Electronic Supporting Information

Towards modulating colour hues of isoindigo-based electrochromic polymers through variation of thiophene-based donor groups

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Content:

1. Optical and electrochemical properties of isoindigo polymers

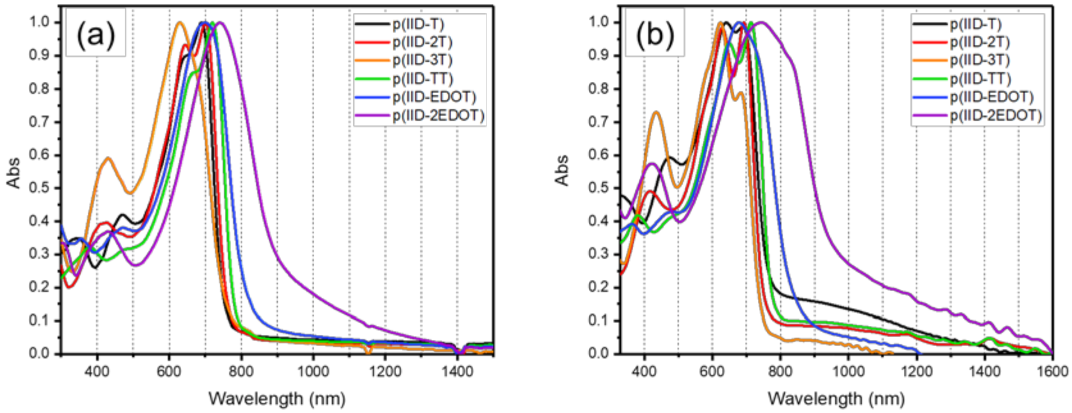


Figure S1. Normalized absorption spectra of the six synthesized isoindigo polymers in solution (a) and thin film (b).

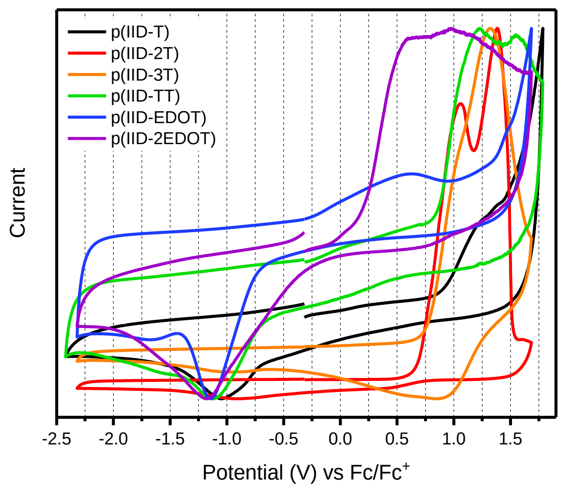


Figure S2. Cyclic voltammograms of the six synthesized isoindigo polymers.

Table S1. Reported optical and electrochemical properties of structurally analogous/similar isoindigo polymers

Analogous/ Similar Polymer	λ_{abs} Solution (nm)	λ_{abs} Thin Film (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elec} (eV)	Ref
p(IID-T)	647	604	775	1.6	-5.8	-3.95	1.86	1
	644, 691	645, 697	785	1.58	-5.8	-3.81	1.99	2
p(IID-2T)	647, 706	637, 701	780	1.59	-5.65	-3.78	1.87	2
p(IID-3T)	628	628, 682	785	1.58	-5.48	-3.70	1.78	2
p(IID-TT)	666, 723	656, 720	800	1.55	-5.70	-3.73	1.97	2
p(IID-EDOT)	-	675, 735 (sh)	802	1.55	-5.34	-3.94	1.40	3
p(IID-2EDOT)	-	424, 736	984	1.26	-4.8	-3.48	-	4
	799	785	932	1.33	-	-	1.45	5

2. Surface morphology of spin-coated polymer thin films

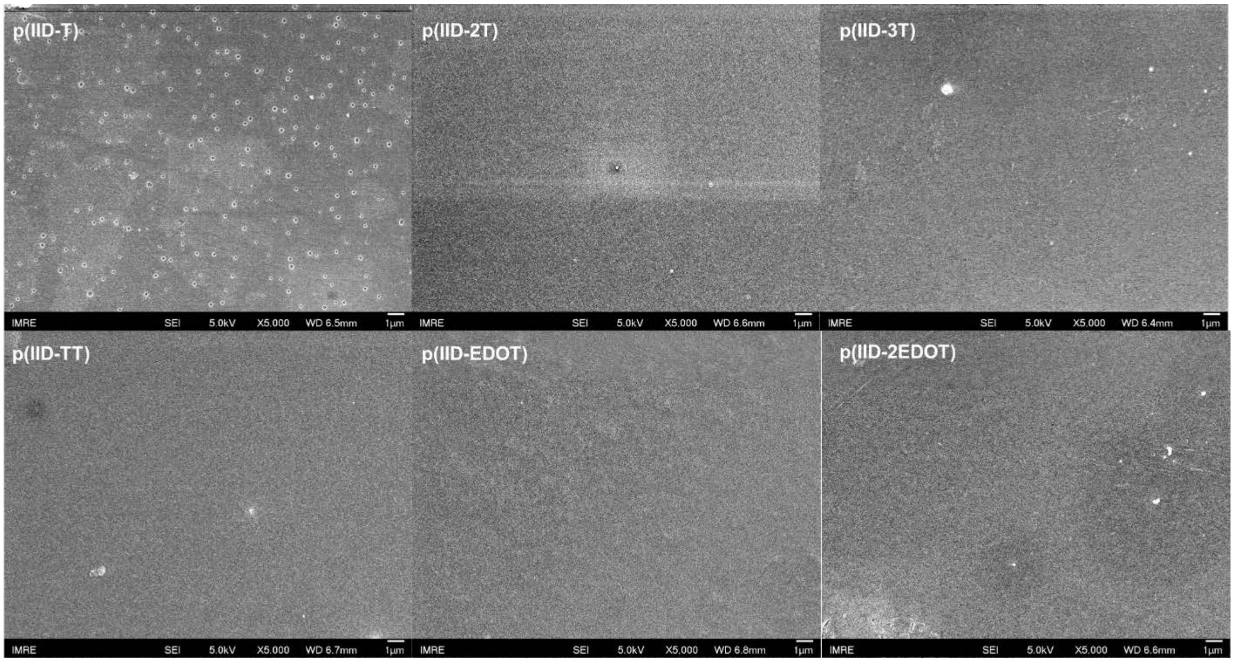


Figure S3. SEM images of the surfaces of the six polymer thin films under 1 μm magnification.

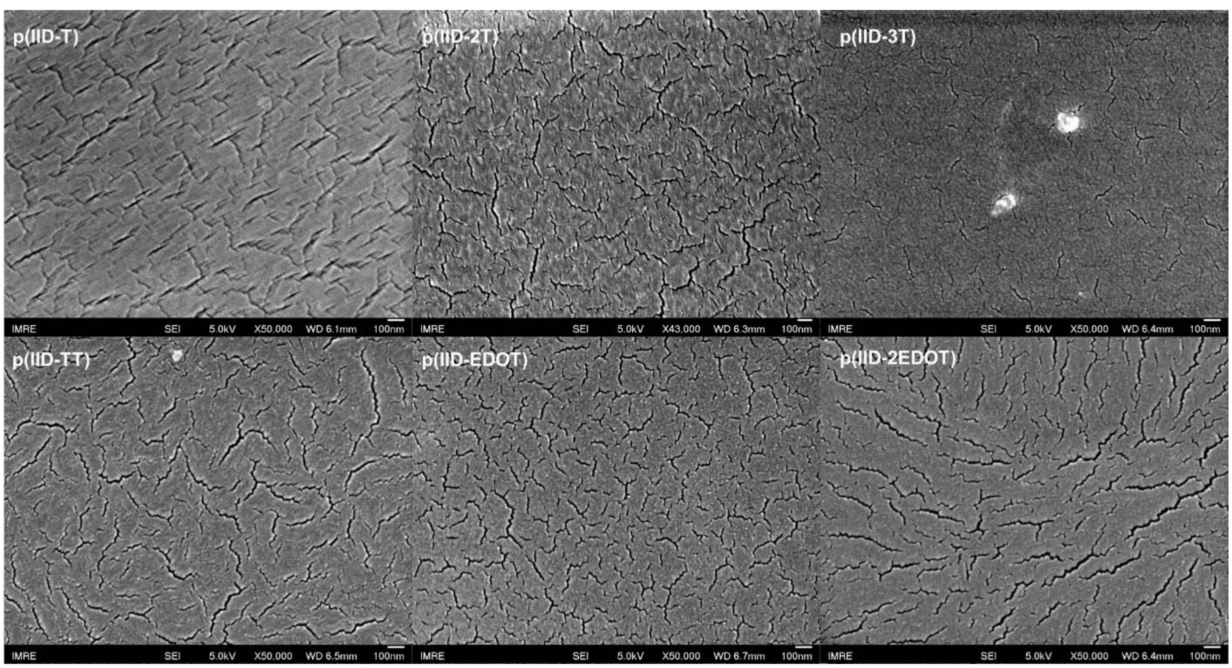


Figure S4. SEM images of the surfaces of the six polymer thin films under 100 nm magnification.

3. Spectroelectrochemistry of polymers under the application of negative voltages

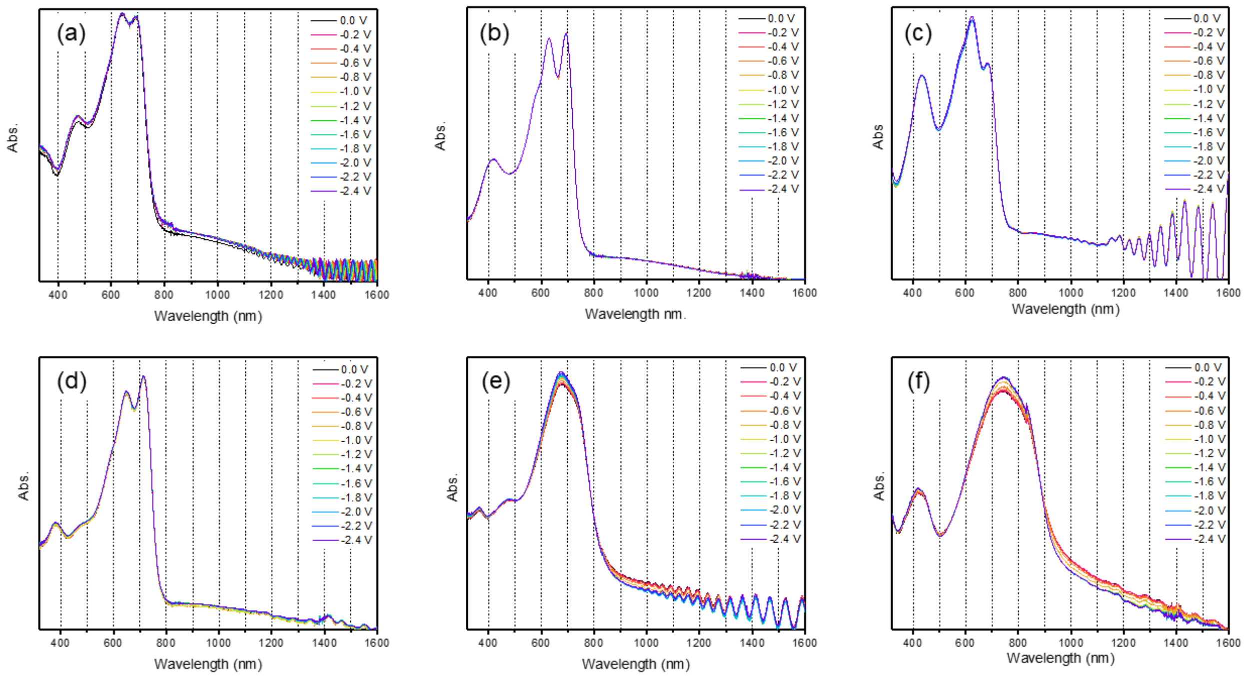


Figure S5. Spectroelectrochemistry of isoindigo polymers (a) **p(IID-T)**, (b) **p(IID-2T)**, (c) **p(IID-3T)**, (d) **p(IID-TT)**, (e) **p(IID-EDOT)** and (f) **p(IID-2EDOT)**, undergo electrochemical reductive doping.

4. Electrochromic switching studies

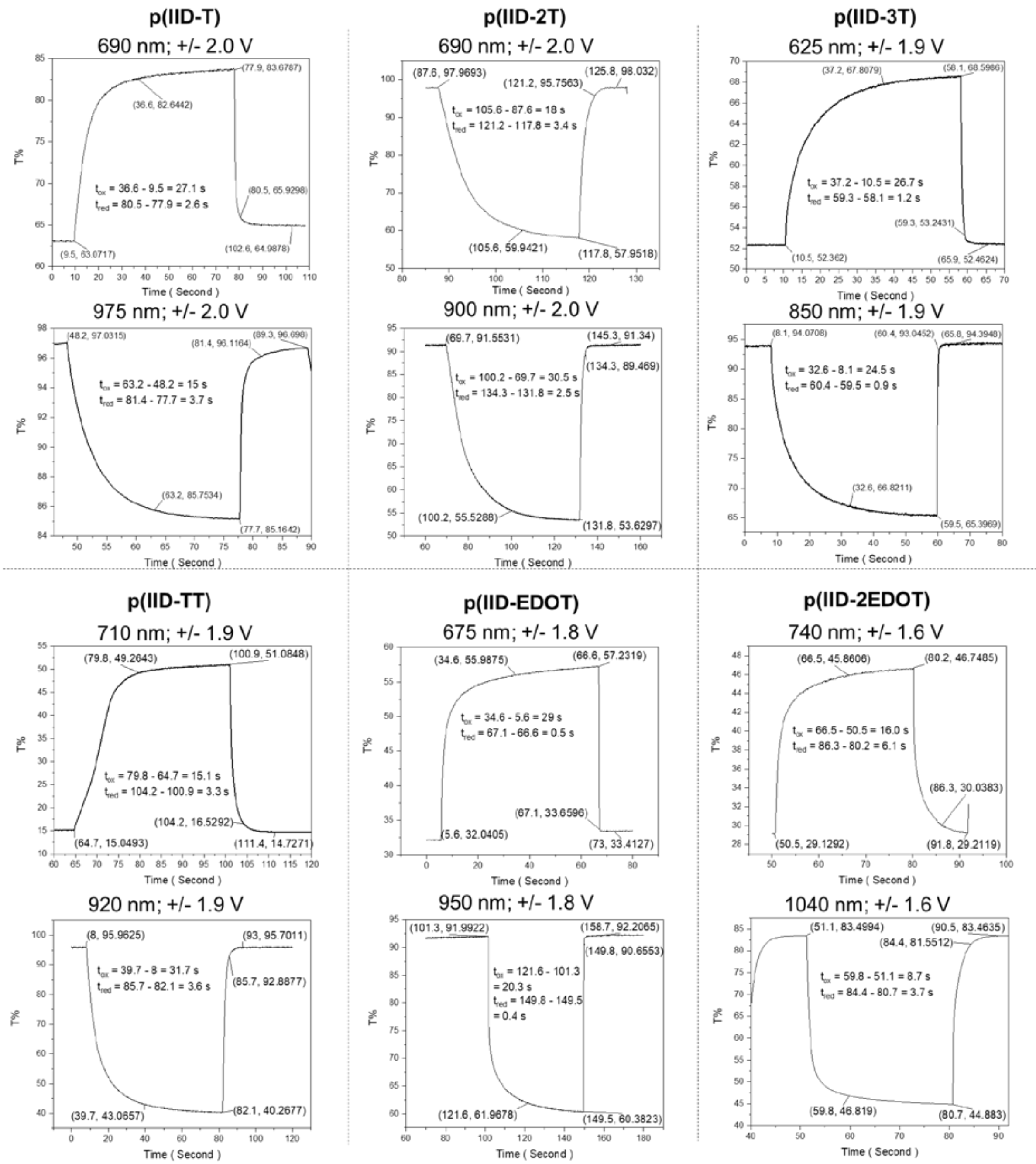


Figure S6. EC switching response time measurements of the six polymers.

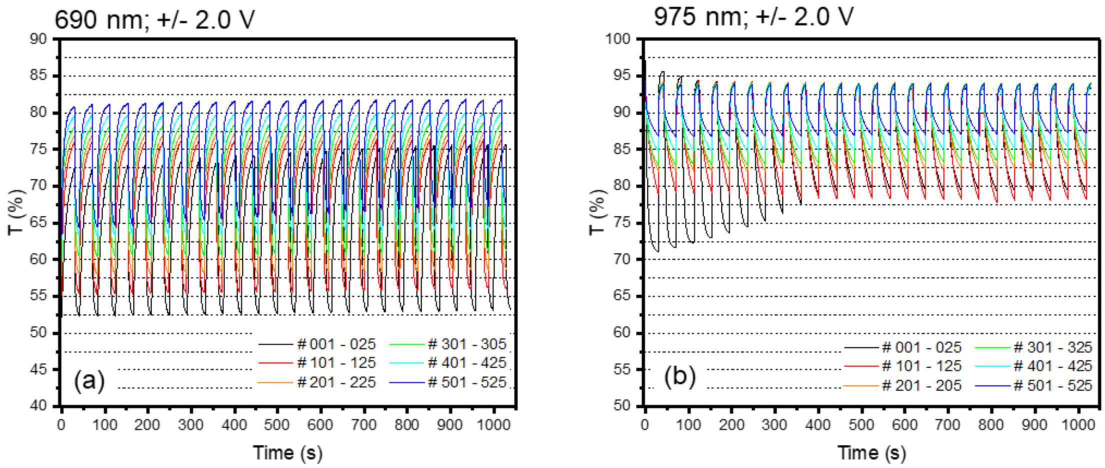


Figure S7. Square-wave potential step absorptiometry of polymer **p(IID-T)** (showing different sets of 25 cycles) undergoing EC switching at (a) 690 nm and (b) 975 nm at +/- 2.0 V, 30s/10s oxidation/reduction cycling intervals.

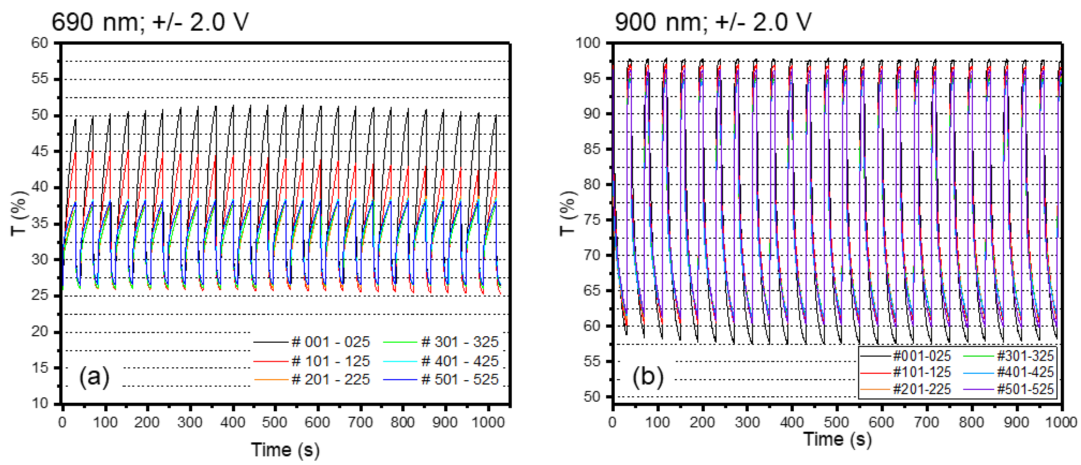


Figure S8. Square-wave potential step absorptiometry of polymer **p(IID-2T)** (showing different sets of 25 cycles) undergoing EC switching at (a) 690 nm and (b) 900 nm at +/- 2.0 V, 30s/10s oxidation/reduction cycling intervals.

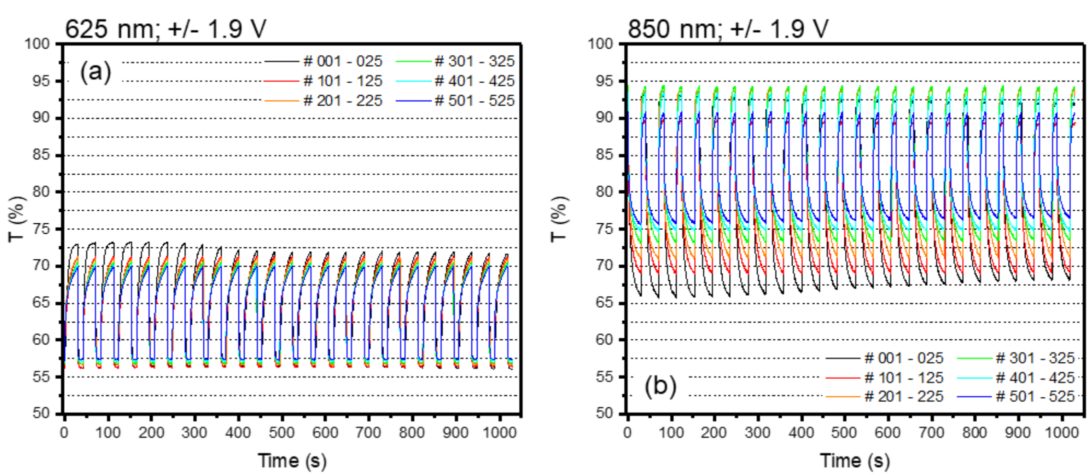


Figure S9. Square-wave potential step absorptiometry of polymer **p(IID-3T)** (showing different sets of 25 cycles) undergoing EC switching at (a) 625 nm and (b) 850 nm at +/- 1.9 V, 30s/10s oxidation/reduction cycling intervals.

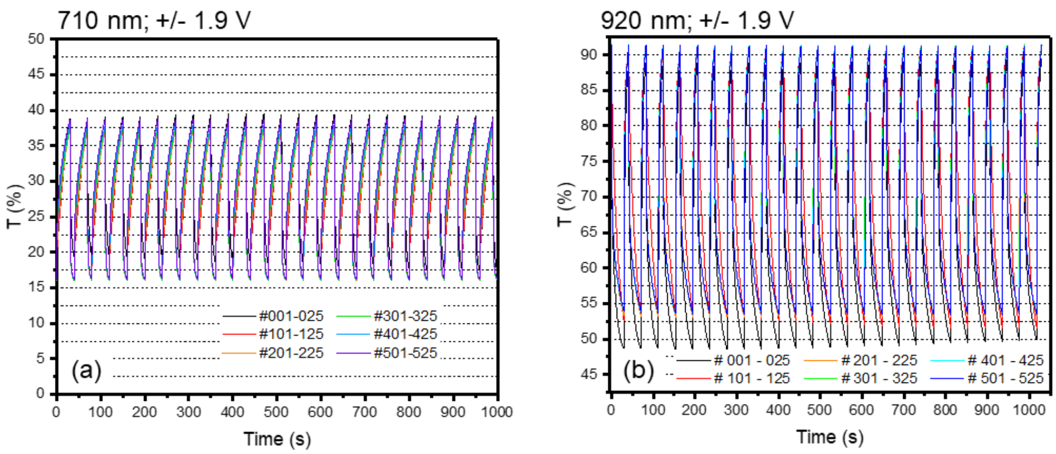


Figure S10. Square-wave potential step absorptiometry of polymer **p(IID-TT)** (showing different sets of 25 cycles) undergoing EC switching at (a) 710 nm and (b) 920 nm at +/- 1.9 V, 30s/10s oxidation/reduction cycling intervals.

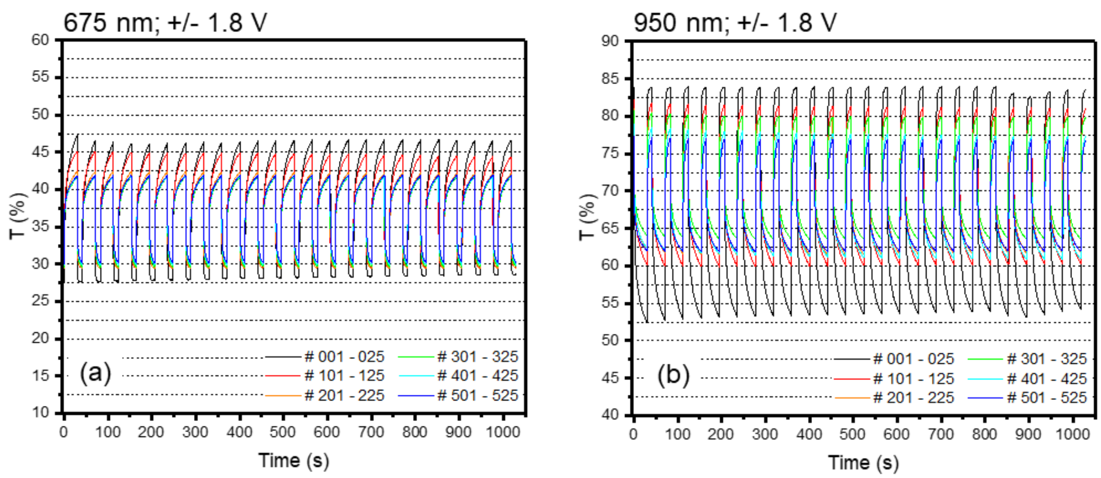


Figure S11. Square-wave potential step absorptiometry of polymer **p(IID-EDOT)** (showing different sets of 25 cycles) undergoing EC switching at (a) 675 nm and (b) 950 nm at +/- 1.8 V, 30s/10s oxidation/reduction cycling intervals.

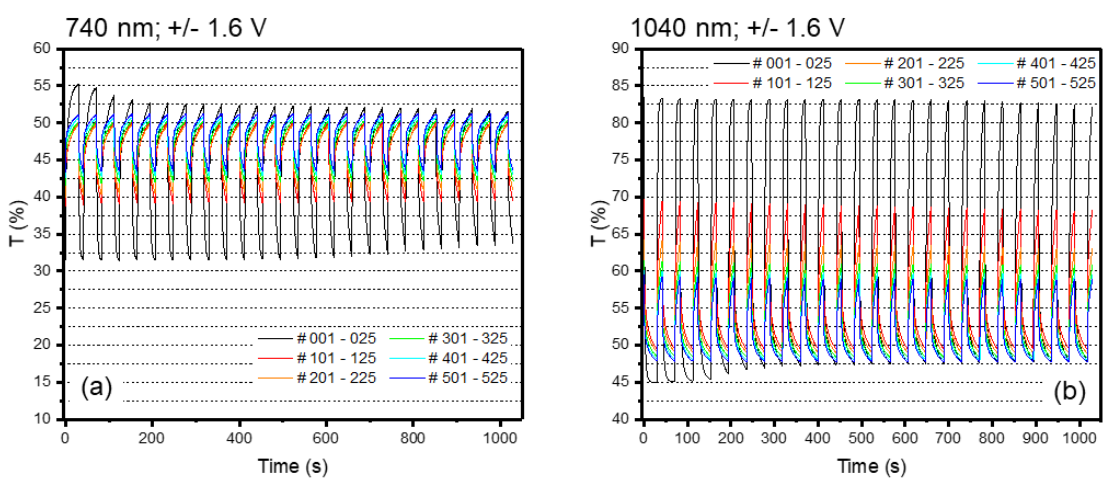
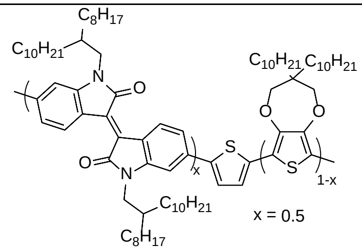
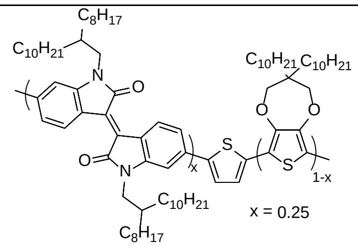
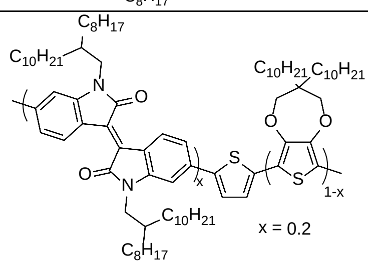
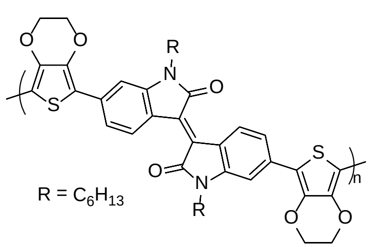
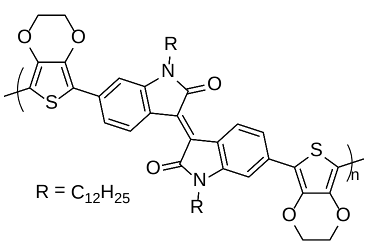
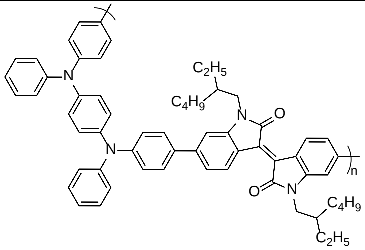
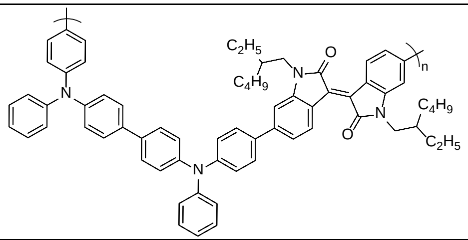
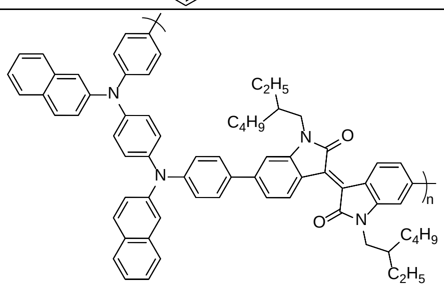
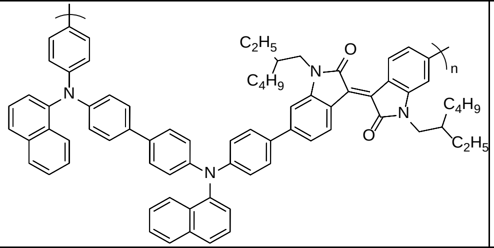
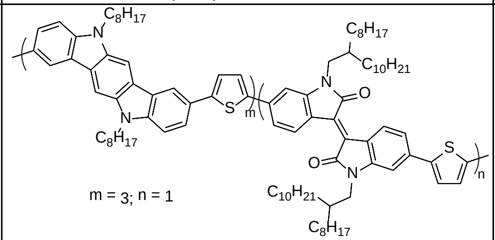
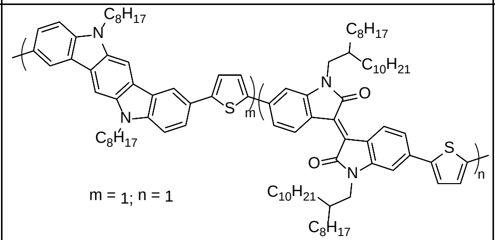
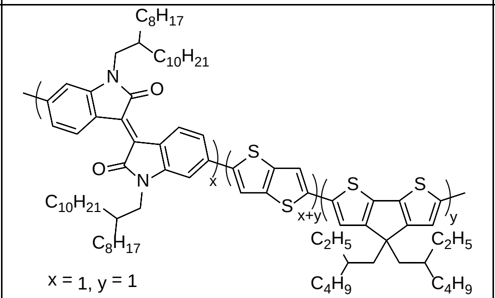


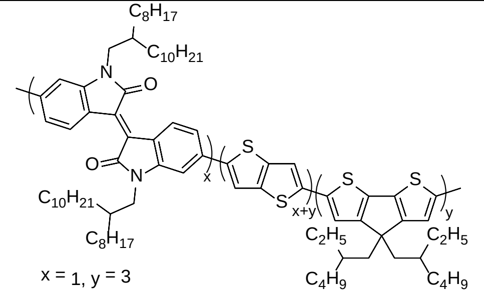
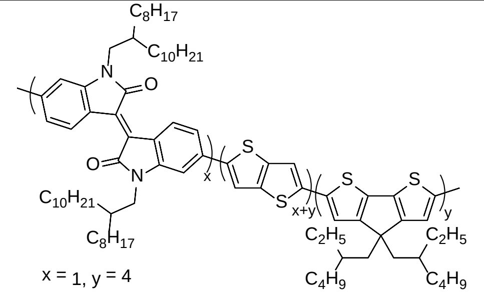
Figure S12. Square-wave potential step absorptiometry of polymer **p(IID-2EDOT)** (showing different sets of 25 cycles) undergoing EC switching at (a) 740 nm and (b) 1040 nm at +/- 1.6 V, 30s/10s oxidation/reduction cycling intervals.

Table S2. EC switching properties of reported isoindigo polymers

S/ No.	Chemical Structure	Neutral Colour	Oxidised Colour	λ_{abs} neutral (nm)	λ_{abs} ox (nm)	$\lambda_{Switching}$ (nm)	Δ%T (%)	τ_B (s)	τ_C (s)	CE (cm^2 C^{-1})	Cycling Intervals	Cycling Stability	Ref
1		Cyan	Transmissive Grey	663	915, 1350	460 660 1600	8.7 11.4 27.4	2.85 2.92 -	- - 0.45	53.15 38.14 162.49	+/- 1.5V 1 – 10 s	~ 40 Cycles	6
2		Black	Transmissive Light Grey	646	903, 1396	520 660 1600	21.0 28.0 34.1	1.90 1.02 -	- - 0.38	155.97 145.61 181.73	+/- 1.5V 1 – 10 s	~ 40 Cycles	6
3		Black	Transmissive Light Grey	482	931, 1330	510 850 1330	20.6 17.8 31.3	0.72 0.88 -	- - 0.77	167.61 50.38 96.88	+/- 1.5V 1 – 10 s	~ 40 Cycles	6
4		Green L* = 72.84 a* = 7.74 b* = 0.03	Wathet Blue L* = 73.81 a* = 3.30, b* = 5.71	424 714	330 to 1600	424 714 1000 1500 1600	35 27 81 78 86	0.98 1.07 0.78 0.75 0.83	0.68 0.66 1.34 1.34 1.39	64 305 292 105 192	0.9 V 1 – 10s	~ 60 Cycles	4

5		Light green L* = 156.41, a* = 6.39 b* = 4.03	Blue L* = 150.35, a* = 10.20, b* = 5.22	427 733	330 to 1600	427 733 1050 1500 1600	50 29 83 91 81	0.77 0.74 0.82 0.91 0.78	0.63 0.51 1.23 1.44 1.36	268 318 362 144 122	1.2 V 1 – 10s	~ 60 Cycles	4
6		Colourless	Green then blue	460	928	460	34.8	3.5	2.8	93	0 – 1.4 V; 5 s	~50 cycles	7
7		Colourless	Green then dark blue	496	1237	496	47.6	3.4	2.6	195	0 – 1.4 V; 5 s	~50 cycles	7
8		Colourless	Green then blue	453	981	453	42.2	3.1	3.9	182	0 – 1.4 V; 5 s	~50 cycles	7

9		Colourless	Pale brown then blue	480	1271	480	43.1	2.8	3.7	131	0 – 1.4 V; 5 s	~50 cycles	7
10	 m = 3; n = 1	Cyan L* = 71.60, a* = −6.79, b* = 0.24	Grey L* = 72.08, a* = −0.45, b* = −0.72	355 674	1500	670, 1500	12 33	2.89 2.36	0.39 2.23	52.94 92.92	0 – 1.35 V; 4s	~ 40 cycles	8
11	 m = 1; n = 1	Cyan L* = 63.25, a* = 8.60, b* = −1.67	Grey L* = 65.15, a* = 0.45, b* = 2.15	353 672	1550	675 1600	18 58	2.04 1.5	0.33 1.35	171.52 153.08	0 – 1.35 V; 4s	~ 40 cycles	8
12	 x = 1, y = 1	Greenish brown	Livid blue	657	1580	700 1520	23.8 72.7	1.85 -	- 0.78	210 467	1.3 V 1 – 10s	~ 200 Cycles	9

13		Antique violet	Greyish blue	554	1600	550 1510	41.1 56.9	0.67 -	- 0.94	254 300	1.3 V 1 – 10s	~ 200 Cycles	9
14		Dark red	Transparent blue	547	1580	545 1550	38.2 80.8	1.26 -	- 0.36	268 389	1.1 V 1 – 10s	~ 200 Cycles	9

References

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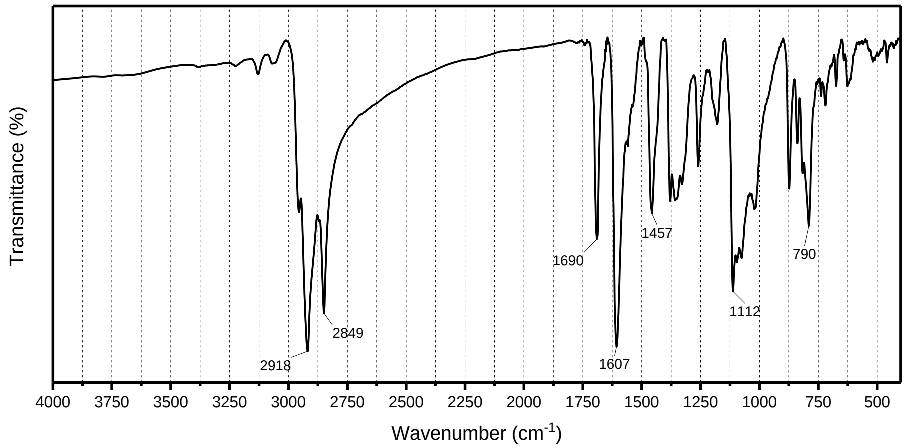
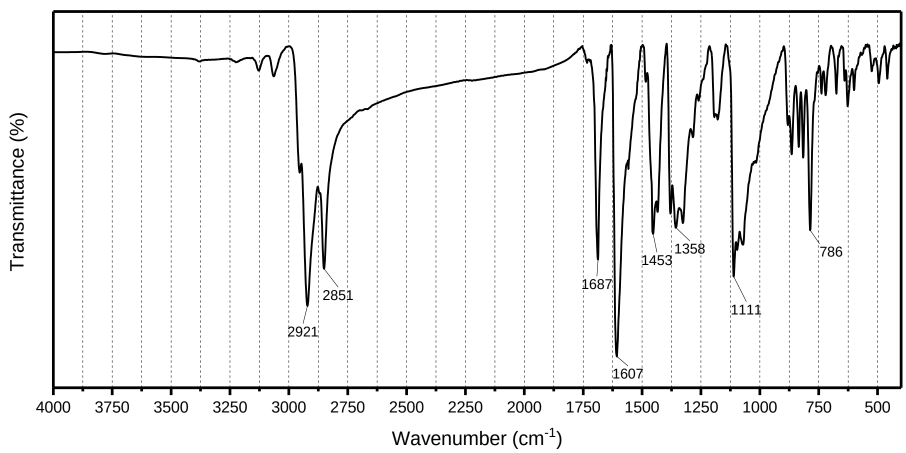
9. X. Cheng, Y. Ma, X. Ju, W. Zhao, J. Zhao, Q. Li, Z. Sang, H. Du and Y. Zhang, *Synthetic Metals*, 2020, **270**, 116589.

APPENDIX

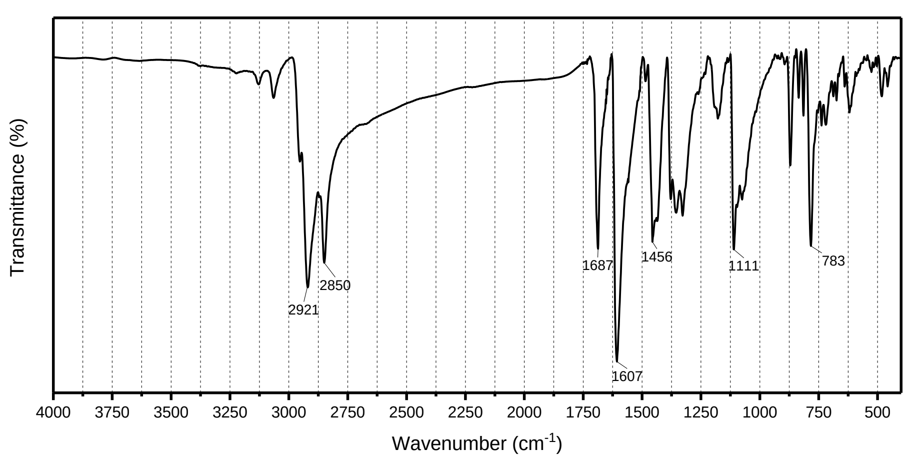
FTIR spectrum of **p(IID-T)**



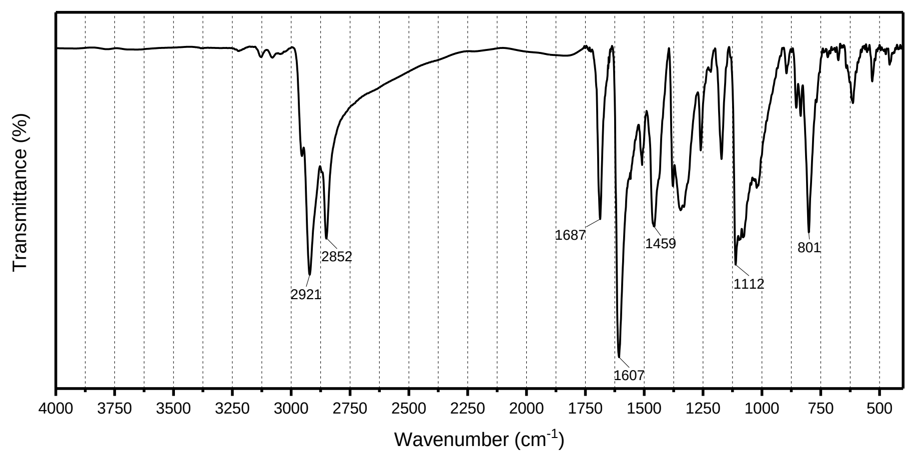
FTIR spectrum of **p(IID-2T)**



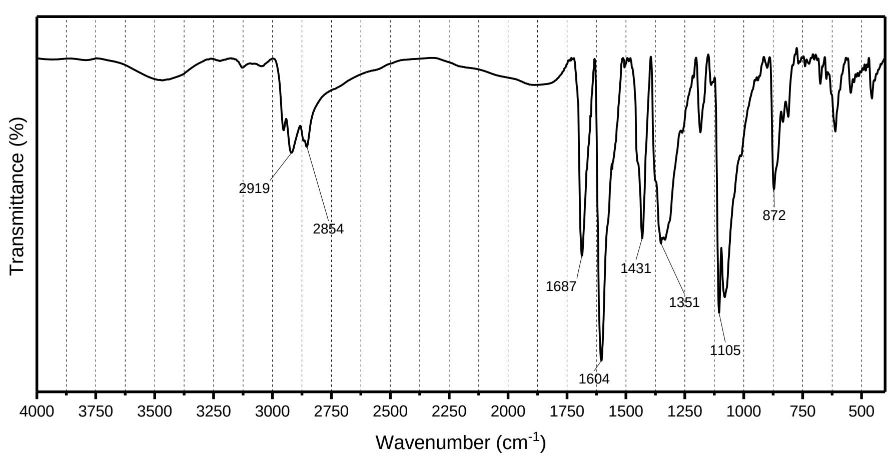
FTIR spectrum of **p(IID-3T)**



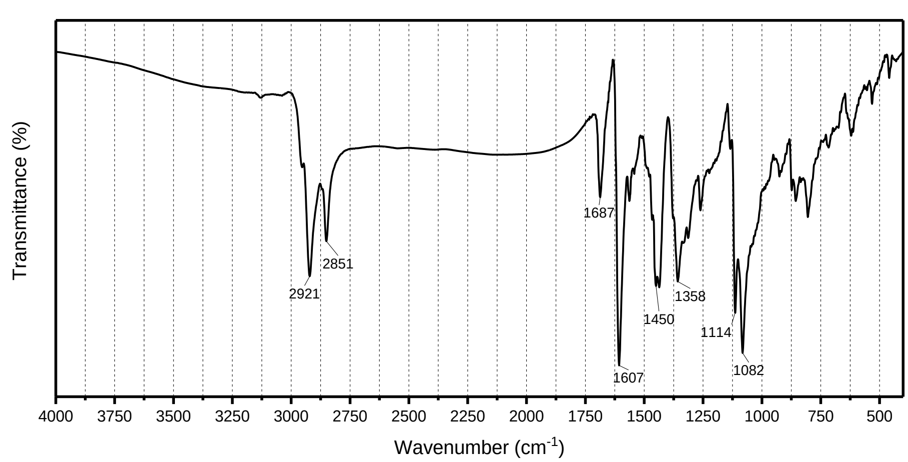
FTIR spectrum of **p(IID-TT)**



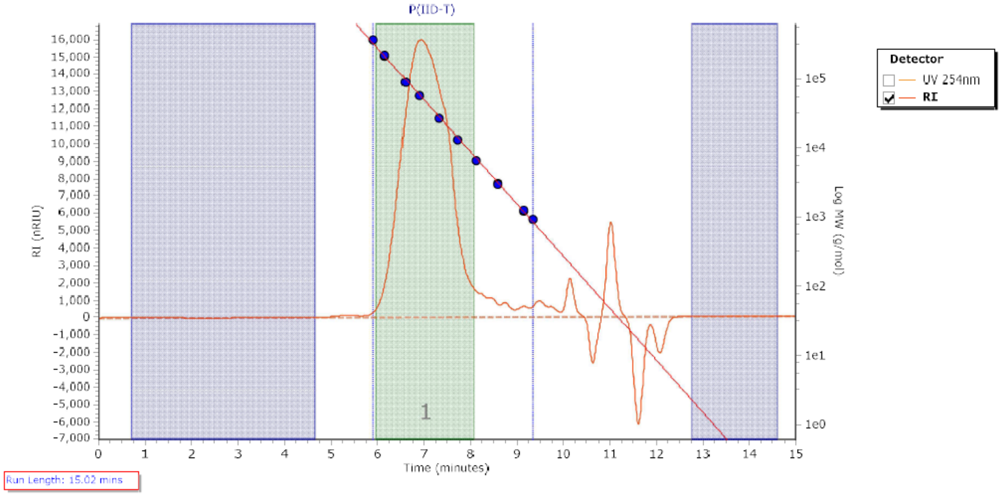
FTIR spectrum of **p(IID-EDOT)**



FTIR spectrum of **p(IID-2EDOT)**



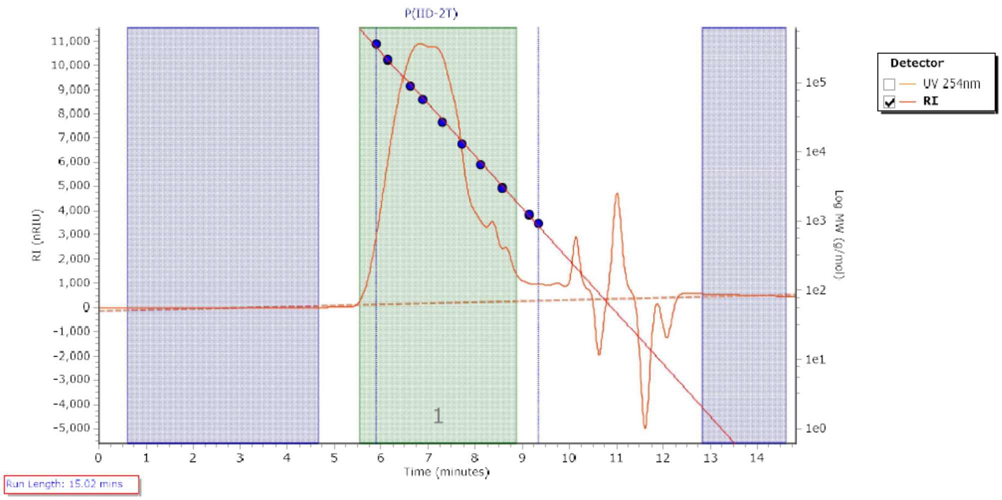
GPC chromatogram of **p(IID-T)**



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	55362	34652	58090	89614	122378	84876	1.676

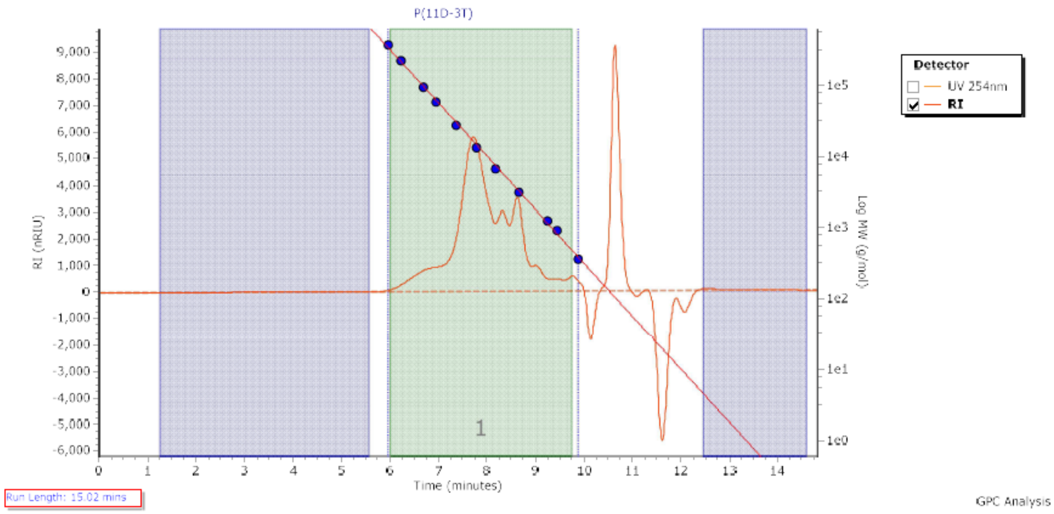
GPC chromatogram of **p(IID-2T)**



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	66811	18835	74570	164097	246688	151779	3.959

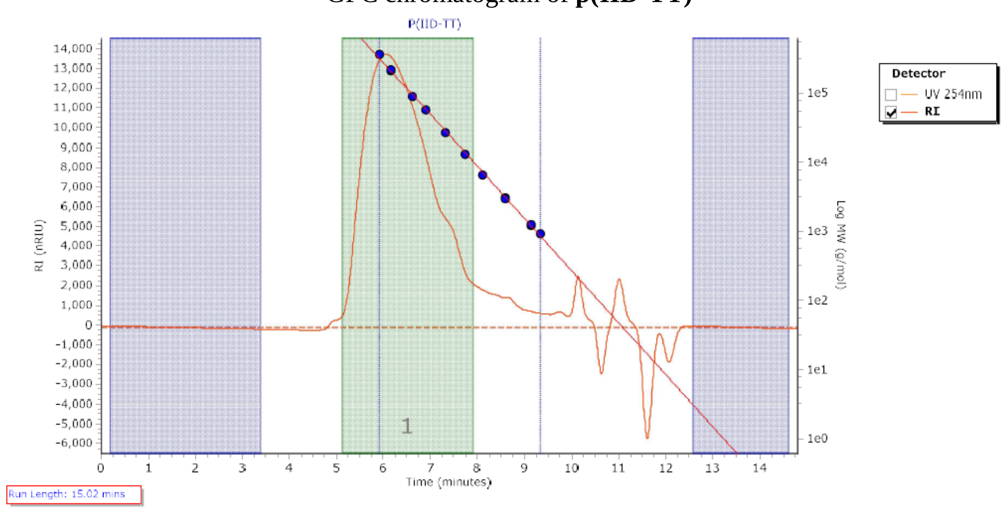
GPC chromatogram of **p(IID-3T)**



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15983	5356	20739	69776	137148	60555	3.872

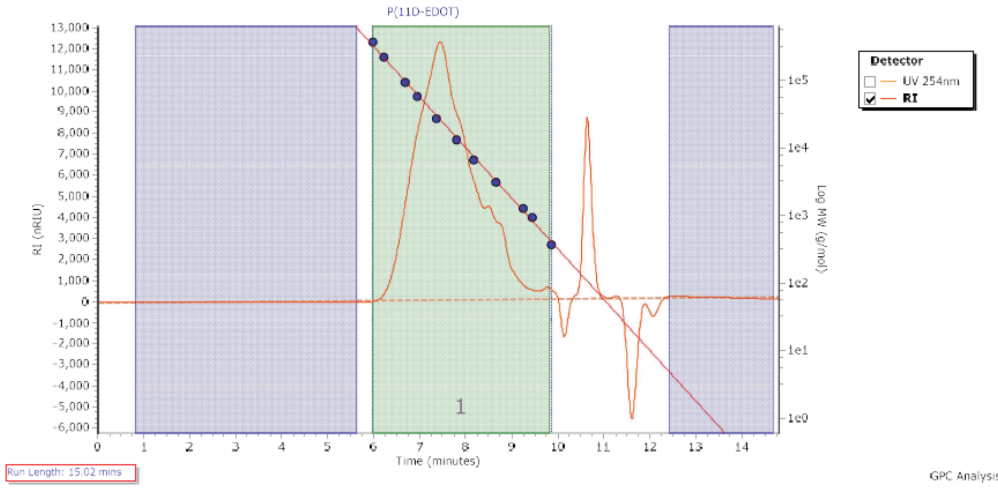
GPC chromatogram of **p(IID-TT)**



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	241965	74865	225342	422193	577679	397513	3.01

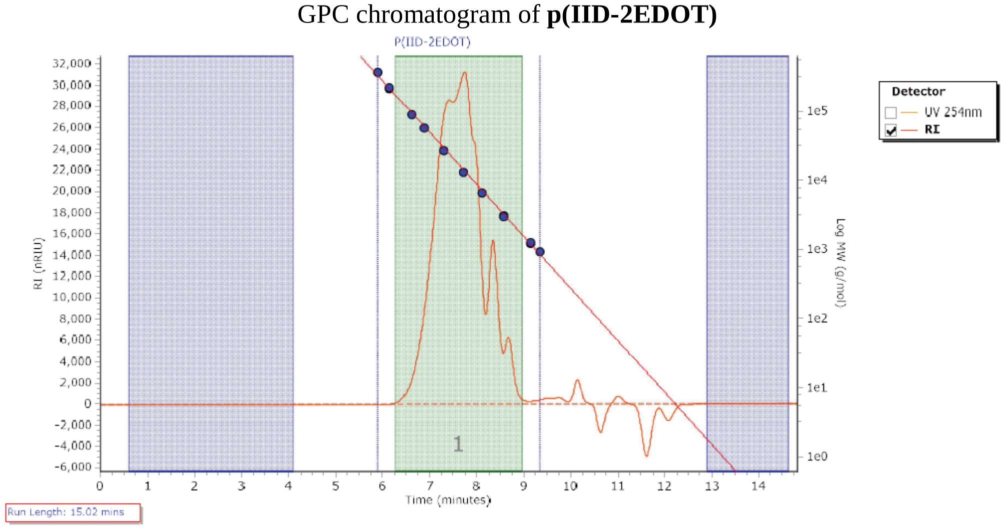
GPC chromatogram of **p(IID-EDOT)**



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	25652	8510	31235	63526	95566	58946	3.67

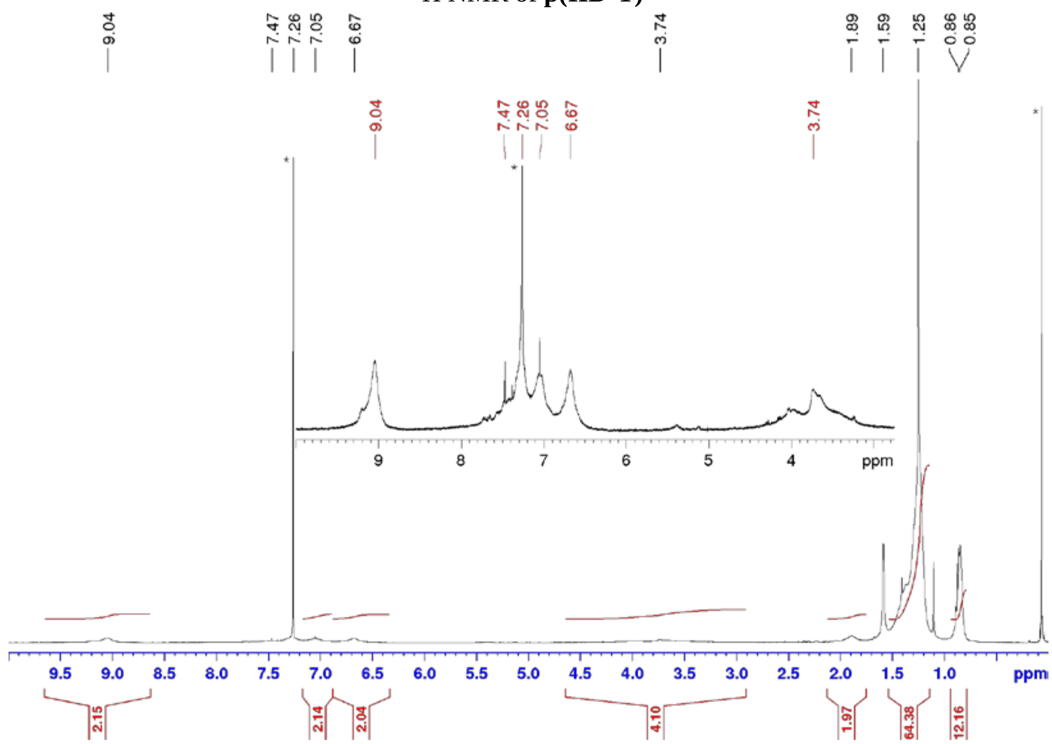
GPC chromatogram of **p(IID-2EDOT)**



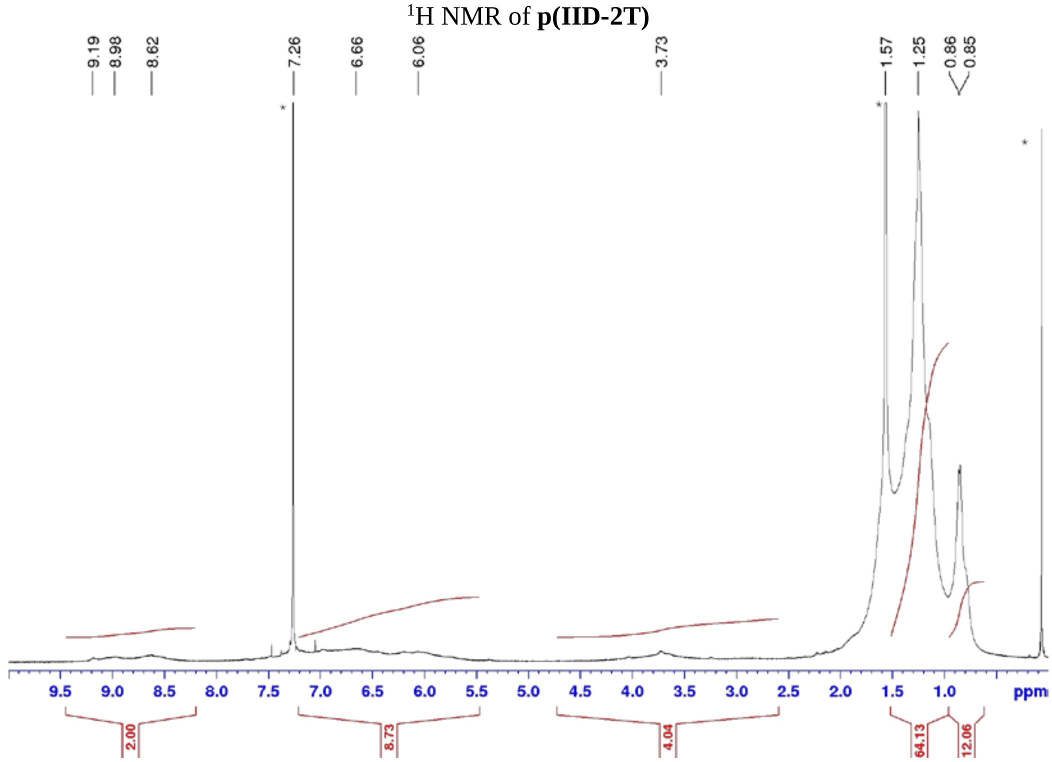
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13421	11088	21703	37087	55440	34644	1.957

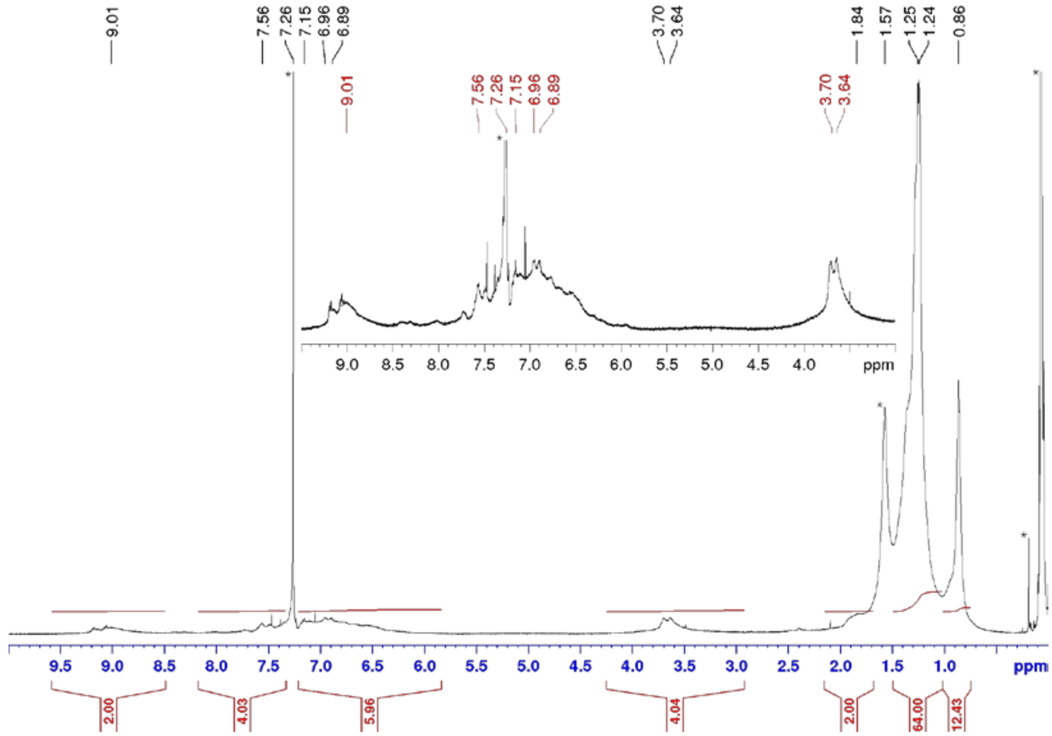
[1]H NMR of **p(IID-T)**



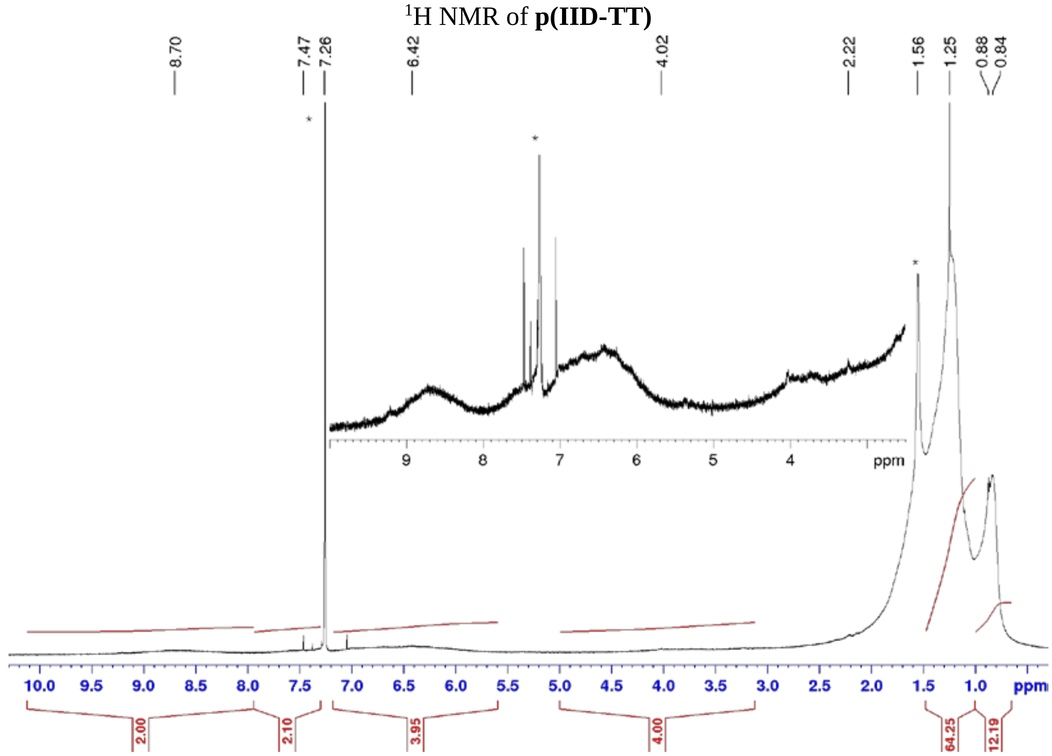
[1]H NMR of **p(IID-2T)**



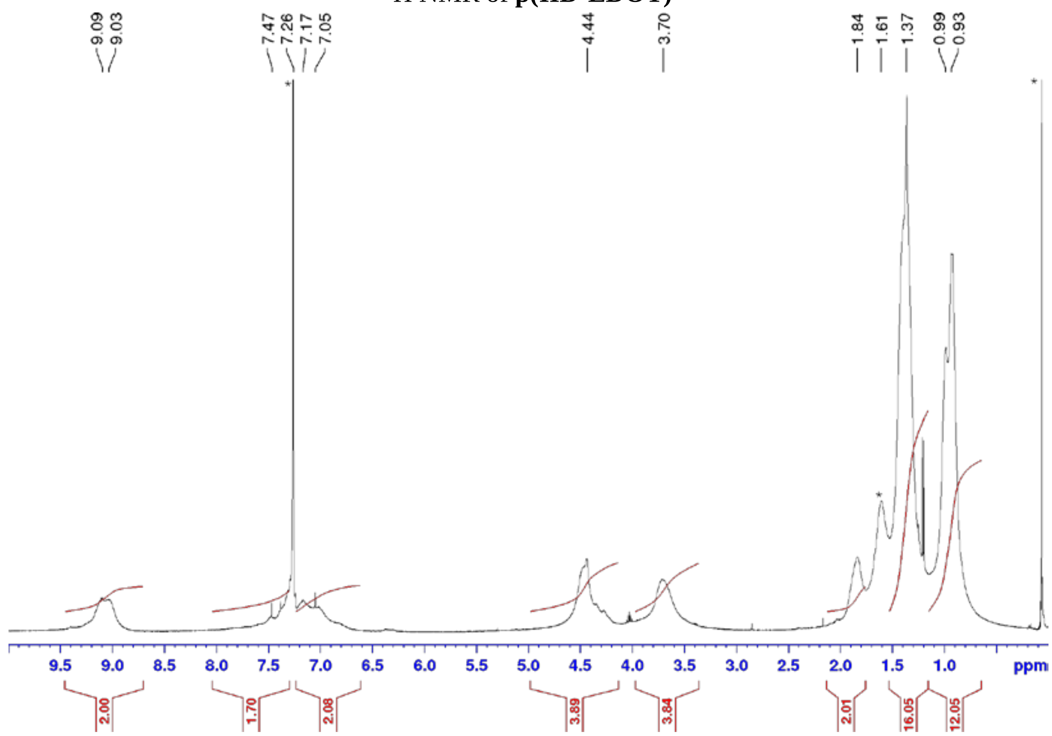
^{1}H NMR of **p(IID-3T)**



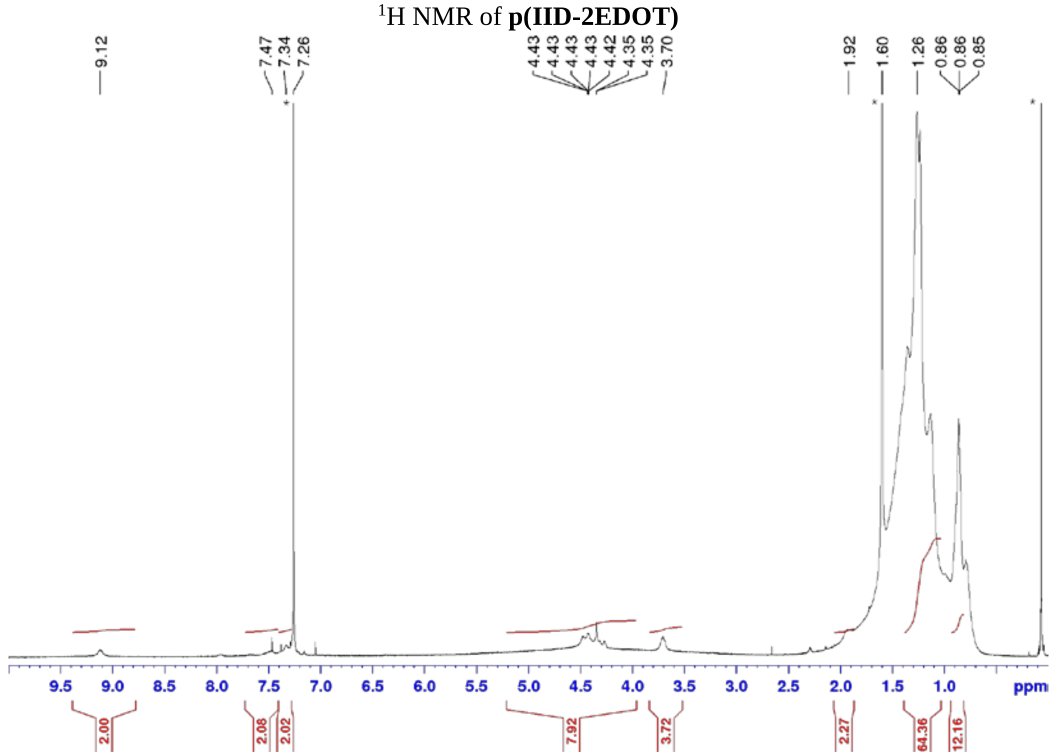
^{1}H NMR of **p(IID-TT)**



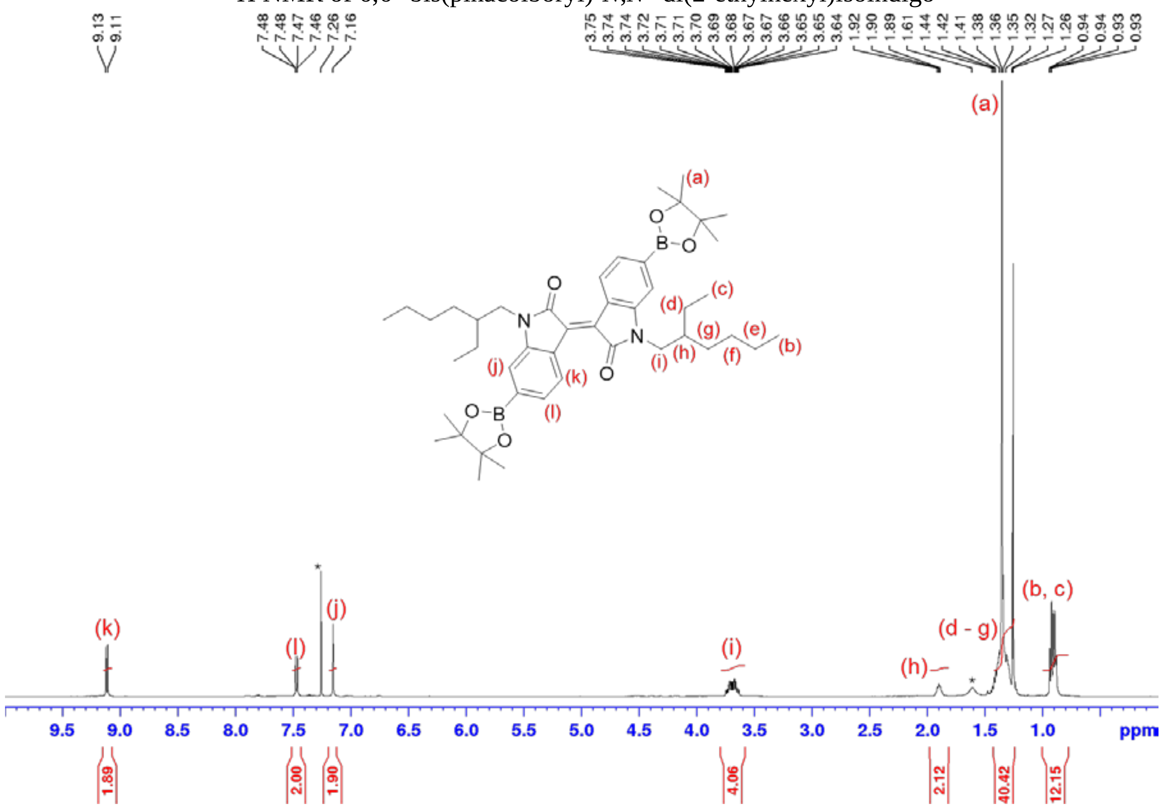
^{1}H NMR of **p(IID-EDOT)**



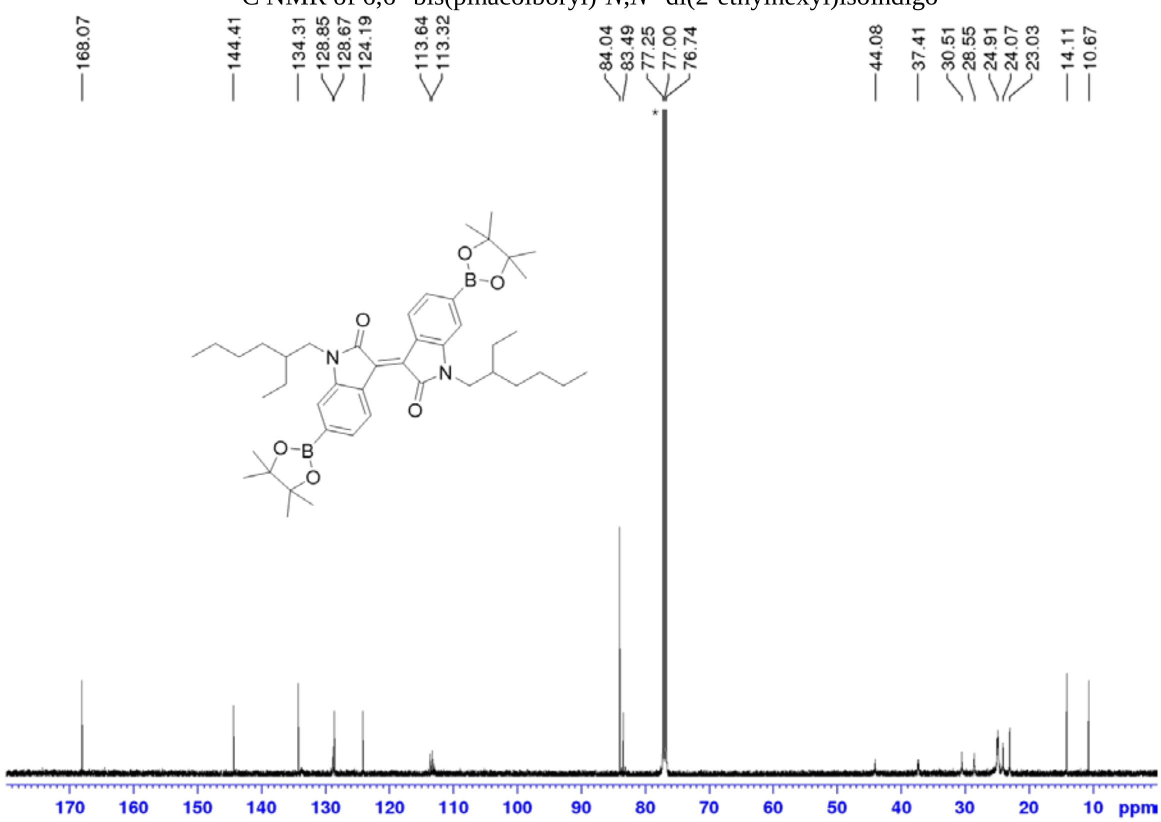
^{1}H NMR of **p(IID-2EDOT)**



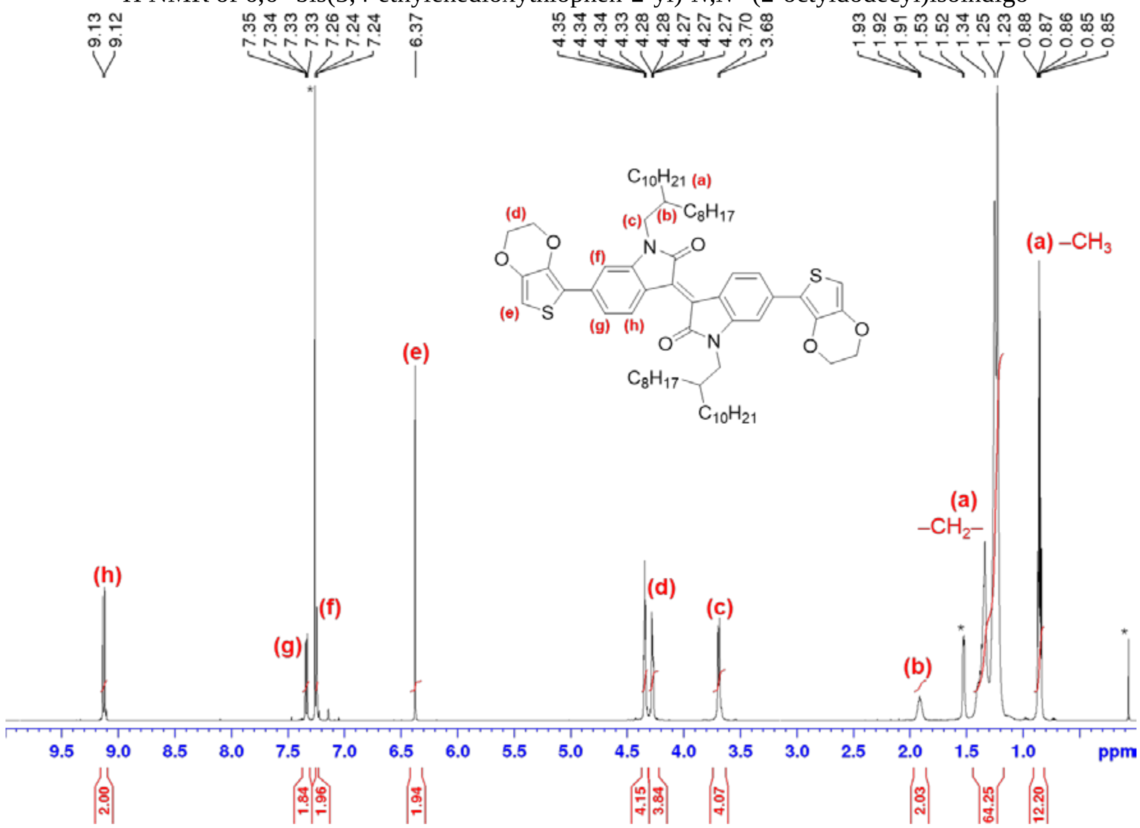
[1]H NMR of 6,6'-bis(pinacolboryl)-*N*,*N*'-di(2-ethylhexyl)isoindigo



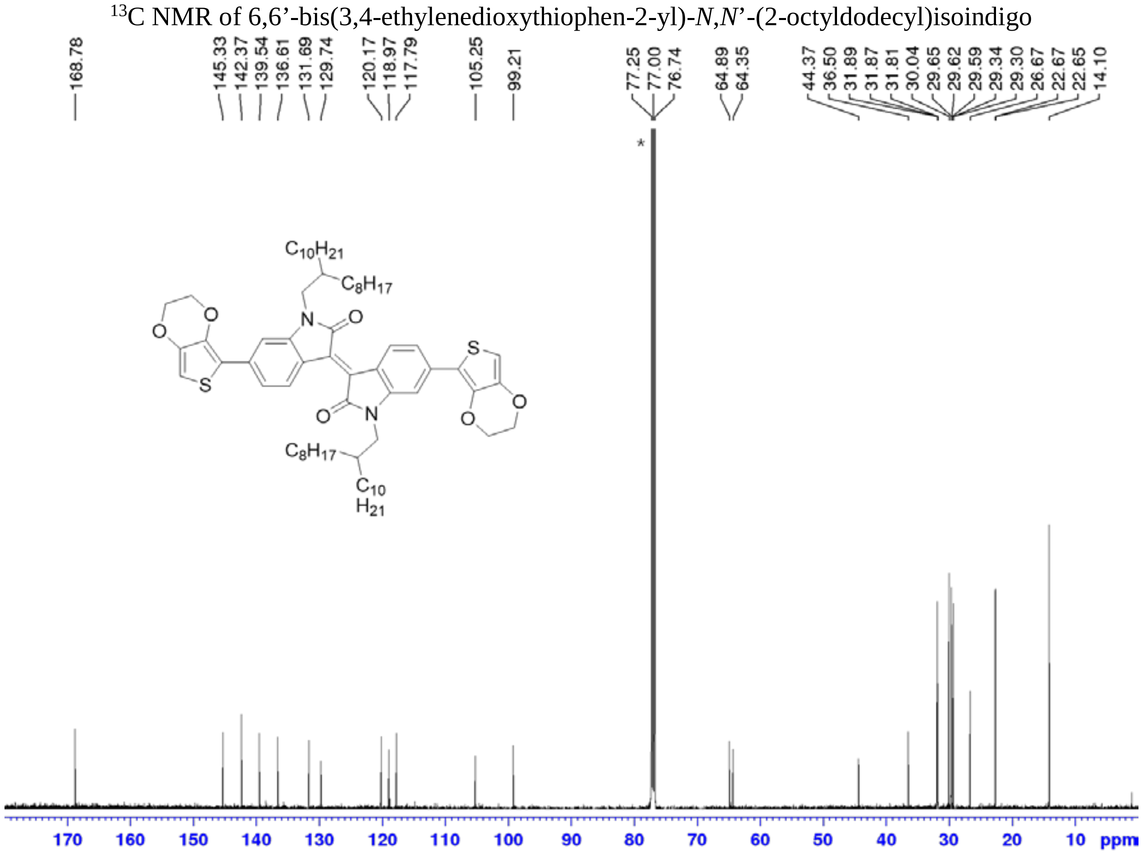
[13]C NMR of 6,6'-bis(pinacolboryl)-*N*,*N*'-di(2-ethylhexyl)isoindigo



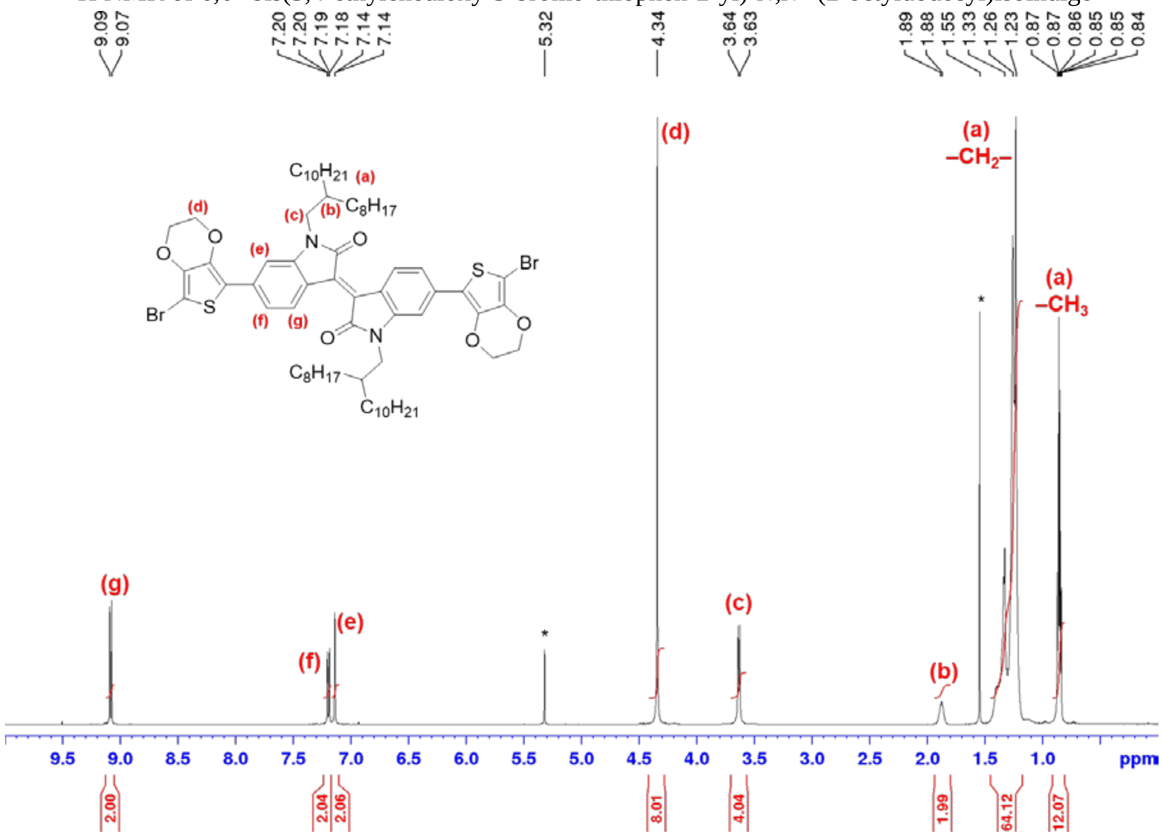
^{1}H NMR of 6,6'-bis(3,4-ethylenedioxythiophen-2-yl)-*N*,*N*'-(2-octyldodecyl)isoindigo



^{13}C NMR of 6,6'-bis(3,4-ethylenedioxythiophen-2-yl)-*N*,*N*'-(2-octyldodecyl)isoindigo



^{1}H NMR of 6,6'-bis(3,4-ethylenedioxy-5-bromo-thiophen-2-yl)-*N*,*N*'-(2-octyldodecyl)isoindigo



^{13}C NMR of 6,6'-bis(3,4-ethylenedioxy-5-bromo-thiophen-2-yl)-*N*,*N*'-(2-octyldodecyl)isoindigo