Effect of Fluorine Substitution on Tetraphenylethene-Benzothiadiazole Based AIE-active Copolymers

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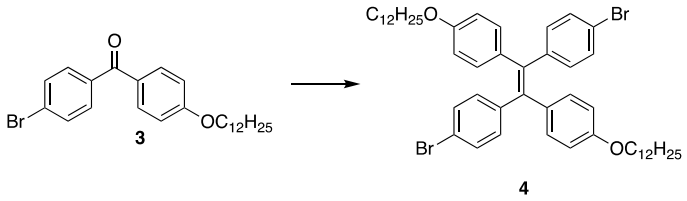
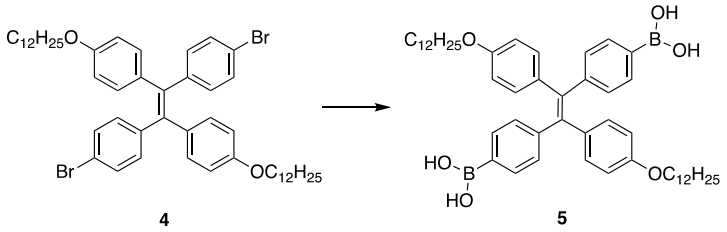
Synthetic details of 4, 5, pBTPE, pBFTPE, BTPE, BFTPE

*Synthesis of compound **4**.*



Titanium tetrachloride (6.6 mL, 60.0 mmol) was added into a mixture of **3** (6.5 g, 15.0 mmol), Zn dust (2.9 g, 45 mmol), pyridine (3.5 mL, 40.0 mmol) in dry THF (145 mL) at 0 ^{o}C, and then, the reaction temperature was increased to 70 ^{o}C. After 18 h, the mixture was cooled and filtered through a celite pad. The filtrate was evaporated in vacuo to give the residue which was recrystallized in CH_2Cl_2/MeOH co-solvent to give **4** as white solid (2.6 g, 41%); mp 77-78 ^{o}C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.88 (t, *J* = 6.9 Hz, 6H), 1.22-1.44 (m, 36H), 1.72 (t, *J* = 6.9 Hz, 4H), 3.87 (t, *J* = 6.6 Hz, 6H), 6.64 (d, *J* = 9.0 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.4 Hz, 4H), 7.24 (d, *J* = 9.0 Hz, 4H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.28, 29.34, 29.4, 29.56, 29.59, 29.6, 29.7, 31.9, 67.9, 113.8, 120.3, 130.8, 132.4, 133.0, 135.2, 139.0, 143.0, 157.9. HRMS (EI) (M^{+}+H) calcd for $C_{50}H_{67}Br_2O_6$: 857.3508 found: 857.3484.

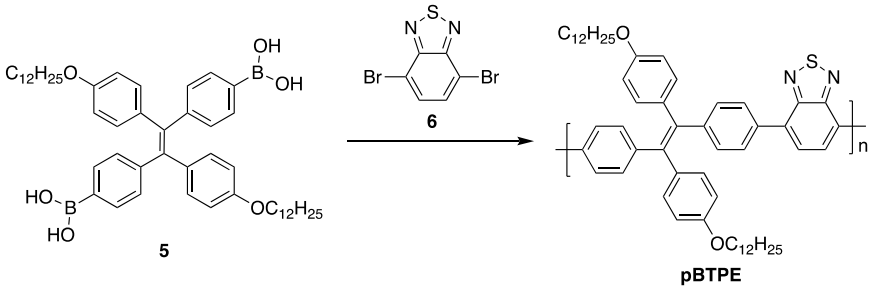
*Synthesis of compound **5**.*



A solution of **4** (0.86 g, 1.0 mmol) in THF (10 mL) at -78 ^{o}C was added dropwisely with a hexane solution of *n*-BuLi (1.2 mL, 2.5 M, 3.0 mmol) under N_2. After 0.5 h, triisopropyl borate (0.6 mL, 3.0 mmol) was introduced and the mixture was gradually warmed to rt. After further stirring for 20 h, the reaction mixture was quenched with sat. $NaHCO_3$. The organic layer was washed with brine, water and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (CH_2Cl_2/hexane = 1/3) to give **5** as a white solid (0.50 g, 56%): mp: 111-112 ^{o}C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.88 (t, *J* = 7.2 Hz, 6H), 1.22-

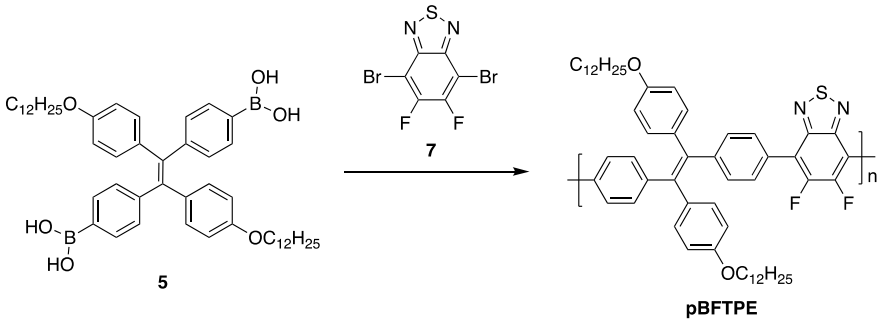
1.45 (m, 36H), 1.72 (t, J = 7.5 Hz, 4H), 3.86 (t, J = 6.6 Hz, 4H), 6.61(d, J = 9.0 Hz, 4H), 6.86 (d, J = 9.0 Hz, 4H), 7.04 (d, J = 8.4 Hz, 4H), 7.50 (d, J = 8.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.28, 29.34, 29.4, 29.57, 29.59, 29.6, 29.7, 31.9, 67.9, 113.8, 120.3, 130.8, 132.4, 133.0, 135.2, 139.0, 142.9, 157.9. HRMS (EI) (M^+) calcd for $C_{50}H_{70}B_2O_6$: 788.5359 found: 788.5351.

*Synthesis of polymer **pBTPE**.*



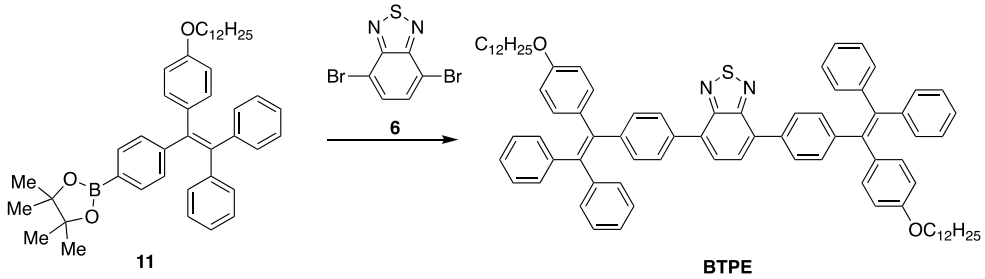
A mixture of **5** (96.3 mg, 0.1 mmol), **6** (29.4 mg, 0.1 mmol), $Pd_2(dba)_3$ (3.5 mg, 0.004 mmol), $^tBu_3PHBF_4$ (1.2 mg, 0.004 mmol), and K_3PO_4 (21.5 mg, 0.1 mmol) in THF (2.5 mL) and H_2O (1.0 mL) was stirred at rt under argon for 16 h and then added to methanol. Precipitate was collected and washed with methanol to obtain the crude polymer which was re-dissolved in THF. Reprecipitation by adding the THF solution to methanol slowly afforded **pBTPE** was obtained as a yellow solid (85.0 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$, δ): 0.80-0.90 (br, 6H), 1.20-1.45 (br, 20H), 1.45-1.75 (br, 20H), 3.86 (s, 4H), 6.50-6.60 (br, 4H), 6.90-7.05 (br, 4H), 7.12-7.25 (br, 8H), 7.55-7.60 (br, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 14.3, 23.1, 26.4, 29.66, 29.71, 29.8, 29.96, 30.00. 30.03, 68.2, 114.1, 126.7, 127.7, 129.6, 132.4, 132.8, 132.9, 136.1, 140.1, 144.2, 145.1, 154.6, 158.4; GPC (THF, polystyrene standard) M_n = 13400, PDI = 1.25.

Synthesis of polymer ***pBFTPE***.



A mixture of **5** (96.3 mg, 0.1 mmol), **7** (33.0 mg, 0.1mmol), $Pd_2(dba)_3$ (3.5 mg, 0.004 mmol) , $^tBu_3PHBF_4$ (1.2 mg, 0.004 mmol), and K_3PO_4 (21.5 mg, 0.1 mmol) in THF (2.5 mL) and H_2O (1.0 mL) was stirred at rt under argon for 16 h and then added to methanol. Precipitate was collected and washed with methanol to obtain the crude polymer which was re-dissolved in THF. Reprecipitation by adding the THF solution to methanol slowly afforded **pBFTPE** was obtained as a yellow solid (98.0 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$, δ): 0.80-0.90 (br, 6H), 1.15-1.40 (br, 36H), 1.60-1.70 (br, 4H), 3.87 (s, 4H), 6.50-6.75 (br, 4H), 6.80-7.20 (br, 6H), 7.20-7.30 (br, 8H), 7.55-7.65 (br, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 14.1, 22.7, 26.1, 29.30, 29.35, 29.4, 29.57, 29.60, 29.63, 29.7, 31.9, 67.8, 113.7, 120.9, 130.9, 131.4, 132.4, 132.5, 132.6, 133.0, 135.3, 135.4, 135.6, 139.0, 139.6, 144.3, 157.9 ; GPC (THF, polystyrene standard) M_n = 12500, PDI = 1.23.

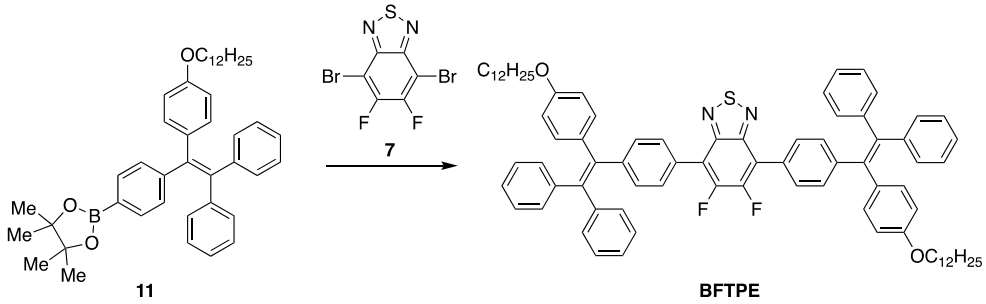
Synthesis of monomer ***BTPE***.



A mixture of **11** (0.711 g, 0.61 mmol), **6** (88.2 mg, 0.30 mmol), $Pd(PPh_3)_4$ (35.8 mg, 0.031 mmol), $Na_2CO_{3(aq)}$ (1.0 mL, 1.2 M) in THF (5.0 mL) was stirred and refluxed under N_2 for 48 h. After cooling to rt, EtOAc (20 mL) was added into the mixture, and the organic layer was washed with brine, water and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (CH_2Cl_2/hexane = 1/3) to give ***BTPE*** as a yellow

solid (0.599 g, 84 %): mp: 74-75 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.87 (t, *J* = 7.2 Hz, 6H), 1.25-1.30 (m, 32H), 1.41 (t, *J* = 7.4 Hz, 4H), 1.72 (t, *J* = 7.2 Hz, 4H), 3.87 (t, *J* = 6.6 Hz, 4H), 6.64 (d, *J* = 9 Hz, 4H), 6.98 (d, *J* = 9 Hz, 4H), 7.05-7.11 (m, 20H), 7.18 (d, *J* = 8.4 Hz, 4H), 7.70 (s, 2H), 7.74 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.1, 22.7, 26.1, 29.3, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 67.9, 113.7, 126.3, 126.4, 127.7, 127.8, 127.9, 128.3, 131.4, 131.4, 131.7, 132.6, 132.6, 135.2, 135.8, 140.2, 140.5, 143.96, 144.09, 144.12, 154.0, 157. 8; HRMS (EI) (M^+) calcd for $C_{82}H_{88}N_2O_2S$: 1164.6567 found: 1164.6552.

Synthesis of monomer ***BFTPE***.



A mixture of **11** (0.318 g, 0.26 mmol), **7** (35.3 mg, 0.12 mmol), $Pd_2(dba)_3$ (15.0 mg, 0.013 mmol), $Na_2CO_{3(aq)}$ (0.5 mL, 1.2 M) in THF (5.0 mL) was stirred and refluxed under N_2 for 48 h. After cooling to rt, EtOAc (20 mL) was added into the mixture, and the organic layer was washed with brine, water and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (CH_2Cl_2/hexane = 1/3) to give ***BFTPE*** as a yellow solid (0.211 g, 68 %): mp: 78-79 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.86 (t, *J* = 7.2 Hz, 6H), 1.24-1.31 (m, 32H), 1.39-1.40 (m, 4H), 1.72 (t, *J* = 7.2 Hz, 4H), 3.87 (t, *J* = 6.6 Hz, 4H), 6.64 (d, *J* = 9 Hz, 4H), 6.98 (d, *J* = 9 Hz, 4H), 7.19 (d, *J* = 8.4, 4H), 7.04-7.12 (m, 20H), 7.57 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.1, 22.7, 26.1, 29.2, 29.7, 31.9, 67.8, 113.7, 126.3, 126.5, 127.7, 127.8, 128.2, 129.7, 131.3, 131.4, 132.6, 135.6, 140.0, 140.9, 143.8, 144.0, 144.8, 150.4, 157.8.; HRMS (EI) (M^++H) calcd for $C_{82}H_{87}F_2N_2O_2S$: 1201.6456 found: 1201.6342.

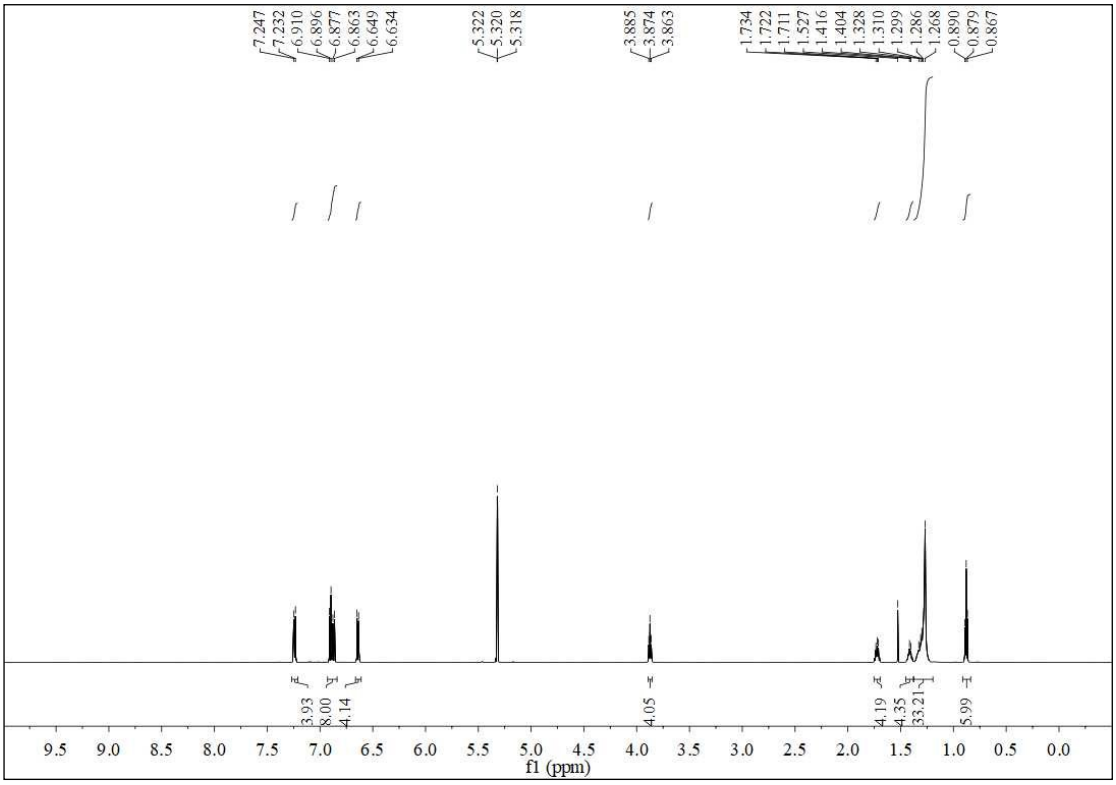


Fig. S1 ^{1}H NMR of **4**.

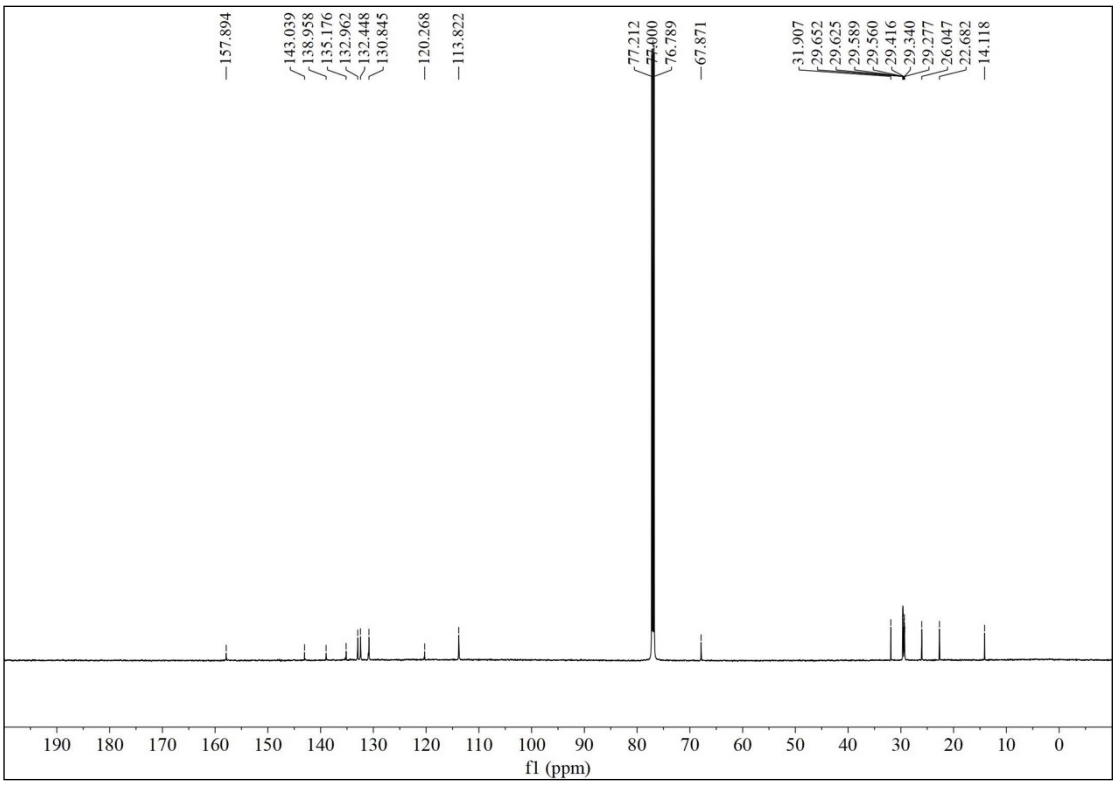


Fig. S2 ^{13}C NMR of **4**.

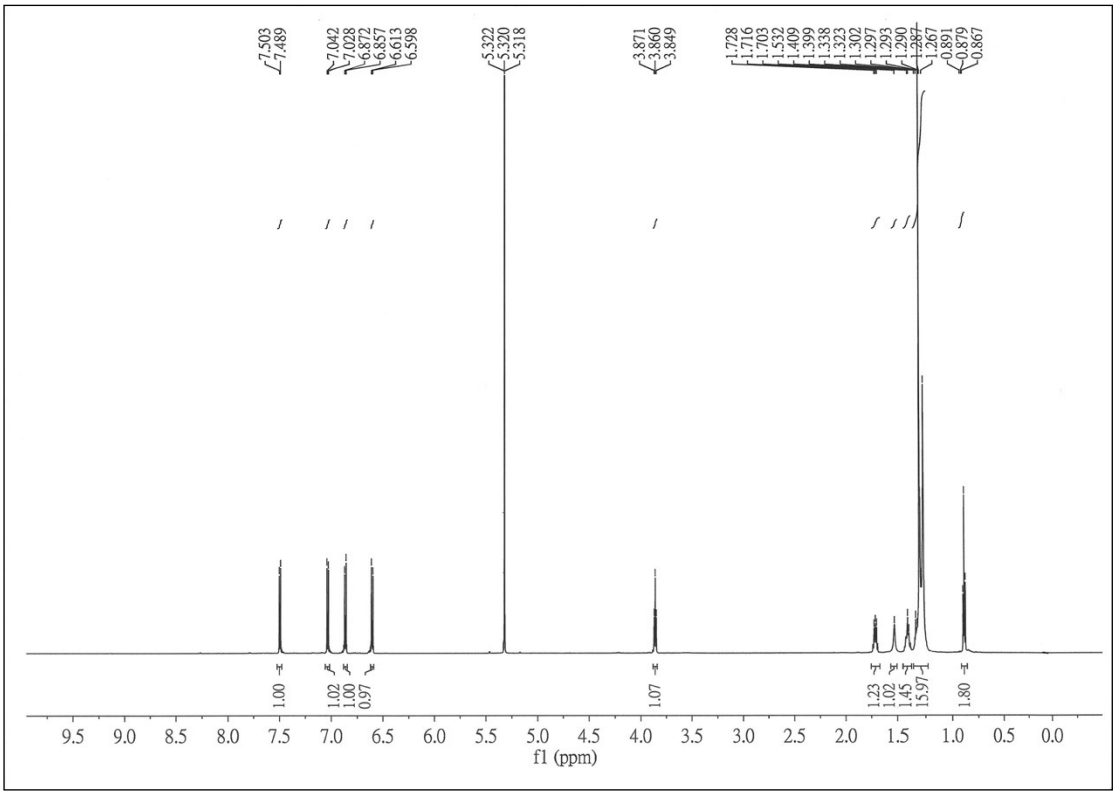


Fig. S3 ^{1}H NMR of **5**.

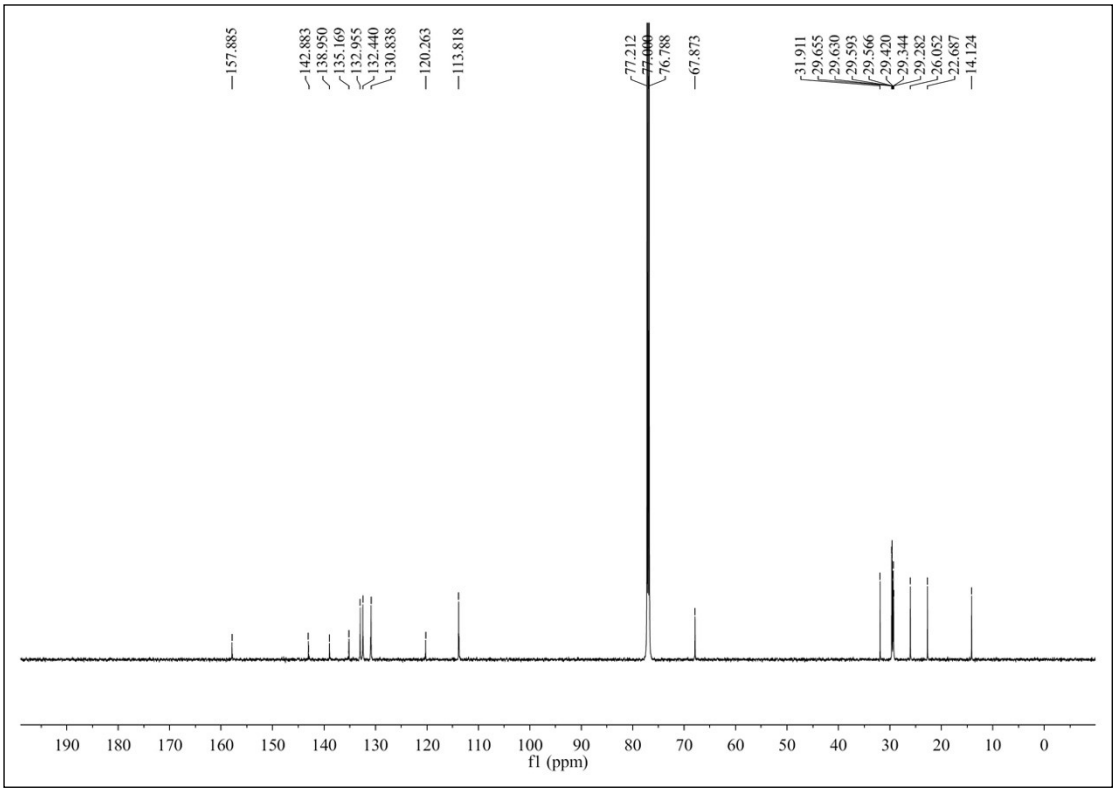


Fig. S4 ^{13}C NMR of **5**.

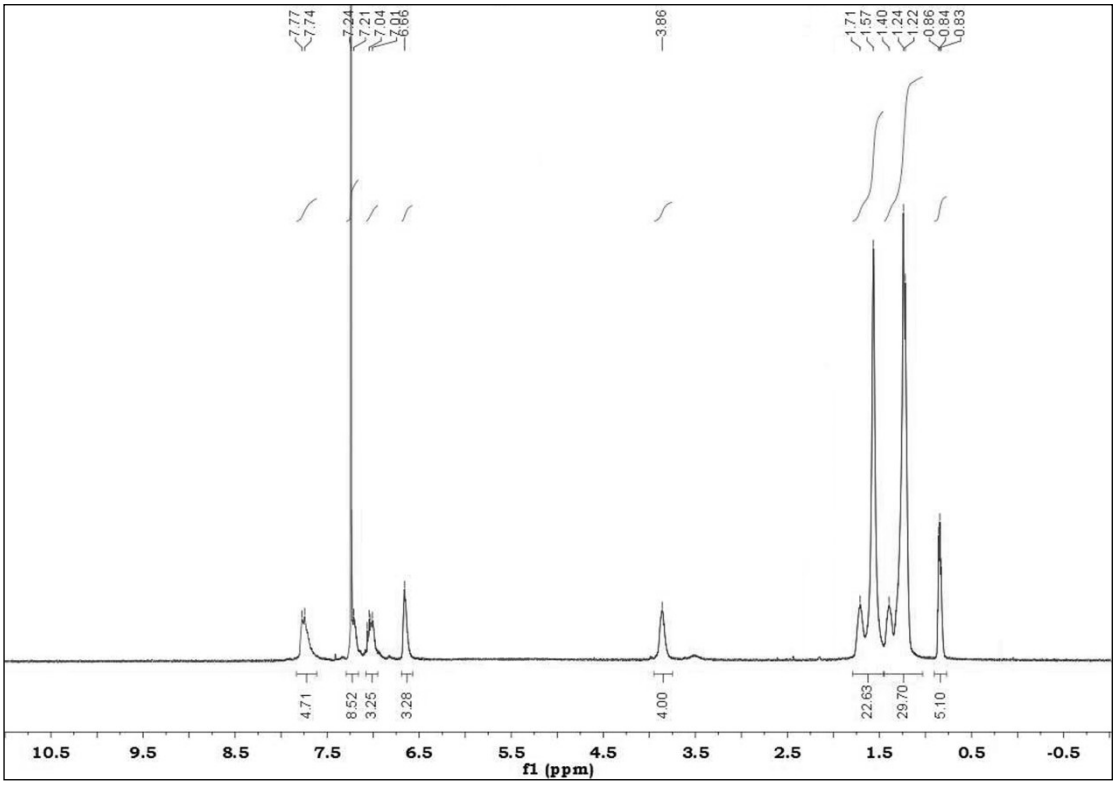


Fig. S5 ^{1}H NMR of **pBTPE**.

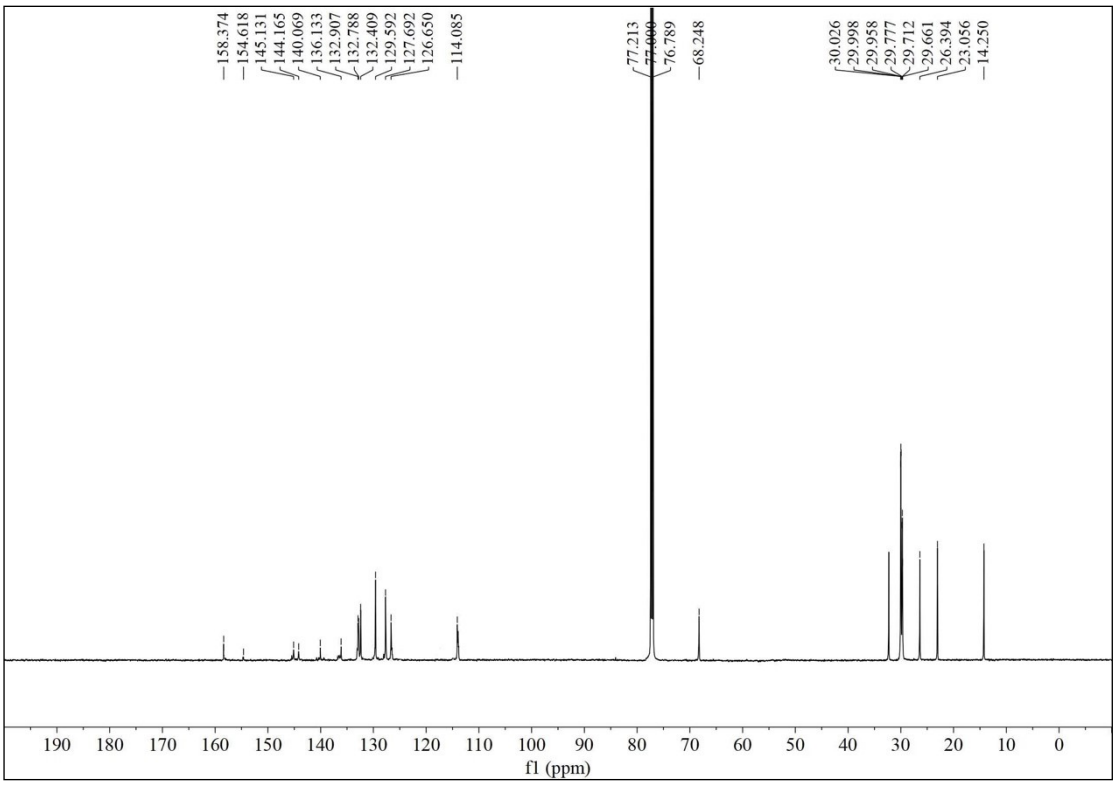


Fig. S6 ^{13}C NMR of **pBTPE**.

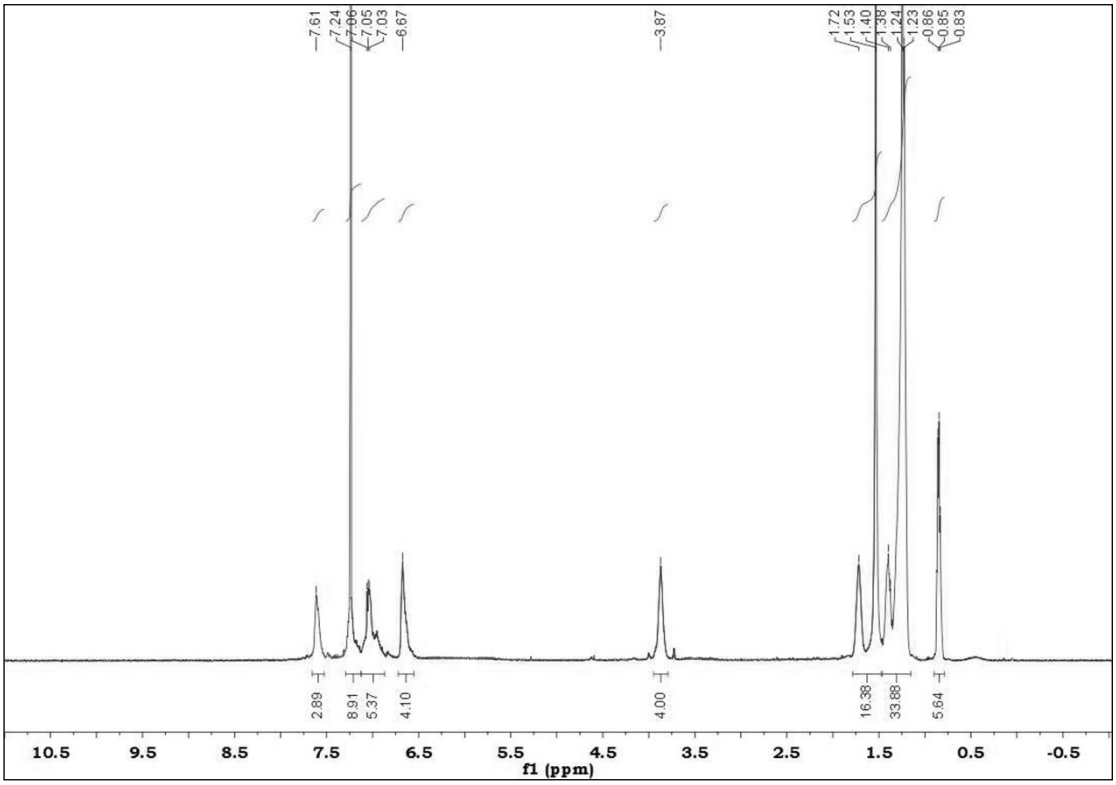


Fig. S7 ^{1}H NMR of **pBFTPE**.

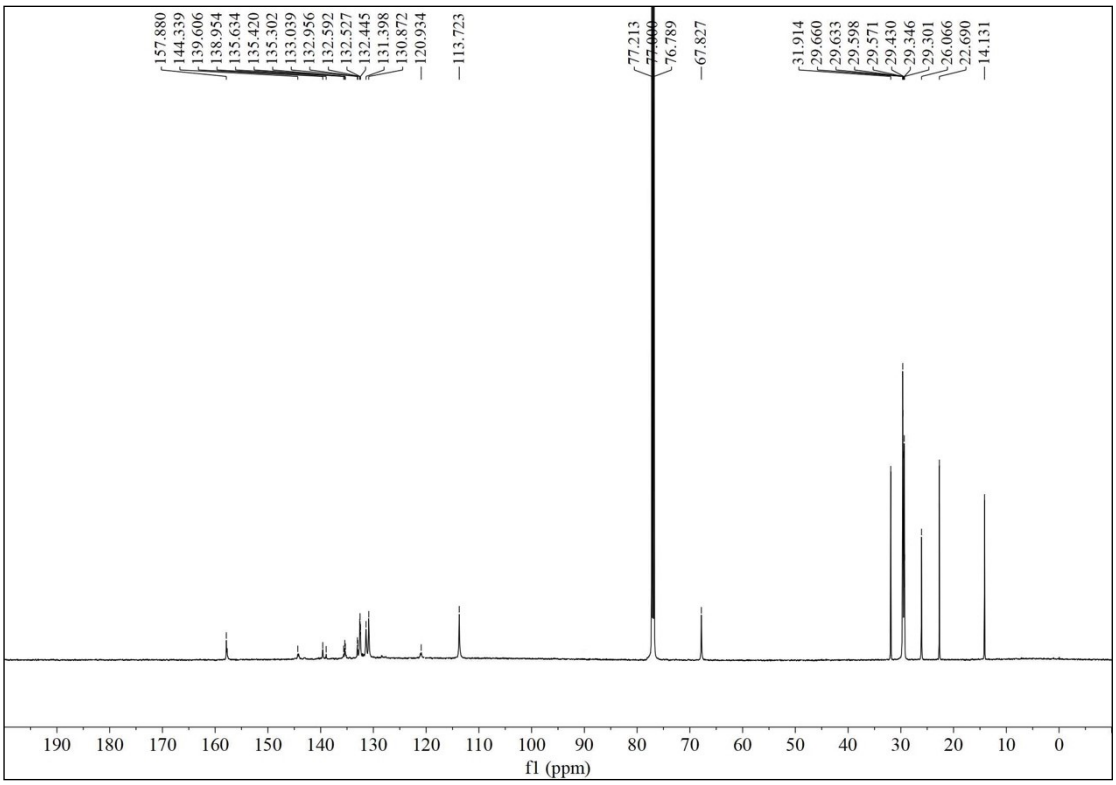


Fig. S8 ^{13}C NMR of **pBFTPE**.

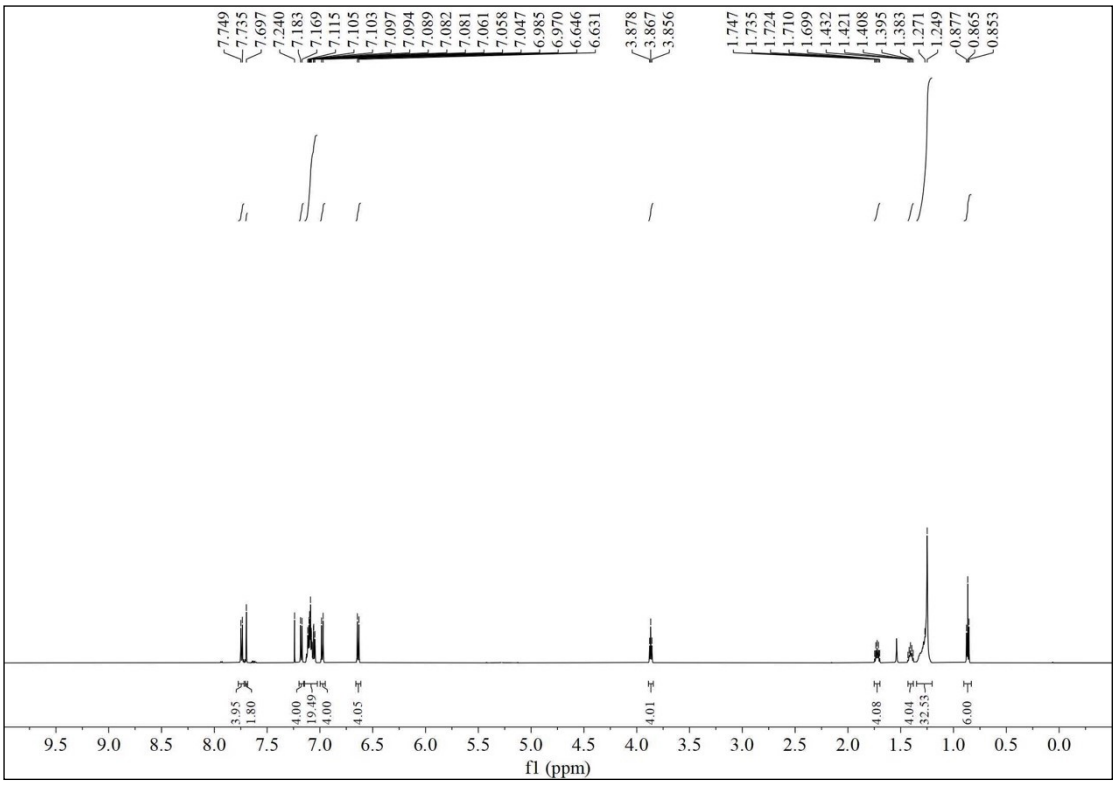


Fig. S9 ^{1}H NMR of **BTPE**.

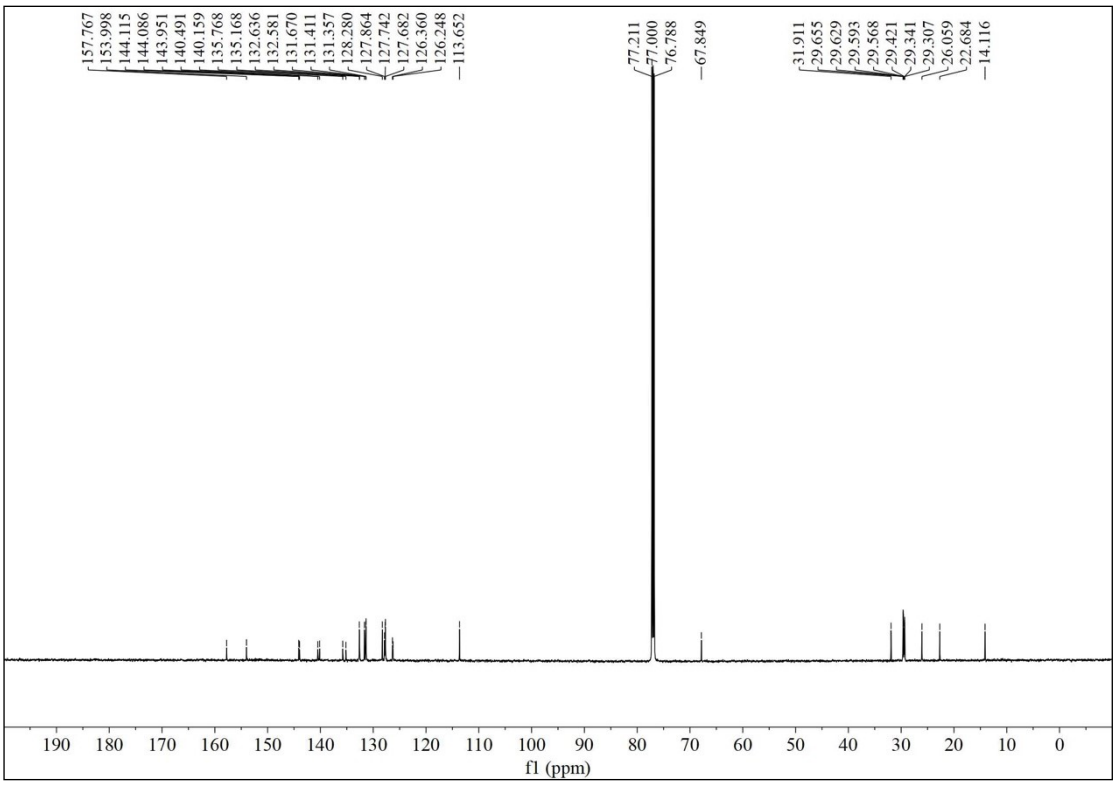


Fig. S10 ^{13}C NMR of **BTPE**.

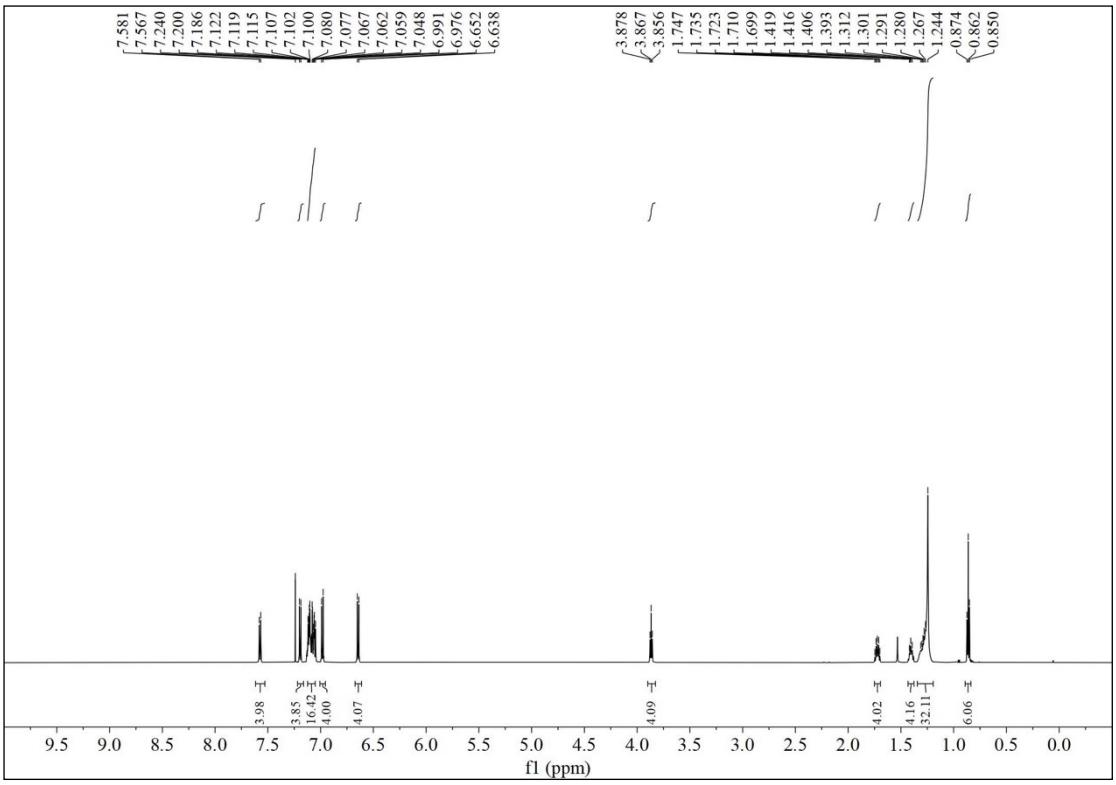


Fig. S11 ^{1}H NMR of **BFTPE**.

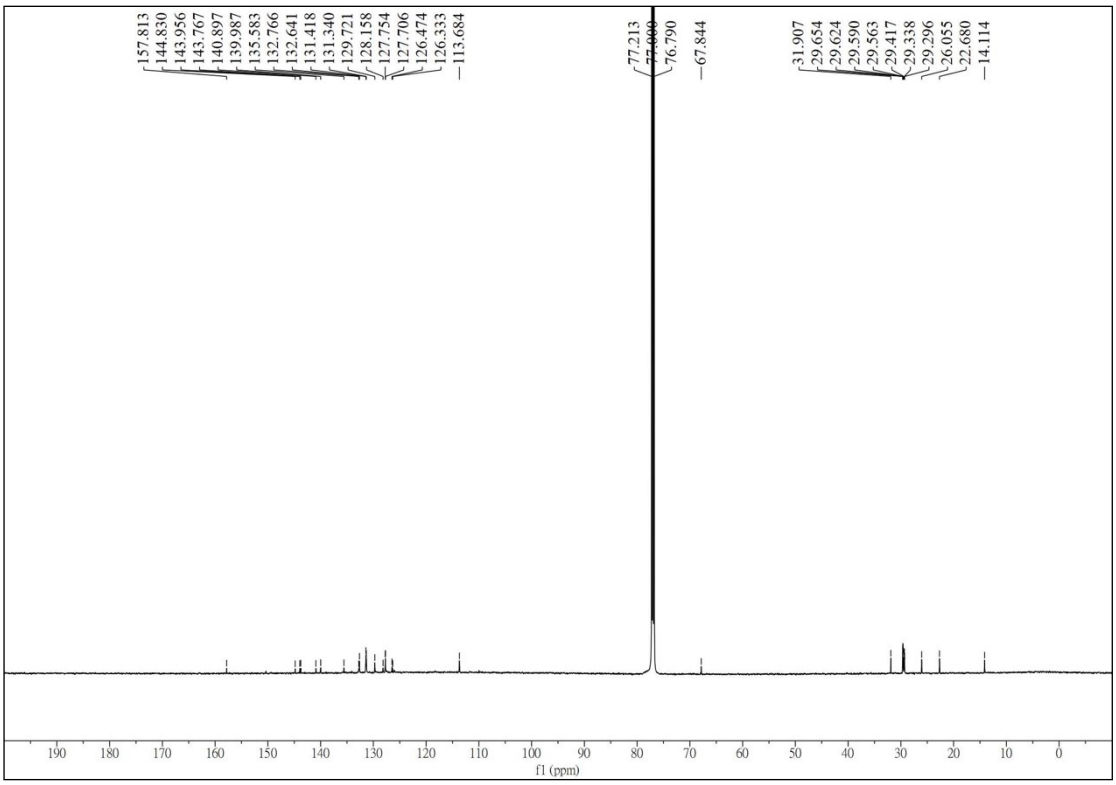


Fig. S12 ^{13}C NMR of **BFTPE**.

Characterization of pBTPE and pBFTPE

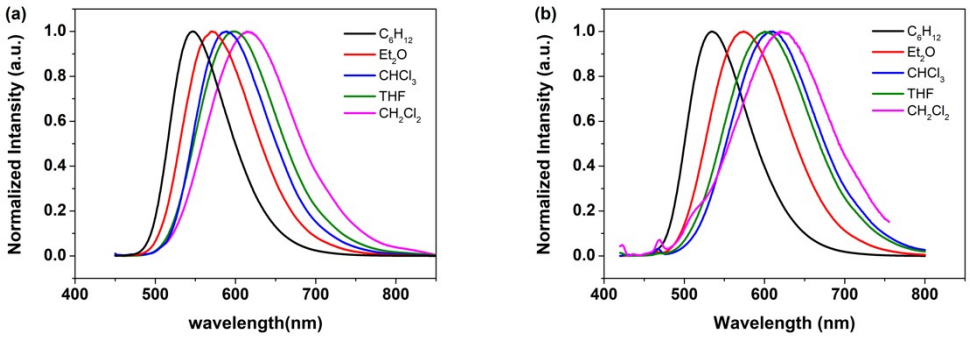


Fig. S13 Solvent-dependent emission spectra of (a) **pBTPE** and (b) **pBFTPE**.

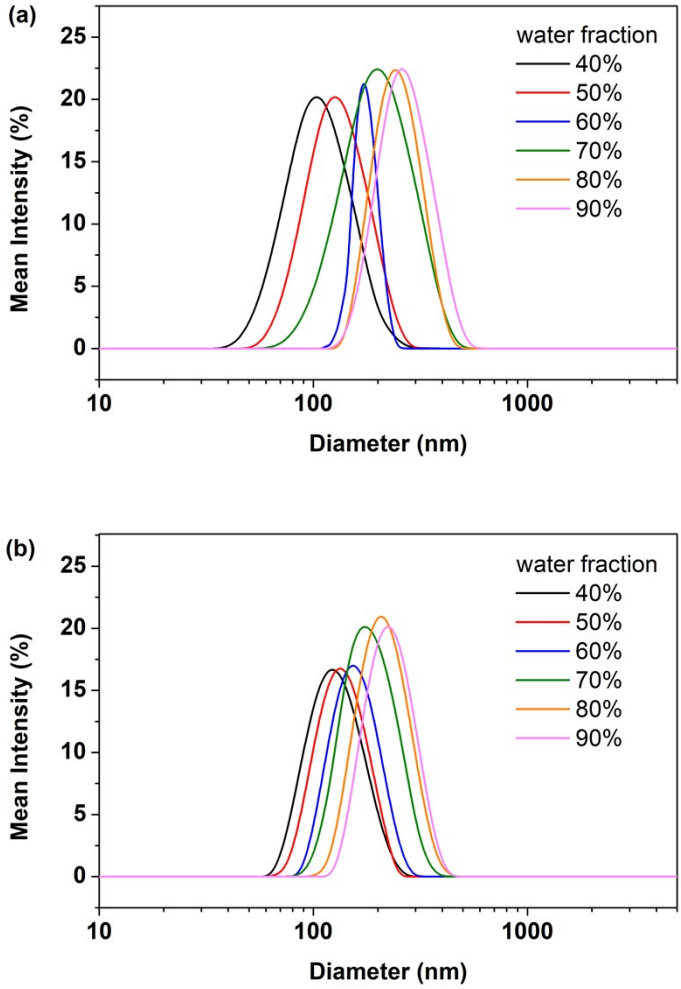


Fig. S14 Particle size distributions of aggregated (a) **pBTPE** and (b) **pBFTPE** with different water fraction.

Molecular simulation of BTPE and BFTPE

Table S1. Computation results of **BTPE**.

Total energy (RB3LYP) = -2971.05859595

Center Number	Atomic Number	Atomic Type	Coordinates (Angstrom)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstrom)		
			X	Y	Z				X	Y	Z
1	6	0	8.075612	-1.072616	-0.261514	52	6	0	0.731693	0.116918	-1.063848
2	6	0	7.312309	0.062633	-0.257263	53	6	0	-0.696646	-0.083399	1.316275
3	6	0	9.556456	-1.049798	-0.059034	54	6	0	-0.688894	0.115116	-1.057178
4	6	0	10.406683	-1.777441	-0.910308	55	1	0	1.230464	0.160511	-2.026858
5	6	0	10.133561	-0.355564	1.017959	56	6	0	-1.448755	0.01739	0.092668
6	6	0	11.786225	-1.783691	-0.711447	57	1	0	-1.197194	0.158224	-2.015253
7	1	0	9.97755	-2.337894	-1.735484	58	16	0	0.043433	-0.21911	3.595101
8	6	0	11.51169	-0.371611	1.224318	59	7	0	1.295613	-0.150816	2.535222
9	1	0	9.491283	0.19703	1.695603	60	7	0	-1.218356	-0.156099	2.546515
10	6	0	12.345212	-1.080536	0.357327	61	6	0	-2.927285	0.025178	0.052272
11	1	0	12.424945	-2.342589	-1.389608	62	6	0	-3.605172	0.817481	-0.892286
12	1	0	11.934758	0.167985	2.066935	63	6	0	-3.703786	-0.759664	0.923407
13	1	0	13.419454	-1.09089	0.51723	64	6	0	-4.9931	0.820987	-0.966836
14	6	0	7.495476	-2.433757	-0.472012	65	1	0	-3.037266	1.465387	-1.55313
15	6	0	7.856598	-3.502652	0.367353	66	6	0	-5.091129	-0.767842	0.833774
16	6	0	6.622602	-2.697467	-1.541293	67	1	0	-3.215316	-1.365178	1.676737
17	6	0	7.336883	-4.779847	0.165602	68	6	0	-5.769104	0.01284	-0.117553
18	1	0	8.54657	-3.323722	1.186474	69	1	0	-5.488336	1.462894	-1.688826
19	6	0	6.111617	-3.977183	-1.750291	70	1	0	-5.664102	-1.387909	1.514906
20	1	0	6.348331	-1.889582	-2.211645	71	6	0	-7.260779	0.050095	-0.179515
21	6	0	6.461582	-5.023189	-0.894751	72	6	0	-8.025109	-1.084212	-0.186649
22	1	0	7.619315	-5.587331	0.835244	73	6	0	-9.503747	-1.062272	0.0334
23	1	0	5.44224	-4.158125	-2.586564	74	6	0	-10.364704	-1.776889	-0.81796
24	1	0	6.06201	-6.02004	-1.056837	75	6	0	-10.067384	-0.38327	1.127128
25	6	0	7.901632	1.43211	-0.332119	76	6	0	-11.741874	-1.785371	-0.602617
26	6	0	7.450348	2.45751	0.511546	77	1	0	-9.945936	-2.325996	-1.656023
27	6	0	8.887374	1.761832	-1.282953	78	6	0	-11.442965	-0.401394	1.349723
28	6	0	7.970957	3.750716	0.444233	79	1	0	-9.416761	0.159126	1.805078
29	1	0	6.677793	2.241539	1.243311	80	6	0	-12.287514	-1.097389	0.482746
30	6	0	9.406925	3.044365	-1.371146	81	1	0	-12.388949	-2.334761	-1.280677
31	1	0	9.244793	0.99655	-1.963556	82	1	0	-11.855179	0.12584	2.205461
32	6	0	8.956817	4.050256	-0.503033	83	1	0	-13.359698	-1.110209	0.655956
33	1	0	7.600272	4.507906	1.12474	84	6	0	-7.849361	1.420824	-0.229497
34	1	0	10.160526	3.296331	-2.109981	85	6	0	-7.391486	2.434575	0.636084
35	6	0	5.821504	0.025601	-0.177172	86	6	0	-8.834499	1.766697	-1.164368
36	6	0	5.034308	0.823966	-1.025657	87	6	0	-7.916694	3.717297	0.590347
37	6	0	5.155323	-0.746787	0.789121	88	1	0	-6.615209	2.205045	1.359631
38	6	0	3.647411	0.818638	-0.935603	89	6	0	-9.365976	3.055257	-1.231347
39	1	0	5.520132	1.459401	-1.759616	90	1	0	-9.195136	1.013733	-1.857168
40	6	0	3.768952	-0.740981	0.893574	91	6	0	-8.911185	4.038761	-0.345464
41	1	0	5.736909	-1.359192	1.469868	92	1	0	-7.571256	4.49219	1.266766
42	6	0	2.981097	0.033659	0.023464	93	1	0	-10.122316	3.278348	-1.9744
43	1	0	3.071316	1.45916	-1.596533	94	6	0	-7.44878	-2.443784	-0.41696
44	1	0	3.290217	-1.340524	1.657772	95	6	0	-7.803613	-3.520749	0.414786
45	8	0	9.531047	5.27765	-0.667787	96	6	0	-6.58579	-2.697696	-1.496591
46	6	0	9.107266	6.335631	0.177208	97	6	0	-7.287391	-4.796441	0.195448
47	1	0	9.309117	6.116789	1.233588	98	1	0	-8.485784	-3.349432	1.24203
48	1	0	9.684214	7.211255	-0.123753	99	6	0	-6.078378	-3.975863	-1.723135
49	1	0	8.037669	6.548896	0.054475	100	1	0	-6.316122	-1.883381	-2.160994

50	6	0	1.503047	0.022189	0.078741	101	6	0	-6.422023	-5.030096	-0.875166
51	6	0	0.762743	-0.080494	1.309593	102	1	0	-7.564754	-5.610287	0.859477
103	1	0	-5.416591	-4.14906	-2.567053						
104	1	0	-6.025143	-6.025705	-1.050897						
105	8	0	-9.358796	5.327937	-0.31644						
106	6	0	-10.366016	5.709539	-1.239977						
107	1	0	-10.574372	6.761733	-1.040877						
108	1	0	-10.027168	5.599743	-2.27814						
109	1	0	-11.285605	5.126956	-1.100692						

Table S2. Computation results of **BFTPE**.

Total energy (RB3LYP) = -3169.51178767

Center Number	Atomic Number	Atomic Type	Coordinates (Angstrom)			Center Number	Atomic Number	Atomic Type	Coordinates (Angstrom)		
			X	Y	Z				X	Y	Z
1	6	0	8.089107	-1.093278	-0.128609	42	6	0	2.997304	0.034038	-0.03011
2	6	0	7.331925	0.045526	-0.160346	43	1	0	3.146247	1.41195	-1.687311
3	6	0	9.563604	-1.074138	0.116059	44	1	0	3.241922	-1.319637	1.63279
4	6	0	10.434296	-1.815104	-0.702324	45	8	0	9.580428	5.248019	-0.563316
5	6	0	10.112682	-0.369518	1.200893	46	6	0	9.132789	6.317948	0.253954
6	6	0	11.807592	-1.824582	-0.464231	47	1	0	9.300041	6.112225	1.31897
7	1	0	10.026342	-2.383156	-1.533007	48	1	0	9.721632	7.188139	-0.039575
8	6	0	11.484282	-0.389024	1.446693	49	1	0	8.068312	6.532131	0.094036
9	1	0	9.45382	0.194112	1.853066	50	6	0	1.518324	0.035716	0.013391
10	6	0	12.338928	-1.111534	0.61204	51	6	0	0.762265	0.014065	1.240995
11	1	0	12.462878	-2.393766	-1.117542	52	6	0	0.734525	0.060326	-1.11679
12	1	0	11.885689	0.158684	2.294645	53	6	0	-0.697314	0.01118	1.24799
13	1	0	13.408114	-1.124421	0.802643	54	6	0	-0.692961	0.058554	-1.109815
14	6	0	7.509098	-2.454359	-0.339633	55	6	0	-1.465174	0.030994	0.028
15	6	0	7.841877	-3.514082	0.52283	56	16	0	0.04303	0.026166	3.530317
16	6	0	6.664772	-2.727512	-1.429283	57	7	0	1.294746	0.024724	2.465732
17	6	0	7.321963	-4.79142	0.322697	58	7	0	-1.218494	0.019388	2.477557
18	1	0	8.50974	-3.32797	1.358533	59	6	0	-2.944491	0.025927	-0.000651
19	6	0	6.153709	-4.007567	-1.63626	60	6	0	-3.653578	0.800703	-0.936419
20	1	0	6.412498	-1.927405	-2.11735	61	6	0	-3.685145	-0.750727	0.907477
21	6	0	6.475186	-5.044207	-0.758429	62	6	0	-5.043087	0.800842	-0.956473
22	1	0	7.582175	-5.591663	1.009806	63	1	0	-3.112482	1.417825	-1.644027
23	1	0	5.506699	-4.195807	-2.48831	64	6	0	-5.074505	-0.764155	0.867714
24	1	0	6.07573	-6.041314	-0.919219	65	1	0	-3.168545	-1.342475	1.653002
25	6	0	7.92875	1.411805	-0.232557	66	6	0	-5.786464	0.003386	-0.068978
26	6	0	7.455913	2.448202	0.58542	67	1	0	-5.565179	1.426468	-1.67367
27	6	0	8.943772	1.727379	-1.157061	68	1	0	-5.620889	-1.376828	1.576638
28	6	0	7.982653	3.738967	0.518921	69	6	0	-7.279547	0.033201	-0.08389
29	1	0	6.66111	2.243211	1.29629	70	6	0	-8.037767	-1.104712	-0.055335
30	6	0	9.47004	3.007177	-1.244272	71	6	0	-9.509968	-1.08615	0.20455
31	1	0	9.318569	0.95339	-1.818141	72	6	0	-10.389913	-1.815507	-0.614204
32	6	0	8.99742	4.024516	-0.401768	73	6	0	-10.047097	-0.394979	1.303946
33	1	0	7.594244	4.505186	1.179115	74	6	0	-11.760795	-1.826906	-0.362048
34	1	0	10.246161	3.248279	-1.96313	75	1	0	-9.991178	-2.373592	-1.456074
35	6	0	5.839115	0.015736	-0.12839	76	6	0	-11.416126	-0.416212	1.563551
36	6	0	5.084649	0.803938	-1.015006	77	1	0	-9.381116	0.159541	1.95671
37	6	0	5.138152	-0.744273	0.822641	78	6	0	-12.280278	-1.127248	0.728645
38	6	0	3.695509	0.802015	-0.979875	79	1	0	-12.423228	-2.387718	-1.015444
39	1	0	5.59778	1.423479	-1.743809	80	1	0	-11.807847	0.120533	2.422985
40	6	0	3.749239	-0.733246	0.876814	81	1	0	-13.347365	-1.142332	0.930699
41	1	0	5.692967	-1.349799	1.531141	82	6	0	-7.875017	1.400942	-0.132421

83	6	0	-7.398049	2.42548	0.709741	97	6	0	-6.119197	-4.007602	-1.606512
84	6	0	-8.885891	1.733117	-1.044471	98	1	0	-6.378377	-1.922631	-2.065927
85	6	0	-7.929059	3.705809	0.664227	99	6	0	-6.43512	-5.051925	-0.735799
86	1	0	-6.602028	2.206569	1.414977	100	1	0	-7.528276	-5.614151	1.03639
87	6	0	-9.423584	3.019069	-1.111226	101	1	0	-5.479236	-4.188779	-2.465386
88	1	0	-9.26175	0.971557	-1.71952	102	1	0	-6.038431	-6.048039	-0.90908
89	6	0	-8.94913	4.013727	-0.248346	103	8	0	-9.400569	5.301422	-0.221276
90	1	0	-7.568601	4.489261	1.322699	104	6	0	-10.431772	5.670275	-1.123466
91	1	0	-10.200093	3.231497	-1.836387	105	1	0	-10.638764	6.723762	-0.929964
92	6	0	-7.461682	-2.464564	-0.284536	106	1	0	-10.118263	5.550889	-2.168474
93	6	0	-7.788882	-3.531812	0.5708	107	1	0	-11.345536	5.086159	-0.955399
94	6	0	-6.62661	-2.728774	-1.383471	108	9	0	1.287725	0.058914	-2.342646
95	6	0	-7.272582	-4.80797	0.354554	109	9	0	-1.258736	0.056803	-2.329886
96	1	0	-8.44941	-3.352623	1.41381						