm)		λ_{onset} (nm)		E_g^{opt} (eV) ^a	$E_{\text{ox, onset}}$ (V) ^b	HOMO (eV) ^c	LUMO (eV) ^d
	Solution	Film	Solution	Film				
P1	463, 708, 774(sh)	462, 712, 784(sh)	860	872	1.42	0.26	-5.06	-3.64
P2	494, 718, 770(sh)	501, 720, 777(sh)	867	883	1.40	0.18	-4.98	-3.58
P3	500, 714, 770(sh)	504, 720, 777(sh)	863	883	1.40	0.21	-5.01	-3.61

^a $E_g^{\text{opt}} = 1240/\lambda_{\text{onset, film}}$. ^b Values are calculated vs ferrocene. ^c $E_{\text{HOMO}} = -(E_{\text{onset, ox vs ferrocene}}) - 4.8$. ^d $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$.

5 Spectroelectrochemical Graphs of P2 and P3 ECDs

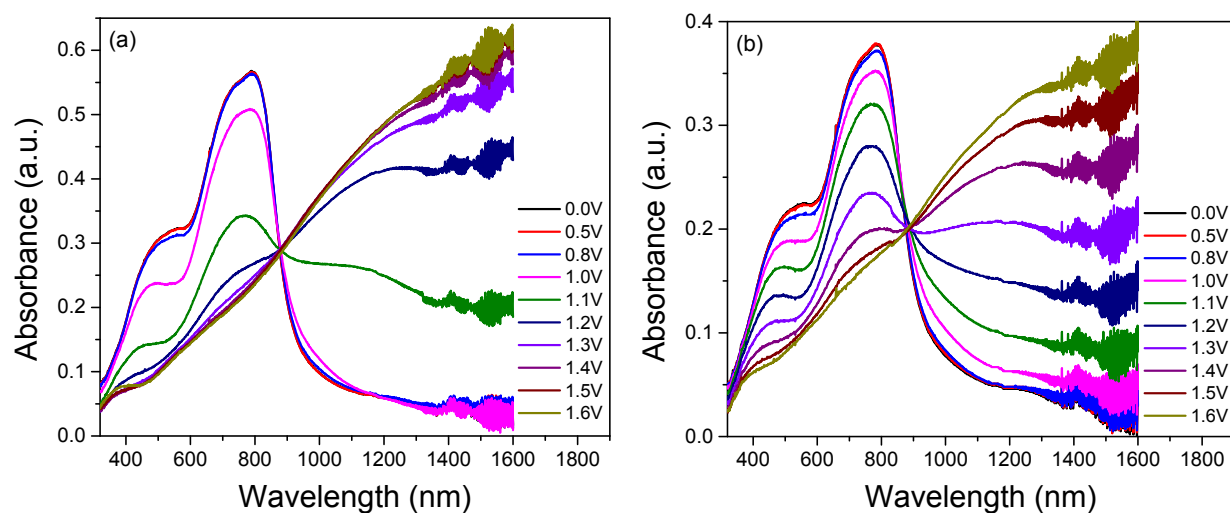


Figure S10 Spectroelectrochemical graphs of (a) **P2** and (b) **P3** ECDs.

6 Device Stability of P1 and P3 ECDs

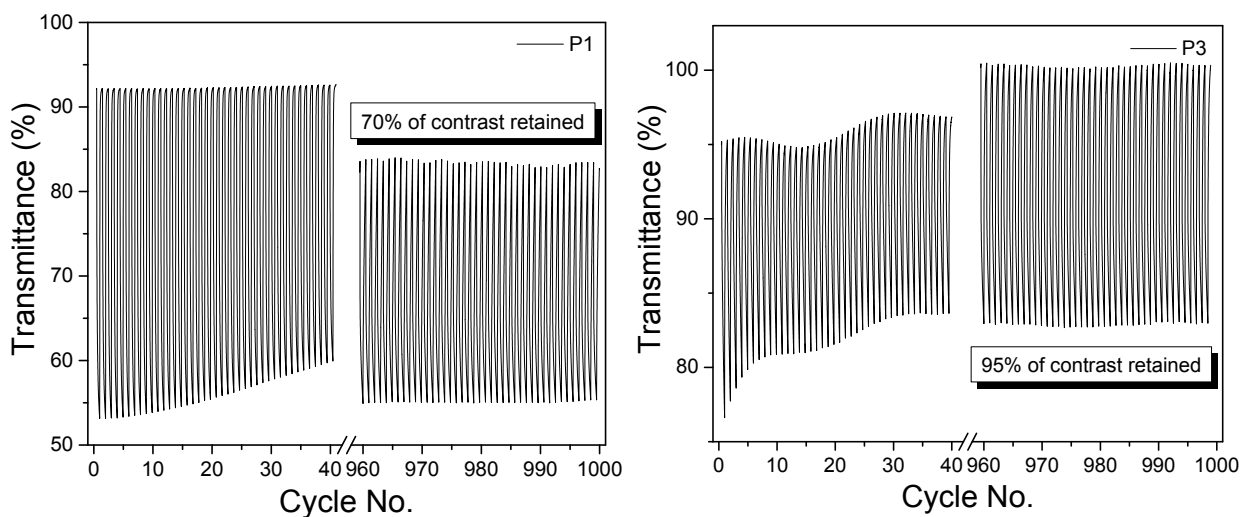


Figure S11 Switching cycles (1-40 and 961-1000) of (a) **P1** and (b) **P3** ECDs switched at 20 s cycles between +1.6 and -1.6 V at 1500 nm. A 'break-in' period of 20 s cycles was allowed.

7 Summary of Electrochromic Performance of P1-P3 ECDs

Table S2 Electrochromic Performance of **P1-P3** ECDs.

Polymer	Absorbance (a.u.)	Photopic Contrast (%) ^a	λ_1^b				λ_2 (1500 nm)			
			Contrast (%)	τ_b (s) ^c	τ_c (s) ^d	CE (cm ² /C) ^e	Contrast (%)	τ_b (s) ^c	τ_c (s) ^d	CE (cm ² /C) ^e
P1	0.62	17.2	26.4	61.38	2.00	200	59.7	4.45	19.89	253
P1	0.70	15.3	25.8	56.35	1.81	182	61.3	4.8	19.77	230
P1	0.82	11.2	17.9	75.95	3.40	130	57.6	11.33	24.51	149
P1	0.91	11.4	11.6	81.36	7.91	95	52.5	28.16	31.88	107
P1	1.08	10.1	11.9	80.41	8.34	98	53.0	29.71	31.52	108
P2	0.63	13.6	23.0	33.99	3.07	130	60.3	5.95	17.72	243
P2	0.73	12.0	21.0	41.42	3.41	115	54.0	9.33	20.39	152
P2	0.85	12.9	18.0	47.73	4.64	100	56.1	14.7	48.51	138
P2	0.93	11.5	18.9	39.88	3.14	93	54.8	11.03	22.57	126
P2	1.06	10.6	15.8	42.72	4.58	101	53.2	17.26	35.38	111
P3	0.61	13.3	15.1	72.91	14.57	107	46.0	29.13	69.39	193
P3	0.70	14.2	15.2	77.99	22.1	118	48.5	32.09	67.41	186
P3	0.81	13.3	15.8	76.89	14.85	134	48.4	27.23	66.35	200
P3	0.90	12.6	13.5	80.54	24.47	115	50.3	38.93	69.52	181
P3	0.98	12.3	15.7	79.08	17.28	147	58.0	28.33	65.42	201

^a $\Delta\%T$ integrated over 400 – 700 nm. ^b P1: 736 nm; P2: 790 nm; P3: 785 nm. ^c Bleaching time where bleaching refers to the process in which the percent transmittance changes from a lower value to a higher value. ^d Coloration time where coloration refers to the process in which the percent transmittance changes from a higher value to a lower value. ^e Coloration efficiency.

8 Computational Calculations

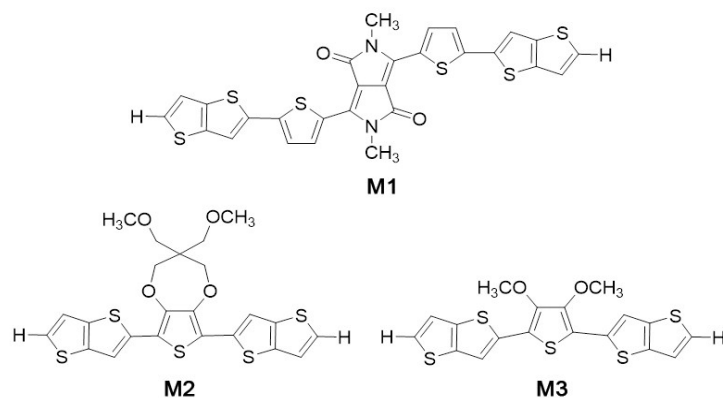
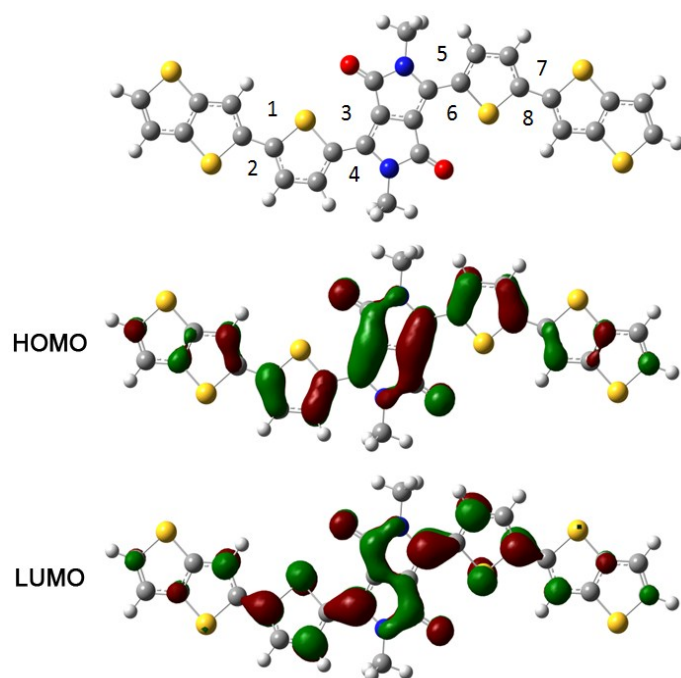
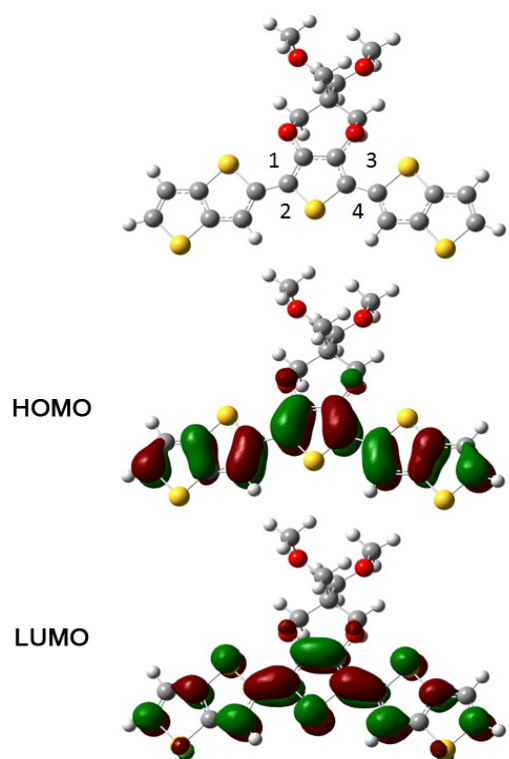


Figure S12 Molecular structures for computational study.



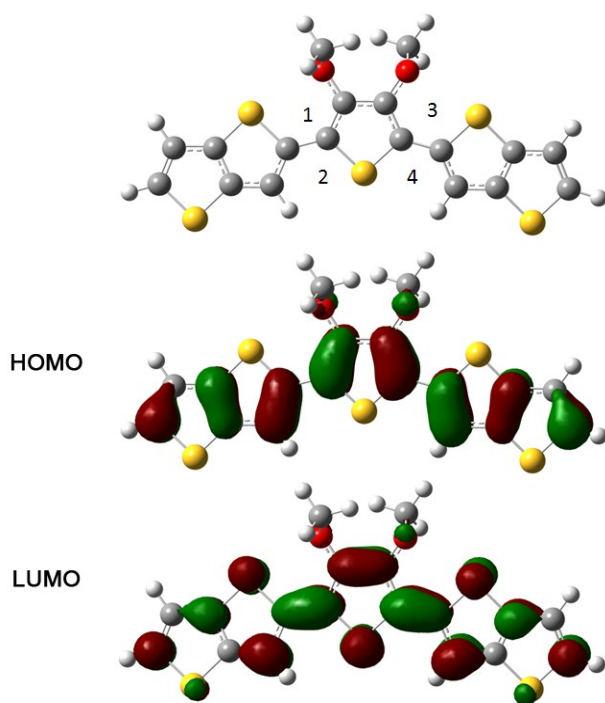
dihedral angle	(degrees)	dihedral angle	(degrees)
1	-9.6980	3	6.9758
2	-10.1765	4	7.0290
dihedral angle	(degrees)	dihedral angle	(degrees)
5	7.0206	7	-10.1565
6	6.9657	8	-9.6791

Figure S13. DFT optimized geometry and HOMO, LUMO (isovalue = 0.03) of **M1**.



dihedral angle	(degrees)	dihedral angle	(degrees)
1	-4.0973	3	3.7340
2	-5.2885	4	4.8614

Figure S14. DFT optimized geometry and HOMO, LUMO (isovalue = 0.03) of **M2**.



dihedral angle	(degrees)	dihedral angle	(degrees)
1	5.3673	3	5.3739
2	4.4677	4	4.4740

Figure S15. DFT optimized geometry and HOMO, LUMO (isovalue = 0.03) of **M3**.

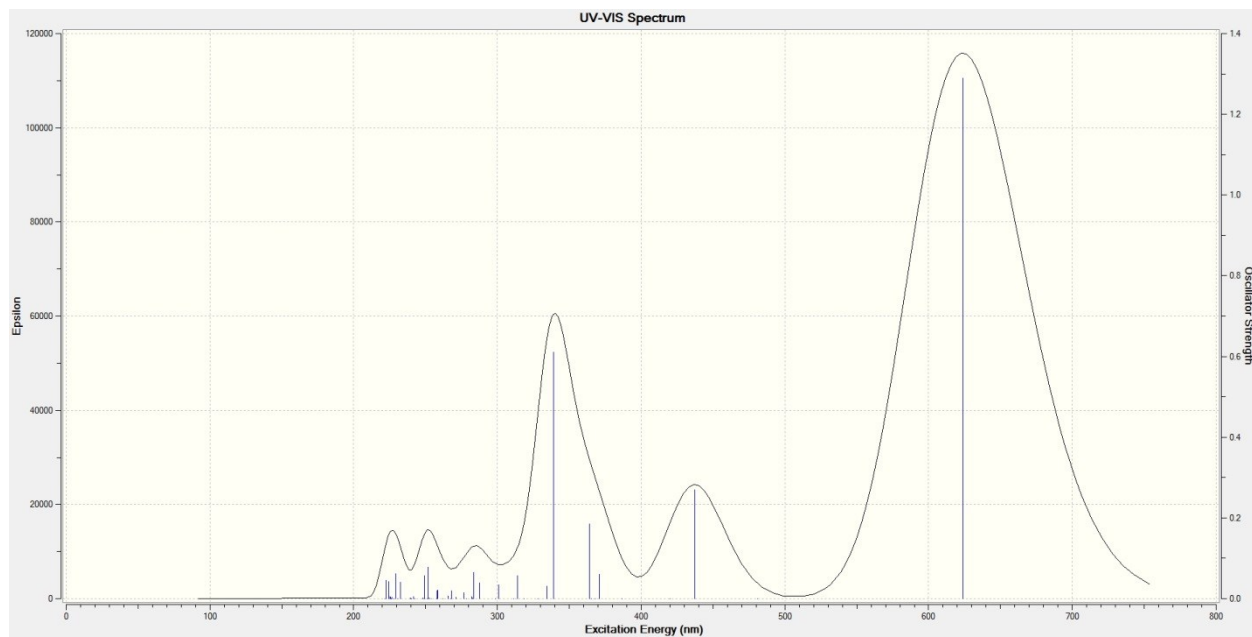


Figure S16. TD-DFT calculated UV-VIS spectrum (plotted with peak half-width at half height 0.15 eV or 1209.83 cm^{-1}) of **M1**.

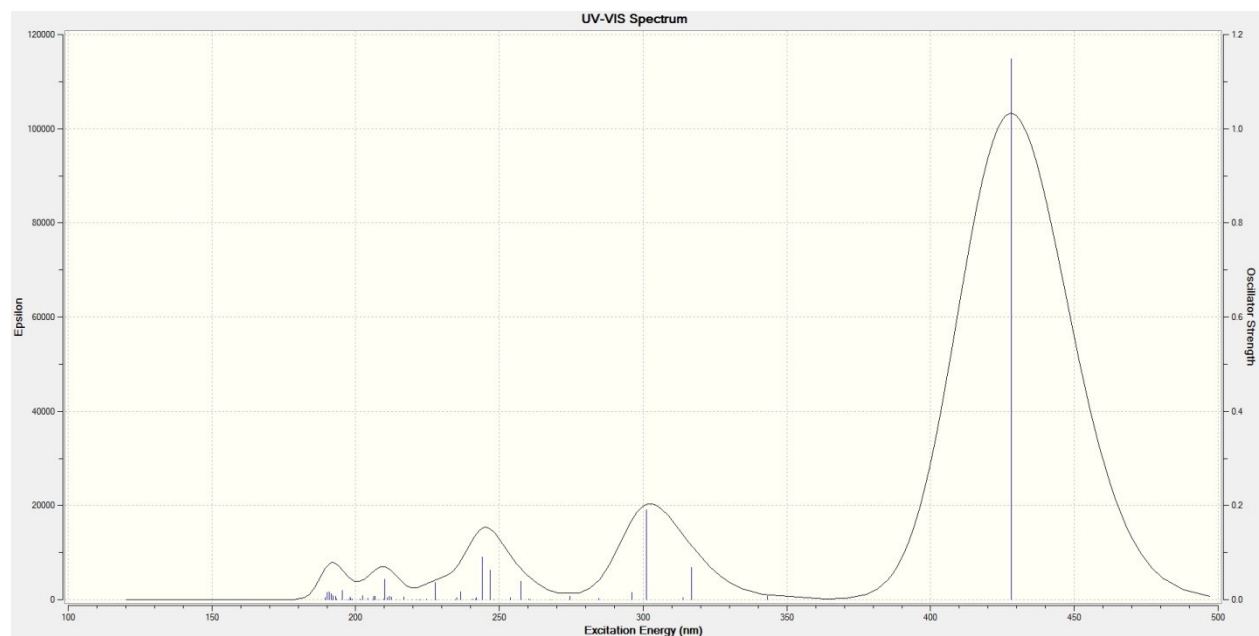


Figure S17. TD-DFT calculated UV-VIS spectrum (plotted with peak half-width at half height 0.15 eV or 1209.83 cm^{-1}) of **M2**.

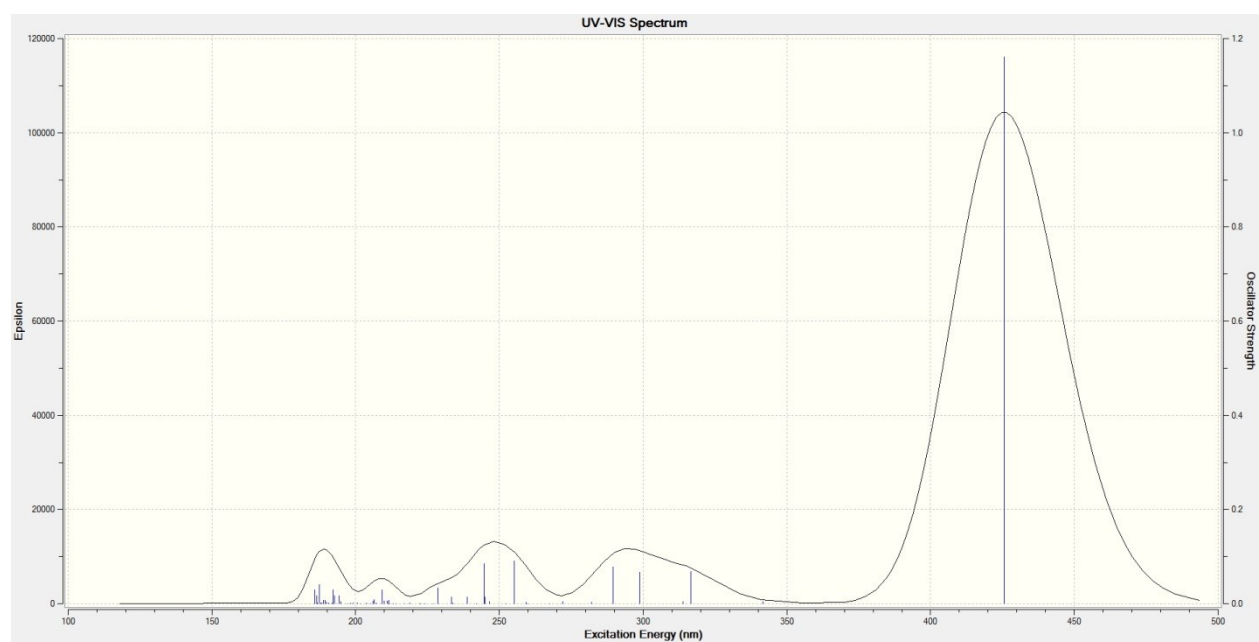


Figure S18. TD-DFT calculated UV-VIS spectrum (plotted with peak half-width at half height 0.15 eV or 1209.83 cm^{-1}) of **M3**.