

Supporting Information

Platinum Complexes of *N*, *N'*, *N''*, *N'''*-Diboronazophenines

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Table S1. Crystallographic data of **BQ**, **5** and **TertPtBQ**.

Compound	BQ	5	TertPtBQ
Formula	C ₅₀ H ₅₄ B ₂ F ₄ N ₄ Si ₄	C ₃₈ H ₂₂ B ₂ F ₄ N ₄	C _{61.50} H ₈₄ BF ₂ N ₂ OP ₄ Pt ₂
Formula weight	920.95	632.22	1430.18
Temp(K)	173(2) K	173(2) K	173(2) K
Wavelength(Å)	1.54178 Å	1.54178 Å	1.54178 Å
Crystal size(mm)	0.010 x 0.400 x 0.500 mm	0.160 x 0.340 x 0.470 mm	0.150 x 0.180 x 0.500 mm
Crystal habit	translucent intense purple Plate	translucent dark green Prism	Metallic dark black Prism
Crystal system	monoclinic	triclinic	triclinic
Space group	P 1 21/c 1	P -1	P -1
a (Å)	23.3666(8)	10.1908(3)	9.1677(3)
b (Å)	8.8672(3)	10.9062(3)	16.8482(5)
c (Å)	12.5679(4)	14.9925(4)	21.8171(7)
α (deg)	90°	78.6710(10)°	72.1240(10)
β (deg)	93.893(2)°	76.2140(10)°	86.5910(10)
γ (deg)	90°	85.7300(10)°	81.2500(10)
Volume(Å³)	2598.01(15)	1586.11(8)	3169.55(17)
Z	4	2	2
Density (calculated)	1.177 g/cm ³	1.324 g/cm ³	1.499
Absorption coefficient	1.476 mm ⁻¹	0.781 mm ⁻¹	9.439
F(000)	968	648	1428
Reflections collected	32305	8881	17751
Independent reflections	4918 [R(int) = 0.1729]	5912 [R(int) = 0.0236]	11782 [R(int) = 0.0276]
Maximum θ angle	70.87°	70.79°	71.18°
Data/restraints/parameters	4918 / 0 / 295	5912 / 0 / 434	11782 / 4 / 664
Goodness-of-fit on F²	0.988	1.138	1.067
R indices (all data)	3245 data; I>2σ(I)	5379 data; I>2σ(I)	10953 data; I>2σ(I)
Largest diff. peak and hole	0.671 and -0.534 eÅ ⁻³	0.277 and -0.202 eÅ ⁻³	2.380 and -2.568 eÅ ⁻³

Table S2. Calculated positions of the pure electronic transitions, oscillator strengths (f), and major contributions for BQ and TertPtBQ.

No	λ (nm)	f	Major contribs for BQ (crystal structure)
1	719	0	HOMO→LUMO (100%)
2	565	0.6166	H-1→LUMO (99%)
3	541	0.7602	H-2→LUMO (100%)
4	463	0	H-3→LUMO (99%)
5	448	0	H-4→LUMO (97%)
6	381	0	H-10→LUMO (94%)
7	381	0.0002	H-11→LUMO (94%)
8	380	0.0037	H-13→LUMO (91%)
9	380	0	H-12→LUMO (97%)
10	366	0.0005	H-6→LUMO (93%)
11	366	0	H-8→LUMO (69%), H-7→LUMO (27%)
12	366	0.0017	H-9→LUMO (32%), H-8→LUMO (13%), H-7→LUMO (49%)
13	366	0.0025	H-9→LUMO (62%), H-8→LUMO (14%), H-7→LUMO (18%)
14	364	0.2314	H-5→LUMO (88%)
15	321	0.5157	HOMO→L+2 (96%)
16	320	0.8914	HOMO→L+1 (93%)
17	313	0.0059	H-14→LUMO (92%)
18	300	0	H-15→LUMO (89%)
19	297	0	H-1→L+2 (32%), HOMO→L+4 (65%)
20	295	0	H-16→LUMO (31%), HOMO→L+3 (62%)
21	291	0	H-16→LUMO (42%), H-1→L+1 (23%), HOMO→L+3 (33%)
22	288	0	H-16→LUMO (22%), H-1→L+1 (68%)
23	288	0	H-1→L+2 (65%), HOMO→L+4 (33%)
24	285	0.0151	H-17→LUMO (92%)
25	279	0	H-2→L+1 (96%)
26	274	0.5992	H-22→LUMO (32%), H-1→L+3 (58%)
27	270	0.001	H-19→LUMO (13%), H-18→LUMO (78%)
28	270	0.0042	H-21→LUMO (15%), H-19→LUMO (66%), H-18→LUMO (15%)
29	270	0.0002	H-21→LUMO (10%), H-20→LUMO (81%)
30	270	0.0002	H-21→LUMO (70%), H-20→LUMO (12%), H-19→LUMO (16%)
31	270	0	H-2→L+2 (85%)
32	269	0.0123	H-22→LUMO (60%), H-1→L+3 (33%)
33	268	0	HOMO→L+6 (66%)
34	268	0.0022	H-1→L+4 (70%), HOMO→L+7 (13%)
35	268	0.0022	HOMO→L+5 (64%)
36	267	0.0304	H-1→L+4 (14%), HOMO→L+7 (60%)
37	267	0	HOMO→L+8 (69%)
38	266	0	H-23→LUMO (84%)
39	261	0.1272	H-3→L+1 (37%), H-2→L+3 (44%)
40	260	0	H-24→LUMO (95%)
41	259	1.0436	H-26→LUMO (10%), H-3→L+2 (15%), H-2→L+4 (66%)
42	257	0.0003	H-25→LUMO (12%), H-3→L+1 (50%), H-2→L+3 (36%)

43	255	0.0007	H-25→LUMO (78%)
44	254	0.1484	H-26→LUMO (21%), H-3→L+2 (65%)
45	253	0.0033	H-26→LUMO (59%), H-3→L+2 (12%), H-2→L+4 (24%)
46	252	0	H-27→LUMO (91%)
47	250	0.0028	H-9→L+3 (16%), H-8→L+1 (21%), H-7→L+2 (17%), H-6→L+4 (14%)
48	250	0.0015	H-9→L+4 (14%), H-8→L+2 (21%), H-7→L+1 (18%), H-6→L+3 (17%)
49	250	0.0001	H-9→L+1 (29%), H-8→L+3 (12%), H-7→L+4 (12%), H-6→L+2 (22%)
50	250	0.0001	H-9→L+2 (24%), H-8→L+4 (13%), H-7→L+3 (12%), H-6→L+1 (24%)
51	248	0.1284	H-4→L+1 (83%)
52	247	0	H-2→L+5 (11%), H-1→L+7 (33%), HOMO→L+6 (18%)
53	247	0.0002	H-2→L+8 (11%), H-1→L+6 (30%), HOMO→L+7 (22%)
54	247	0.0001	H-2→L+6 (12%), H-1→L+8 (33%), HOMO→L+5 (18%)
55	247	0	H-2→L+7 (12%), H-1→L+5 (31%), HOMO→L+8 (23%)
56	245	0.0002	H-4→L+2 (87%)
57	244	0	H-3→L+3 (89%)
58	242	0.0001	H-3→L+4 (87%)
59	237	0	H-2→L+7 (38%), H-1→L+5 (40%)
60	237	0	H-2→L+5 (35%), H-1→L+7 (46%)
61	237	0.0068	H-2→L+8 (40%), H-1→L+6 (40%)
62	237	0.002	H-2→L+6 (33%), H-1→L+8 (48%)
63	236	0	H-5→L+1 (20%), H-4→L+3 (65%)
64	236	0.0984	HOMO→L+9 (87%)
65	235	0	H-5→L+2 (22%), H-4→L+4 (66%)
66	229	0	H-37→LUMO (23%), H-36→LUMO (14%), H-32→LUMO (35%), H-28→LUMO (14%)
67	228	0	H-5→L+1 (65%), H-4→L+3 (22%)
68	226	0.0004	H-5→L+2 (69%), H-4→L+4 (26%)
69	226	0.2189	HOMO→L+10 (73%)
70	226	0.0002	H-2→L+13 (14%), H-1→L+9 (19%), H-1→L+14 (15%), HOMO→L+12 (28%)
71	225	0.0002	H-3→L+12 (10%), H-2→L+14 (16%), H-1→L+13 (19%), HOMO→L+11 (36%)
72	225	0.0097	H-3→L+14 (11%), H-2→L+12 (15%), H-1→L+11 (19%), HOMO→L+13 (37%)
73	225	0.0038	H-3→L+13 (11%), H-2→L+11 (16%), H-1→L+12 (19%), HOMO→L+14 (39%)
74	224	0.0086	H-13→L+2 (14%), H-12→L+2 (10%), H-11→L+1 (39%), H-10→L+1 (20%)
75	224	0.0138	H-12→L+2 (19%), H-11→L+1 (22%), H-10→L+1 (39%)
76	224	0.0002	H-12→L+1 (60%), H-10→L+2 (29%)
77	223	0	H-13→L+1 (58%), H-11→L+2 (23%)
78	223	0	H-11→L+2 (16%), H-2→L+7 (10%), H-1→L+9 (42%)
79	222	0.0006	H-33→LUMO (55%), H-29→LUMO (32%)
80	222	0	H-13→L+2 (28%), H-3→L+8 (23%), H-2→L+5 (27%)
81	222	0.0011	H-10→L+2 (19%), H-3→L+7 (27%), H-2→L+6 (30%)
82	221	0.0747	H-12→L+2 (20%), H-3→L+5 (28%), H-2→L+8 (36%)
83	221	0	H-3→L+6 (22%), H-2→L+7 (22%), H-1→L+9 (18%)
84	221	0.0008	H-7→L+1 (32%), H-7→L+2 (35%)
85	221	0	H-9→L+1 (15%), H-9→L+2 (22%), H-6→L+1 (33%), H-6→L+2 (21%)
86	221	0.0005	H-8→L+1 (37%), H-8→L+2 (41%)
87	221	0.0001	H-9→L+1 (24%), H-9→L+2 (16%), H-7→L+1 (13%), H-6→L+1 (10%), H-6→L+2 (17%)
88	220	0	H-34→LUMO (58%), H-31→LUMO (21%), H-1→L+10 (16%)

89	220	0.0019	H-30→LUMO (96%)
90	220	0	H-34→LUMO (17%), H-31→LUMO (76%)
91	220	0	H-32→LUMO (24%), H-28→LUMO (60%)
92	220	0.0015	H-33→LUMO (23%), H-29→LUMO (62%), H-5→L+3 (10%)
93	218	0.0004	H-33→LUMO (10%), H-5→L+3 (77%)
94	218	0	H-36→LUMO (55%), H-32→LUMO (13%), H-28→LUMO (17%)
95	216	0.0173	H-35→LUMO (81%)
96	216	0.0698	H-12→L+2 (29%), H-10→L+1 (15%), H-5→L+4 (13%), H-3→L+5 (25%)
97	216	0.0001	H-3→L+8 (23%), H-2→L+9 (45%)
98	216	0	H-12→L+1 (18%), H-10→L+2 (29%), H-3→L+7 (33%)
99	216	0	H-13→L+1 (19%), H-11→L+2 (31%), H-3→L+6 (25%)
10	216	0	H-13→L+2 (23%), H-11→L+1 (14%), H-3→L+8 (13%), H-2→L+9 (25%)
0			

No.	λ (nm)	f	Major contribs for TertPtBQ (crystal structure)
1	872	0.0002	HOMO→LUMO (97%)
2	794	0.6029	H-1→LUMO (99%)
3	763	0.6554	H-2→LUMO (98%)
4	701	0.0009	H-3→LUMO (99%)
5	644	0.0336	H-4→LUMO (94%)
6	613	0.1571	H-5→LUMO (96%)
7	563	0.09	H-6→LUMO (96%)
8	552	0.0248	H-7→LUMO (85%)
9	543	0.0036	H-8→LUMO (80%)
10	533	0.0912	H-10→LUMO (17%), H-9→LUMO (70%), H-8→LUMO (10%)
11	523	0.0235	H-10→LUMO (70%), H-9→LUMO (19%)
12	493	0.0035	H-12→LUMO (36%), H-11→LUMO (51%)
13	473	0.0104	H-12→LUMO (46%), H-11→LUMO (47%)
14	453	0.0195	H-18→LUMO (36%), H-13→LUMO (49%)
15	450	0.0216	H-18→LUMO (12%), H-16→LUMO (30%), H-14→LUMO (48%)
16	448	0.0004	H-15→LUMO (75%), H-14→LUMO (18%)
17	448	0.0016	H-18→LUMO (39%), H-15→LUMO (12%), H-13→LUMO (44%)
18	448	0.0028	H-16→LUMO (62%), H-14→LUMO (30%)
19	447	0.0002	H-17→LUMO (97%)
20	443	0.0023	H-19→LUMO (80%)
21	422	0.0154	H-20→LUMO (96%)
22	391	0.3612	H-21→LUMO (91%)
23	382	0	H-27→LUMO (43%), H-26→LUMO (55%)
24	382	0.0001	H-28→LUMO (54%), H-27→LUMO (20%), H-26→LUMO (21%)
25	382	0.0011	H-28→LUMO (38%), H-27→LUMO (36%), H-26→LUMO (23%)
26	381	0.0192	H-29→LUMO (92%)
27	370	0	H-22→LUMO (100%)
28	369	0	H-24→LUMO (100%)
29	369	0.0001	H-23→LUMO (100%)
30	369	0.0001	H-25→LUMO (100%)
31	363	2.2157	H-1→L+3 (20%), HOMO→L+1 (62%)
32	358	0.0001	H-1→L+1 (54%), HOMO→L+3 (24%)

33	353	0.4572	H-34→LUMO (16%), H-30→LUMO (33%), HOMO→L+2 (20%)
34	350	1.1209	H-30→LUMO (20%), H-2→L+4 (13%), HOMO→L+2 (39%)
35	346	0.0003	H-31→LUMO (99%)
36	346	0.0037	H-34→LUMO (34%), H-33→LUMO (15%), H-32→LUMO (10%), H-30→LUMO (40%)
37	346	0.0001	H-32→LUMO (88%)
38	345	0.0002	H-34→LUMO (31%), H-33→LUMO (69%)
39	344	0.0143	H-3→L+4 (14%), H-2→L+2 (42%), HOMO→L+4 (20%)
40	340	0.0001	H-35→LUMO (88%)
41	334	0.0051	H-36→LUMO (93%)
42	332	0.2603	H-3→L+1 (24%), H-1→L+3 (32%), HOMO→L+1 (21%)
43	330	0.0202	H-37→LUMO (37%), H-2→L+1 (33%)
44	330	0.0044	H-37→LUMO (52%), H-2→L+1 (27%)
45	330	0.1488	H-38→LUMO (18%), H-3→L+2 (18%), H-2→L+4 (10%), HOMO→L+2 (17%)
46	329	0.0182	H-38→LUMO (64%)
47	328	0.0064	H-2→L+1 (26%), H-1→L+1 (26%), HOMO→L+3 (33%)
48	326	0.0139	H-39→LUMO (36%), H-1→L+2 (36%)
49	326	0.0025	H-39→LUMO (43%), H-1→L+2 (24%)
50	323	0.0108	H-4→L+2 (10%), H-4→L+4 (12%), H-1→L+2 (14%), HOMO→L+4 (15%)
51	322	0.002	H-10→L+1 (10%), H-6→L+1 (27%), H-6→L+3 (21%)
52	321	0.0001	H-8→L+1 (43%), H-8→L+3 (35%)
53	319	0.0005	H-3→L+1 (37%), H-2→L+3 (14%), H-1→L+3 (27%)
54	319	0.0011	H-5→L+4 (11%), HOMO→L+4 (24%)
55	316	0.0006	H-7→L+2 (11%), H-7→L+4 (17%), H-5→L+2 (14%), HOMO→L+4 (21%)
56	314	0.0034	H-3→L+1 (18%), H-2→L+3 (71%)
57	314	0.0003	H-40→LUMO (50%), H-1→L+4 (31%)
58	313	0.0132	H-40→LUMO (29%), H-1→L+4 (50%)
59	310	0.0002	H-3→L+3 (78%)
60	308	0.0094	H-3→L+2 (33%), H-2→L+4 (21%)
61	307	0.009	H-4→L+1 (64%), H-3→L+2 (11%)
62	306	0.0121	H-41→LUMO (87%)
63	305	0.0017	H-3→L+4 (56%), H-2→L+2 (15%), H-2→L+5 (12%)
64	302	0.1924	H-2→L+4 (12%), HOMO→L+5 (56%)
65	300	0.0038	H-5→L+1 (44%), H-4→L+3 (19%)
66	299	0.0125	H-5→L+2 (20%)
67	297	0.0359	H-5→L+1 (12%), HOMO→L+6 (11%)
68	297	0.0229	HOMO→L+6 (38%)
69	296	0.028	H-5→L+1 (13%)
70	296	0.0019	H-1→L+15 (37%), HOMO→L+15 (25%)
71	296	0.0034	H-1→L+14 (16%), H-1→L+16 (18%), HOMO→L+14 (12%), HOMO→L+16 (10%)
72	295	0.0008	H-42→LUMO (63%)
73	294	0.0021	H-3→L+4 (10%), H-2→L+5 (19%), H-1→L+6 (10%)
74	293	0.001	H-4→L+3 (17%), H-1→L+5 (46%), H-1→L+6 (10%)
75	293	0.0039	H-3→L+13 (19%), H-2→L+13 (35%), HOMO→L+13 (17%)
76	293	0.0029	H-3→L+14 (15%), H-3→L+16 (11%), H-2→L+14 (22%), H-2→L+16 (19%)
77	292	0.0005	H-5→L+1 (11%), H-4→L+3 (10%), HOMO→L+6 (11%)

78	291	0.0013	H-4→L+3 (31%), H-1→L+5 (19%)
79	289	0.0108	H-43→LUMO (18%), H-3→L+5 (14%)
80	289	0.0066	H-43→LUMO (19%), H-1→L+6 (18%)
81	288	0.0523	H-43→LUMO (36%), H-3→L+5 (18%)
82	288	0.023	H-1→L+9 (10%), HOMO→L+9 (11%), HOMO→L+11 (30%)
83	287	0.0091	H-1→L+6 (10%), HOMO→L+9 (18%), HOMO→L+11 (16%), HOMO→L+12 (12%)
84	287	0.0002	H-4→L+4 (36%)
85	286	0.0058	H-5→L+3 (46%)
86	286	0.0084	H-5→L+3 (13%), HOMO→L+10 (33%)
87	286	0.0131	HOMO→L+10 (16%), HOMO→L+12 (20%)
88	284	0.0064	H-5→L+2 (12%), H-5→L+4 (27%)
89	283	0.0027	HOMO→L+7 (41%)
90	283	0.0056	H-44→LUMO (51%), H-6→L+1 (12%)
91	282	0.0036	H-7→L+1 (32%)
92	282	0.0032	H-44→LUMO (22%), H-7→L+1 (10%), HOMO→L+7 (19%)
93	281	0.0009	H-2→L+6 (74%)
94	280	0.0648	H-6→L+2 (20%), H-3→L+5 (10%)
95	279	0.0027	H-6→L+2 (29%)
96	279	0.0125	H-6→L+2 (25%), H-3→L+6 (18%)
97	278	0.0011	HOMO→L+8 (60%)
98	277	0.0386	H-3→L+6 (14%), H-1→L+7 (10%), H-1→L+8 (11%)
99	277	0.03	H-7→L+1 (11%), H-3→L+6 (11%)
100	276	0.1143	H-45→LUMO (11%), H-1→L+7 (47%)

^1H NMR, ^{13}C NMR and MALDI-TOF spectra

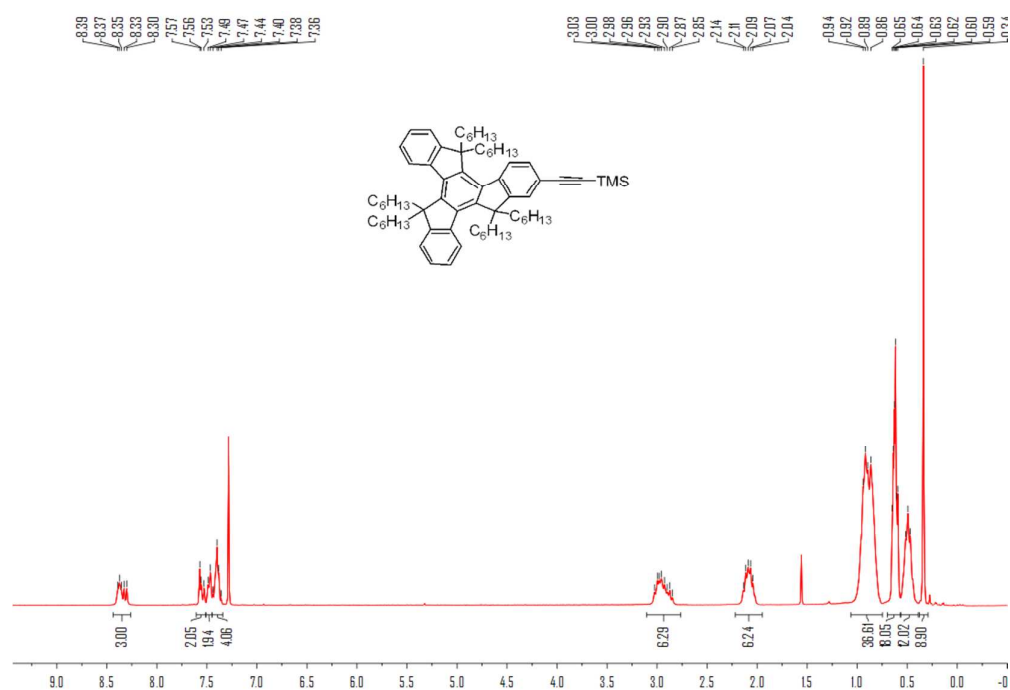


Figure S1. ^1H NMR spectrum of **2** (CDCl₃, 300 MHz, 298 K).

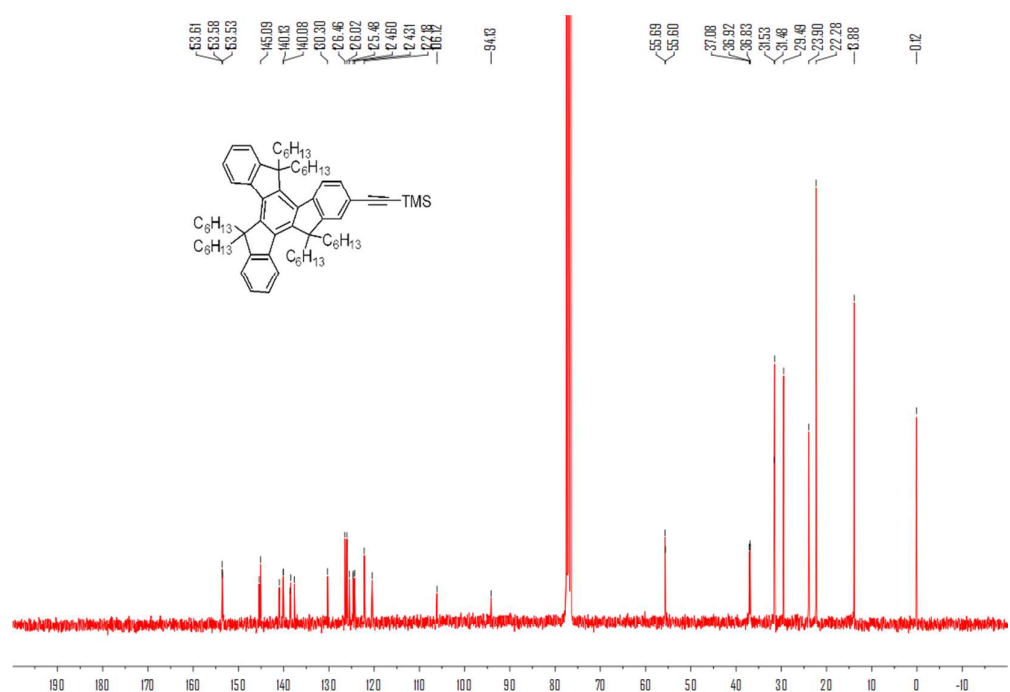


Figure S2. ^{13}C NMR spectrum of **2** (CDCl₃, 76 MHz, 298 K).

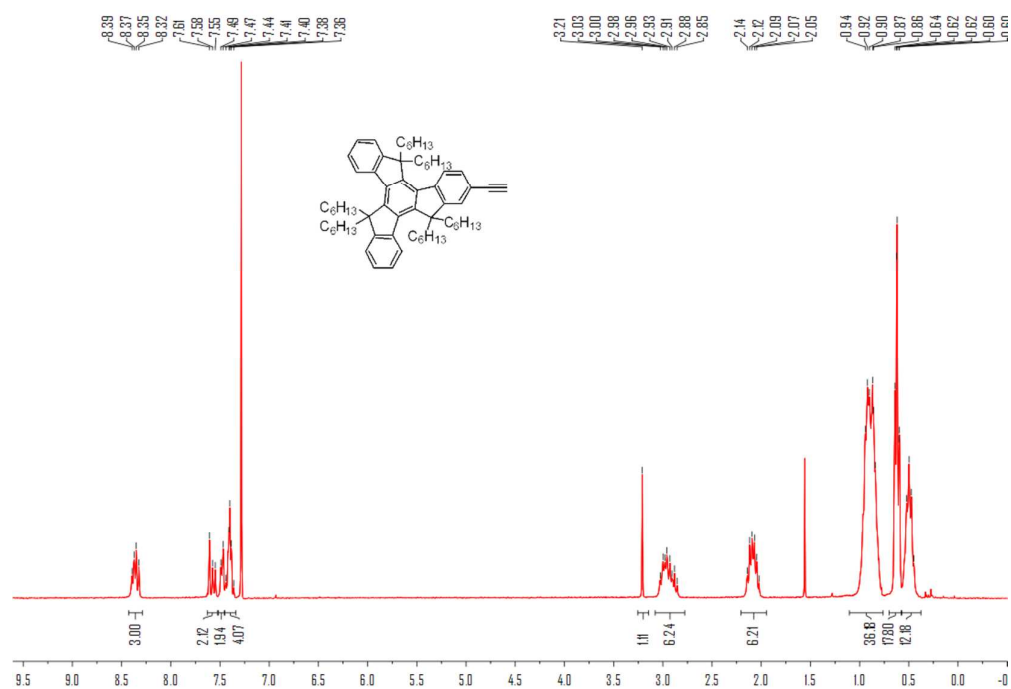


Figure S3. ¹H NMR spectrum of **3a** (CDCl₃, 300 MHz, 298 K).

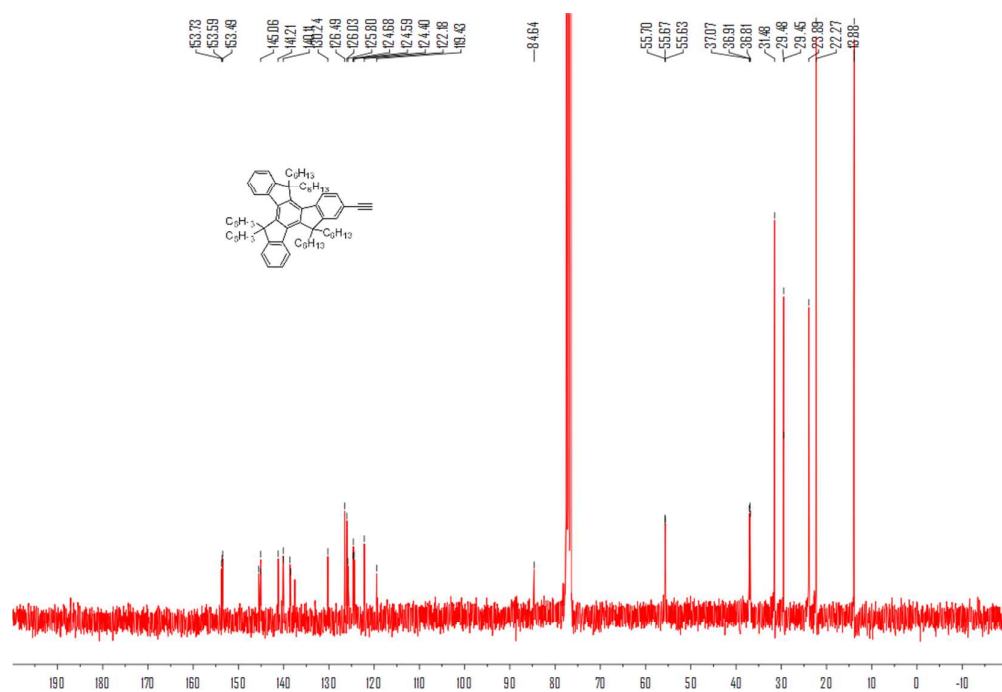


Figure S4. ¹³C NMR spectrum of **3a** (CDCl₃, 76 MHz, 298 K).

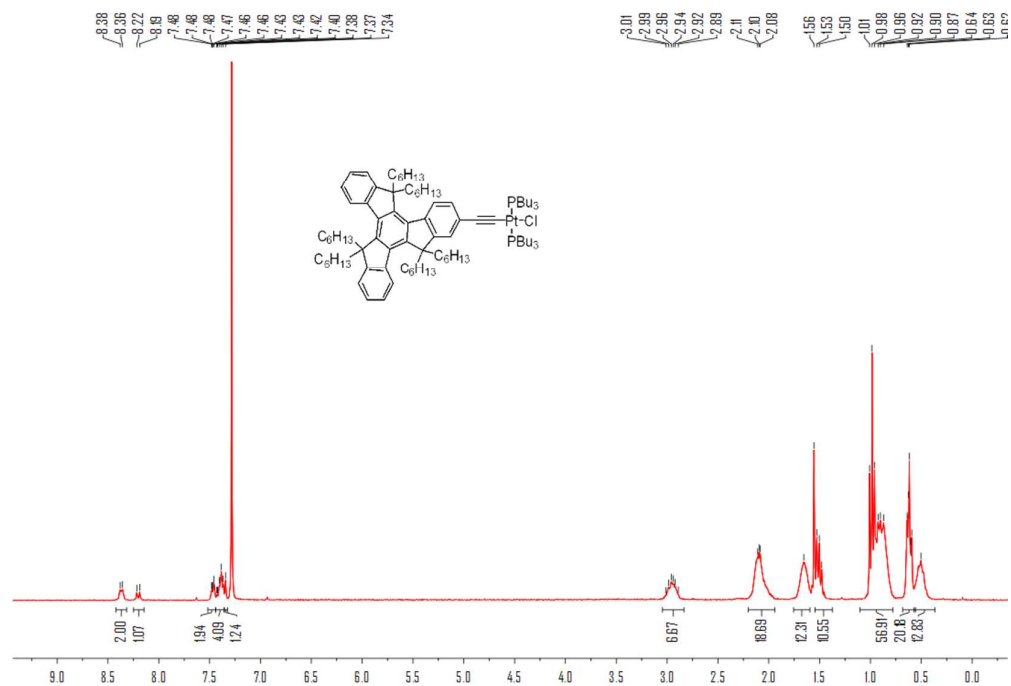


Figure S5. ^1H NMR spectrum of **3** (CDCl_3 , 300 MHz, 298 K).

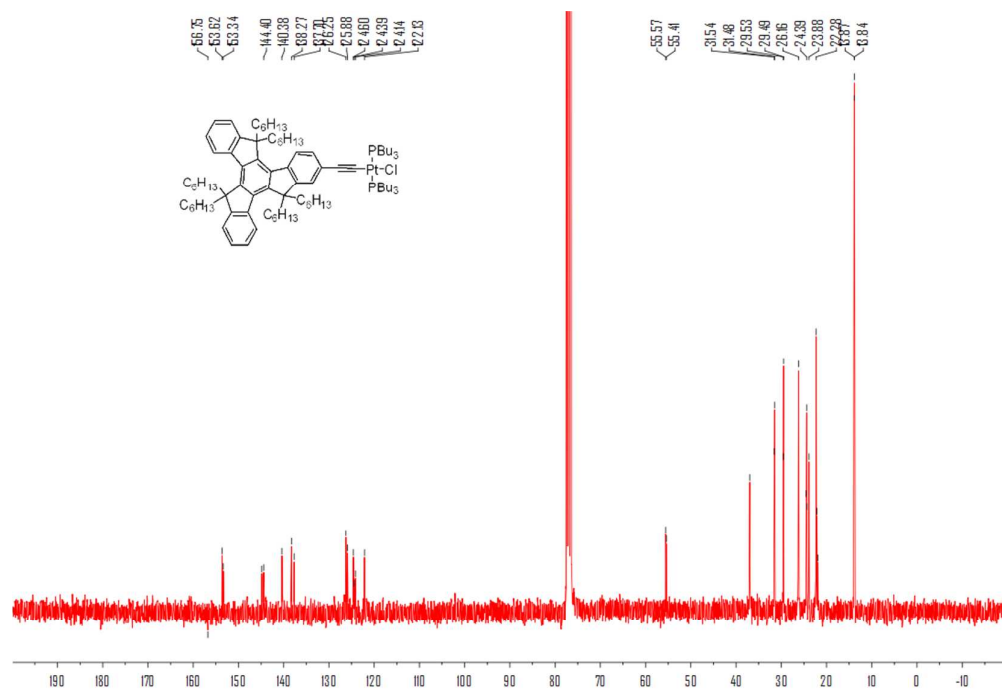


Figure S6. ^{13}C NMR spectrum of **3** (CDCl_3 , 76 MHz, 298 K).

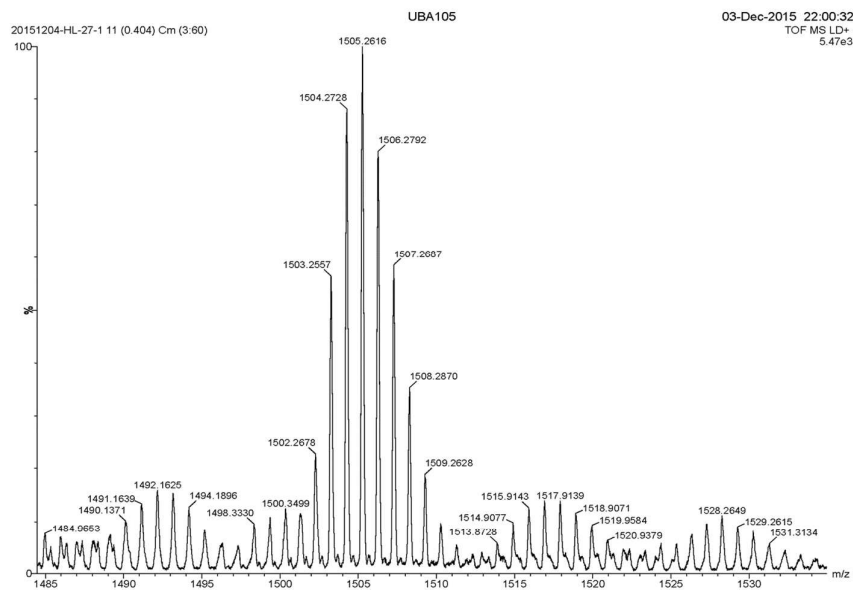


Figure S7. MALDI-TOF spectrum of **3**.

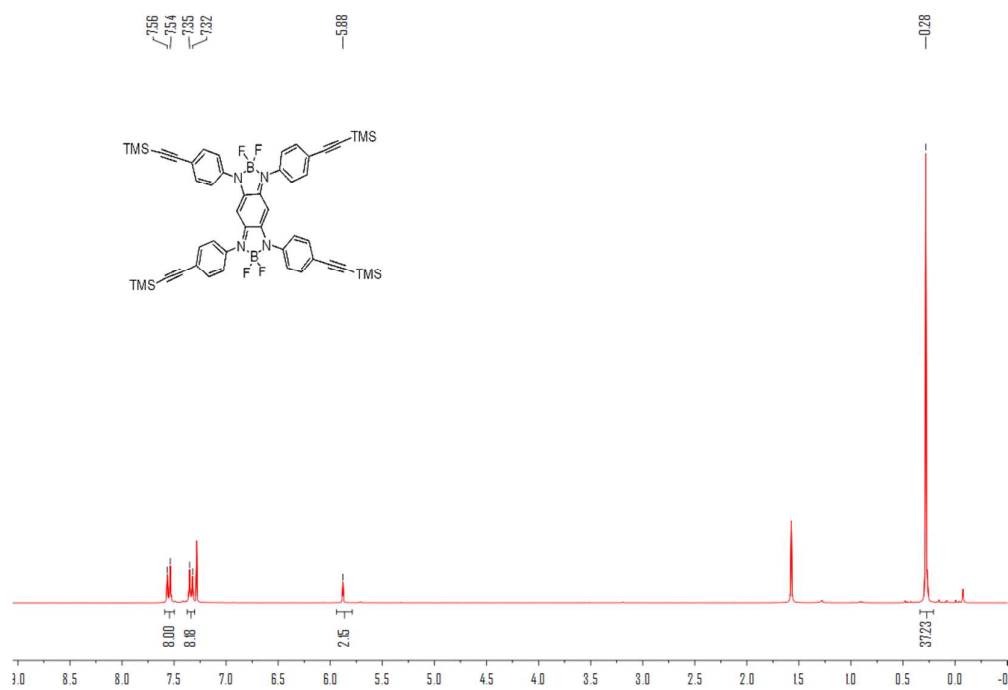


Figure S8. ^1H NMR spectrum of **BQ** (CDCl_3 , 300 MHz, 298 K).

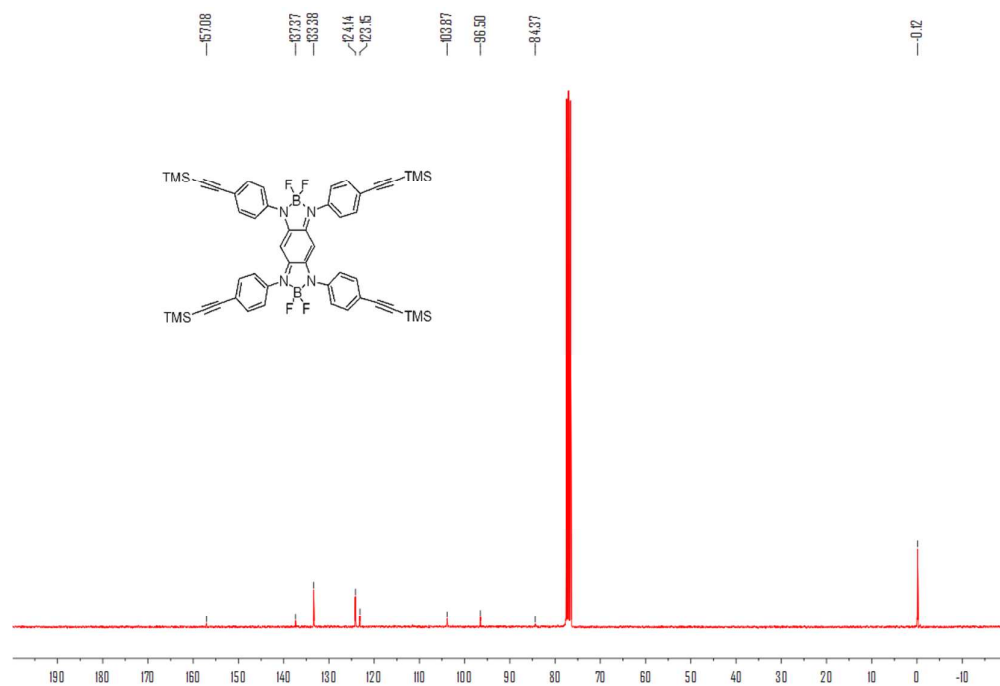


Figure S9. ¹³C NMR spectrum of BQ (CDCl₃, 76 MHz, 298 K).

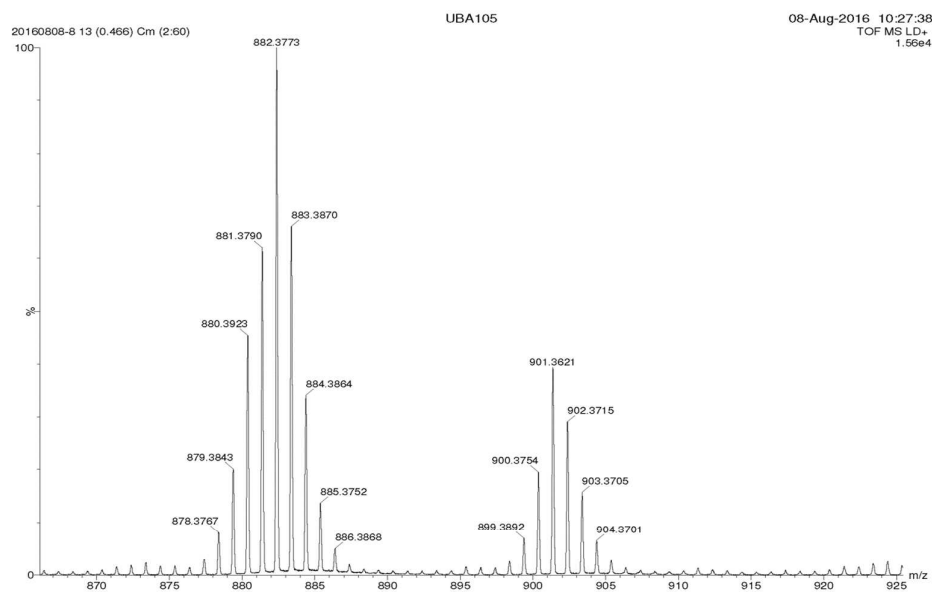


Figure S10. MALDI-TOF spectrum of BQ.

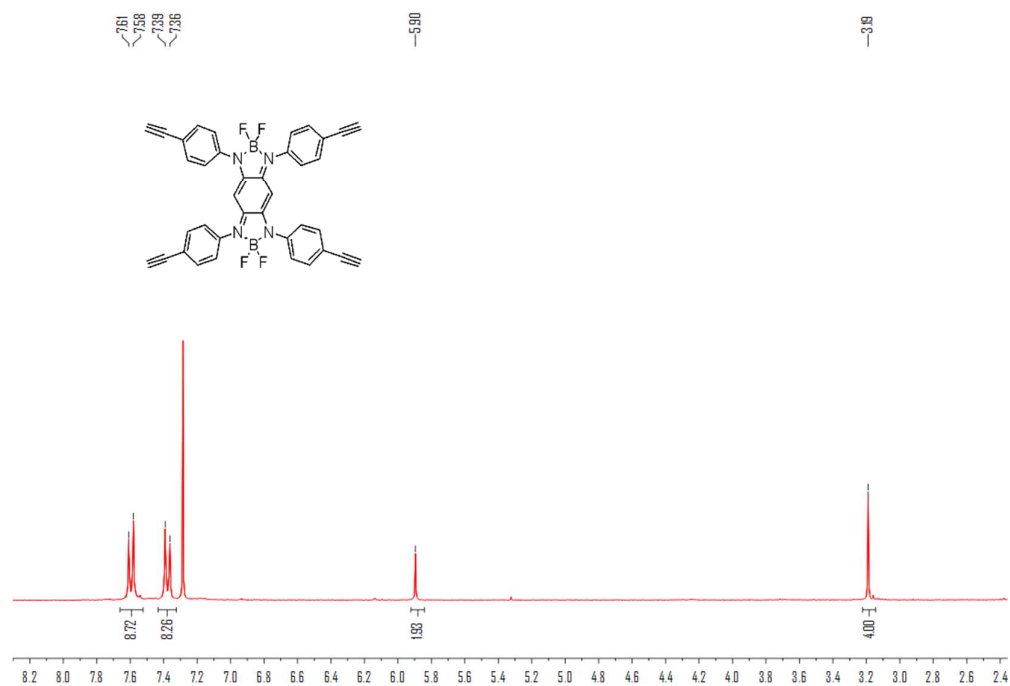


Figure S11. ^1H NMR spectrum of **5** (CDCl_3 , 76 MHz, 298 K).

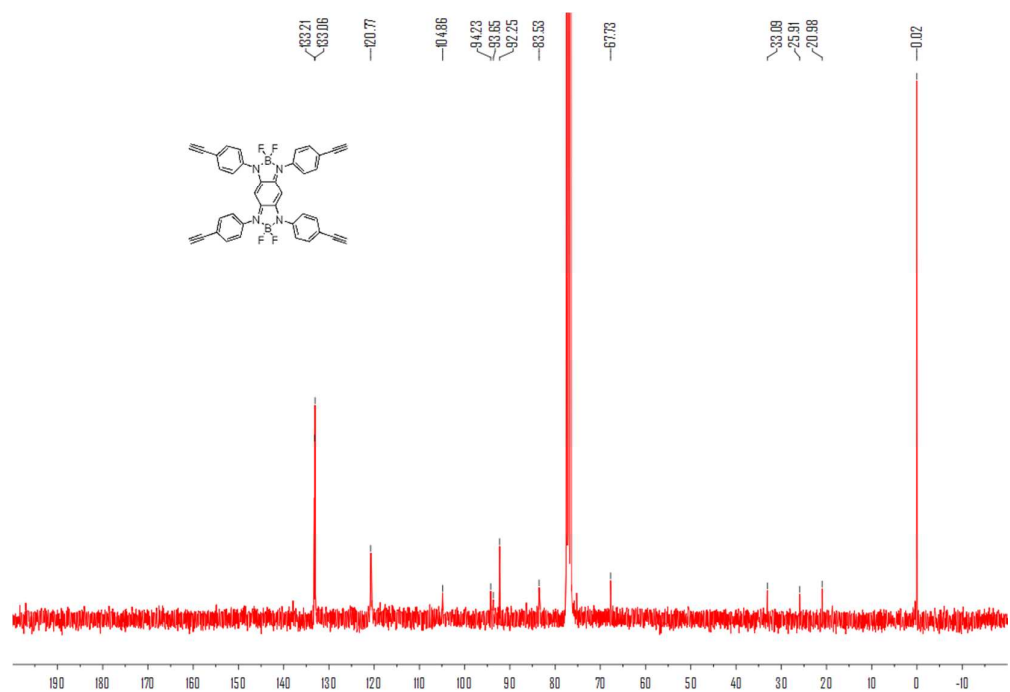


Figure S12. ^{13}C NMR spectrum of **5** (CDCl_3 , 76 MHz, 298 K).

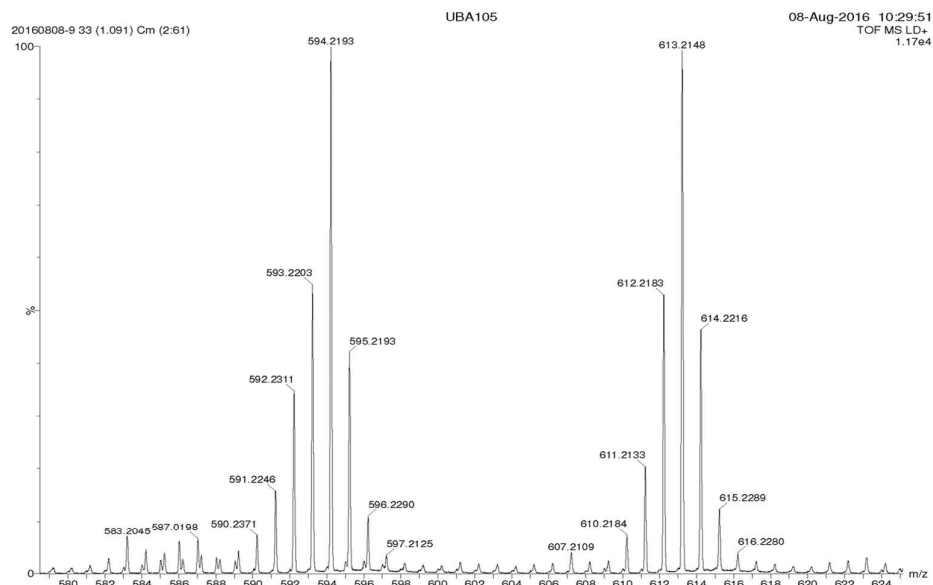


Figure S13. MALDI-TOF spectrum of **5**.

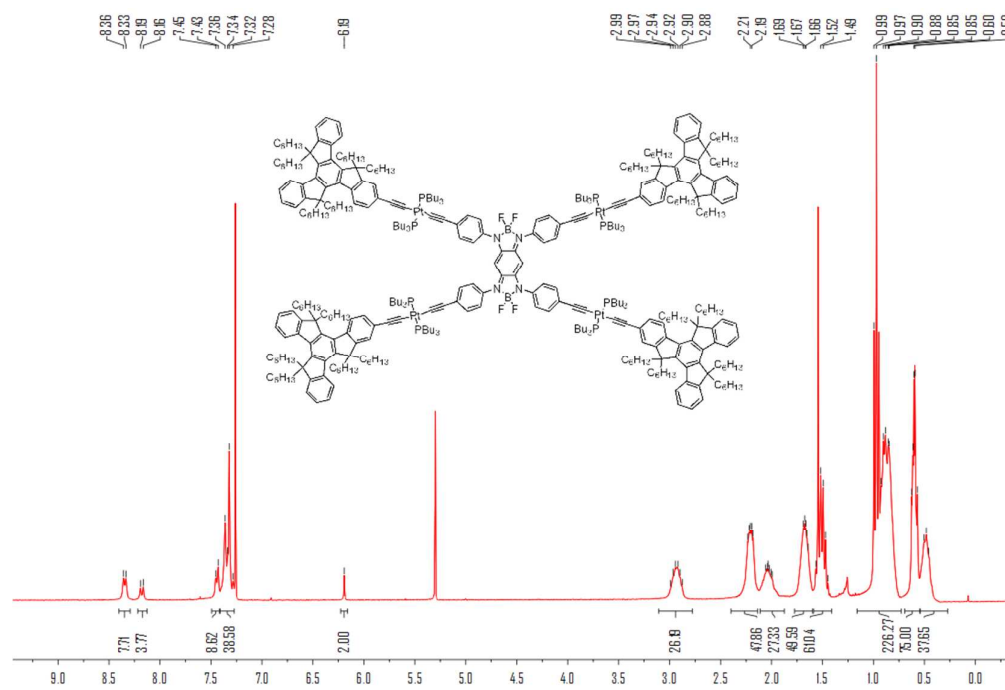


Figure S14. ^1H NMR spectrum of **TertTruPtBQ** (CDCl_3 , 76 MHz, 298 K).

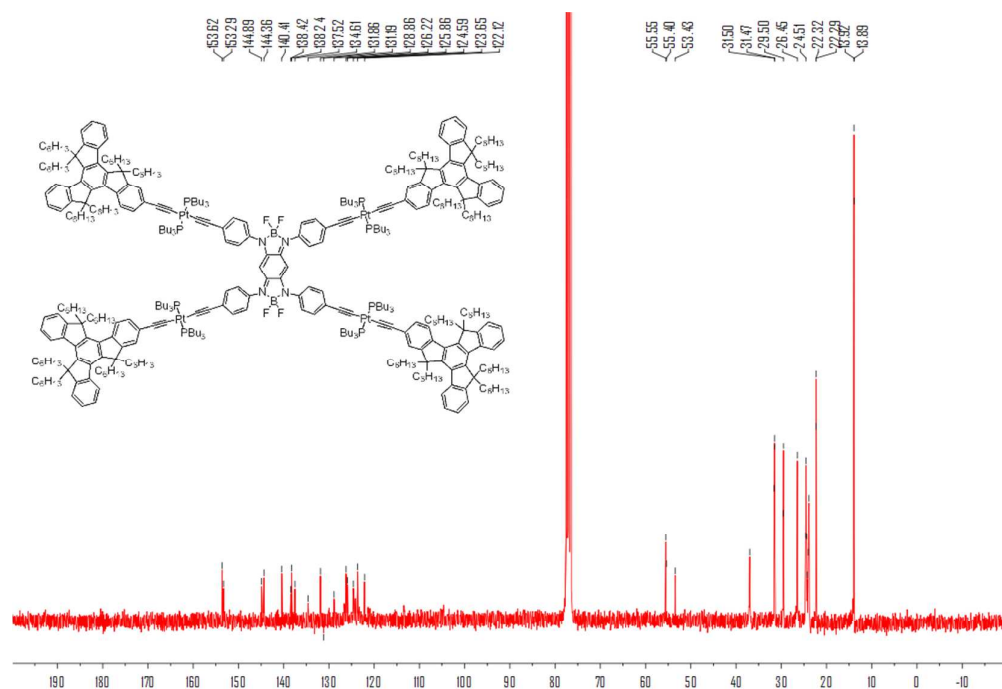


Figure S15. ^{13}C NMR spectrum of **TertTruPtBQ** (CDCl_3 , 76 MHz, 298 K).

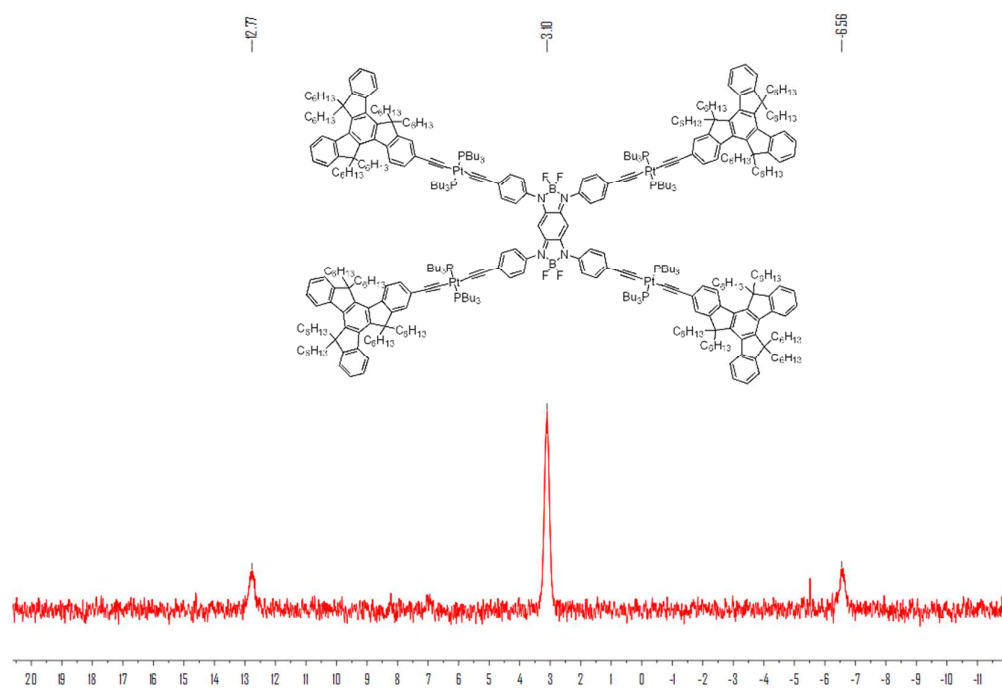


Figure S16. ^{31}P NMR spectrum of **TertTruPtBQ** (CDCl_3 , 76 MHz, 298 K).

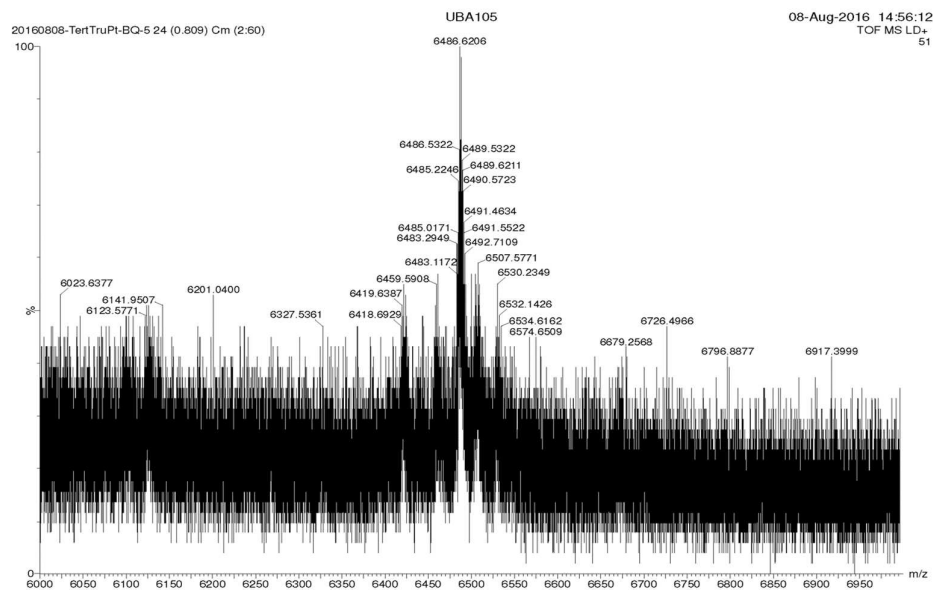


Figure S17. MALDI-TOF spectrum of **TertTruPtBQ**.

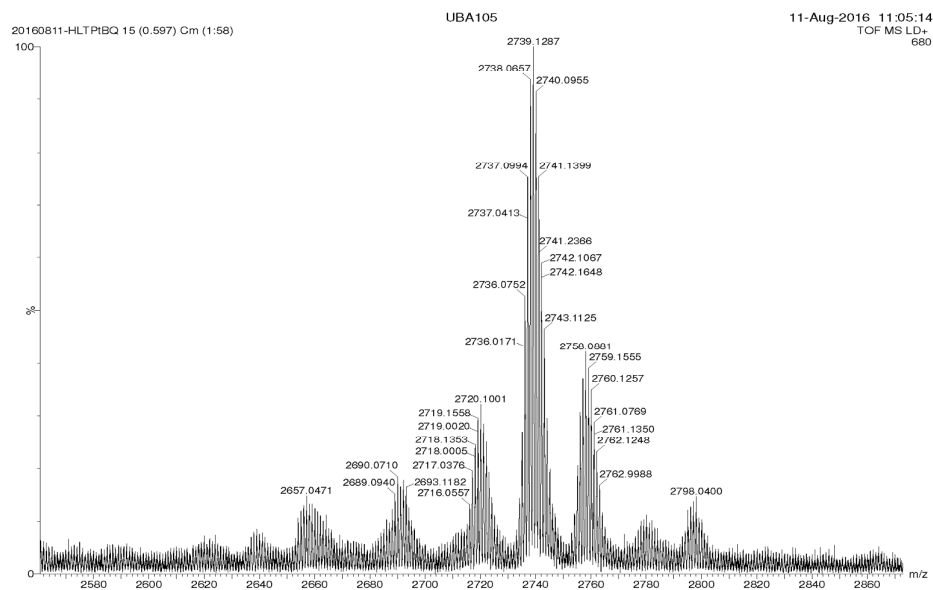


Figure S18. MALDI-TOF spectrum of **TertPtBQ**.