Electronic Supplementary Material (ESI) for Polymer Chemistry.

Ultrahighly Electron-Deficient Pyrrolo-acenaphtho-pyridazine-dione Based Donor-Acceptor Conjugated Polymers for Electrochromic Applications

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[‡] These authors contribute equally to this work.

Contents

1. NMR Spectra of all new compounds

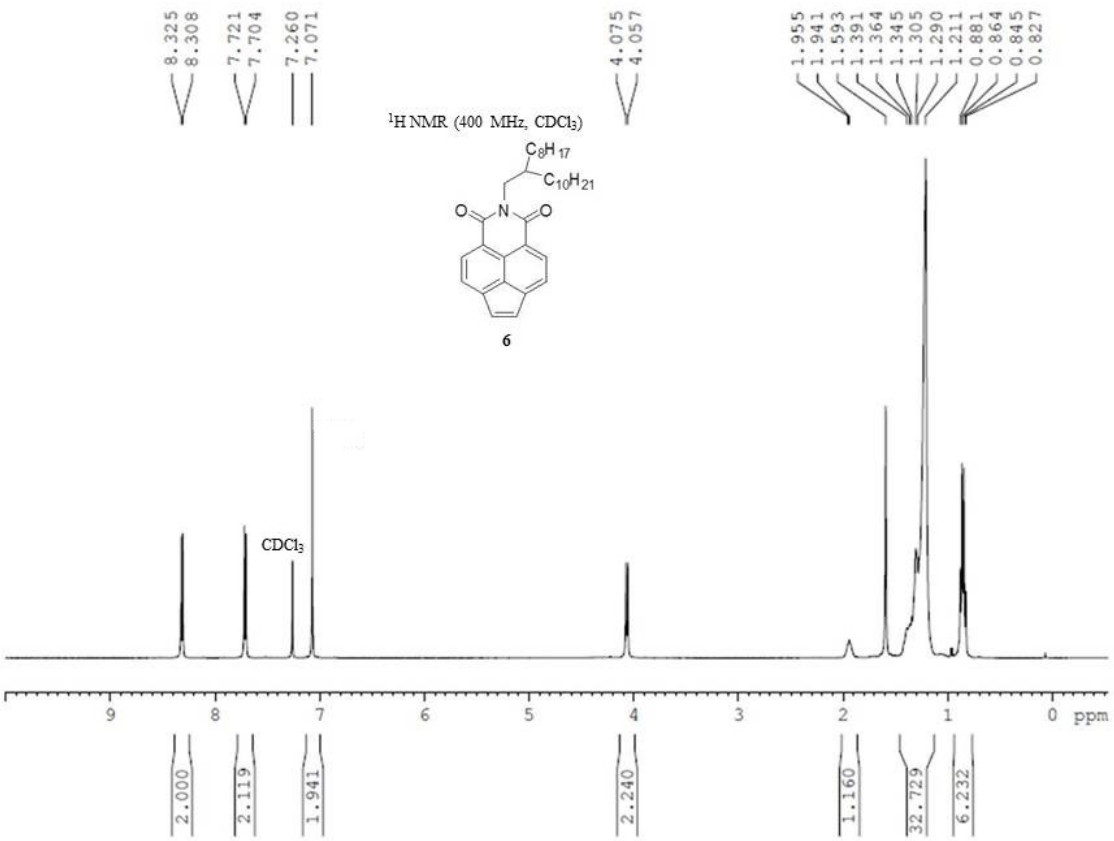


Figure S1. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, room temperature).

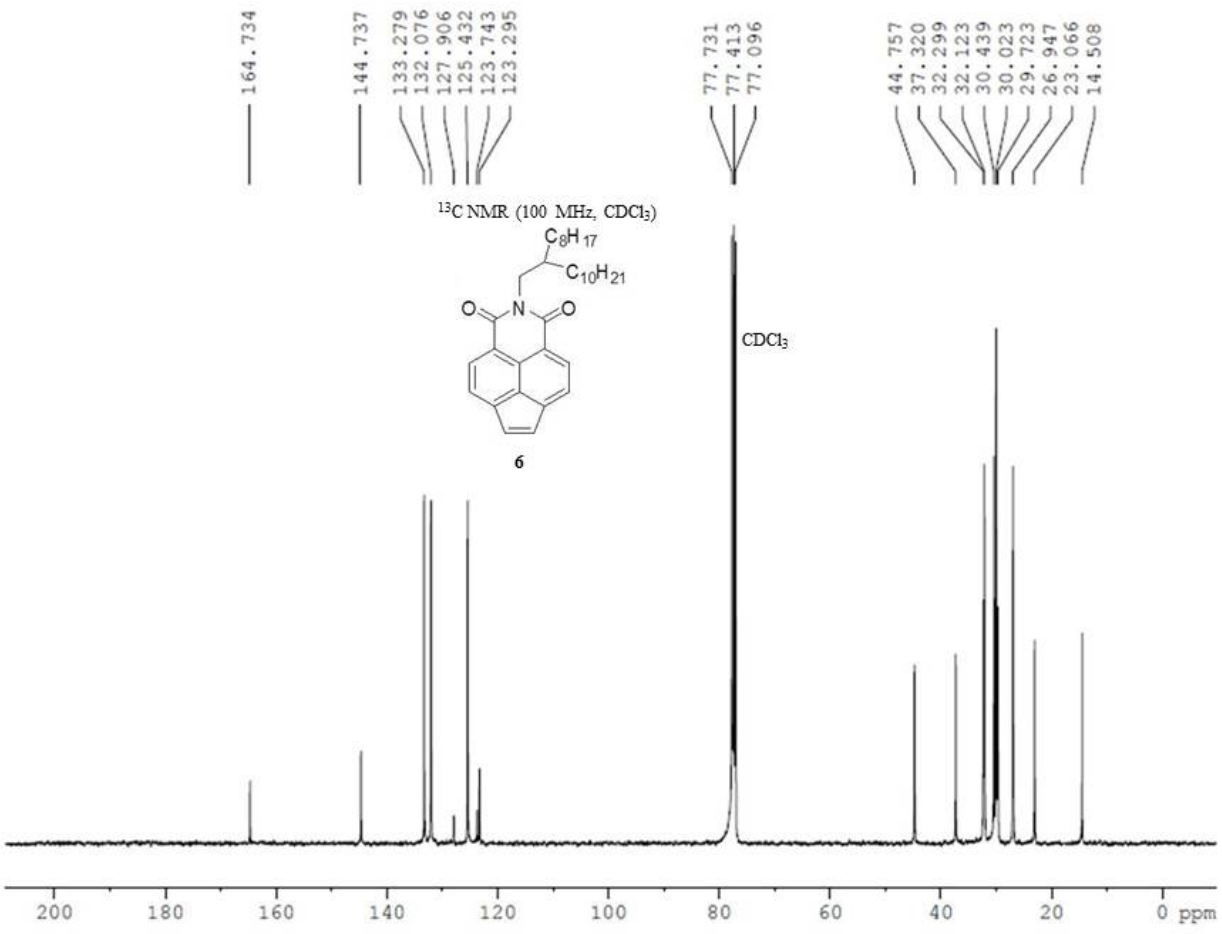


Figure S2. ^{13}C NMR spectrum of compound **6** ($CDCl_3$, room temperature).

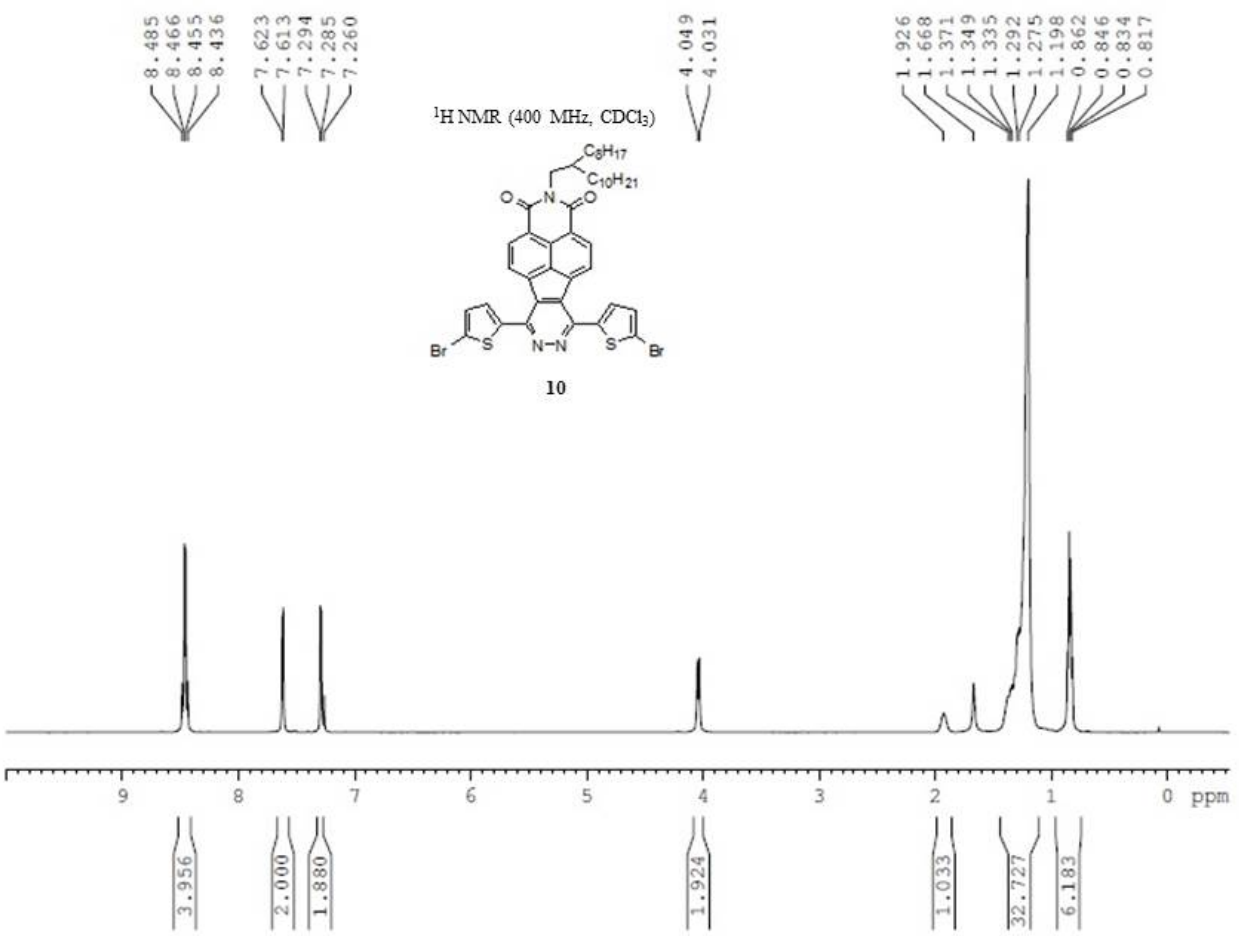


Figure S3. ^{1}H NMR spectrum of compound **10** ($CDCl_3$, room temperature).

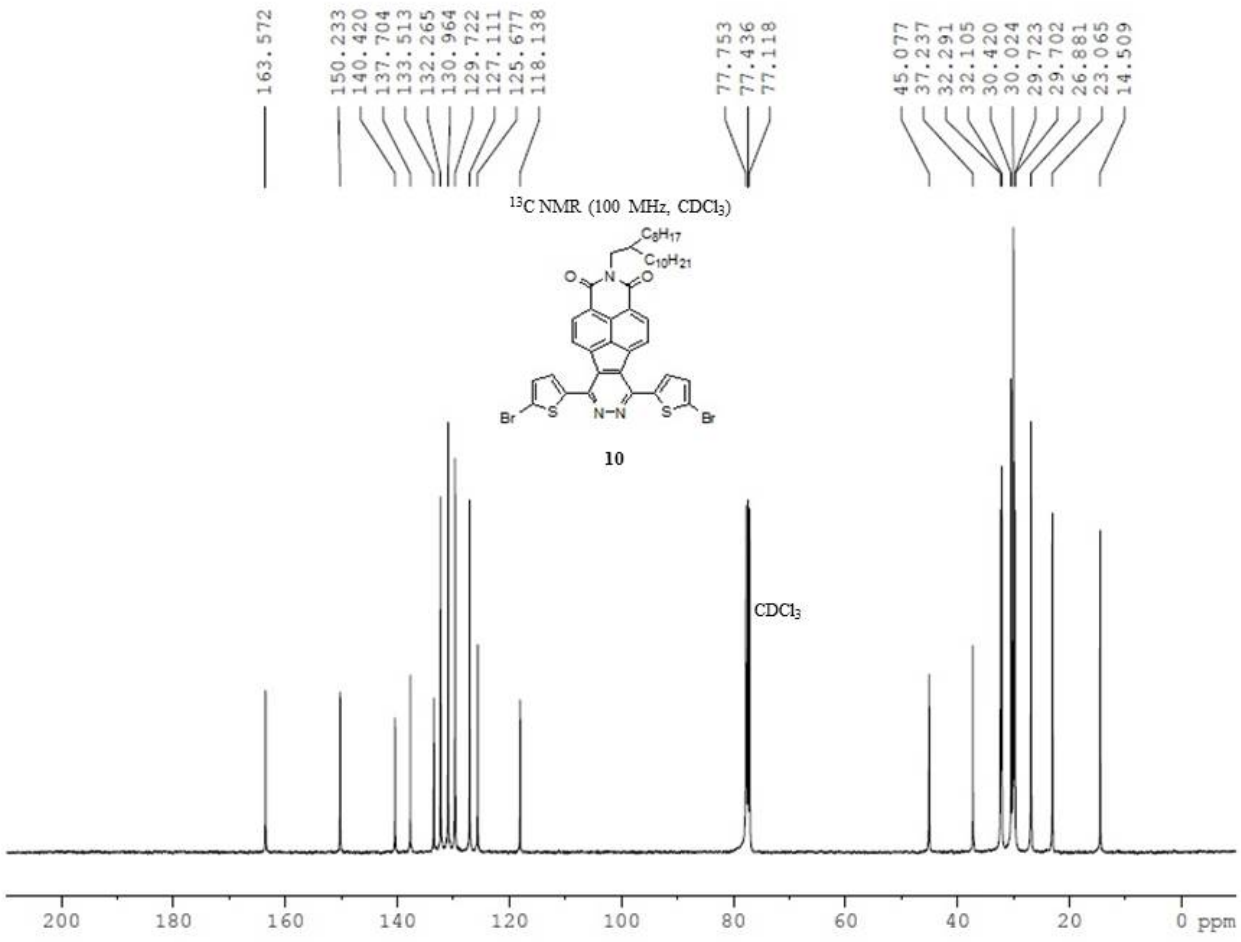


Figure S4. ^{13}C NMR spectrum of compound **10** ($CDCl_3$, room temperature).

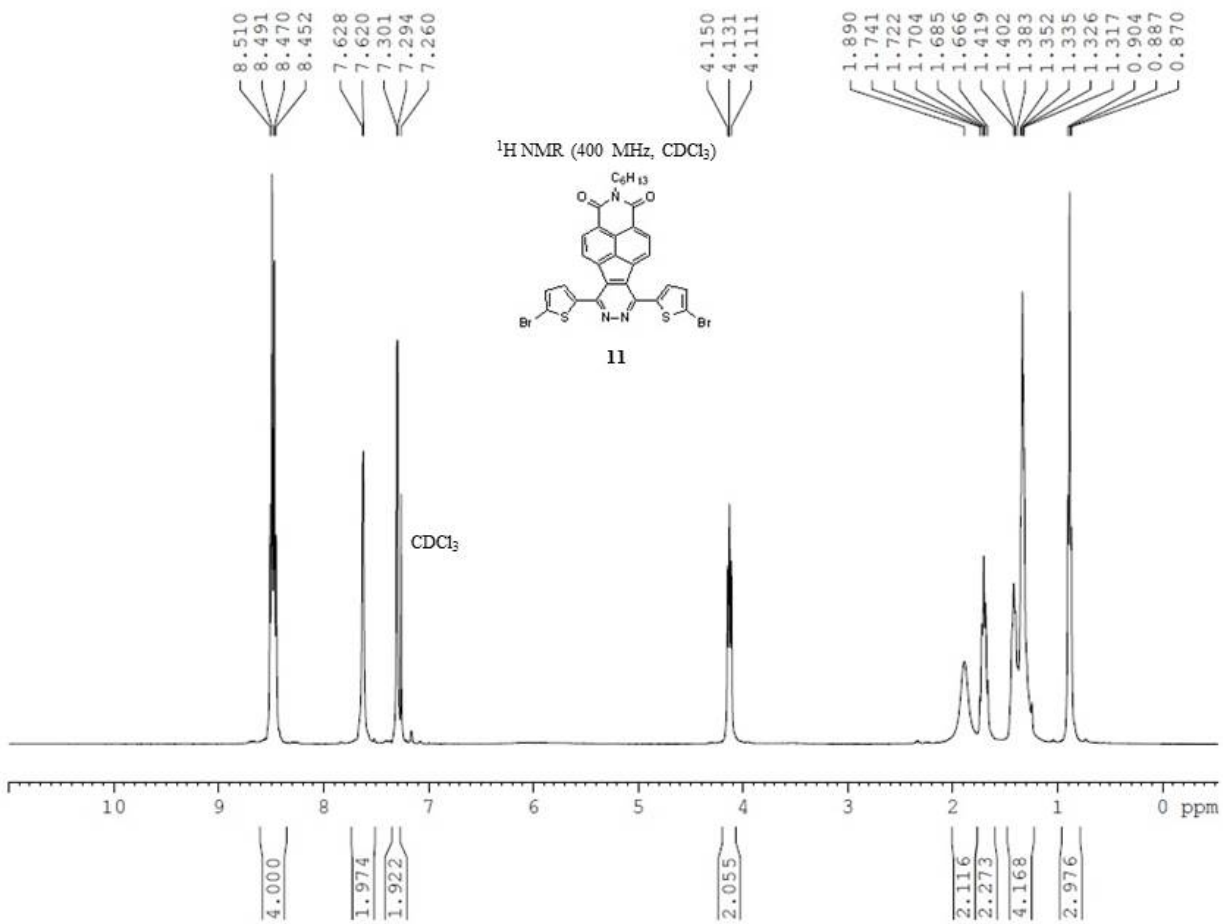


Figure S5. ^{1}H NMR spectrum of compound **11** ($CDCl_3$, room temperature).

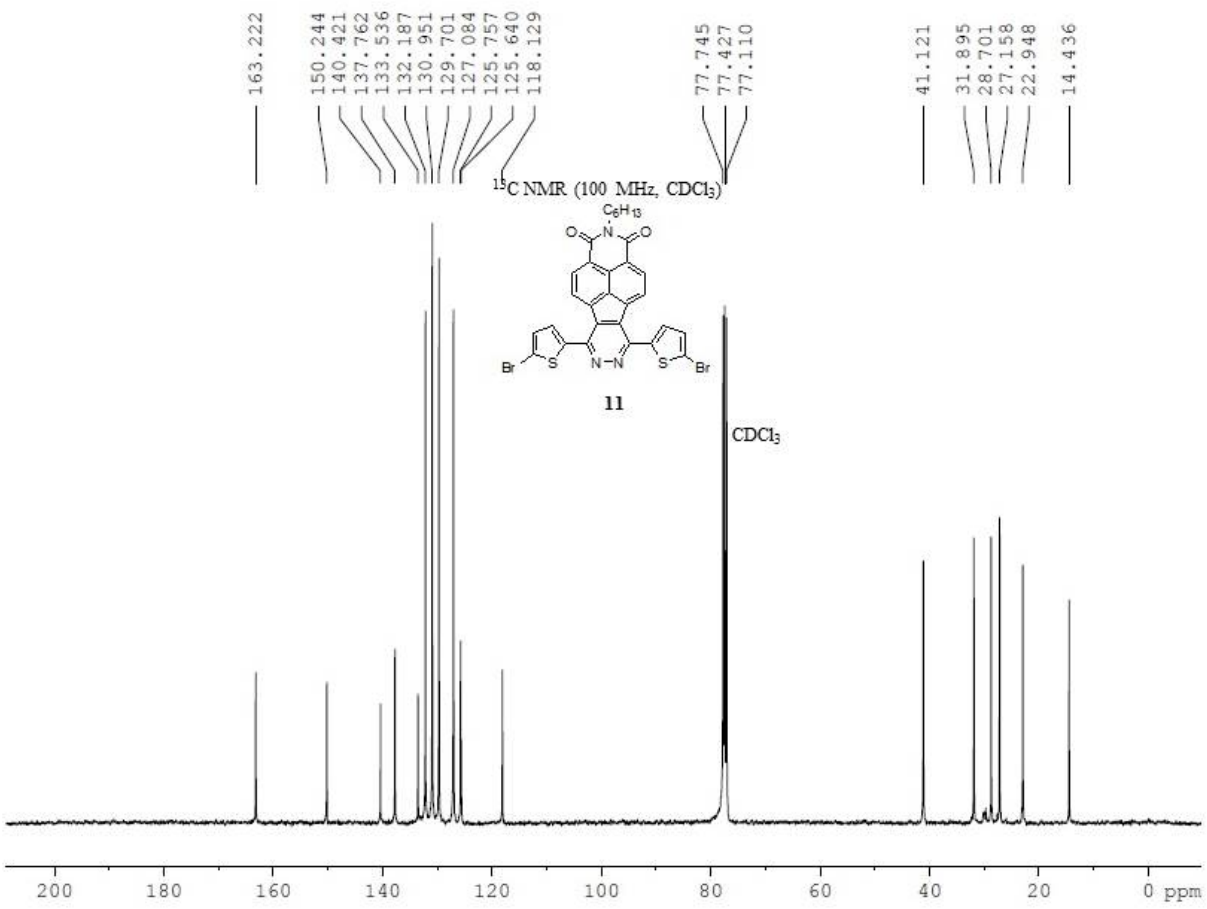


Figure S6. ^{13}C NMR spectrum of compound **11** ($CDCl_3$, room temperature).

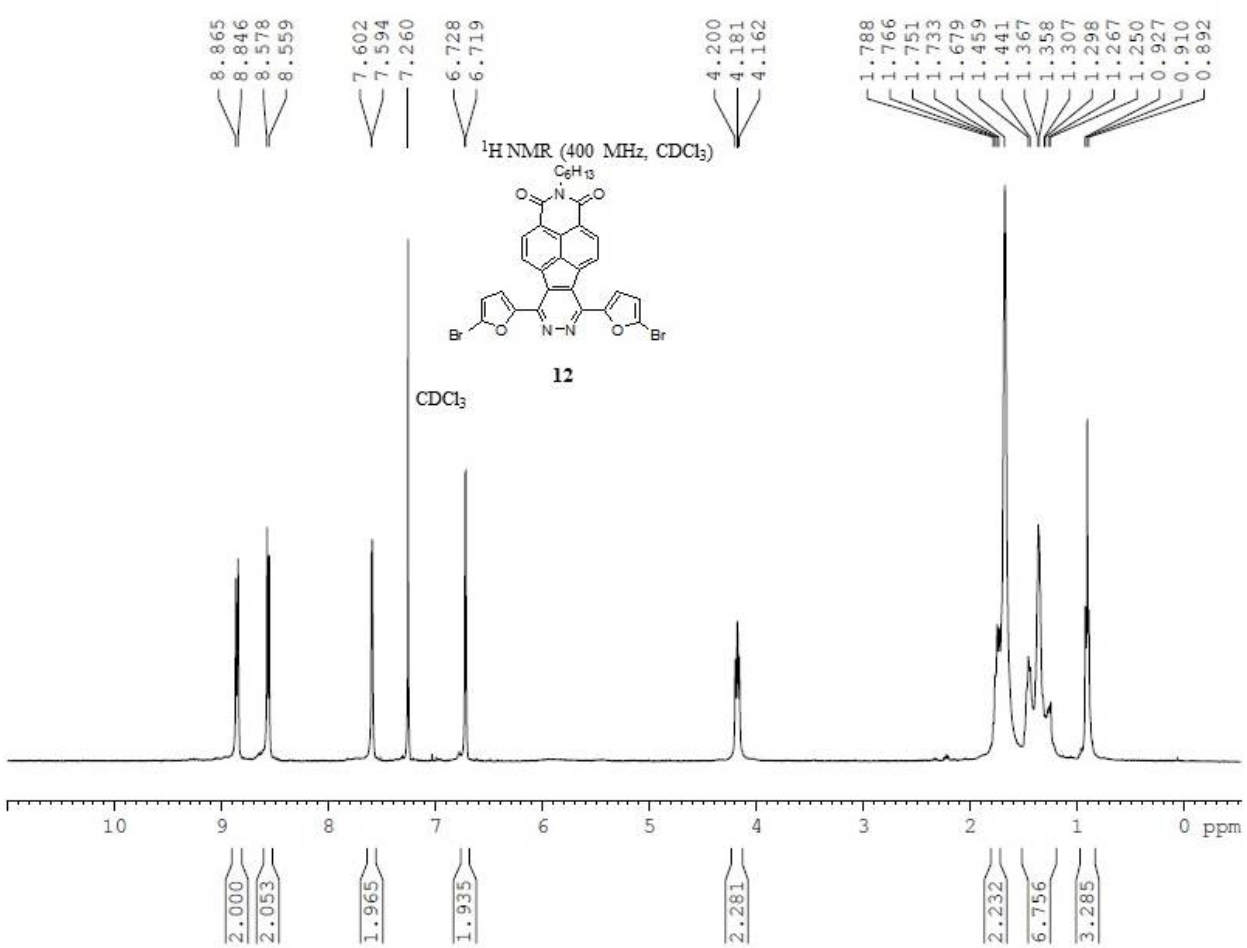


Figure S7. ^{1}H NMR spectrum of compound **12** ($CDCl_3$, room temperature).

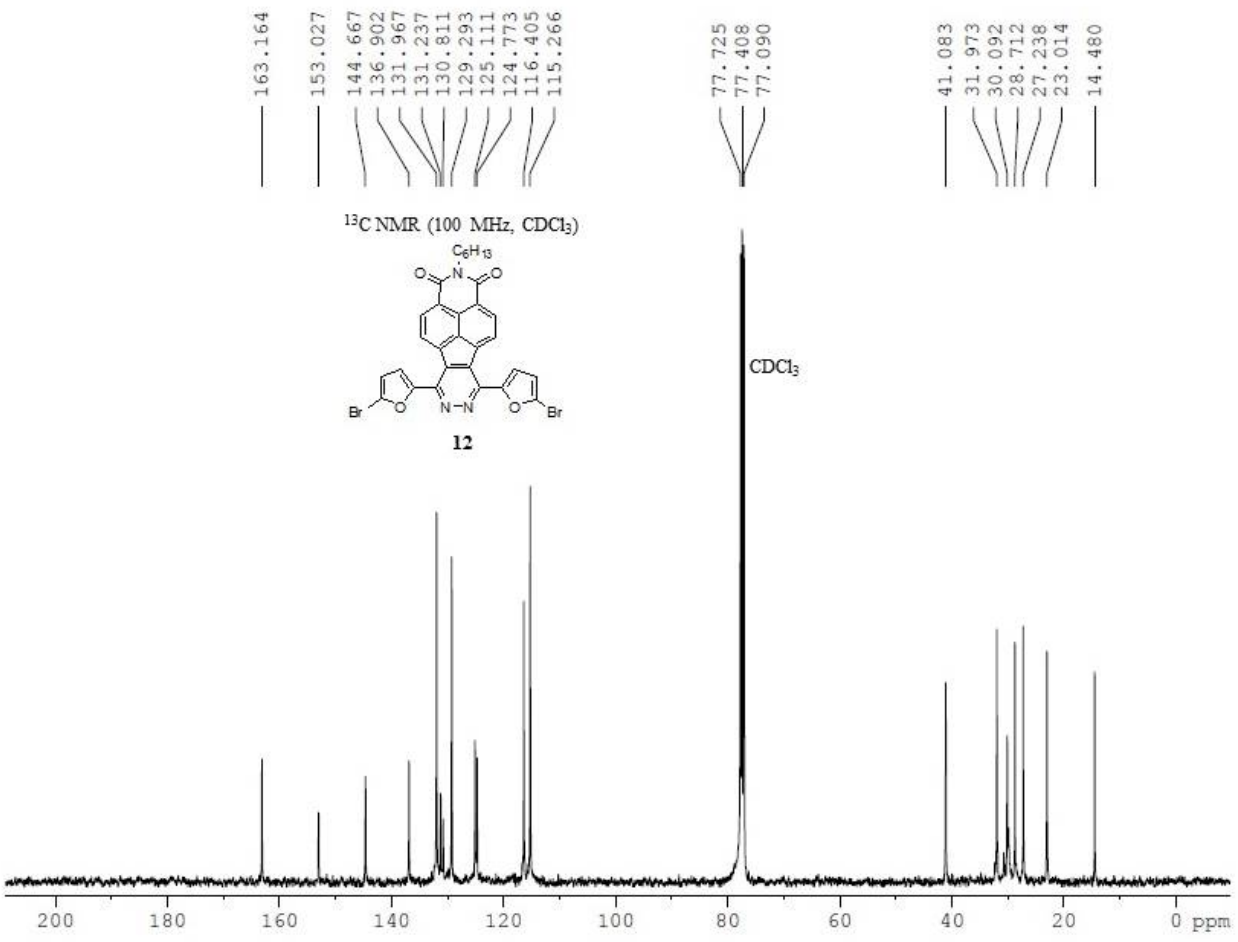


Figure S8. ^{13}C NMR spectrum of compound **12** ($CDCl_3$, room temperature).

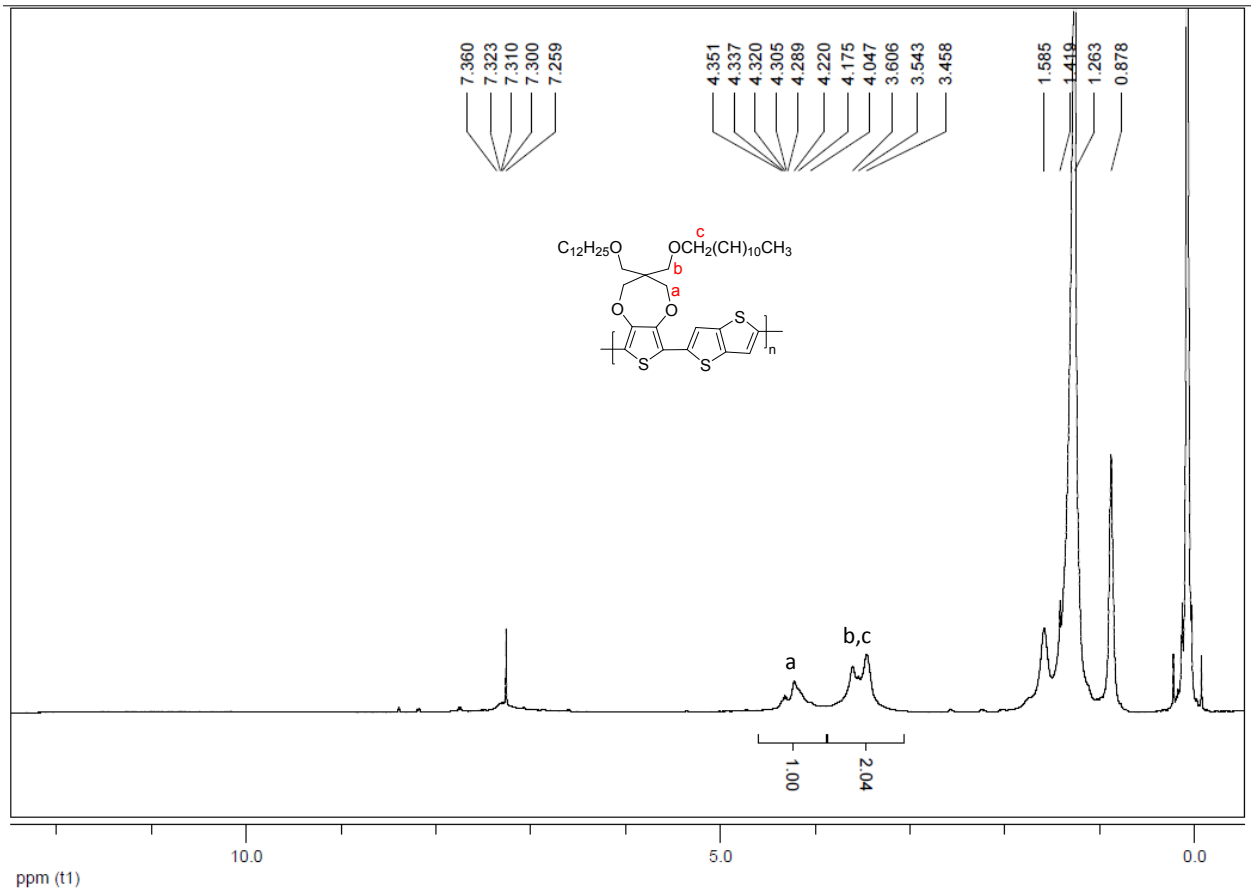


Figure S9. ^{1}H NMR spectrum of Polymer **P1** ($CDCl_3$, room temperature).

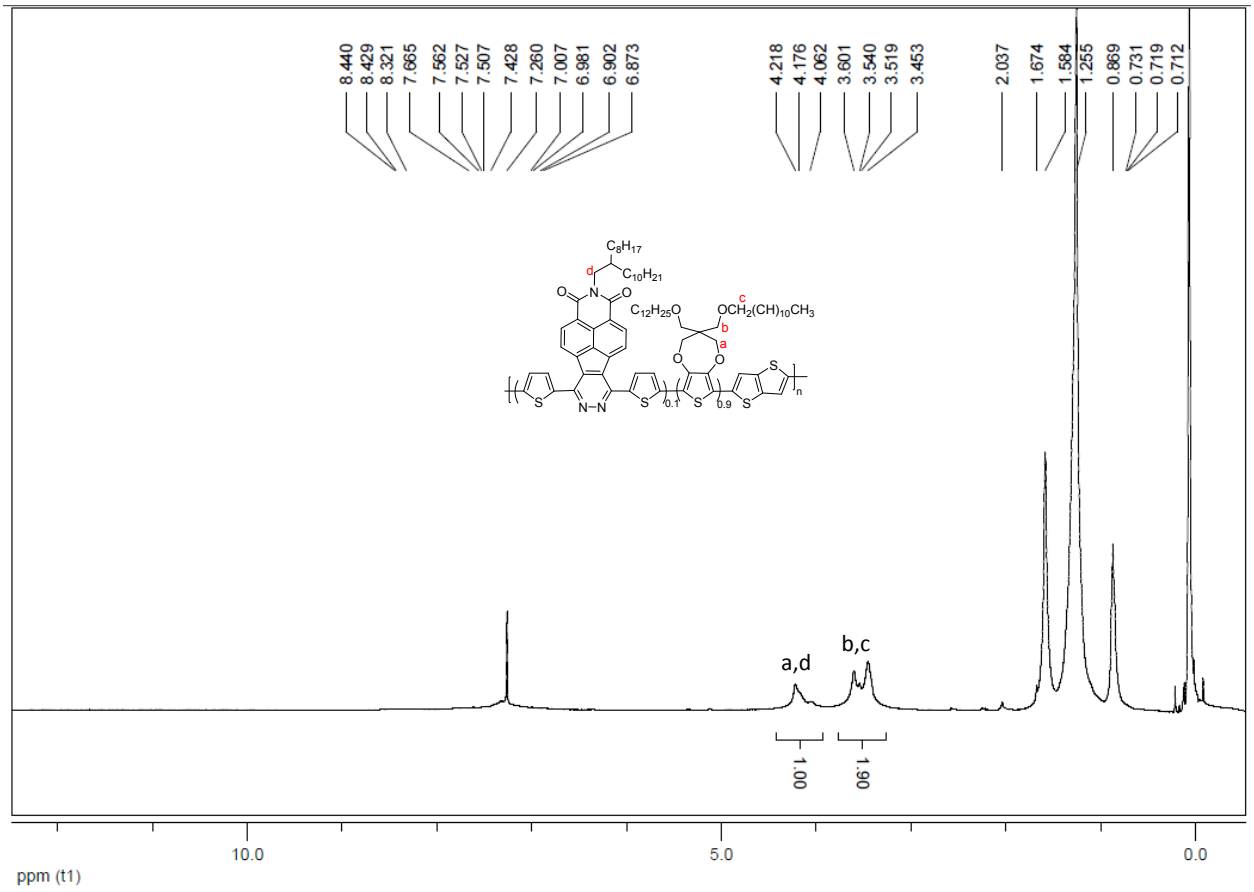


Figure S10. ^{1}H NMR spectrum of Polymer **P2** ($CDCl_3$, room temperature).

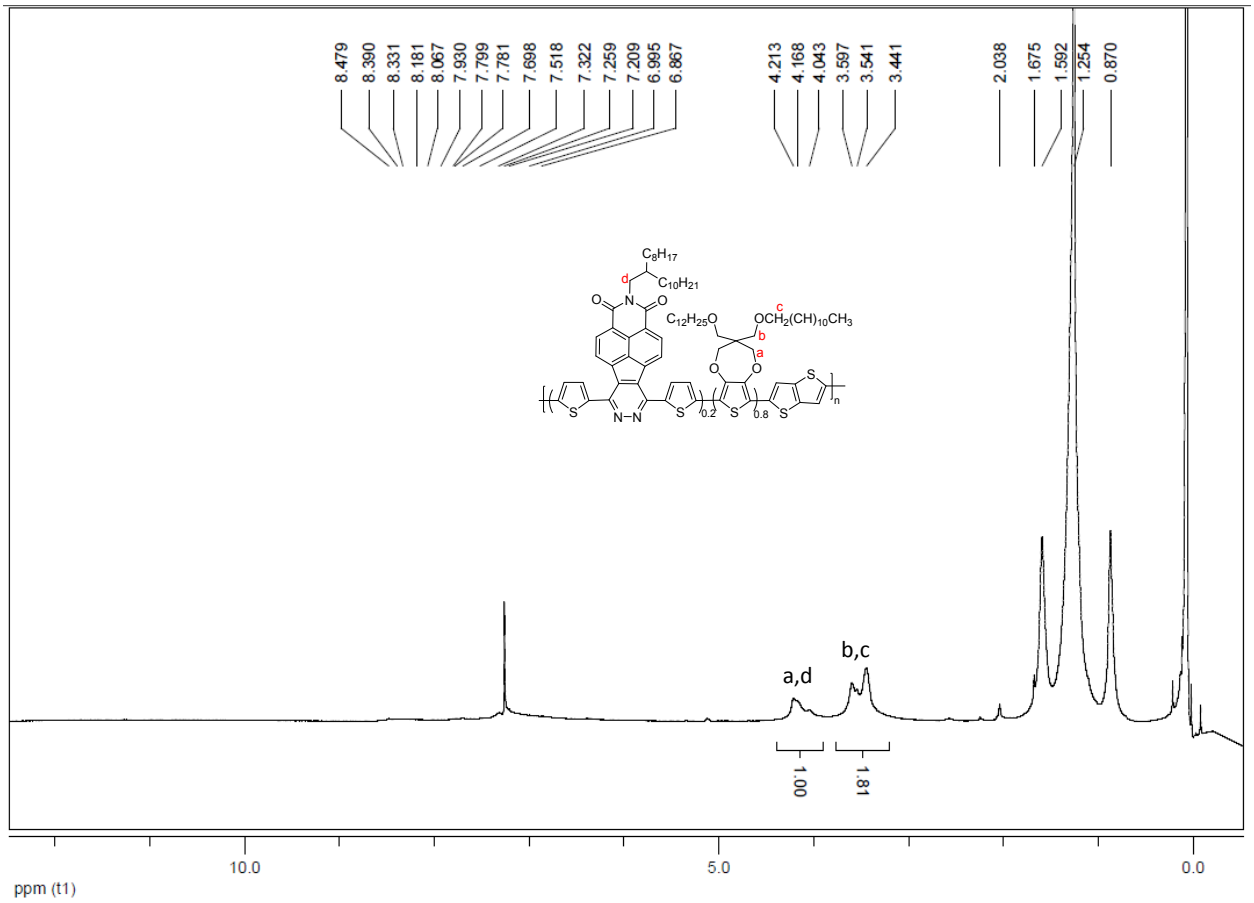


Figure S11. ^{1}H NMR spectrum of Polymer **P3** ($CDCl_3$, room temperature).

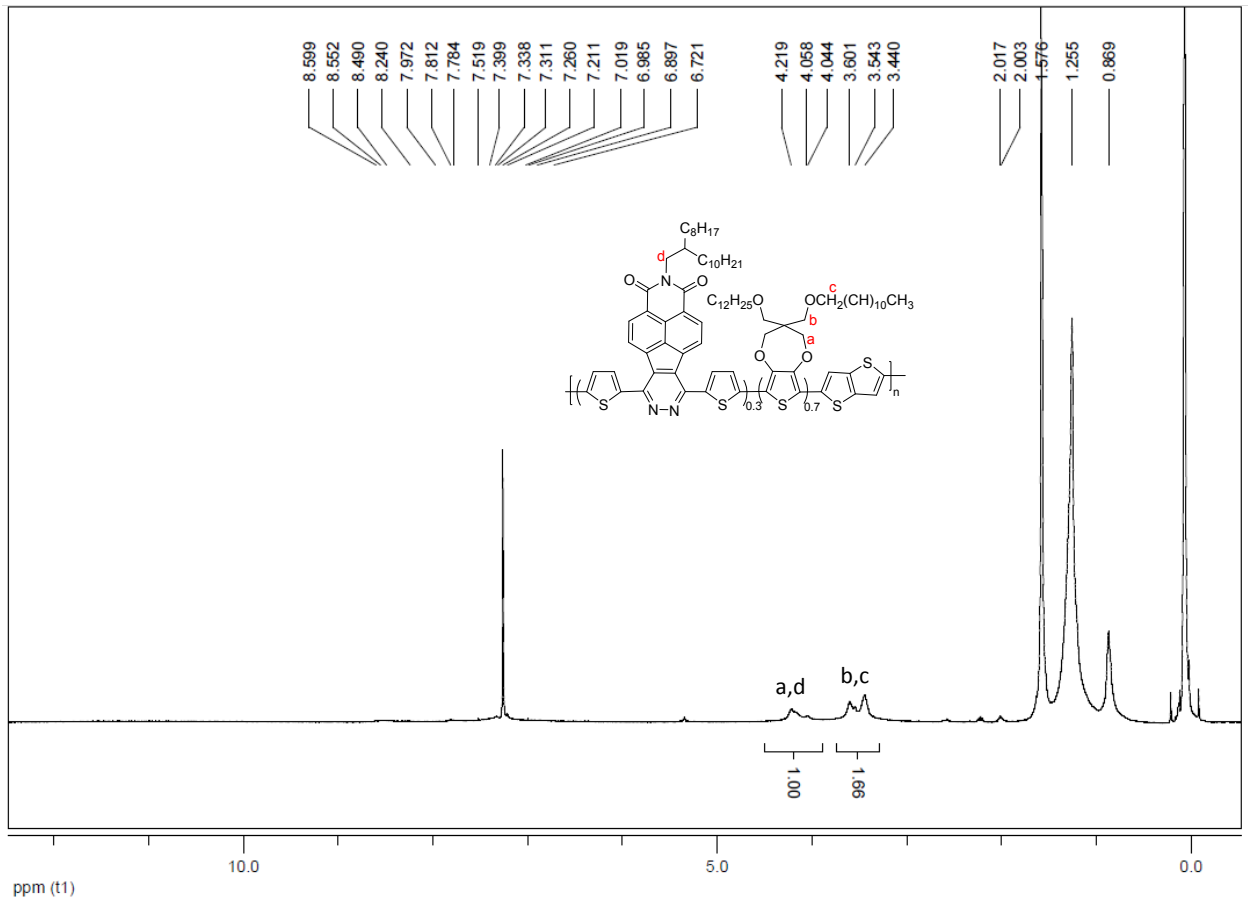


Figure S12. ^{1}H NMR spectrum of Polymer **P4** ($CDCl_3$, room temperature).

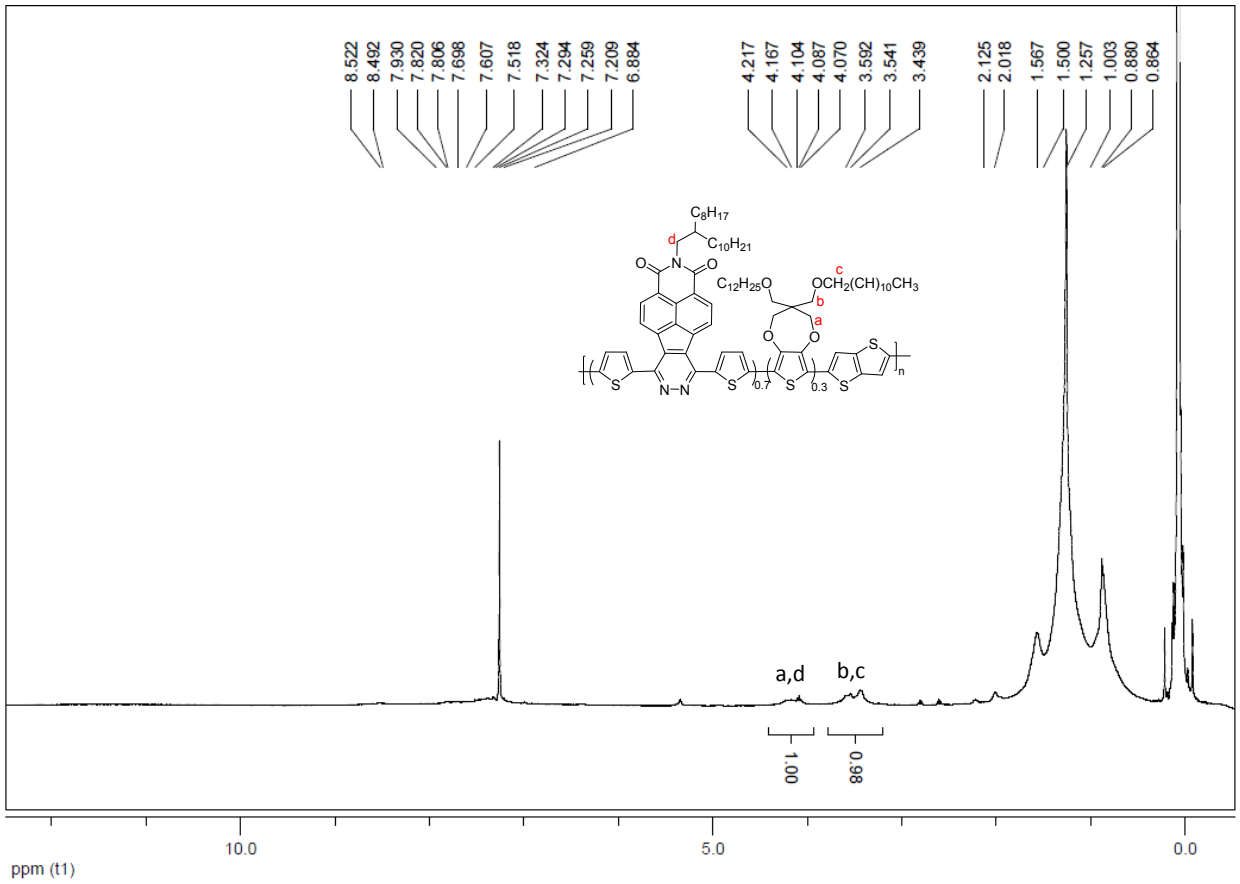
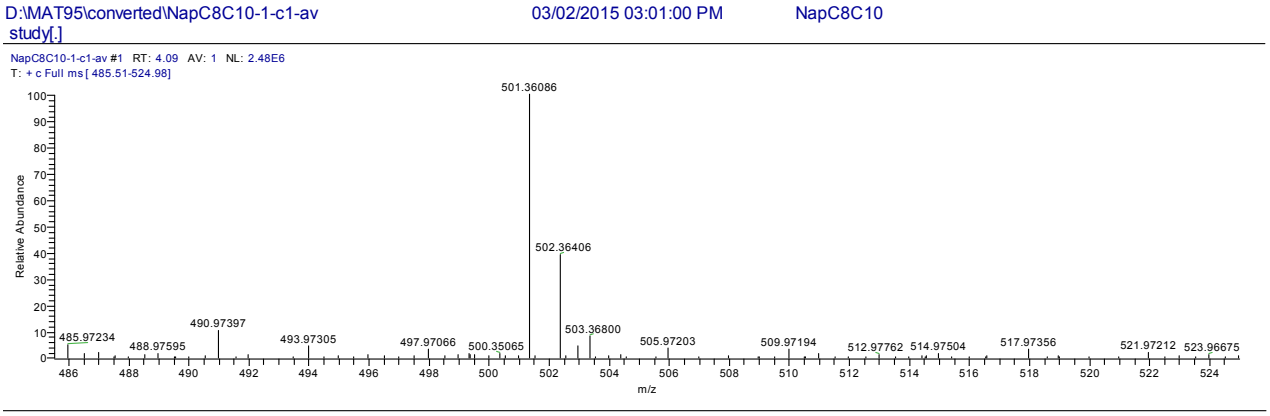


Figure S13. ^{1}H NMR spectrum of Polymer **P5** ($CDCl_3$, room temperature).

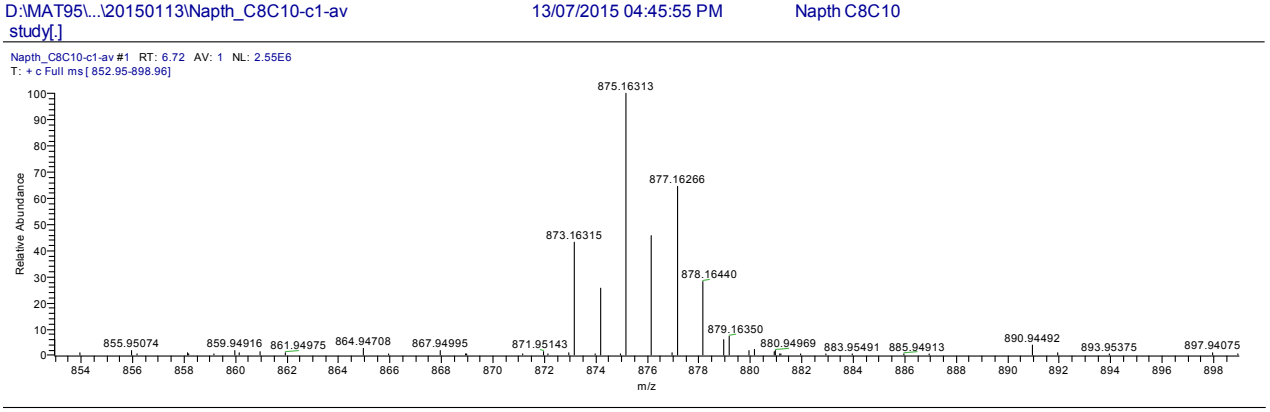
2. High resolution MS data of all new compounds



NapC8C10-1-c1-av#1 RT: 4.09
T: + c Full ms [485.51-524.98]

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
501.36086	2483799.0	100.00	501.36013	1.44	12.0	$C_{34}H_{47}O_2N_1$

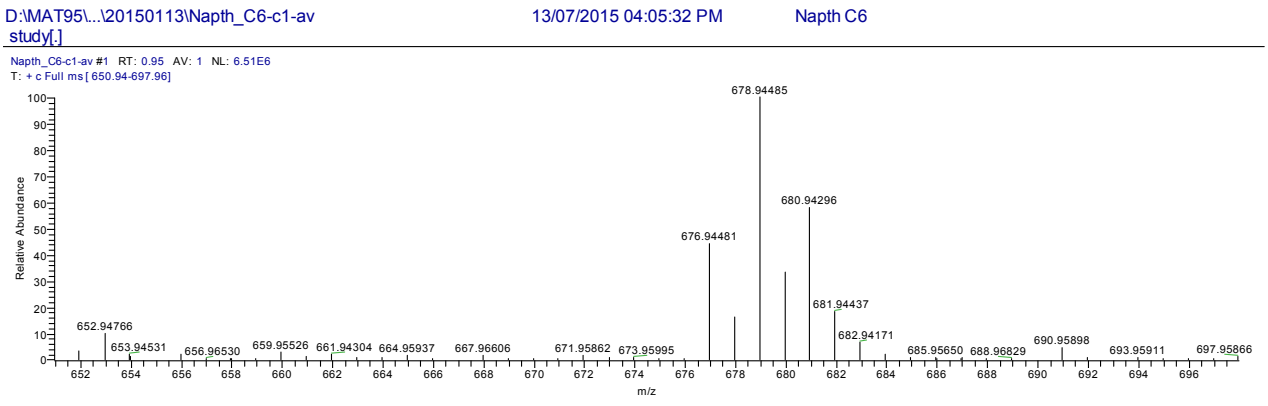
Figure S14. HR-EI-MS spectrum of compound **6**.



Napth_C8C10-c1-av#1 RT: 6.72
T: + c Full ms [852.95-898.96]
m/z= 872.96694-873.39376

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
873.16315	1091169.0	100.00	873.16275	0.46	21.0	$C_{44}H_{49}O_2N_3{}^{79}Br_2{}^{32}S_2$

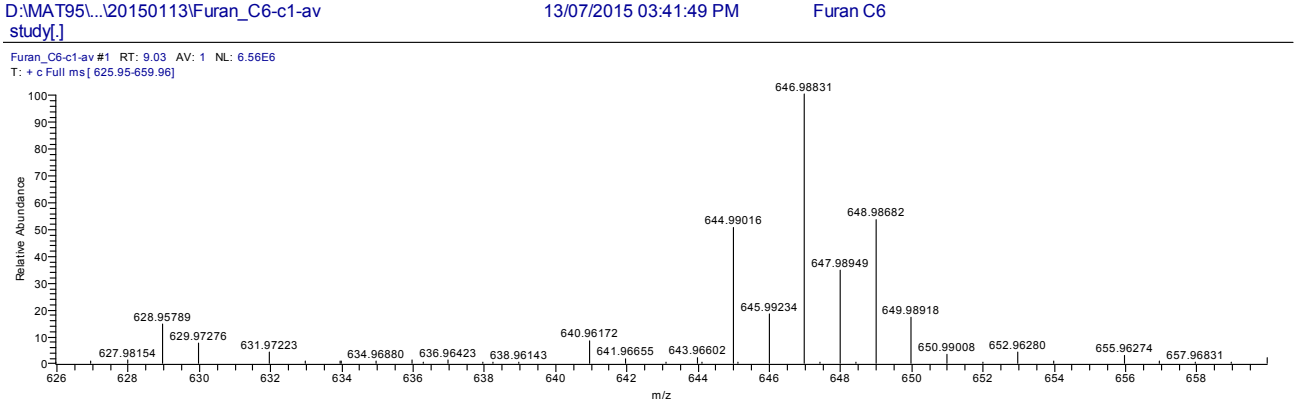
Figure S15. HR-EI-MS spectrum of compound **10**.



Napth_C6-c1-av#1 RT: 0.95
T: + c Full ms [650.94-697.96]
m/z= 676.67285-677.23989

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
676.94481	2884069.0	100.00	676.94364	1.72	21.0	$C_{30}H_{21}O_2N_3{}^{79}Br_2{}^{32}S_2$

Figure S16. HR-EI-MS spectrum of compound **11**.



Furan_C6-c1-av#1 RT: 9.03
T: + c Full ms [625.95-659.96]
m/z= 644.84867-645.06951

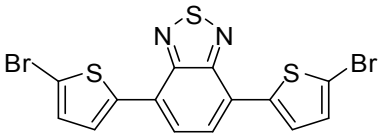
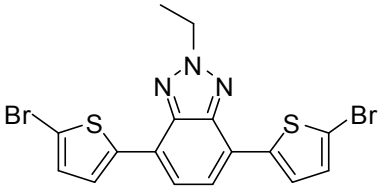
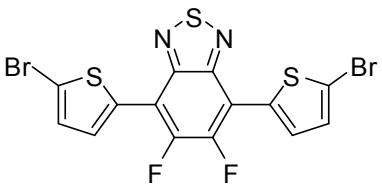
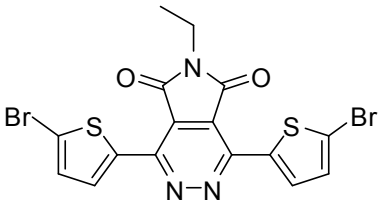
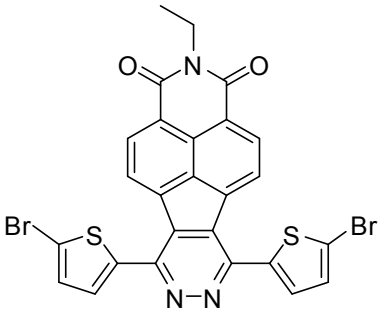
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
644.99016	3303838.0	100.00	644.98933	1.28	21.0	$C_{30}H_{21}O_4N_3{}^{79}Br_2$

Figure S17. HR-EI-MS spectrum of compound **12**.

3. TD-DFT Calculation Details

The model compounds were built using GaussView and then optimized using DFT at the level of theory: B3LYP/6-31G with Gaussian 09.[1] The HOMO, LUMO and other properties were obtained at the DFT optimized geometries and summarized in Table S1.

Table S1. Summary of the frontier orbital energy levels of the model compounds listed in Figure 1.

Molecule Model	HOMO (eV)	LUMO (eV)	Dipole Moment (D)	Stoichiometry
	-5.434	-2.871	3.1025	C14H6Br2N2S3
	-5.237	-2.185	0.6424	C16H11Br2N3S2
	-5.622	-2.982	1.1988	C14H4Br2F2N2S3
	-5.906	-3.084	0.4392	C16H9Br2N3O2S2
	-6.086	-3.418	0.7746	C26H13Br2N3O2S2

[1]Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S2. Summary of the calculated free energies of molecules and reactions using (DMol^3: GGA-PW91-VPSR/dnp (fine)).

Molecule	Et electronic (ha)	ZPVE (ha)	G, T=298.15K (ha)	Et (ha) T=0K	Et (ha) T=298.15K	Imaginary frequency (cm-1)
Reactants						
C10H4N4S2Br2_c	-6538.6029492	0.1217351	0.0729996	-6538.4812141	-6538.5299496	none
C10H4N4S2Br2_t	-6538.6029970	0.1220251	0.0731367	-6538.4809719	-6538.5298603	none
C10H4N4O2Br2_c	-5890.9393366	0.1272394	0.0823843	-5890.8120972	-5890.8569523	One, -9.7?
C10H4N4O2Br2_t	-5890.9396775	0.1279023	0.0809868	-5890.8117752	-5890.8586907	none
C16H11NO2	-822.4178467	0.2279119	0.1869038	-822.1899348	-822.2309429	none
Intermediates						
C26H15N5O2S2Br2	-7360.9828332	0.3503084	0.2873086	-7360.6325248	-7360.6955246	One, -3.6
C26H15N5O2S2Br2_2	-7360.9653869	0.3520948	0.2870169	-7360.6132921	-7360.6783700	none
C26H15N5O4Br2	-6713.3249086	0.3574429	0.2939618	-6712.9674657	-6713.0309468	none
C26H15N5O4Br2_2	-6713.3080570	0.3569776	0.2956479	-6712.9510794	-6713.0124091	One, -7.0

4. Cyclic voltammetry of Compound 10

Figure S18. Cyclic voltammetry of compound **10** and its LUMO energy level.

5. Switching behaviour of devices

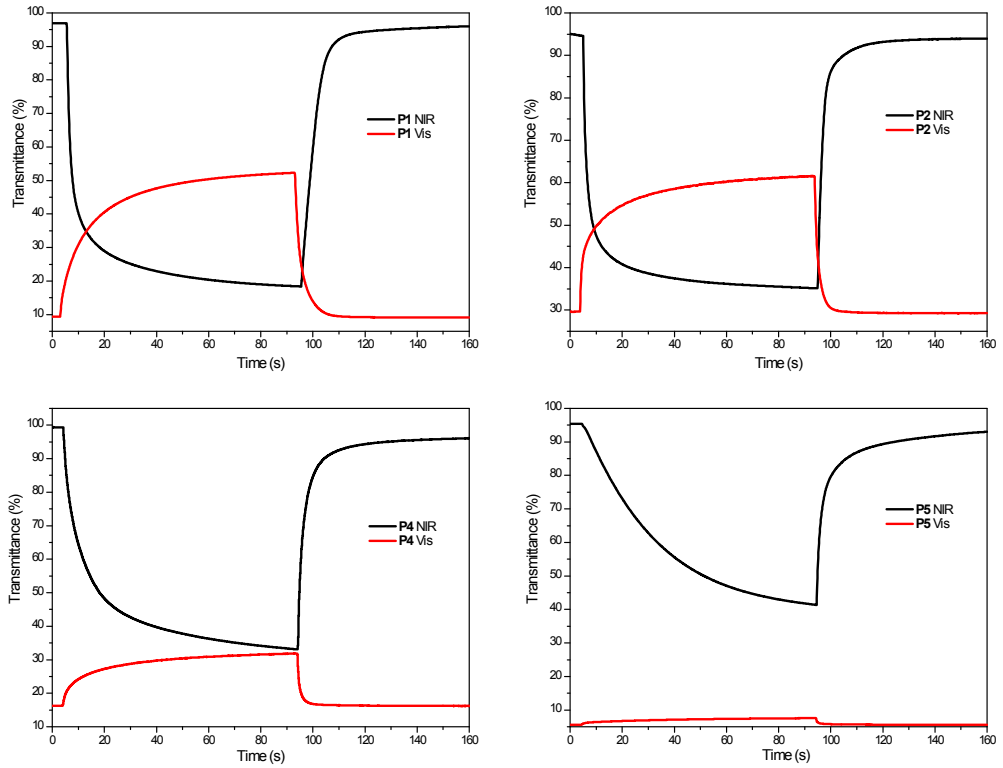


Figure S19. Switching behaviour of **P1**, **P2**, **P4** and **P5** device between + 1.6 and -1.6 V.

6. Stability studies

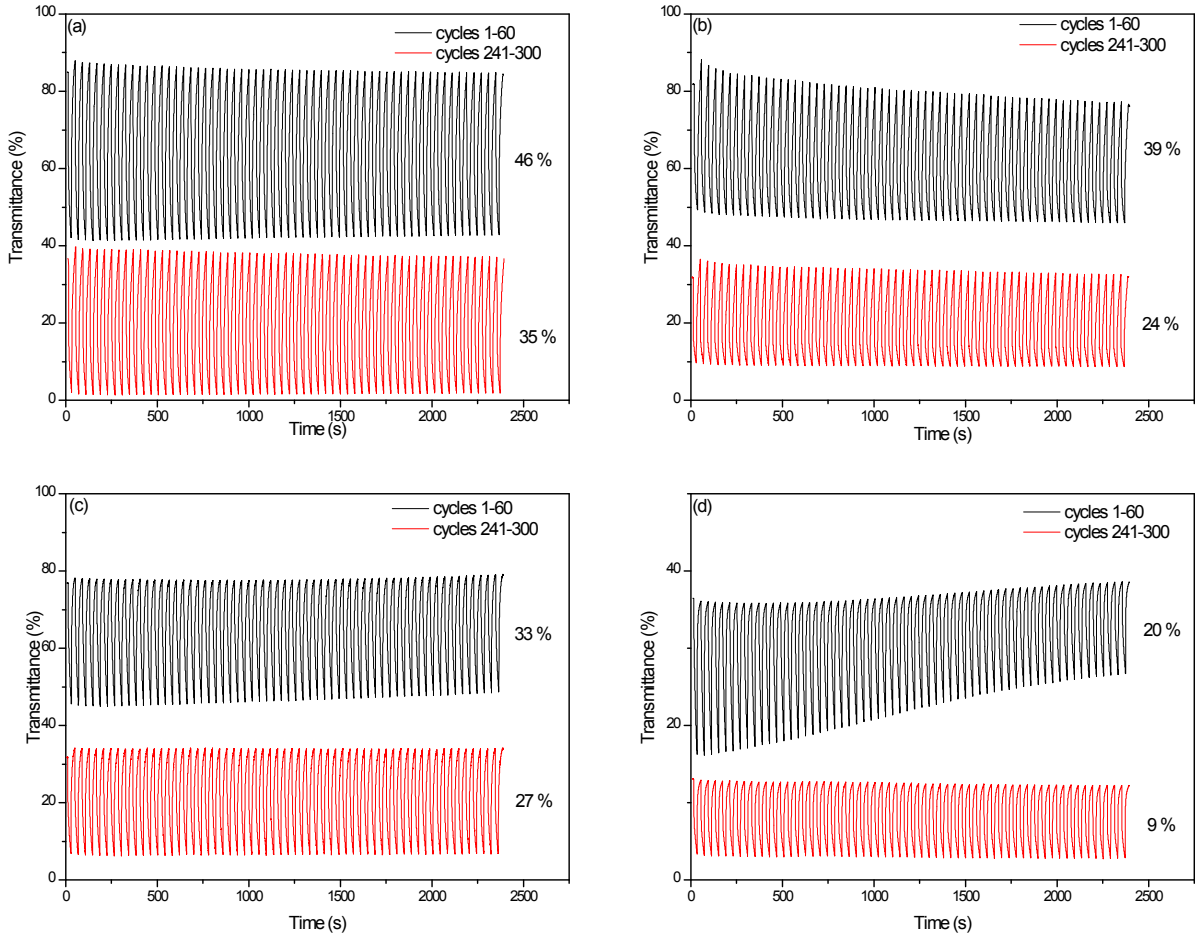


Figure S20. Stability studies of (a) **P1**, (b) **P2**, (c) **P4** and (d) **P5** devices in the NIR region.

7. X-ray crystallographic data

Table S3. Crystal data and structure refinement for **11**.

Empirical formula	$C_{30}H_{21}Br_2N_3O_2S_2$
Formula weight	679.44
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 8.2952(4) Å, α = 90°
	b = 20.7323(9) Å, β = 100.587(2)°
	c = 22.0577(10) Å, γ = 90°
Volume	3728.9(3) $Å^3$

Z	4
Density (calculated)	1.210 Mg/m^3
Absorption coefficient	4.010 mm^{-1}
F(000)	1360
Crystal size	0.178 x 0.101 x 0.098 mm^3
Theta range for data collection	2.949 to 54.230°
Index ranges	-8<=h<=8, -21<=k<=15, -23<=l<=18
Reflections collected	9028
Independent reflections	4225 [R(int) = 0.0332]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4225 / 78 / 432
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0776, wR2 = 0.2322
R indices (all data)	R1 = 0.0891, wR2 = 0.2454
Extinction coefficient	n/a
Largest diff. peak and hole	0.651 and -0.594 e.$Å^{-3}$

Table S4. Crystal data and structure refinement for **12**.

Empirical formula	$C_{30}H_{21}Br_2N_3O_4$
Formula weight	647.315
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 13.4552(6) Å, α = 78.712(2)°
	b = 13.6974(7) Å, β = 73.880(2)°
	c = 14.8065(6) Å, γ = 76.746(2)°
Volume	2526.2(2) $Å^3$
Z	4
Density (calculated)	1.702 Mg/m^3
Absorption coefficient	3.253 mm^{-1}
F(000)	1296
Crystal size	0.321 x 0.150 x 0.100 mm^3
Theta range for data collection	2.259 to 28.078°
Index ranges	-16<=h<=17, -17<=k<=18, -19<=l<=19

Reflections collected	57642
Independent reflections	12264 [R(int) = 0.0751]
Completeness to theta = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12264 / 0 / 705
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0760
R indices (all data)	R1 = 0.0842, wR2 = 0.0876
Extinction coefficient	n/a

8. TGA thermograms

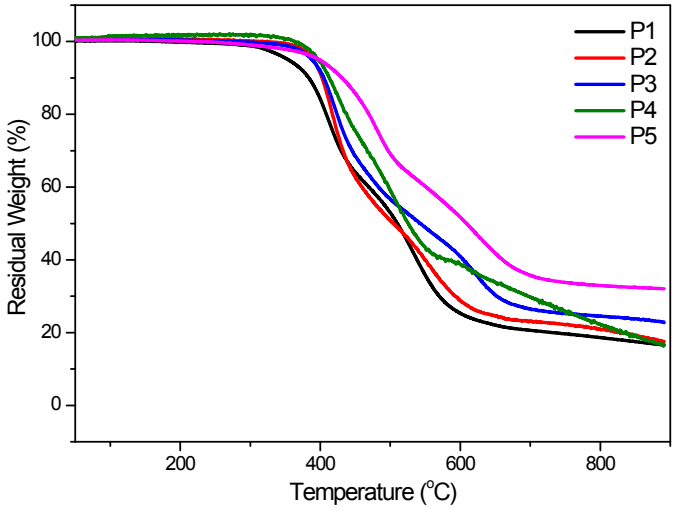


Figure S21. TGA thermograms of **P1** – **P5**.

9. DSC thermograms

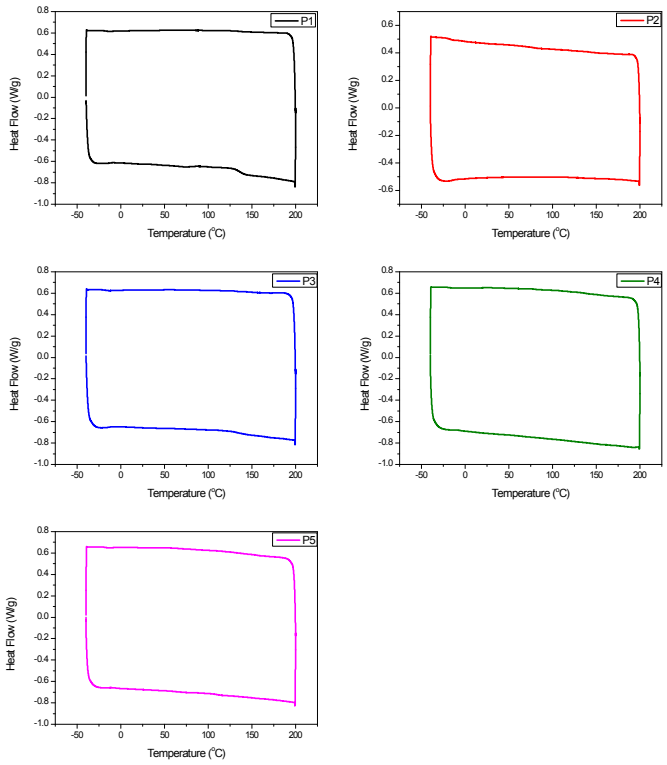


Figure S22. DSC thermograms of **P1 – P5.**

10. XRD diffractograms

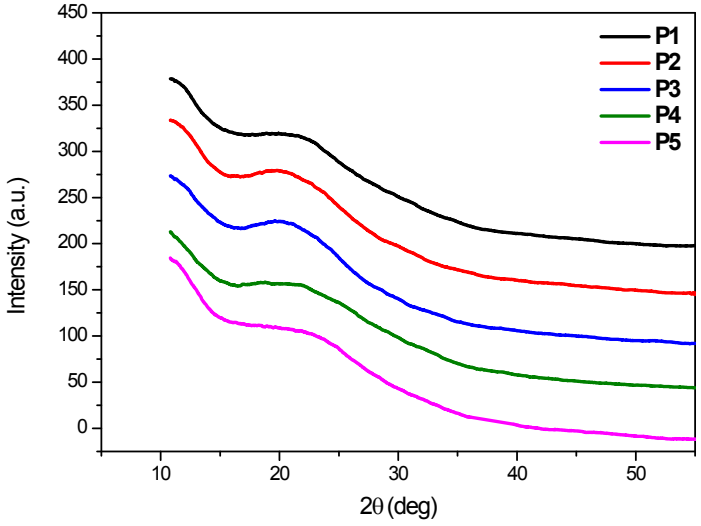


Figure S23. XRD diffractograms of **P1 – P5**

11. GPC chromatograms

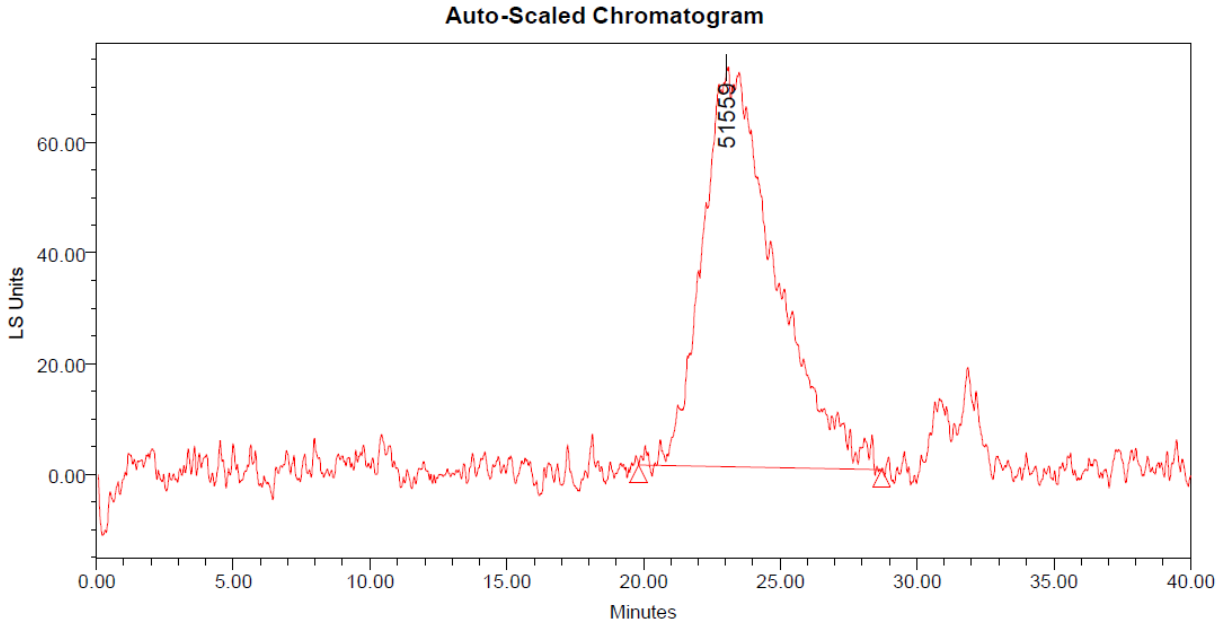


Figure S24. GPC chromatogram of **P1**.

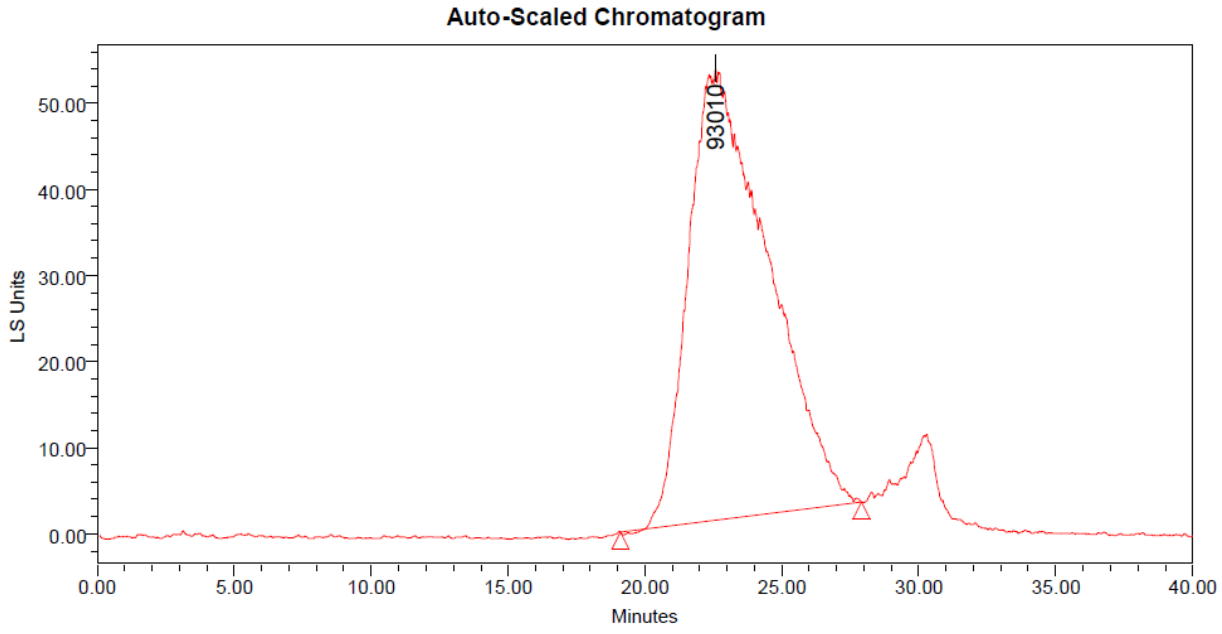


Figure S25. GPC chromatogram of **P2**.

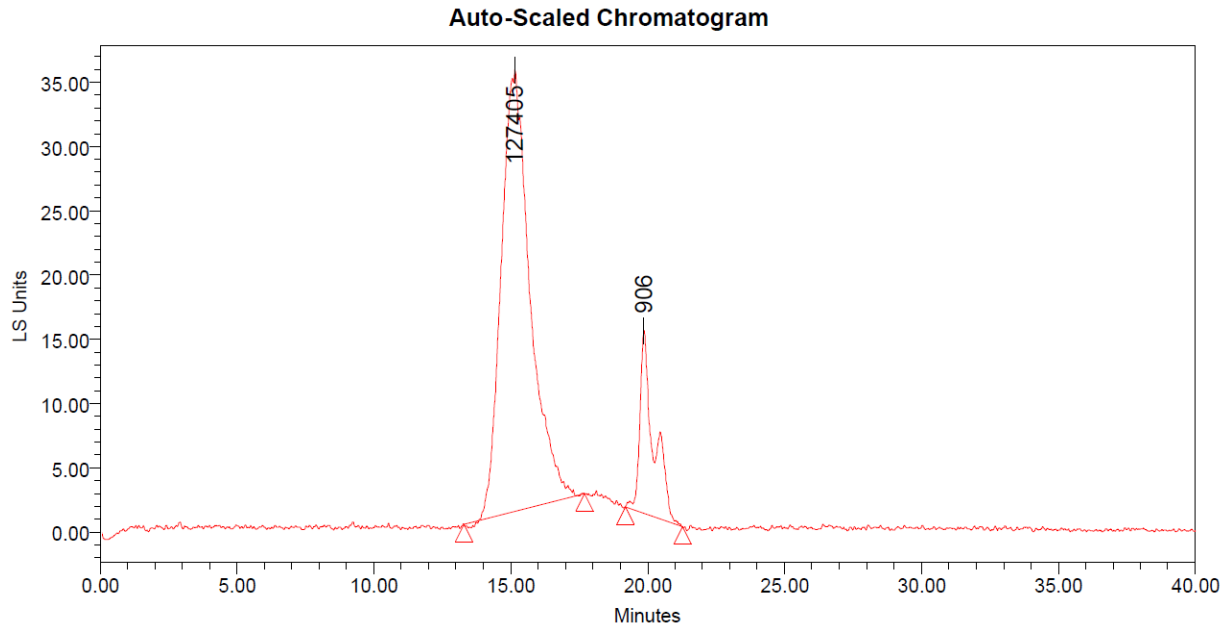


Figure S26. GPC chromatogram of **P3**.

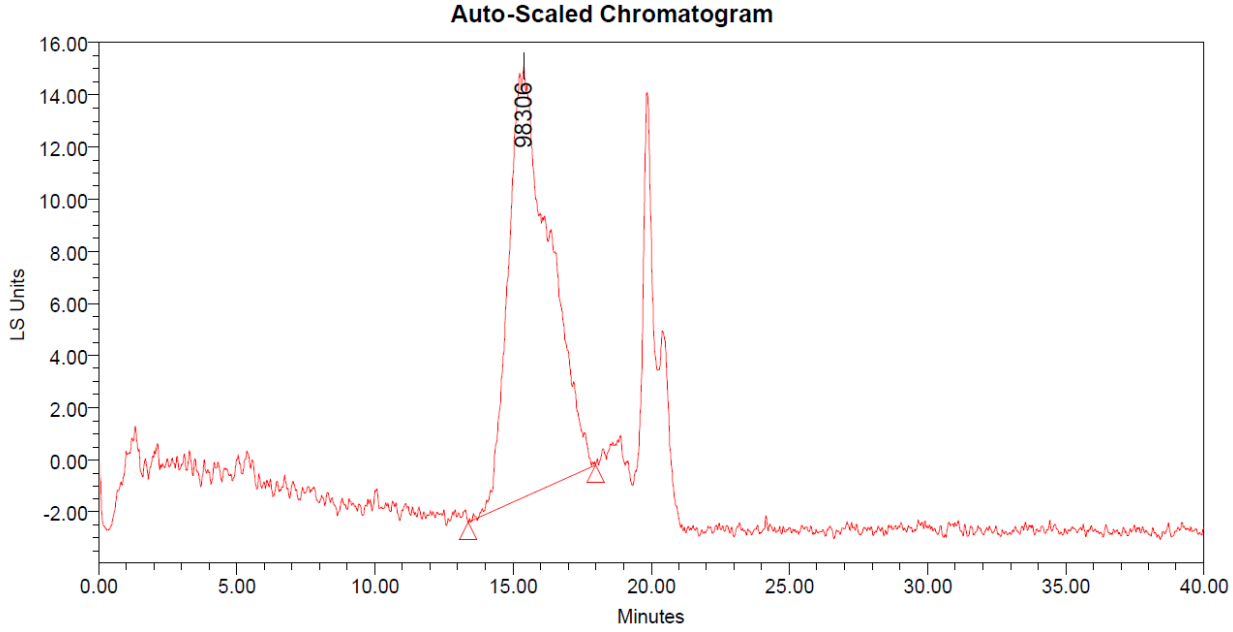


Figure S27. GPC chromatogram of **P4**.

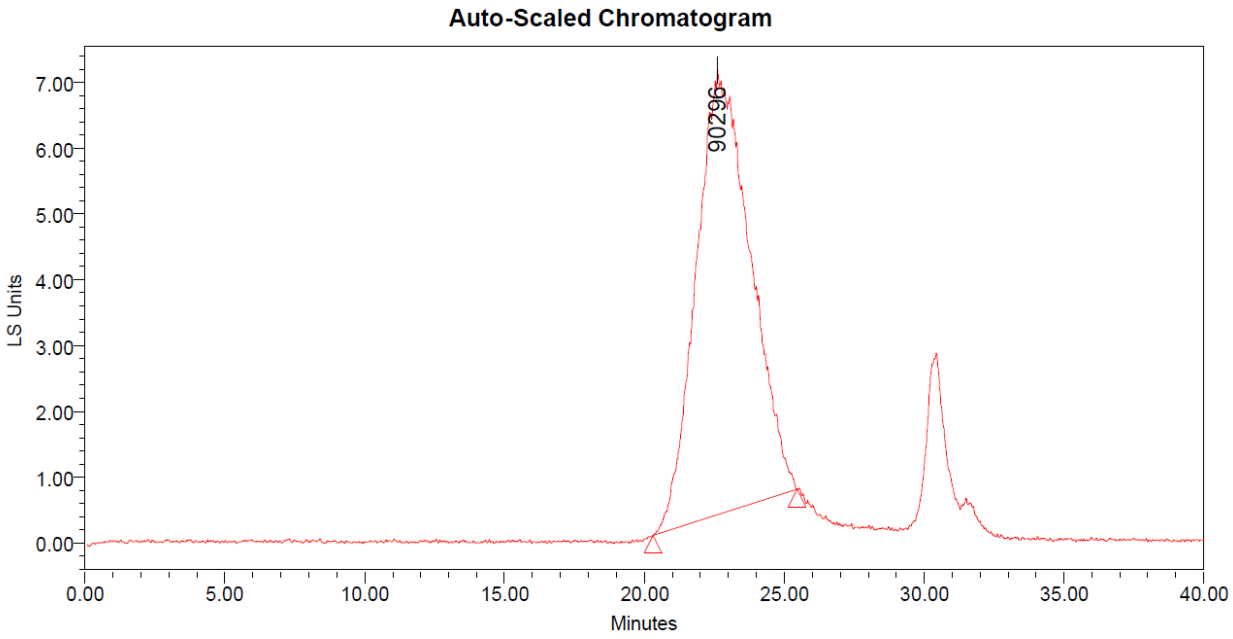


Figure S28. GPC chromatogram of **P5**.