D-A-D-π-D-A-D Type Diketopyrrolopyrrole Based Small Molecule Electron Donor for Bulk Heterojunction Organic Solar Cell

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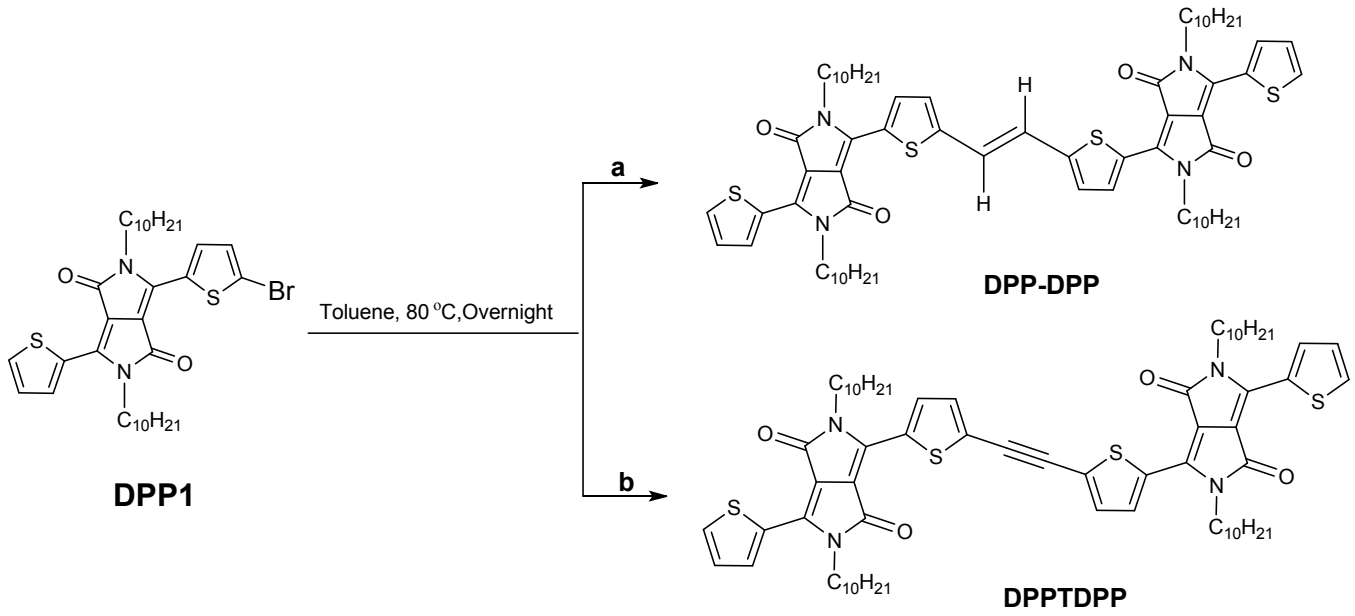

Reagents: **a** = bis(tributylstannyl)ethene , **b** = bis(tributylstannyl)acetylene

Scheme S1. Synthesis of **DPP-DPP** and **DPPTDPP**

Experimental details

General Methods:

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon by using standard Schlenk methods. The ^{1}H and ^{13}C NMR spectroscopic data were recorded at 400 and 100 MHz, respectively, by using $CDCl_3$ as the solvent. The 1H NMR chemical shifts are reported in parts per million (ppm) relative to the residual proton signal of the solvent (CHCl3, δ = 7.26 ppm). The multiplicity of each resonance is described as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), and the coupling constants (J) are given in Hertz (Hz). The chemical shifts of the ^{13}C NMR spectra are reported relative to the solvent signal (CDCl3, δ = 77.0 ppm). The UV/Vis absorption spectra of the DPPs were recorded in chloroform with a UV/Vis spectrophotometer. The TGA analyses were performed with a thermal analysis system that was set to a heating rate of 10 °C min–1 under nitrogen. Cyclic voltammograms and differential voltammograms were recorded with an electrochemical analyzer that used glassy carbon as the working electrode, Pt wire as the counter electrode, and saturated Ag/Ag+ as the reference electrode.

Device fabrication and characterization

The solution processed BHJ organic solar cells with ITO/PEDOT:PSS/ active layer/Al were prepared as follow: The indium tin oxide (ITO) coated glass substrates were cleaned ultrasonically and subsequently in aqueous detergent, deionized water, isopropyl alcohol and acetone and finally dried under ambient conditions. An aqueous solution of PEDOT:PSS (Heraeus, clevious PVP, Al 4083) was pin cast on the ITO substrates to obtain a film with thickness of about 40 nm and dried for 10 min at a temperature of 120° C. Mixture of **DPP-DPP** and $PC_{71}BM$ with weight ratios of 1:0.5, 1:1, 1:1.5, 1:2 and 1:2.5 in chloroform solution (concentration 14 mg/mL) were prepared and then spin cast onto the top of the PEDOT:PSS layer and dried at ambient conditions. Finally, the aluminum (Al) top electrode was thermally deposited on the top of active layer in a vacuum of 10^{-5} Torr through a shadow mask of 20 mm^2. For the two step annealing (TSA) treatment, first the active layer was thermally annealed at 120 °C for 10 min and cooled down to room temperature then the active layer was kept in the petri dish containing 100 μL THF for 20 min. All the devices were fabricated and tested under an ambient atmosphere without encapsulation. The hole-only and electron-only devices with ITO/PEODT:PSS/**DPP-DPP**:$PC_{71}BM$/Au and ITO/Al/**DPP-DPP**:$PC_{71}BM$/Al architectures were also fabricated in an analogous way, in order to measure the hole and electron mobility, respectively. The current-voltage (J-V) characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley 2400 source meter in dark as well as under simulated AM1.5G illumination of 100 mW/cm^2. A xenon light source coupled with optical filter was used to give the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured illuminating the device through the light source and monochromator and the resulting current was measured using a Keithley electrometer under short circuit condition.

Synthesis of DPP-DPP

In 100 ml round bottom flask monobromodiketopyrrolopyrrole **DPP1** (0.100 g, 0.15 mmol) and bis(tributylstannyl)ethene (0.040 ml, 0.075 mmol) were dissolved in dry toluene (20 ml). The reaction mixture was degassed with argon for 10 minutes and $Pd(PPh_3)_4$ (0.035g, 0.030 mmol), was then added. The reaction mixture was stirred at 80 ^oC overnight. After completion of reaction, the reaction mixture was allowed to cool down to room temperature.

The solvent was removed under vacuo and the product was purified by repeated silica-column chromatography with hexane : dichloromethane (1:1) as an eluent in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.95 (2H, d, J = 4 Hz), 8.90 (2H, d, J = 4 Hz), 7.28 (4H, d, J = 4 Hz), 7.23 (2H, s), 4.09 (8H, m), 2.17 (16H, s), 1.76 (8H, m), 1.26 (40H, s), 0.86 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 161.4, 161.2, 147.0, 139.9,139.1, 136.3, 135.4, 130.8, 129.8, 129.3, 128.7, 1285, 122.8, 108.6, 108.1, 42.34, 42.26, 31.9, 30.1, 30.0, 29.6, 29.5, 29.30, 29.27, 26.93, 26.91, 22.7, 14.1.

Synthesis of DPPTDPP

In 100 ml round bottom flask monobromodiketopyrrolopyrrole **DPP1** (0.100 g, 0.15 mmol) and bis(tributylstannyl)acetylene (0.040 ml, 0.075 mmol) were dissolved in dry toluene (20 ml). The reaction mixture was degassed with argon for 10 minutes and $Pd(PPh_3)_4$ (0.035g, 0.030 mmol), was then added. The reaction mixture was stirred at 80 ^{o}C overnight. After completion of reaction, the reaction mixture was allowed to cool down to room temperature. The solvent was removed under vacuo and the product was purified by repeated silica-column chromatography with hexane : dichloromethane (1:1) as an eluent in 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.98 (2H, d, J = 4 Hz), 8.92 (2H, d, J = 4 Hz), 7.67 (2H, s), 7.45 (2H, s), 7.30 (2H, s), 4.08 (8H, m), 1.75 (8H, s), 1.44 (8H, m), 1.26 (46H, s), 0.87 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 161.3, 161.2, 140.6, 138.4,135.8, 135.2, 135.1, 133.7, 132.2, 132.1, 131.6, 131.2, 13.4, 129.7, 128.7, 128.6, 128.4, 128.1, 127.9, 126.9, 109.0, 107.9, 90.5, 42.3, 31.9, 30.1, 29.9, 29.7, 29.5, 29.4, 29.3, 29.2, 26.2, 22.7, 14.1.

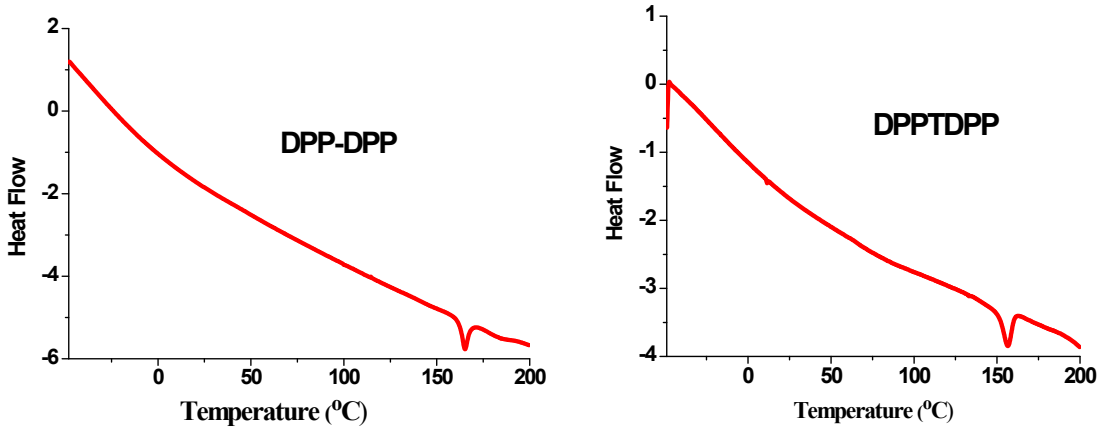

Fig.S1 DSC curves of **DPP-DPP** and **DPPTDPP** with a heating rate of 10 °C min^{-1} under N_2.

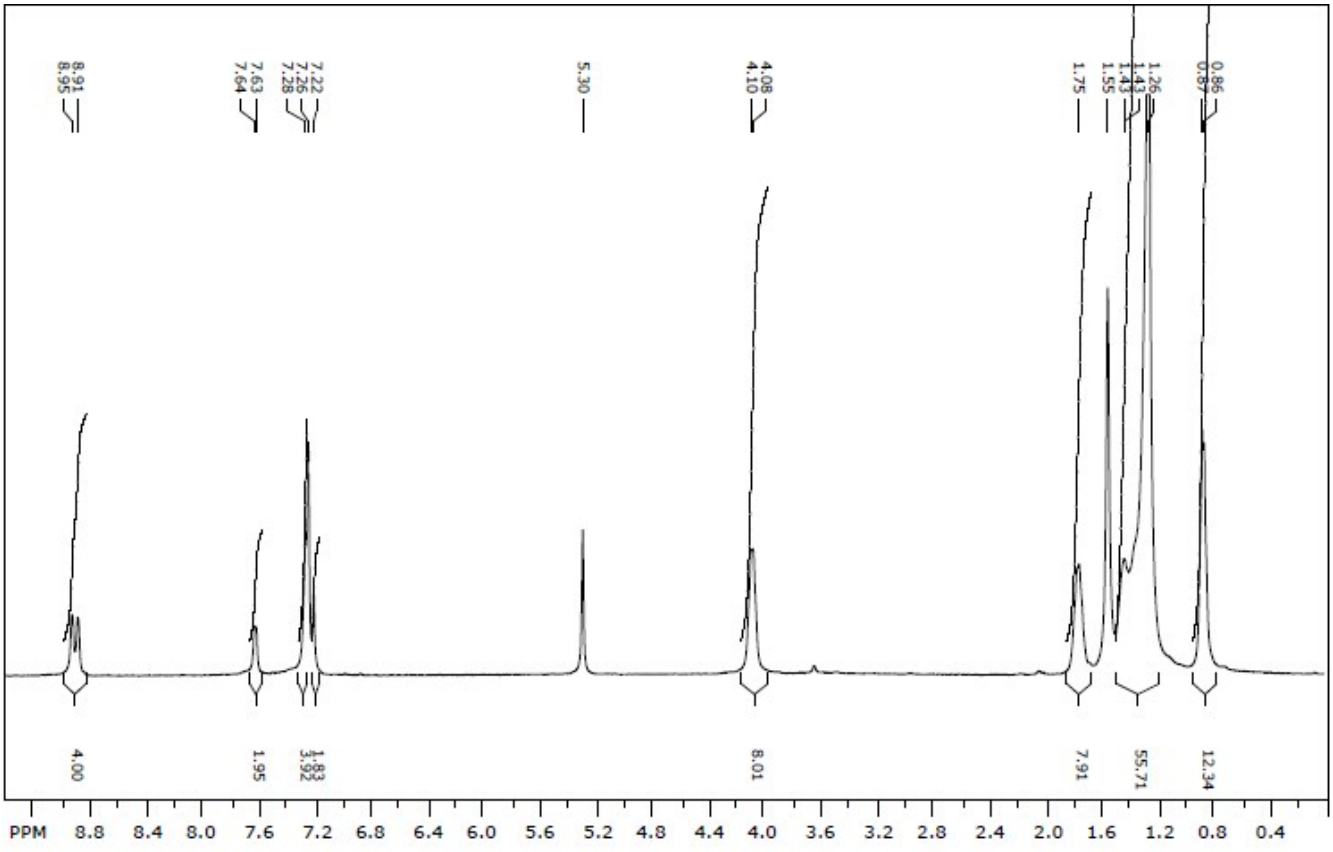

Fig. S2 ^{1}H NMR spectra of **DPP-DPP**

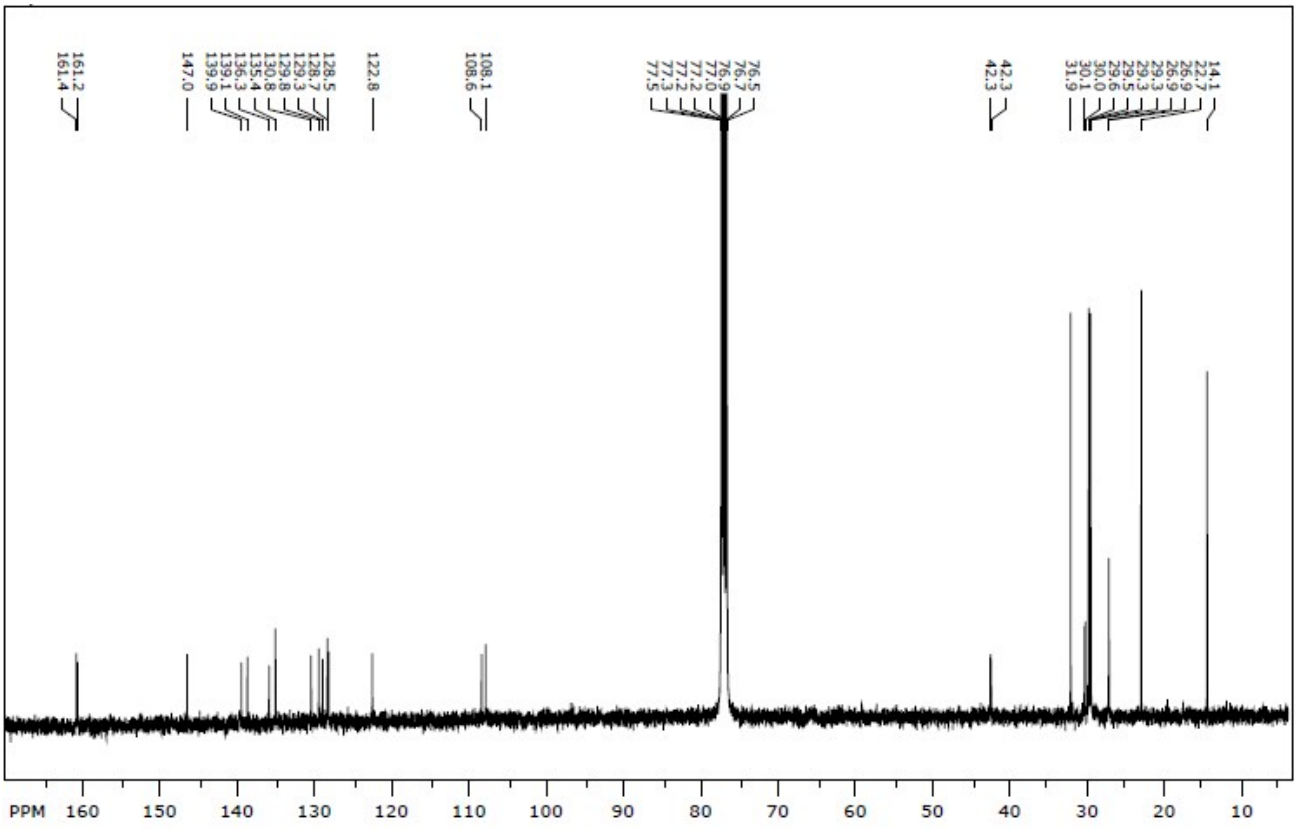

Fig. S3 ^{13}C NMR spectra of **DPP-DPP**

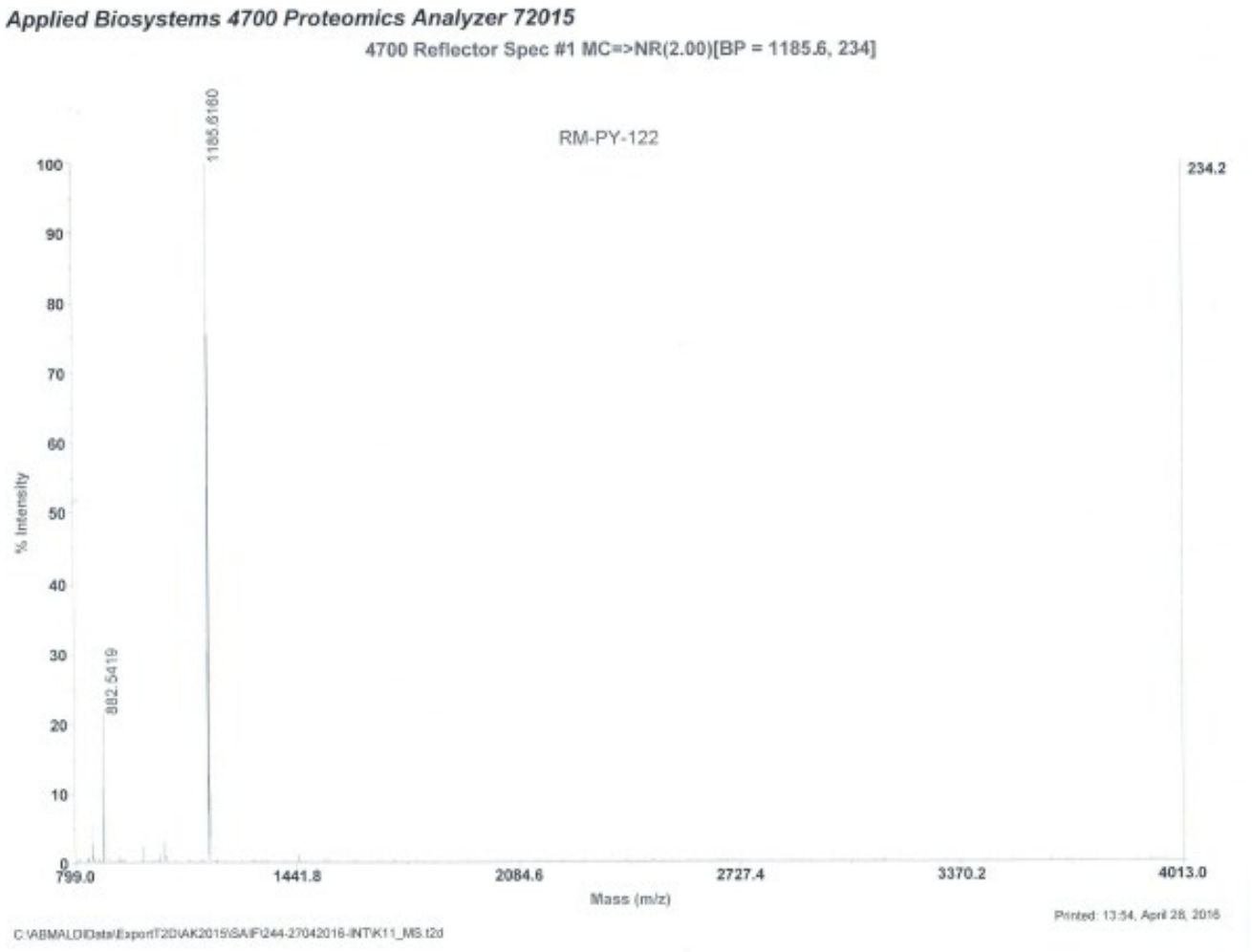

Fig. S4 Mass spectra of **DPP-DPP**

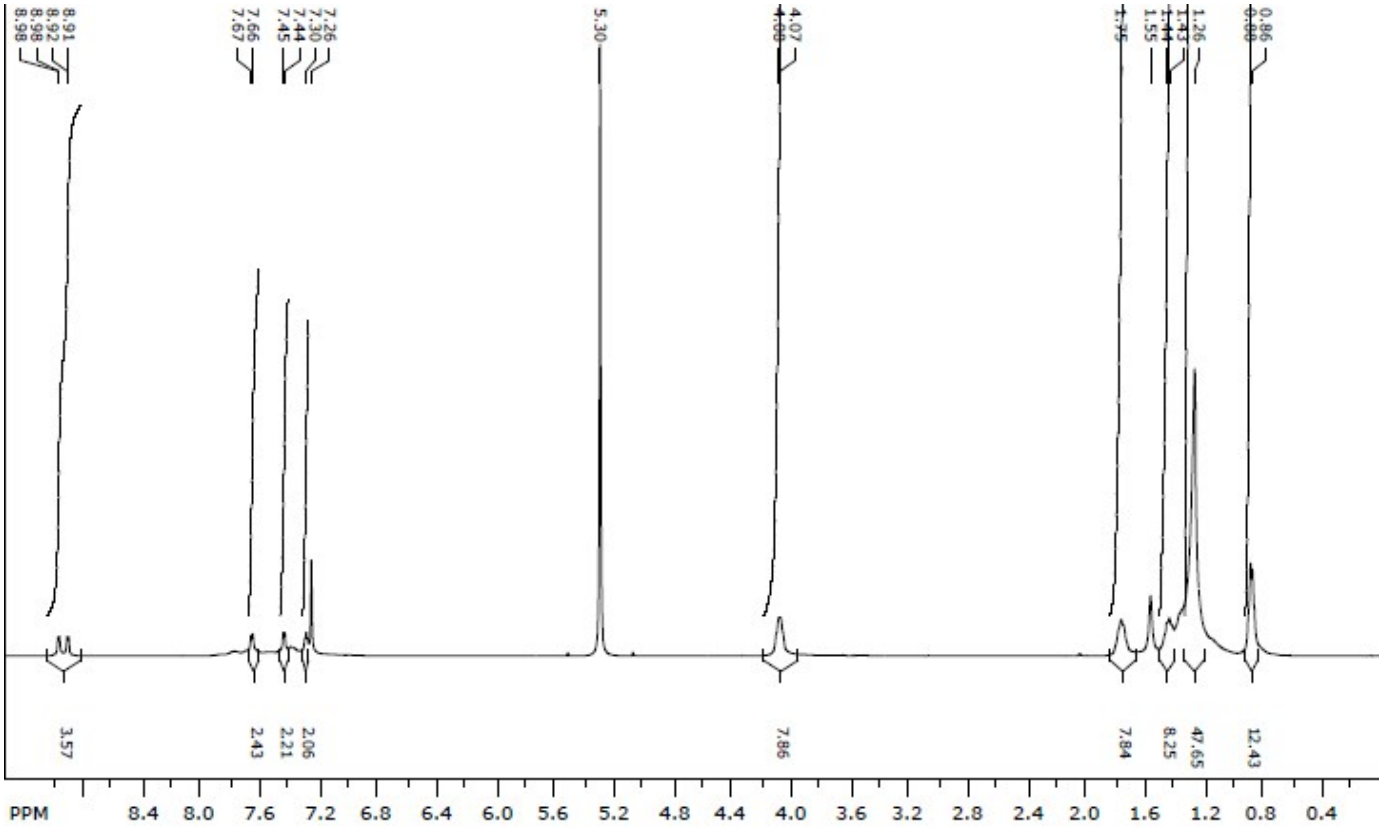

Fig. S5 ^{1}H NMR spectra of **DPPTDPP**

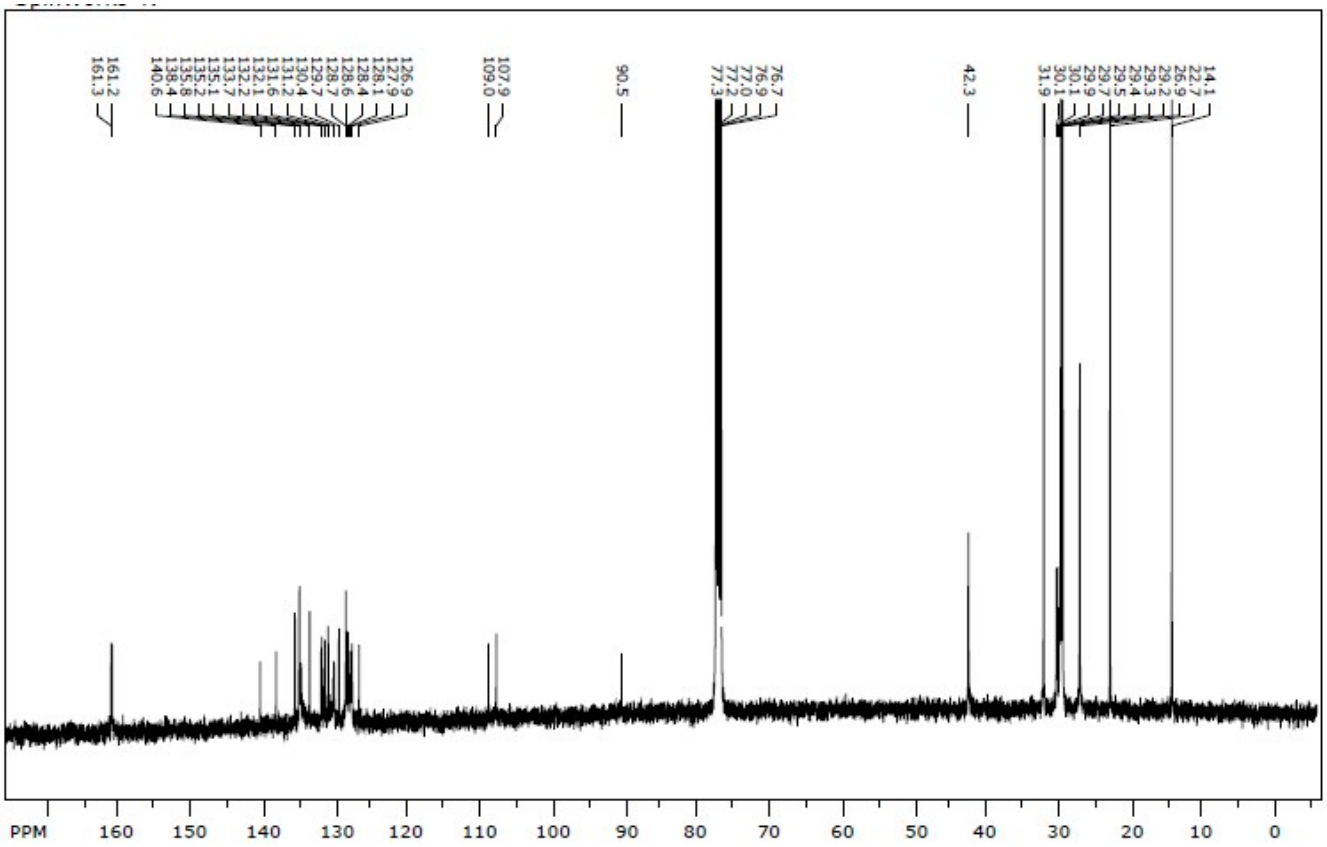

Fig. S6 ^{13}C NMR spectra of **DPPTDPP**

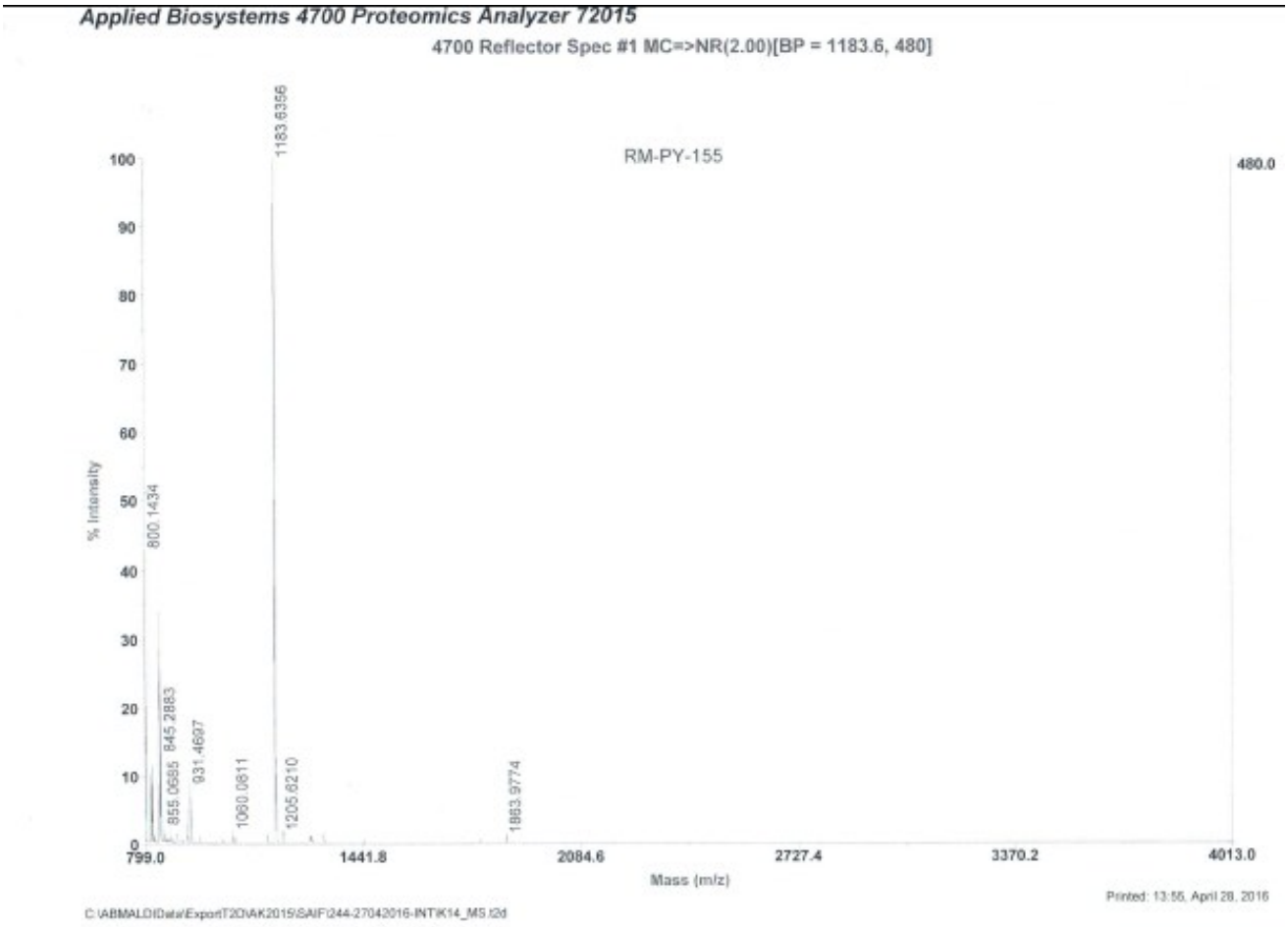

Fig. S7 Mass spectra of **DPPTDPP**

DFT calculations

Calculation method: B3LYP/6-31+G** for C, H, N, O, S with Gaussian 09.

DPP-DPP

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.746619	1.777239	-0.578894
2	6	0	-5.464271	1.287003	-0.406245
3	6	0	-6.176724	0.123068	-0.122923
4	6	0	-7.570656	0.392108	-0.191754
5	6	0	-6.003118	-1.248072	0.311869
6	6	0	-8.282210	-0.730536	0.219753
7	6	0	-9.709864	-0.892729	0.360415
8	6	0	-10.432736	-1.818949	1.100369
9	16	0	-10.811046	0.214853	-0.453293
10	6	0	-11.835431	-1.653377	1.001969
11	1	0	-9.974402	-2.571332	1.725967
12	6	0	-12.184542	-0.605729	0.188105
13	1	0	-12.553299	-2.279966	1.517970
14	1	0	-13.178445	-0.257618	-0.058303
15	6	0	-4.041175	1.493119	-0.393890
16	6	0	-3.308314	2.676433	-0.341743
17	16	0	-2.948887	0.109050	-0.407705
18	6	0	-1.917666	2.480978	-0.329426
19	1	0	-3.759623	3.655597	-0.276603
20	6	0	-1.540940	1.144831	-0.370984
21	1	0	-1.195660	3.288522	-0.281216
22	6	0	-6.217289	3.621129	-1.238484
23	1	0	-5.271319	3.641837	-1.782408
24	1	0	-7.022816	3.766014	-1.963687
25	6	0	-7.543527	-3.139876	0.801347
26	1	0	-8.510036	-3.440642	0.393511
27	1	0	-6.765020	-3.672875	0.248522
28	6	0	-7.417336	-3.479170	2.288957
29	1	0	-7.571898	-4.551907	2.444591
30	1	0	-6.416186	-3.222058	2.642999
31	1	0	-8.145163	-2.934039	2.898020
32	6	0	-6.298903	4.724141	-0.179942
33	1	0	-7.283130	4.707133	0.294237
34	1	0	-5.541864	4.603230	0.601170
35	1	0	-6.159446	5.704837	-0.646510
36	7	0	-6.409375	2.280325	-0.688669
37	7	0	-7.341723	-1.720411	0.516573
38	8	0	-8.731710	2.462748	-0.829678
39	8	0	-5.021692	-1.967736	0.464896
40	6	0	1.541009	-1.145038	-0.371047
41	16	0	2.948947	-0.109241	-0.407534
42	6	0	1.917741	-2.481188	-0.329673
43	6	0	4.041257	-1.493310	-0.393871
44	6	0	3.308391	-2.676633	-0.341944
45	1	0	1.195742	-3.288749	-0.281645
46	6	0	5.464343	-1.287135	-0.406216
47	1	0	3.759681	-3.655815	-0.276985
48	6	0	6.176722	-0.123115	-0.123018
49	7	0	6.409511	-2.280377	-0.688699
50	6	0	7.570672	-0.392050	-0.191921
51	6	0	6.003042	1.247981	0.311887
52	6	0	7.746730	-1.777193	-0.578967
53	6	0	6.217522	-3.621265	-1.238319
54	6	0	8.282159	0.730594	0.219694

55	7	0	7.341619	1.720390	0.516606
56	8	0	5.021578	1.967576	0.465001
57	8	0	8.731866	-2.462675	-0.829635
58	1	0	5.271654	-3.642084	-1.782422
59	1	0	7.023185	-3.766242	-1.963348
60	6	0	6.298985	-4.724115	-0.179591
61	6	0	9.709801	0.892869	0.360407
62	6	0	7.543353	3.139891	0.801275
63	1	0	7.283151	-4.707037	0.294716
64	1	0	5.541848	-4.603092	0.601408
65	1	0	6.159594	-5.704884	-0.646026
66	6	0	10.432561	1.819014	1.100564
67	16	0	10.811098	-0.214504	-0.453405
68	1	0	8.509925	3.440621	0.393567
69	1	0	6.764930	3.672847	0.248288
70	6	0	7.416950	3.479312	2.288835
71	6	0	11.835275	1.653596	1.002167
72	1	0	9.974127	2.571248	1.726273
73	6	0	12.184505	0.606135	0.188111
74	1	0	7.571458	4.552068	2.444391
75	1	0	6.415764	3.222194	2.642767
76	1	0	8.144720	2.934261	2.898040
77	1	0	12.553074	2.280172	1.518278
78	1	0	13.178447	0.258176	-0.058355
79	6	0	-0.191608	0.651733	-0.368180
80	1	0	0.570872	1.429275	-0.362024
81	6	0	0.191674	-0.651948	-0.368249
82	1	0	-0.570804	-1.429493	-0.362222

Total Energy (HF)= -3580.018786 Hartree

DPPTDPP

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.990152	1.741230	-0.625505
2	6	0	-5.729369	1.157834	-0.464801
3	6	0	-6.486594	0.040429	-0.124117
4	6	0	-7.868494	0.366477	-0.183720
5	6	0	-6.363218	-1.318037	0.363220
6	6	0	-8.619231	-0.708221	0.283528
7	6	0	-10.050021	-0.803740	0.450039
8	6	0	-10.800880	-1.672708	1.230683
9	16	0	-11.114749	0.323873	-0.384769
10	6	0	-12.196282	-1.449048	1.146513
11	1	0	-10.366486	-2.424247	1.874090
12	6	0	-12.512040	-0.414071	0.303201
13	1	0	-12.932612	-2.026528	1.692852
14	1	0	-13.493668	-0.031205	0.059104
15	6	0	-4.296247	1.298918	-0.477979
16	6	0	-3.515095	2.452989	-0.473890
17	16	0	-3.267244	-0.128830	-0.459026
18	6	0	-2.132553	2.208312	-0.473430

19	1	0	-3.927129	3.450704	-0.435308
20	6	0	-1.818464	0.854869	-0.478567
21	1	0	-1.375708	2.982752	-0.461049
22	6	0	-6.390546	3.485229	-1.387331
23	1	0	-5.450762	3.439676	-1.940491
24	1	0	-7.197062	3.632052	-2.111036
25	6	0	-7.971894	-3.121834	0.953565
26	1	0	-8.953018	-3.400772	0.565596
27	1	0	-7.220114	-3.708026	0.417974
28	6	0	-7.845160	-3.402803	2.453241
29	1	0	-8.041437	-4.460811	2.655481
30	1	0	-6.831005	-3.172454	2.788289
31	1	0	-8.544201	-2.803241	3.044589
32	6	0	-6.412079	4.637993	-0.380205
33	1	0	-7.391090	4.687901	0.102367
34	1	0	-5.653427	4.519014	0.399687
35	1	0	-6.233377	5.588820	-0.892867
36	7	0	-6.633347	2.180067	-0.774879
37	7	0	-7.716459	-1.724919	0.606548
38	8	0	-8.947764	2.459008	-0.891283
39	8	0	-5.408323	-2.069202	0.529251
40	6	0	1.818468	-0.854847	-0.478573
41	16	0	3.267239	0.128869	-0.459228
42	6	0	2.132569	-2.208287	-0.473322
43	6	0	4.296253	-1.298872	-0.478044
44	6	0	3.515112	-2.452950	-0.473803
45	1	0	1.375729	-2.982730	-0.460822
46	6	0	5.729376	-1.157779	-0.464886
47	1	0	3.927158	-3.450656	-0.435091
48	6	0	6.486605	-0.040419	-0.124079
49	7	0	6.633348	-2.180019	-0.774959
50	6	0	7.868501	-0.366483	-0.183653
51	6	0	6.363241	1.318053	0.363248
52	6	0	7.990153	-1.741185	-0.625600
53	6	0	6.390530	-3.485167	-1.387436
54	6	0	8.619248	0.708192	0.283630
55	7	0	7.716486	1.724947	0.606528
56	8	0	5.408342	2.069201	0.529337
57	8	0	8.947768	-2.459023	-0.891198
58	1	0	5.450785	-3.439557	-1.940654
59	1	0	7.197078	-3.632025	-2.111101
60	6	0	6.411921	-4.637937	-0.380317
61	6	0	10.050048	0.803666	0.450133
62	6	0	7.971923	3.121887	0.953440
63	1	0	7.390871	-4.687866	0.102376
64	1	0	5.653170	-4.518947	0.399478
65	1	0	6.233261	-5.588756	-0.893009
66	6	0	10.800966	1.672593	1.230767
67	16	0	11.114706	-0.324017	-0.384662
68	1	0	8.953059	3.400793	0.565482
69	1	0	7.220165	3.708029	0.417766
70	6	0	7.845116	3.402983	2.453086
71	6	0	12.196358	1.448877	1.146554
72	1	0	10.366629	2.424160	1.874177
73	6	0	12.512055	0.413952	0.303158
74	1	0	8.041404	4.461003	2.655247
75	1	0	6.830938	3.172686	2.788101
76	1	0	8.544113	2.803460	3.044524

77	1	0	12.932728	2.026337	1.692862
78	1	0	13.493663	0.031090	0.058973
79	6	0	-0.548971	0.267499	-0.478219
80	6	0	0.548970	-0.267488	-0.478221

Total Energy (HF)= -3578.7625601Hartree