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Supporting Information

The Adjustment of Band Gap and Coplanarity of Diketopyrrolopyrrole-based Copolymers Through Fine-tuning the Conjugated Backbones, and Applications in Thin Film Field Effect Transistors

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1. Characterization techniques.

All Chemicals were purchased from Alfa-Aesar, J&K and Sigma-Aldrich, and used without further purification. All solvents were purified and dried following standard procedures unless otherwise stated.IR spectra were recorded on a JASCO FT/IR-480 plus Fourier transform infrared spectrometer.^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE III 400 and 500 MHz spectrometers. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. Gel permeation chromatography (GPC) analysis was performed on an PL-GPC 220 high temperature chromatograph at 150 °C equipped with a IR5 detector; polystyrene was used as the calibration standard and 1,2,4-trichlorobenzene as eluent; the flow rate was 1.0 mL/min. UV-vis absorption spectra were measured with JASCO V-570 UV-vis spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was measured by AXIS ULTRA DLD with the illuminant of He I. Thermal gravimetric analysis (TGA) measurements were carried out on a SHIMADZU DTG-60 instruments under a dry nitrogen flow, heating from room temperature to 550 °C, with a heating rate of 10 °C/min. Atomic force microscopy (AFM) images of the thin films were obtained on a NanoscopeIII AFM (Digital instruments) operating in tapping mode. AFM samples and microscopic images were identical to those used in organic field-effect transistors. The GIXRD data were obtained at 1W1A, Beijing Synchrotron Raidation Facility.

2. Thermogravimetric Analysis of polymers P1, P2 and P3

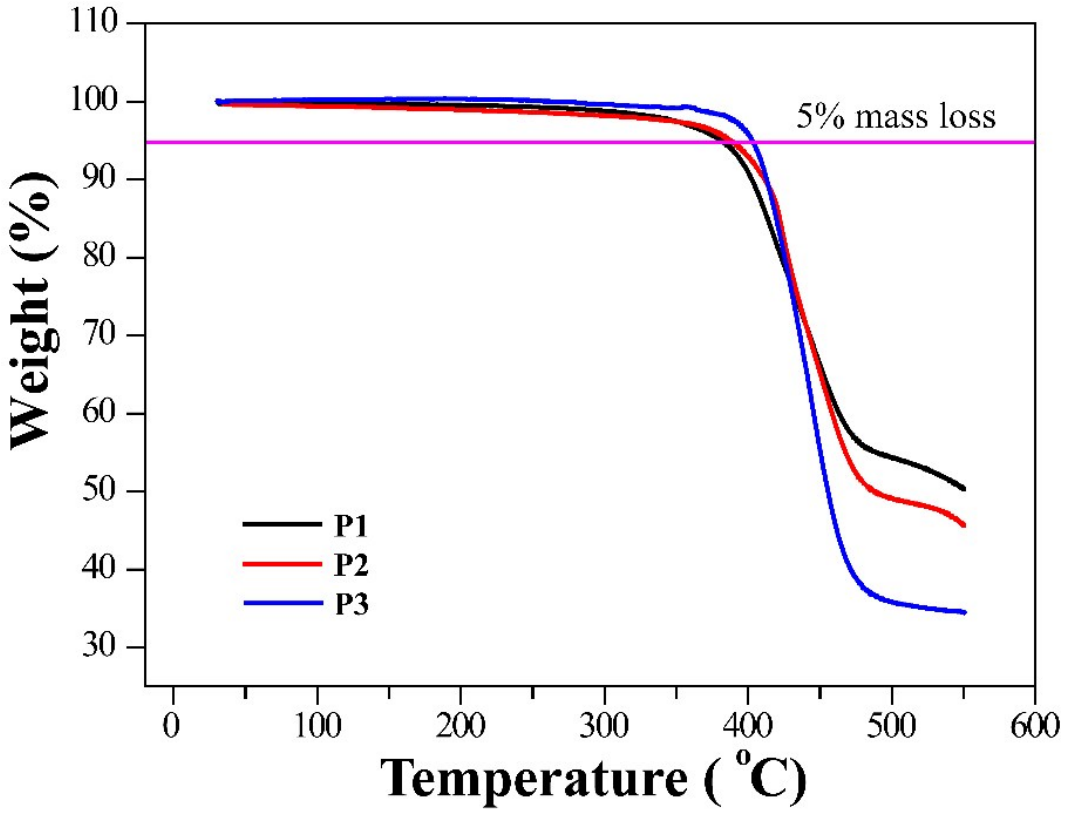

Fig. S1 TGA curves of **P1**, **P2**, and **P3**: heating rate: 10 °C min^{-1}. From 25 °C to 550 °C under nitrogen atmosphere. Decomposition temperatures (at 5% mass loss) are 381 °C, 387 °C, and 403 °C for **P1**, **P2** and **P3**, respectively.

3. Full width at half maxima absorption of polymers P1, P2 and P3

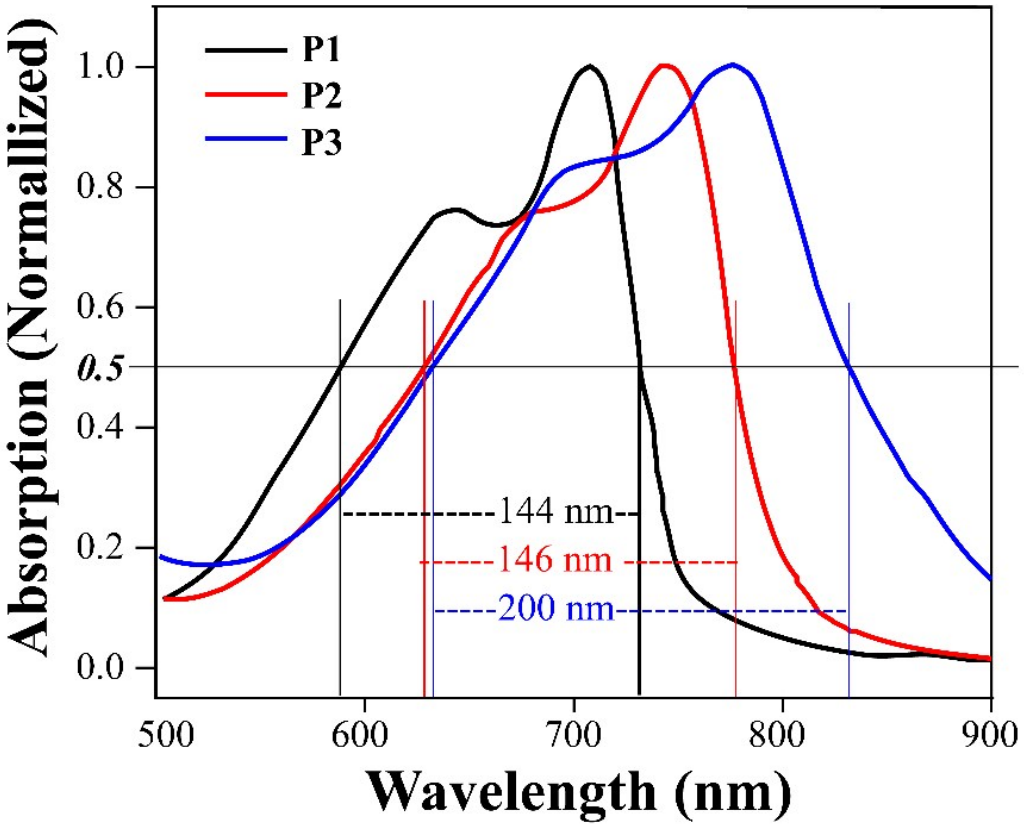

Fig. S2 Full width at half maxima absorption for polymers **P1**, **P2** and **P3** based their thin films absorption spectra.

4. Ultraviolet photoelectron spectroscopy polymers P1, P2 and P3

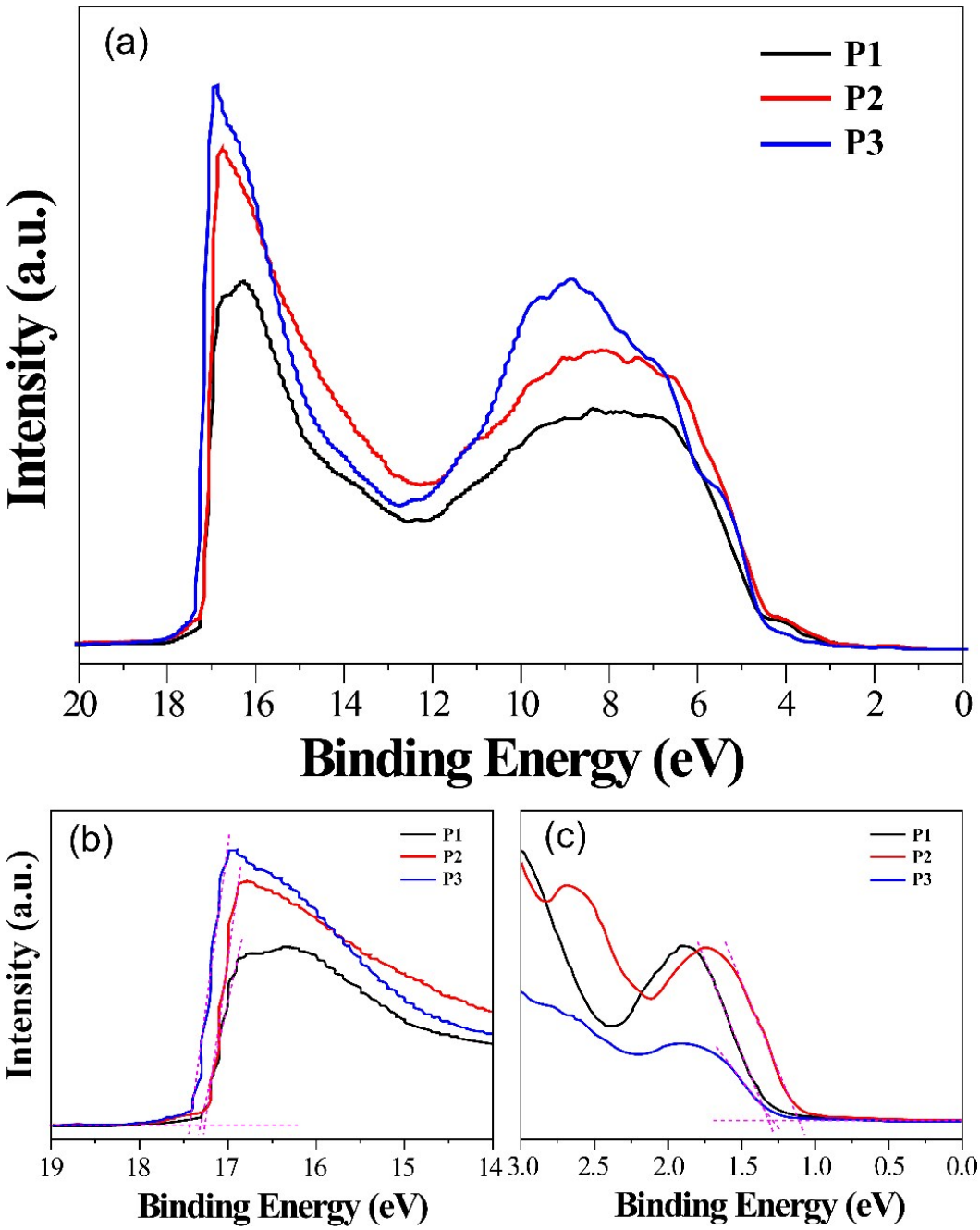

Fig. S3 (a) UPS spectra of thin films of polymers **P1**, **P2** and **P3**; (b) high-energy region, and (c) low-energy region.

5. Fabrication of FET devices.

BG/BCFETs were fabricated. A heavily doped n-type Si wafer and a layer of dry oxidized SiO_2 (300 nm, with roughness lower than 0.1 nm and capacitance of 11 nF cm^{-2}) were used as a gate electrode and gate dielectric layer, respectively. The drain-source (D-S) gold contacts were fabricated by photolithography. The substrates were first cleaned by sonication in acetone and water for 5.0 min and immersed in piranha solution (2:1 mixture of sulfuric acid and 30% hydrogen peroxide) for 20 min. This was followed by rinsing with deionized water, and isopropyl alcohol for several times, and it was blow-dried with nitrogen. Then, the surface was modified with *n*-octadecyltrichlorosilane (OTS). After that, the substrates were cleaned in *n*-hexane, $CHCl_3$ and isopropyl alcohol. The films of polymers (**P1**, **P2** and **P3**) were fabricated by spin-coating its *o*-dichlorobenzene solution (5 mg/mL) at 2000 rpm. The annealing process was carried out in vacuum for 30 min at each temperature. Field-effect characteristics of the devices were determined in air using a Keithley 4200 SCS semiconductor parameter analyzer.

The mobility of the OFETs in the saturation region was extracted from the following equation:

$$I_{DS} = \frac{W}{2L}\mu C_i(V_{GS} - V_{th})^2$$

Where I_{DS} is the drain electrode collected current; L and W are the channel length and width, respectively; μ is the mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer; V_{GS} is the gate voltage, and V_{th} is the threshold voltage. The V_{th} of the device was determined by extrapolating the $(I_{DS,\,sat})^{1/2}$*vs*. V_{GS} plot to I_{DS} =0.

6. DFT calculations

Geometries optimization and frequency analysis were performed at the level of B3LYP/6-31G (d,p) by using Gaussian09 (revision A.02)[S1]. **Table S1**, **S2**, and **S3** list the coordinates and energies at the optimized geometries for two repeated units of **P1**, **P2** and **P3**, and there were no any imaginary frequencies. Then the molecular orbitals were analyzed, the energy gaps between HOMO and LUMO were obtained.

Table S1. Coordinates and energies of two repeated units of **P1**

Labels	Atoms	X	Y	Z
1	C	12.55289	0.202345	0.242351
2	C	13.93216	0.498973	0.411378
3	C	14.11446	1.924712	0.246954
4	N	12.79399	2.40952	-0.0457
5	C	11.85664	1.373072	-0.04898
6	C	12.37455	-1.22598	0.383395
7	N	13.70466	-1.71845	0.612405
8	C	14.63973	-0.68052	0.627623
9	O	15.08895	2.662587	0.334826
10	O	11.38992	-1.95633	0.361604
11	C	10.45403	1.547527	-0.3206
12	C	16.05655	-0.8657	0.823045
13	C	9.767788	2.651128	-0.81655
14	C	8.383137	2.442687	-0.96259
15	C	7.971298	1.17812	-0.58072
16	S	9.326496	0.22359	-0.03673
17	C	16.81213	-2.03179	0.834565
18	C	18.19325	-1.81245	1.050847
19	C	18.49541	-0.48355	1.206693
20	S	17.10717	0.529184	1.076313
21	C	12.58133	3.838584	-0.17691
22	C	13.8937	-3.12795	0.899569
23	C	3.982648	-0.27127	-0.6351
24	C	5.039391	-1.19891	-0.66611
25	C	6.350826	-0.7494	-0.64966
26	C	6.618742	0.629156	-0.60017
27	C	5.492042	1.475745	-0.56848
28	N	4.234153	1.054459	-0.59127
29	C	2.556647	-0.67434	-0.65591

30	C	1.55772	0.299331	-0.83497
31	C	0.214771	-0.04625	-0.86719
32	C	-0.1972	-1.384	-0.71108
33	C	0.802343	-2.35682	-0.51731
34	C	2.146062	-2.00977	-0.49448
35	C	-7.49052	-0.28673	-0.29732
36	C	-6.07869	-0.17292	-0.39854
37	C	-5.73519	1.232393	-0.42226
38	N	-7.00655	1.898483	-0.35678
39	C	-8.06098	0.984575	-0.28183
40	C	-7.83596	-1.69171	-0.30319
41	N	-6.57093	-2.35702	-0.43838
42	C	-5.5143	-1.44345	-0.49573
43	O	-4.66924	1.836472	-0.45959
44	O	-8.89783	-2.29605	-0.19845
45	C	-9.45086	1.350656	-0.21474
46	C	-4.13104	-1.81052	-0.63843
47	C	-10.0651	2.583617	-0.4085
48	C	-11.4663	2.549758	-0.27231
49	C	-11.9618	1.294401	0.032654
50	S	-10.6687	0.12902	0.145078
51	C	-3.5573	-3.03653	-0.96118
52	C	-2.15145	-3.00837	-1.01815
53	C	-1.60895	-1.76548	-0.74013
54	S	-2.86771	-0.60466	-0.40849
55	C	-7.04039	3.345472	-0.25942
56	C	-6.52477	-3.80548	-0.37234
57	C	-16.0426	0.307023	0.645022
58	C	-15.1442	-0.71819	0.300675
59	C	-13.8066	-0.41905	0.090741
60	C	-13.3528	0.902204	0.241485
61	C	-14.3234	1.847951	0.627796
62	N	-15.6092	1.573521	0.81395
63	C	-17.4913	0.063043	0.859208
64	C	-18.2645	1.020761	1.537868
65	C	-19.6225	0.810996	1.759995
66	C	-20.2398	-0.35598	1.304119
67	C	-19.4859	-1.3098	0.618785
68	C	-18.1259	-1.10264	0.397599
69	H	10.24665	3.576451	-1.09895
70	H	7.711056	3.189266	-1.36864
71	H	16.39879	-3.01569	0.672938
72	H	18.93007	-2.60621	1.085787
73	H	19.46571	-0.03888	1.381947

74	H	13.52522	4.312058	0.097805
75	H	12.33937	4.122671	-1.20658
76	H	11.78965	4.184312	0.49321
77	H	14.41458	-3.64398	0.086031
78	H	14.44336	-3.27108	1.833643
79	H	12.89407	-3.55485	0.994331
80	H	4.844905	-2.26306	-0.72702
81	H	7.167276	-1.46424	-0.69732
82	H	5.629087	2.553419	-0.50255
83	H	1.861379	1.332229	-0.95559
84	H	-0.52679	0.729327	-1.03485
85	H	0.520181	-3.39177	-0.35364
86	H	2.8761	-2.7929	-0.31993
87	H	-9.5307	3.48345	-0.67332
88	H	-12.0985	3.415997	-0.42707
89	H	-4.12877	-3.92516	-1.18369
90	H	-1.55233	-3.86924	-1.29004
91	H	-6.00368	3.665999	-0.14491
92	H	-7.4465	3.806472	-1.16611
93	H	-7.62205	3.670748	0.6074
94	H	-6.26756	-4.25078	-1.3394
95	H	-5.81326	-4.14389	0.385575
96	H	-7.53071	-4.12975	-0.10117
97	H	-15.4834	-1.74303	0.205922
98	H	-13.1156	-1.2061	-0.19756
99	H	-14.0282	2.88001	0.807915
100	H	-17.7773	1.924931	1.8837
101	H	-20.2017	1.56016	2.292151
102	H	-21.2996	-0.5186	1.477021
103	H	-19.9583	-2.21497	0.248457
104	H	-17.5658	-1.84651	-0.15977

Total energy: = -4301.670181 Hartrees

Table S2. Coordinates and energies of two repeated units of **P2**

Labels	Atoms	X	Y	Z
1	C	12.35977	0.39931	0.084381
2	C	13.77505	0.492029	0.167114
3	C	14.3199	-0.84805	0.153927
4	N	13.16195	-1.69006	0.035185
5	C	11.98423	-0.93913	-0.00846
6	C	11.81647	1.73948	0.076719

7	N	12.97806	2.582861	0.134656
8	C	14.15486	1.831799	0.186835
9	O	15.45856	-1.29279	0.241321
10	O	10.6735	2.182997	0.055147
11	C	10.6662	-1.50131	-0.13968
12	C	15.48011	2.398301	0.236152
13	C	10.27088	-2.80184	-0.43643
14	C	8.875236	-2.9735	-0.49724
15	C	8.16338	-1.8132	-0.24587
16	S	9.245079	-0.47969	0.065671
17	C	15.89789	3.713124	0.068451
18	C	17.29814	3.883644	0.179763
19	C	17.95173	2.704728	0.433575
20	S	16.87768	1.360411	0.526799
21	C	13.32986	-3.13002	0.087984
22	C	12.79994	4.018957	0.238651
23	C	1.651554	-2.51652	0.00109
24	C	0.279625	-2.18807	-0.0277
25	C	0.033308	-0.83995	-0.22465
26	S	1.547825	0.036412	-0.37369
27	C	2.485367	-1.43011	-0.1728
28	C	3.944803	-1.44167	-0.19431
29	C	4.717996	-0.2807	-0.37842
30	C	6.099696	-0.37893	-0.40004
31	C	6.716158	-1.63139	-0.23043
32	C	5.849046	-2.72795	-0.0349
33	N	4.525393	-2.65047	-0.02243
34	C	-7.30358	-0.30118	-0.07718
35	C	-5.94554	-0.71197	-0.065
36	C	-5.90662	-2.14704	0.107669
37	N	-7.29016	-2.52525	0.173453
38	C	-8.13143	-1.41521	0.059715
39	C	-7.34351	1.132253	-0.26453
40	N	-5.96139	1.50563	-0.37214
41	C	-5.11809	0.396139	-0.25251
42	O	-4.99061	-2.95666	0.20598
43	O	-8.25889	1.946451	-0.31847
44	C	-9.56818	-1.4771	0.075532
45	C	-3.68444	0.448254	-0.32514
46	C	-10.4209	-2.57613	0.03234
47	C	-11.7872	-2.23921	0.047784
48	C	-12.0207	-0.87617	0.10677
49	S	-10.5168	0.00784	0.139086
50	C	-2.83455	1.51873	-0.5944

51	C	-1.47091	1.182713	-0.58614
52	C	-1.23195	-0.15491	-0.30993
53	S	-2.73188	-1.01537	-0.05763
54	C	-7.62952	-3.91275	0.425913
55	C	-5.62315	2.908252	-0.51824
56	C	-18.3166	0.873191	0.67343
57	C	-19.4889	1.674717	0.613307
58	C	-19.242	2.94416	0.16311
59	S	-17.564	3.181785	-0.19633
60	C	-17.1785	1.535264	0.268668
61	C	-15.8206	0.993607	0.212081
62	C	-14.7114	1.751701	-0.20394
63	C	-13.4588	1.16082	-0.24698
64	C	-13.3053	-0.18416	0.132968
65	C	-14.4774	-0.84643	0.553994
66	N	-15.6844	-0.2966	0.589045
67	H	10.96188	-3.60671	-0.63662
68	H	8.405647	-3.91606	-0.75203
69	H	15.22868	4.532325	-0.14621
70	H	17.79798	4.839127	0.073005
71	H	19.01422	2.548603	0.562706
72	H	14.37995	-3.30391	0.328084
73	H	12.69907	-3.57414	0.862769
74	H	13.11275	-3.60225	-0.87603
75	H	13.33157	4.422186	1.104678
76	H	13.12978	4.537585	-0.66768
77	H	11.7281	4.183212	0.35969
78	H	2.04646	-3.5141	0.142011
79	H	-0.51404	-2.91795	0.086754
80	H	4.2427	0.685494	-0.51394
81	H	6.701231	0.51024	-0.56462
82	H	6.264988	-3.71886	0.13636
83	H	-10.0788	-3.59725	-0.03933
84	H	-12.579	-2.97593	-0.01666
85	H	-3.17853	2.519308	-0.80484
86	H	-0.68116	1.898246	-0.7849
87	H	-6.68576	-4.42418	0.621589
88	H	-8.28358	-4.00941	1.296901
89	H	-8.10423	-4.38105	-0.44277
90	H	-4.97191	3.249574	0.291757
91	H	-5.14777	3.112859	-1.48298
92	H	-6.5683	3.451489	-0.47226
93	H	-18.2845	-0.1581	1.000139
94	H	-20.4757	1.324267	0.892678

95	H	-19.9419	3.755618	0.020056
96	H	-14.8302	2.78878	-0.50052
97	H	-12.6029	1.734771	-0.58992
98	H	-14.4193	-1.87817	0.895414

Total energy: = -4943.178513 Hartrees

Table S3. Coordinates and energies of two repeated units of **P3**

Labels	Atoms	X	Y	Z
1	C	12.37483	-0.14843	0.018176
2	C	13.78509	0.010696	-0.01545
3	C	14.07974	1.416912	-0.18192
4	N	12.78512	2.038724	-0.22206
5	C	11.75903	1.096613	-0.10228
6	C	12.08037	-1.55244	0.196074
7	N	13.37492	-2.16952	0.277711
8	C	14.39972	-1.22889	0.151615
9	O	15.12442	2.048327	-0.29311
10	O	11.03424	-2.18927	0.260062
11	C	10.3561	1.410654	-0.1025
12	C	15.80601	-1.54338	0.201613
13	C	9.708635	2.642896	-0.1151
14	C	8.305889	2.552221	-0.10776
15	C	7.836846	1.248379	-0.09065
16	S	9.162395	0.109011	-0.07229
17	C	16.44706	-2.7356	0.517428
18	C	17.85855	-2.65468	0.463071
19	C	18.29911	-1.4059	0.105559
20	S	17.0053	-0.29901	-0.15926
21	C	12.69958	3.469788	-0.44073
22	C	13.45902	-3.61341	0.39052
23	C	5.988373	-0.50676	-0.07703
24	N	4.639427	-0.663	-0.07306
25	C	4.016567	0.494798	-0.07535
26	S	5.103573	1.890721	-0.08347
27	C	6.471968	0.788655	-0.08303
28	C	1.801604	1.770013	-0.06217
29	C	0.418318	1.497967	-0.06418
30	C	0.121492	0.14386	-0.07718
31	S	1.592835	-0.81253	-0.08595
32	C	2.58458	0.629775	-0.07328
33	C	-7.23483	-0.06775	0.008097

34	C	-5.86143	0.284165	0.029134
35	C	-5.76239	1.718585	0.181289
36	N	-7.12819	2.154102	0.257109
37	C	-8.01658	1.079166	0.153583
38	C	-7.33423	-1.50296	-0.13697
39	N	-5.96849	-1.94193	-0.18349
40	C	-5.0798	-0.86721	-0.08263
41	O	-4.81301	2.493296	0.233588
42	O	-8.28451	-2.27303	-0.22376
43	C	-9.44797	1.194105	0.20105
44	C	-3.64844	-0.98745	-0.09004
45	C	-10.2549	2.306307	0.425624
46	C	-11.6323	2.028312	0.401728
47	C	-11.923	0.695625	0.157753
48	S	-10.4579	-0.23598	-0.0415
49	C	-2.84081	-2.12281	-0.10762
50	C	-1.46441	-1.84558	-0.10385
51	C	-1.17291	-0.48998	-0.08428
52	S	-2.63879	0.461314	-0.06135
53	C	-7.40762	3.572623	0.370253
54	C	-5.69124	-3.35272	-0.37578
55	C	-13.5307	-1.26244	-0.13565
56	N	-14.8511	-1.58617	-0.17994
57	C	-15.6147	-0.53132	-0.0152
58	S	-14.7147	0.974489	0.210082
59	C	-13.2165	0.067323	0.066536
60	C	-17.9669	0.452465	0.151506
61	C	-19.3166	0.014847	0.08906
62	C	-19.4223	-1.33532	-0.1231
63	S	-17.8762	-2.1022	-0.25122
64	C	-17.0572	-0.57214	-0.01441
65	H	10.224	3.590717	-0.11908
66	H	7.653684	3.418178	-0.11383
67	H	15.929	-3.64032	0.795902
68	H	18.51731	-3.48662	0.682339
69	H	19.32067	-1.06985	-0.01021
70	H	13.72419	3.812507	-0.59361
71	H	12.10453	3.703911	-1.3283
72	H	12.28307	3.989469	0.428325
73	H	14.06563	-4.04027	-0.41291
74	H	13.86354	-3.9227	1.359819
75	H	12.43569	-3.98268	0.307746
76	H	6.620737	-1.38771	-0.07543
77	H	2.214565	2.772464	-0.05204

78	H	-0.34321	2.269435	-0.0562
79	H	-9.87217	3.297236	0.613138
80	H	-12.3943	2.782242	0.563075
81	H	-3.22397	-3.13115	-0.11311
82	H	-0.70279	-2.61696	-0.11376
83	H	-6.43945	4.074096	0.329475
84	H	-8.03052	3.925082	-0.4571
85	H	-7.88902	3.816663	1.322756
86	H	-5.08542	-3.52269	-1.27056
87	H	-5.19248	-3.79058	0.494823
88	H	-6.66155	-3.8354	-0.50185
89	H	-12.7921	-2.04717	-0.25605
90	H	-17.6755	1.484335	0.313323
91	H	-20.1702	0.673409	0.197087
92	H	-20.3234	-1.92634	-0.21171

Total energy: = -5584.702103 Hartrees

References

(S1) 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.; Peralta, Jr., 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, J. M.; 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

7. ^{1}H and ^{13}C NMR spectra, FTIR, and GPC traces of P1, P2 and P3

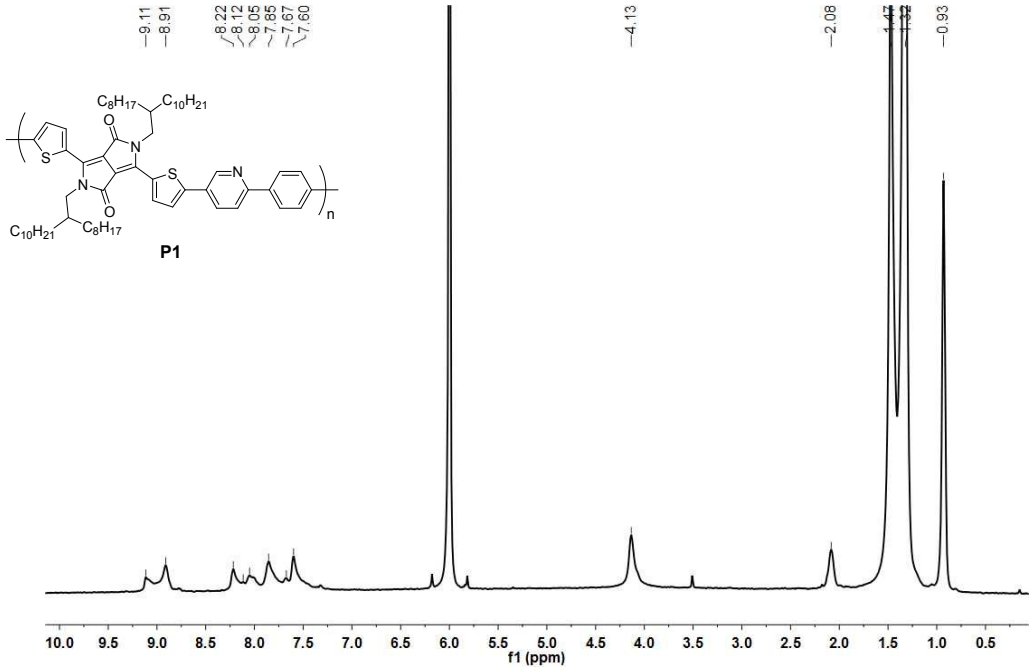

Fig. S4 High temperature ^{1}H NMR spectrum of **P1** (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

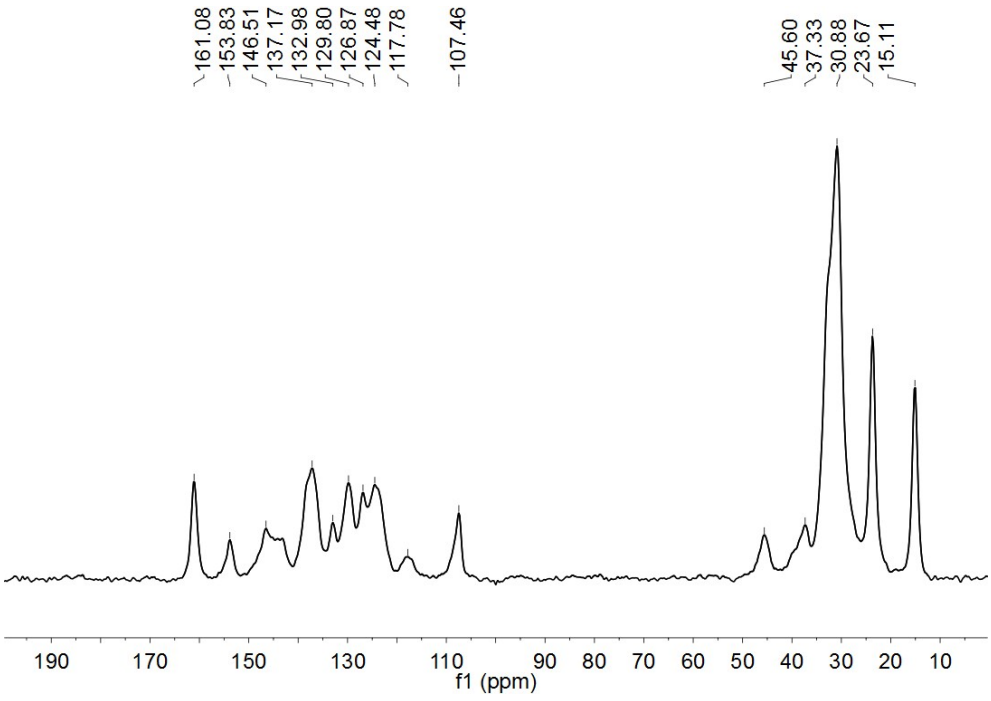

Fig. S5 ^{13}C NMR spectrum of **P1** (100 MHz, solid).

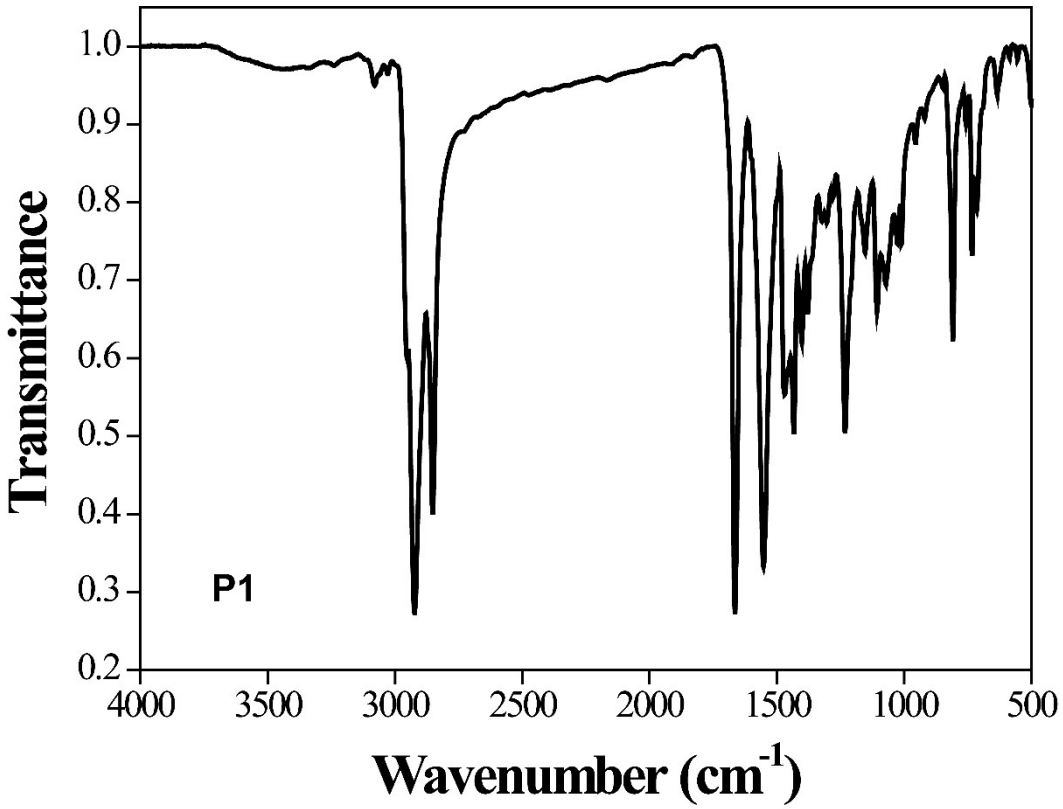

Fig. S6 FTIR spectrum of **P1.**

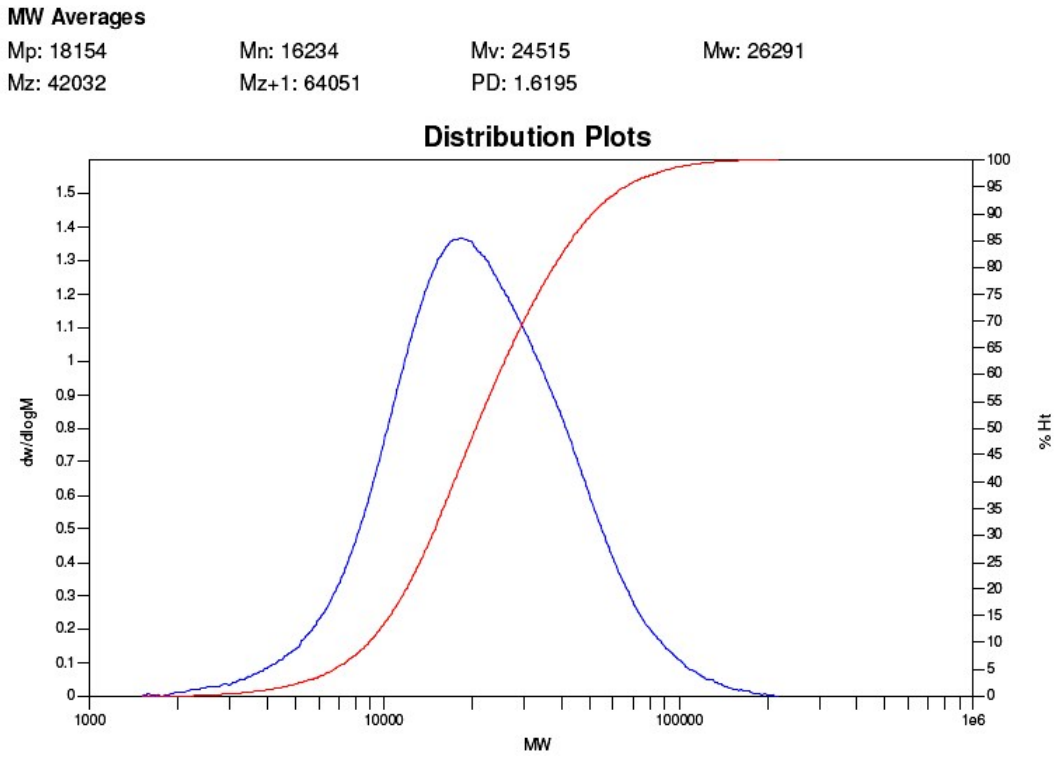

Fig. S7 GPC trace for **P1.**

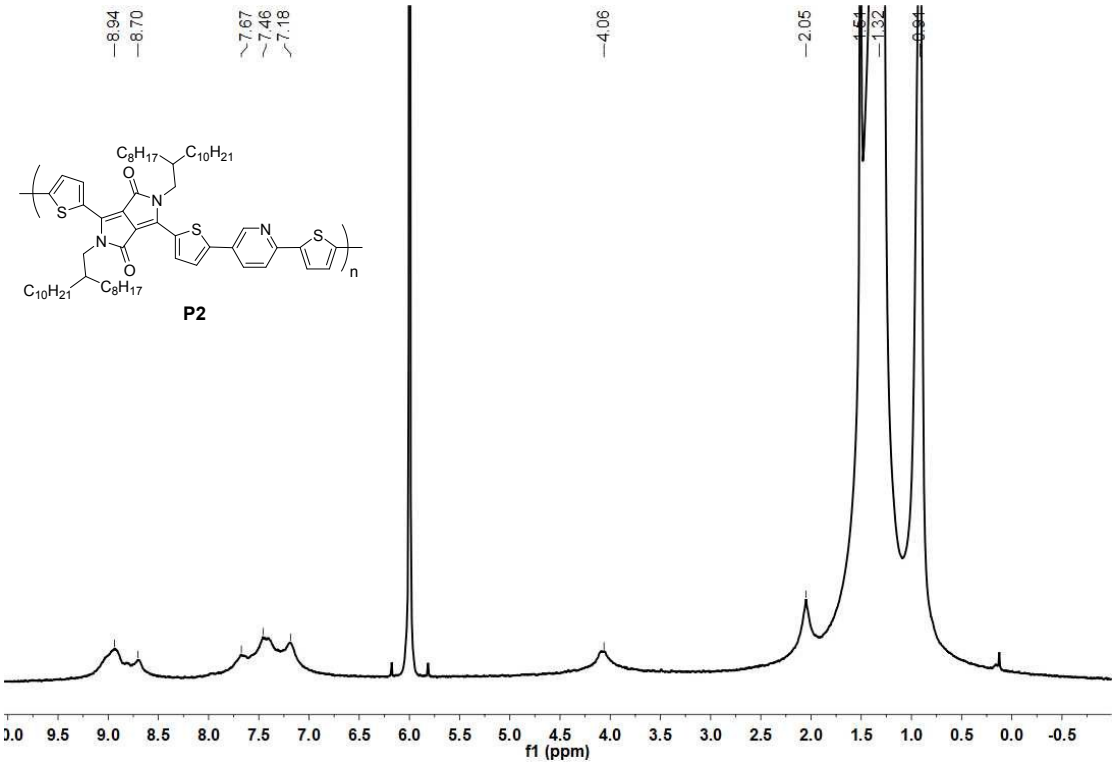

Fig. S8 High temperature ^{1}H NMR spectrum of **P2** (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

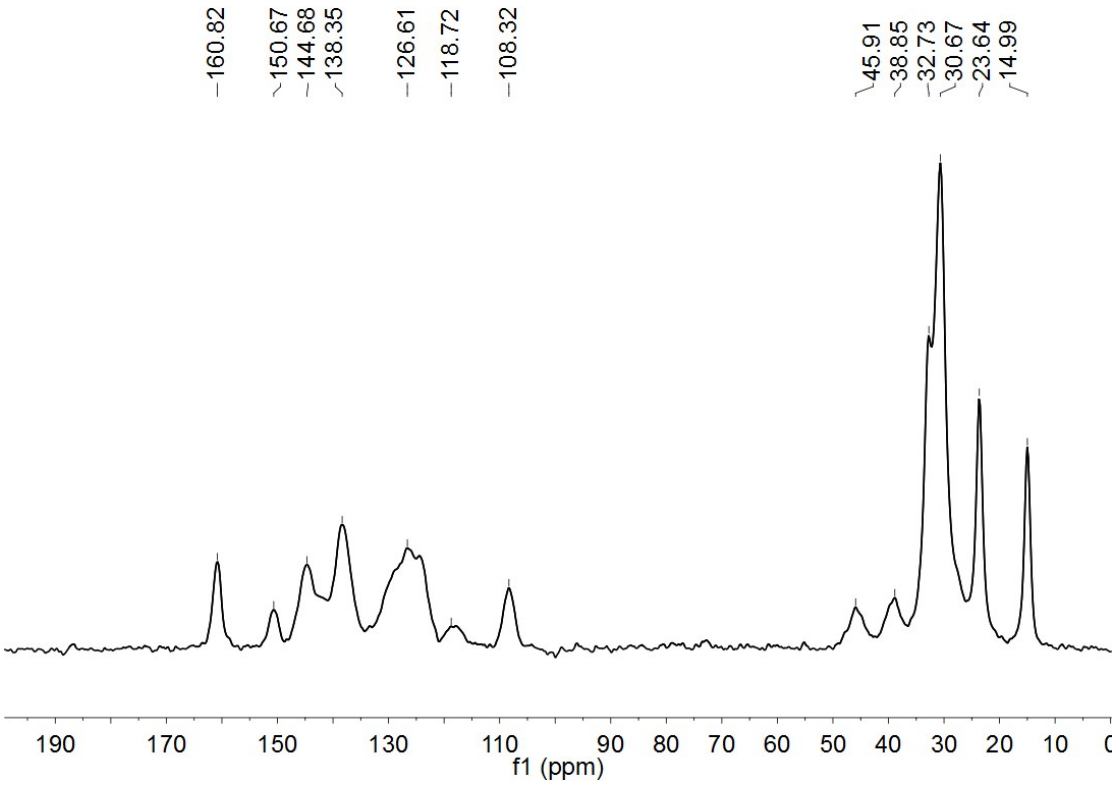

Fig. S9 ^{13}C NMR spectrum of **P2** (100 MHz, solid).

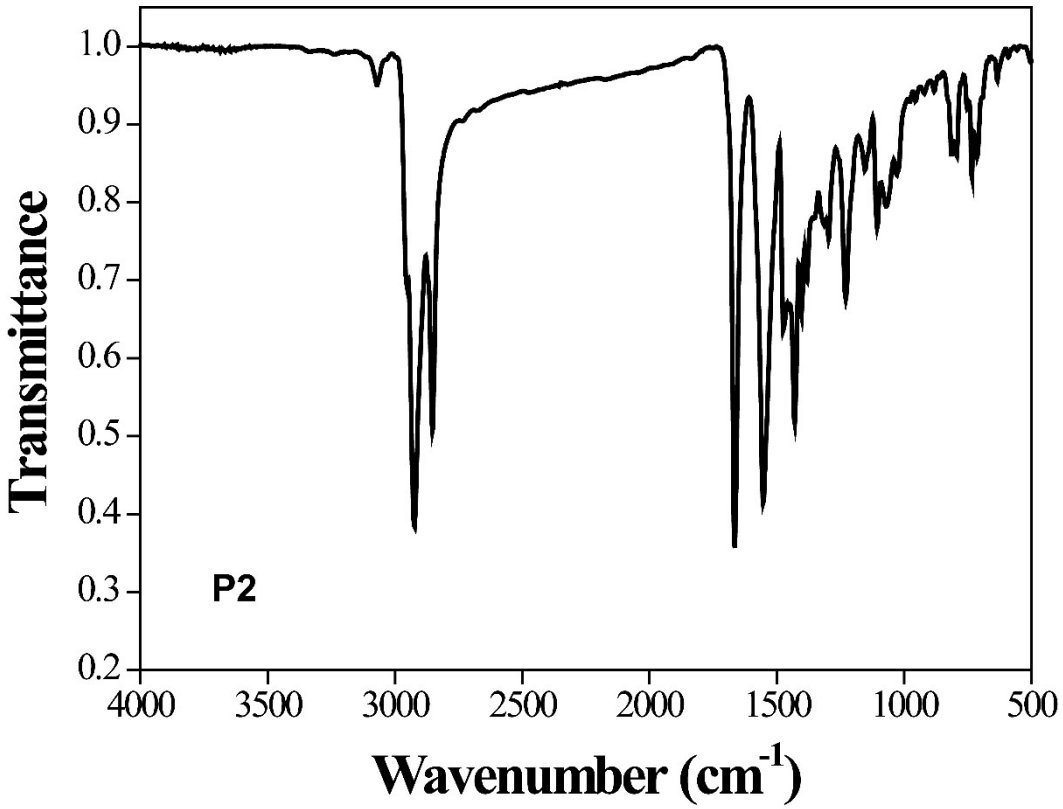

Fig. S10 FTIR spectrum of **P2**

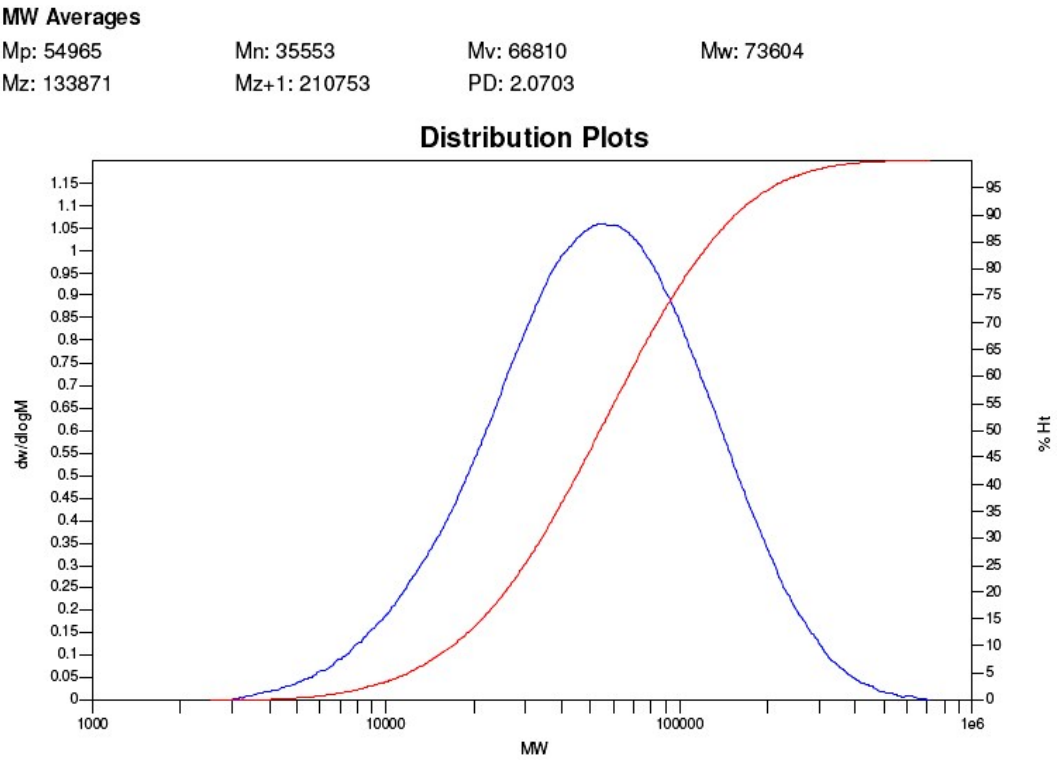

Fig. S11 GPC trace for **P2**

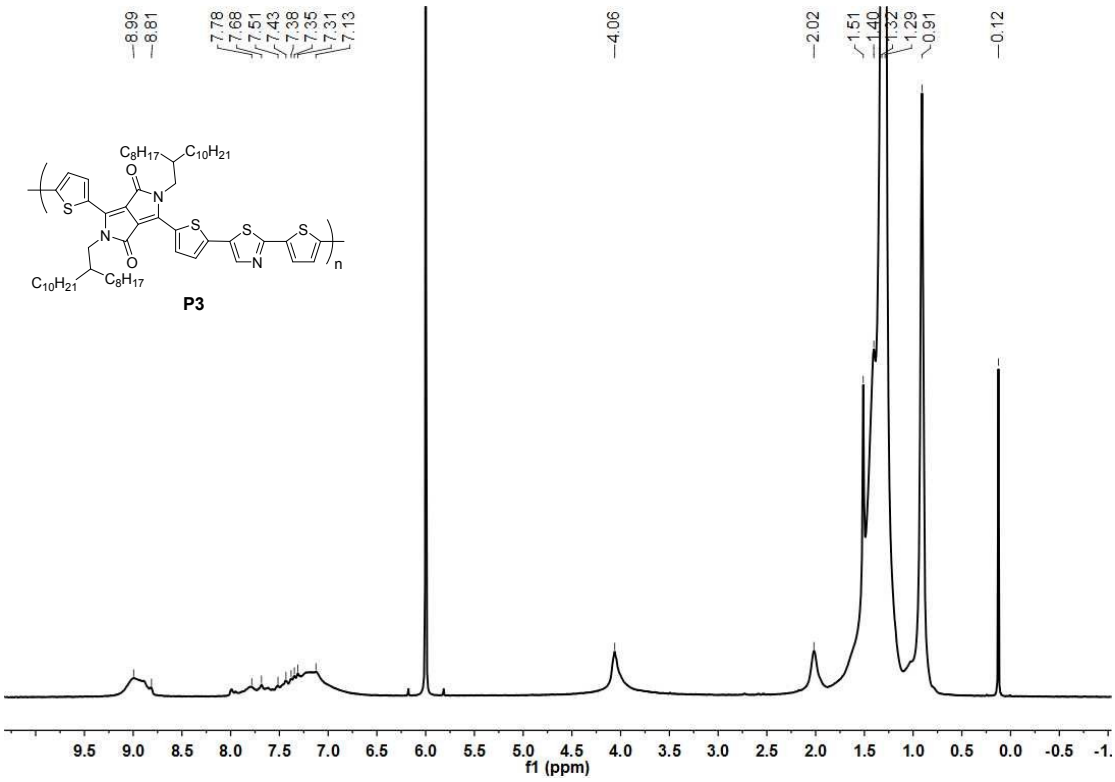

Fig. S12 High temperature ^{1}H NMR spectrum of **P3** (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

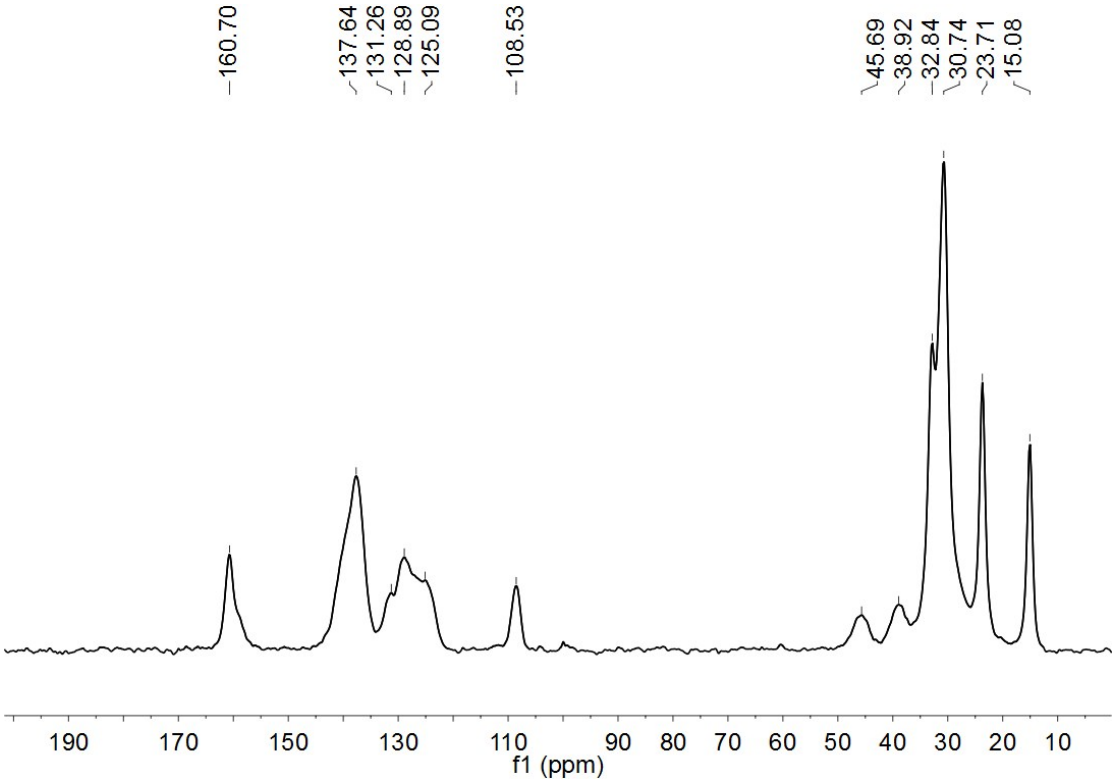

Fig. S13 ^{13}C NMR spectrum of **P3** (100 MHz, solid)

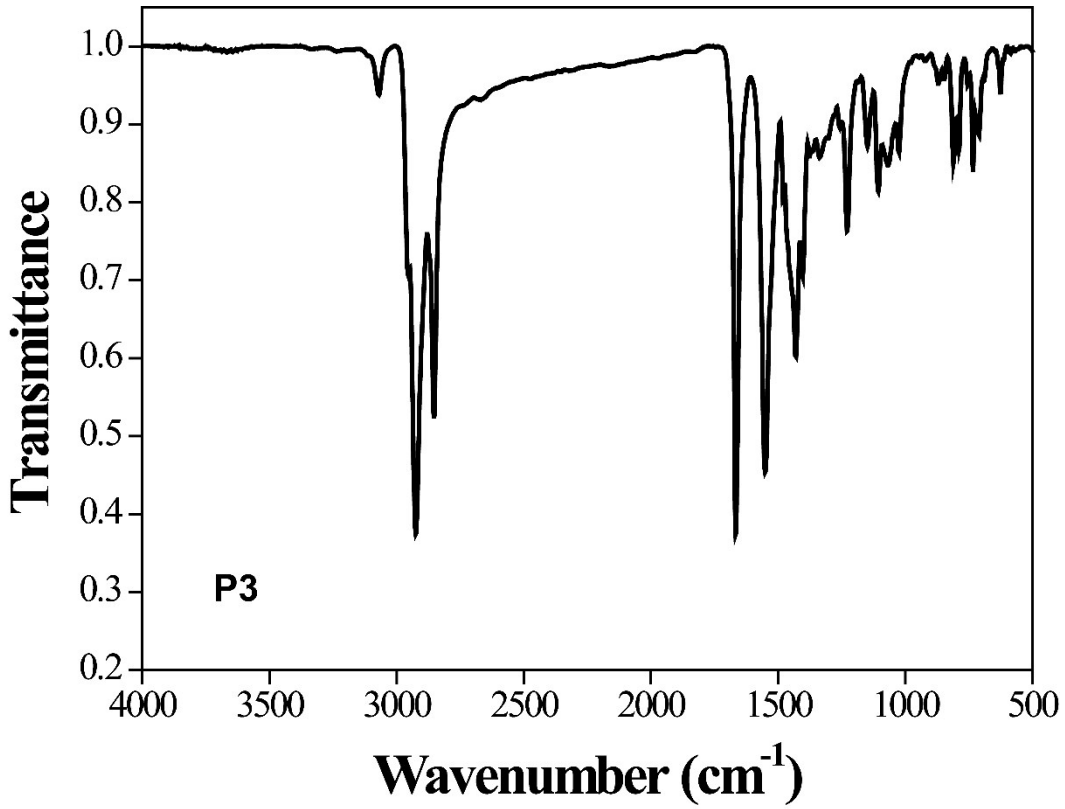

Fig. S14 FTIR spectrum of **P3**

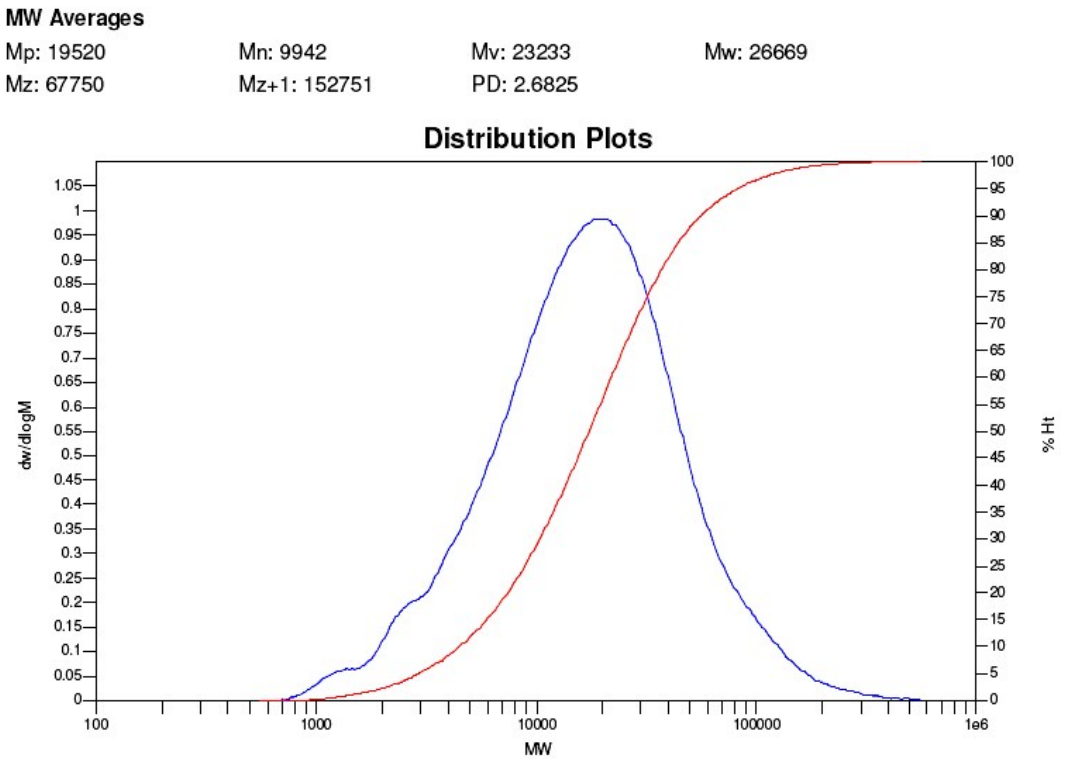

Fig. S15 GPC trace for **P3**