Supporting Information

Synthesis and Isolation of Dinuclear N,C-Chelate Organoboron Compounds Bridged by Neutral, Anionic and Dianionic 4,4'-Bipyridine via Reductive Coupling of Pyridines

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Table of Contents

S1. Experimental Materials and Methods

General methods

Starting materials were purchased from Sigma-Aldrich, TCI, J&K, and others without further purification. The compounds **BN1** and **BN3** were prepared by the reported method.[S1, S2] All reactions were carried out under nitrogen atmosphere. THF was dried by standard methods and freshly distilled over sodium before use. Other solvents were purified by an Mbraun SPS-800 Solvent Purification System. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker Avance 500, 600 spectrometers and deuterated solvents were purchased from Cambridge Isotopes, J&K. High-resolution mass spectra (HRMS) were obtained using a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer using ESI source. Elemental analyses were tested on a Vario EL elemental analyzer at the Analytical Center of Peking University. Infrared Spectra of solid samples were recorded on a Bruker AlphaII using a KBr pellet. X-ray single-crystal diffraction analyses were performed on an XtaLAB PRO 007HF(Mo). Cyclic voltammetry was performed on a CHI660E electrochemical workstation with platinum as the working electrode and $Ag/AgNO_3$ (0.1 M in CH_3CN) as the reference electrode under an argon atmosphere. UV/Vis absorption spectra were measured on an Agilent Cary 60 UV-Vis spectrophotometer. EPR spectra were obtained using a Bruker Elexsys E580 spectrometer and simulated with MATLAB software. The photochemical reactor was purchased from Shanghai Lanyi (LY-GHX-V).

Synthesis of BN2. In the nitrogen filled glovebox, compound **BN1** (100.0 mg, 0.25 mmol) was dissolved in 15 mL THF, KC_8 (33.5 mg, 0.25 mmol) was added to the solution at room temperature, the reaction mixture was stirred at room temperature overnight. After completion of the reaction, the solution was taken out of the glovebox and quenched with water immediately and keep stirring for several minutes. The solvent was removed with a rotary evaporator and concentrated under vacuum, the residue was extracted with dichloromethane (15 mL × 3). The organic layer was collected, then dried with sodium sulfate and concentrated under vacuum. Further purification by column chromatography on silica gel (dichloromethane:hexanes = 1:3) to afford compound **BN2** as bright yellow solid in 17% yield (17 mg). ^{1}H NMR (600 MHz, CD_2Cl_2): 8.75 (d, J = 6.2 Hz, 2H), 8.30 (d, J = 1.6 Hz, 2H), 8.01 (d, J = 7.3 Hz, 2H), 7.77 (d, J = 7.3 Hz, 2H), 7.54 (dd, J = 6.2,

1.9 Hz, 2H), 7.37 (td, *J* = 7.3, 1.2 Hz, 2H), 7.34 (td, *J* = 7.3, 1.2 Hz, 2H), 6.65 (s, 8H), 2.16 (s, 12H), 1.81 (s, 24H); ^{13}C NMR (151 MHz, CD_2Cl_2): 161.5, 150.0, 148.3, 146.6, 141.2, 135.7, 135.3, 132.9, 132.3, 131.2, 128.1, 126.9, 123.3, 121.0, 117.4, 26.2, 21.7; ^{11}B NMR (193 MHz, CD_2Cl_2): 0.26; HRMS (ESI), calcd for $C_{58}H_{59}B_2N_2$ $[M+H]^+$: 805.4859, found: 805.4862.

Synthesis of BN3. The synthetic procedure was similar as **BN2**, compound **BN3** (100.0 mg, 0.24 mmol) reacted with 1 equivalent of KC_8 (32.3 mg, 0.24 mmol) for 12 hours, the crude product was purified by column chromatography on silica gel (dichloromethane:hexanes = 1:4) to afford **BN4** as bright yellow solid in 41% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): 8.66 (d, *J* = 6.3 Hz, 2H), 8.16 (d, *J* = 2.0 Hz, 2H), 7.63–7.59 (m, 2H), 7.53 (dd, *J* = 6.3, 2.1 Hz, 2H), 7.08–7.02 (m, 4H), 6.82–6.77 (m, 2H), 6.49 (s, 8H); 2.74 (s, 4H), 2.05 (s, 12H), 1.79 (s, 24H); ^{13}C NMR (126 MHz, CD_2Cl_2): 157.5, 149.0, 148.3, 148.0, 141.7, 133.8, 131.5, 130.1, 129.8, 129.0, 128.7, 126.3, 124.6, 121.6, 120.7, 29.7, 24.8, 20.3; ^{11}B NMR (161 MHz, CD_2Cl_2): 1.27; HRMS (ESI), calcd for $C_{60}H_{63}B_2N_2$ $[M+H]^+$: 833.5172, found: 833.5189.

Synthesis of BN2K and BN2K(crypt). In the nitrogen-filled glovebox, compound **BN2** (10.4 mg, 0.013 mmol) was dissolved in 10 mL of THF, KC_8 (1.7 mg, 0.013 mmol) was added to the solution at room temperature, the reaction mixture was stirred at room temperature overnight. The solution was filtered through Celite to give a green THF solution of **BN2K**. The THF solution of 2,2,2-cryptand (4.9 mg, 0.013 mmol) was added to the green solution and stirred at room temperature for 30 minutes. The solvent was removed under vacuum to give a green solid. The solid was washed with hexane for three times (2 mL × 3), and further purification was achieved by recrystallization in THF/diethyl ether/hexane mixture solvent at -30 ℃ to give **BN2K(crypt)** as a green solid in near quantitative yield (15.8 mg). Anal. Calcd (%). for $C_{80}H_{102}B_2KN_4O_7$ [**BN2K(crypt)**THF]: C 74.35%, H 7.95%, N 4.34%. Found: C 74.18%, H 8.48%, N 4.14%.

Synthesis of $BN2K_2$ and $BN2K_2(18C6)_2$. The synthetic procedure was similar to **BN2K**. Compound **BN2** (10.4 mg, 0.013 mmol) reacted with 2 equivalent of KC_8 at room temperature overnight to generate **BN2K** as THF solution. Then 18-crown-6 (6.6 mg 0.025 mmol) was added to the solution at room temperature, the reaction mixture was

stirred at room temperature overnight. The resultant brown solution was filtered and concentrated under vacuum to give a brown solid. The solid was washed with hexane for three times (2 mL × 3), and further purification was achieved by recrystallization in THF/diethyl ether/hexane mixture solvent at -30 ℃ to give **$BN2K_2(18c6)_2$** as brown solid in 90% yield (15.5 mg). Anal. Calcd (%). for $C_{106}H_{154}B_2K_2N_2O_{18}$ [**$BN2K_2(18c6)_2$**$(THF)_6$]: C 69.04%, H 8.42%, N 1.52%. Found: C 68.36%, H 8.24%, N 1.82%. NMR for **$BN2K_2$**: ^{1}H NMR (600 MHz, THF-d_8): 7.38 – 7.34 (m, 2H), 7.32 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.78–6.71 (m, 3H), 6.45 (s, 4H), 6.43 (s, 4H), 6.06 (d, J = 7.7 Hz, 1H), 5.89 (d, J = 1.8 Hz, 1H), 5.70 (d, J = 1.8 Hz, 1H), 5.09 (dd, J = 7.7, 1.8 Hz, 1H), 4.87 (dd, J = 7.5, 1.7 Hz, 1H), 2.08 (s, 6H), 2.07 (s, 6H), 1.97 (s, 24H); ^{13}C NMR (126 MHz, THF-d_8): 164.2, 154.1, 148.5, 148.5, 140.9, 140.8, 140.7, 138.2, 133.7, 131.7, 131.6, 131.3, 131.2, 129.6, 129.6, 127.7, 125.8, 125.8, 123.3, 123.2, 118.6, 118.5, 107.9, 107.9, 104.4, 96.8, 96.6, 26.5, 26.4, 21.1; ^{11}B NMR (193 MHz, THF-d_8): - 0.55.

S2. NMR and HRMS Data

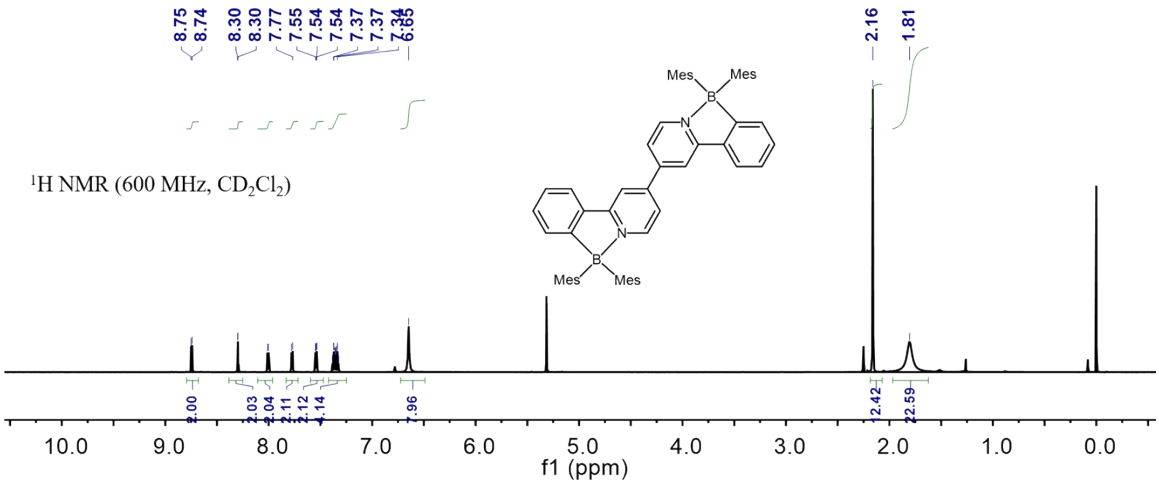

Figure S1. ^{1}H NMR spectrum of **BN2** in CD_2Cl_2.

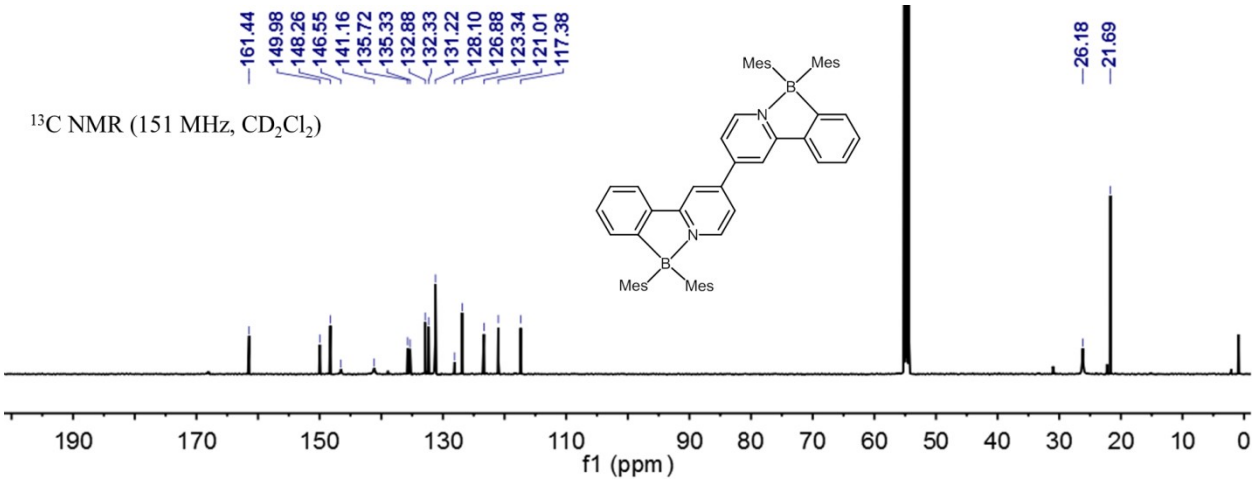

Figure S2. ^{13}C NMR spectrum of **BN2** in CD_2Cl_2.

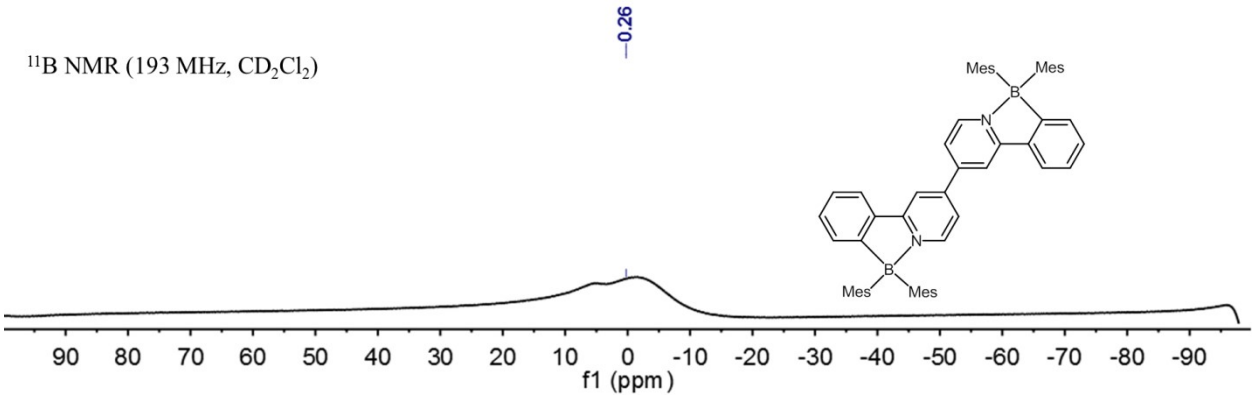

Figure S3. ^{11}B NMR spectrum of **BN2** in CD_2Cl_2.

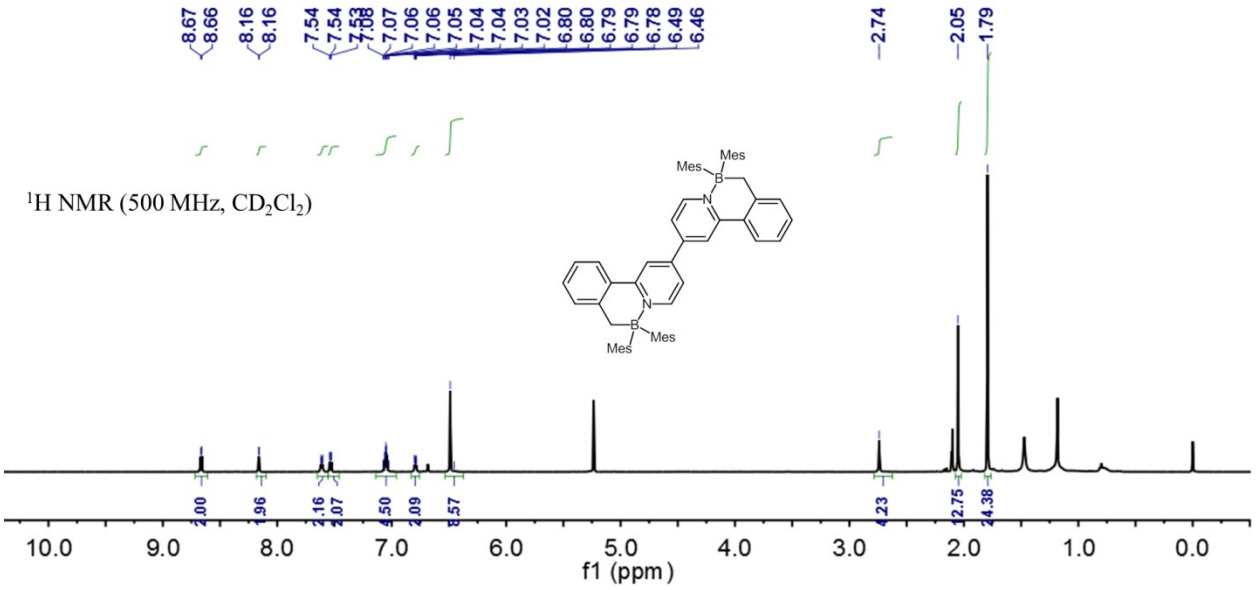

Figure S4. ^{1}H NMR spectrum of **BN4** in CD_2Cl_2.

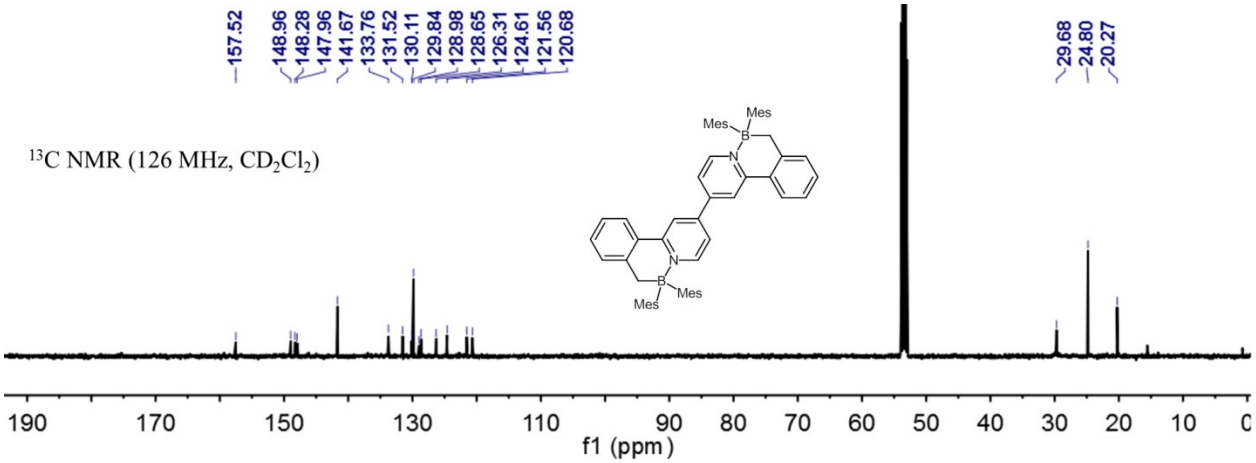

Figure S5. ^{13}C NMR spectrum of **BN4** in CD_2Cl_2.

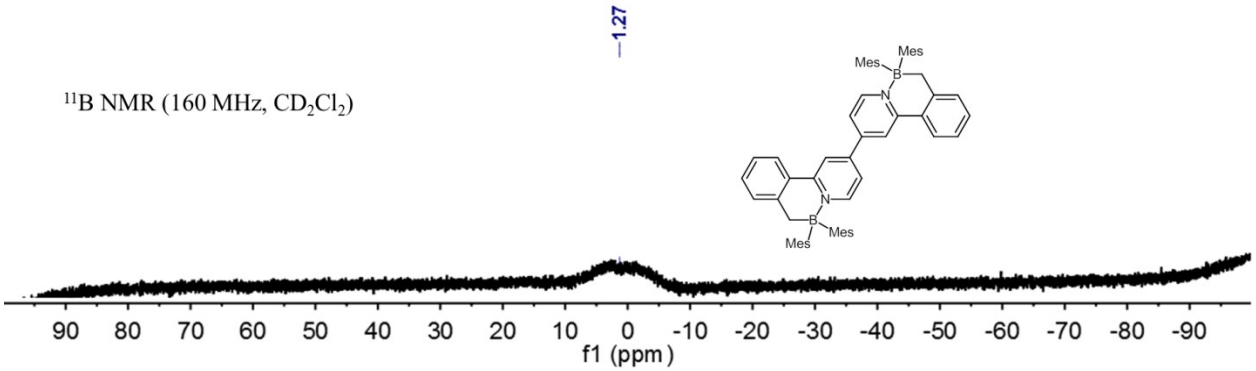

Figure S6. ^{11}B NMR spectrum of **BN4** in CD_2Cl_2.

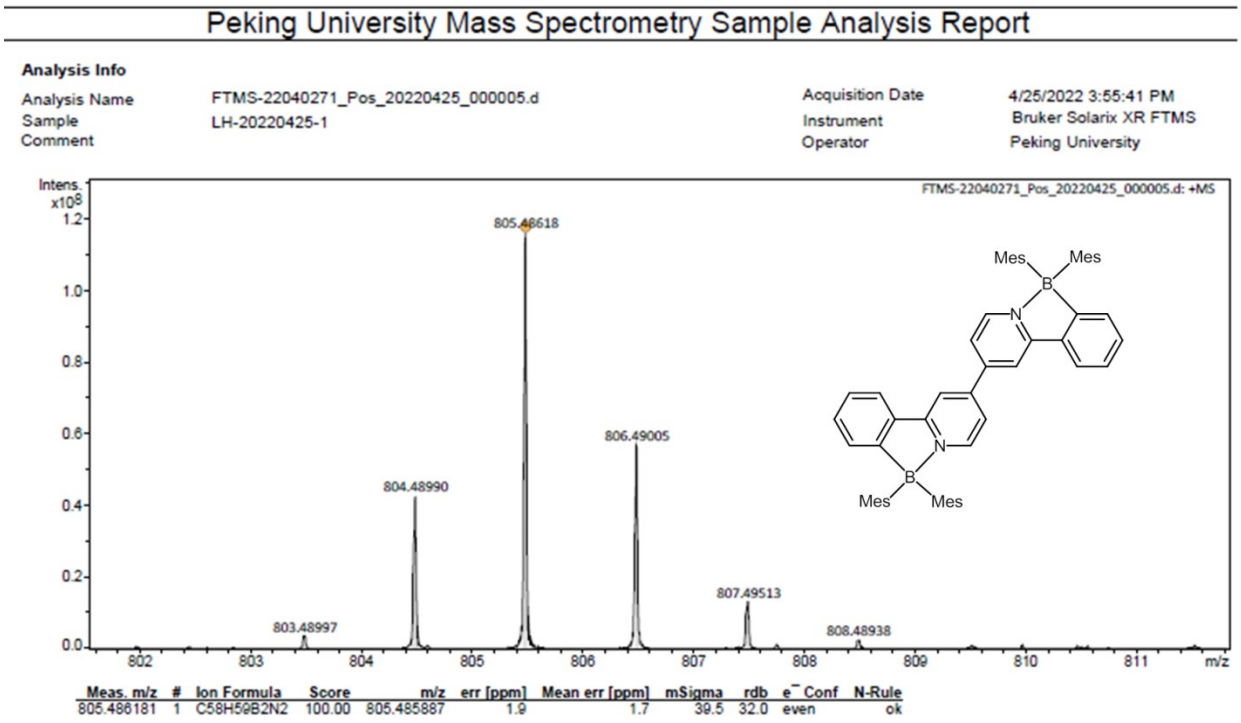

Figure S7. HRMS spectrum of **BN2**.

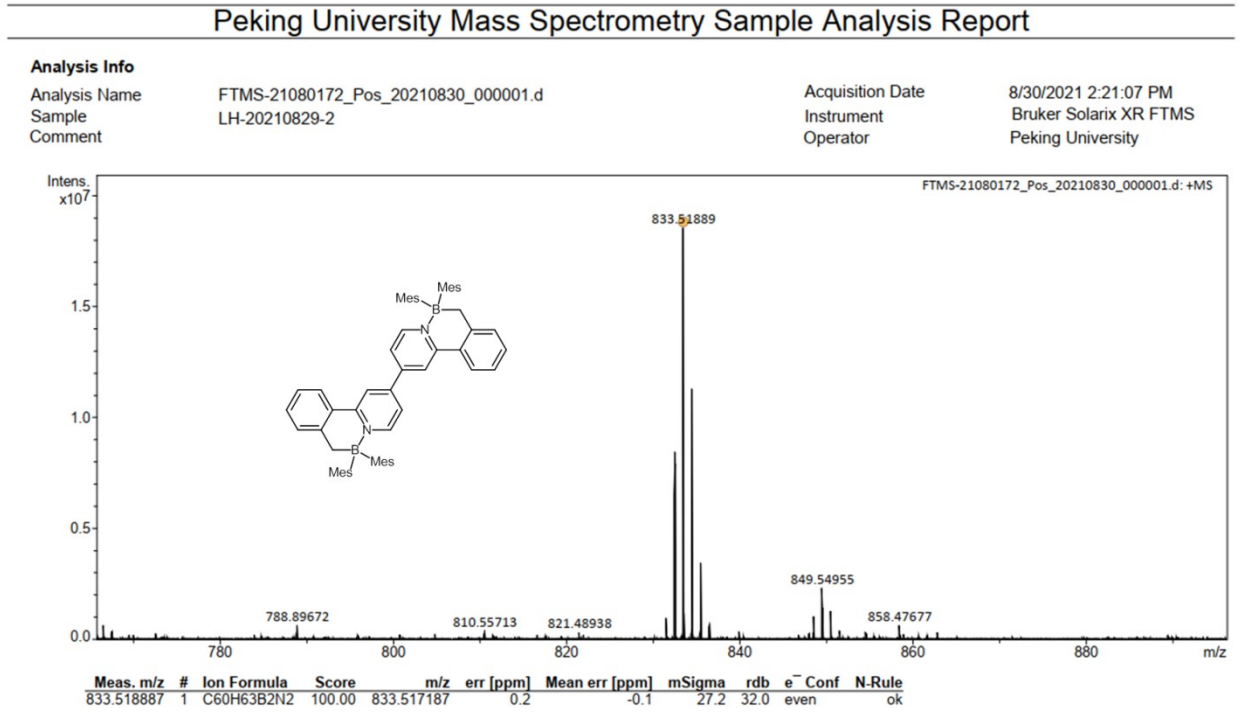

Figure S8. HRMS spectrum of **BN4**.

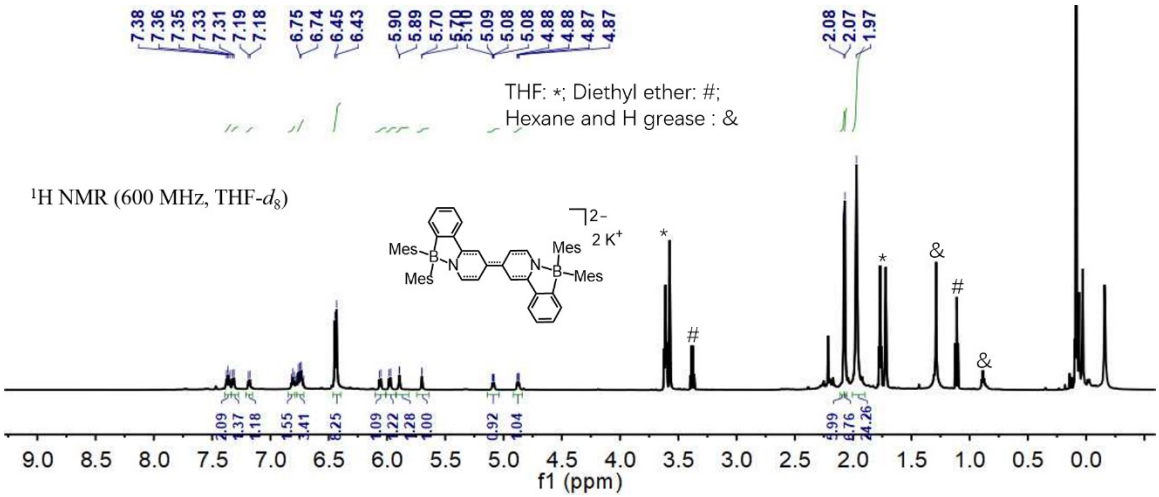

Figure S9. ^{1}H NMR spectrum of **BN2K2** in THF-d_8.

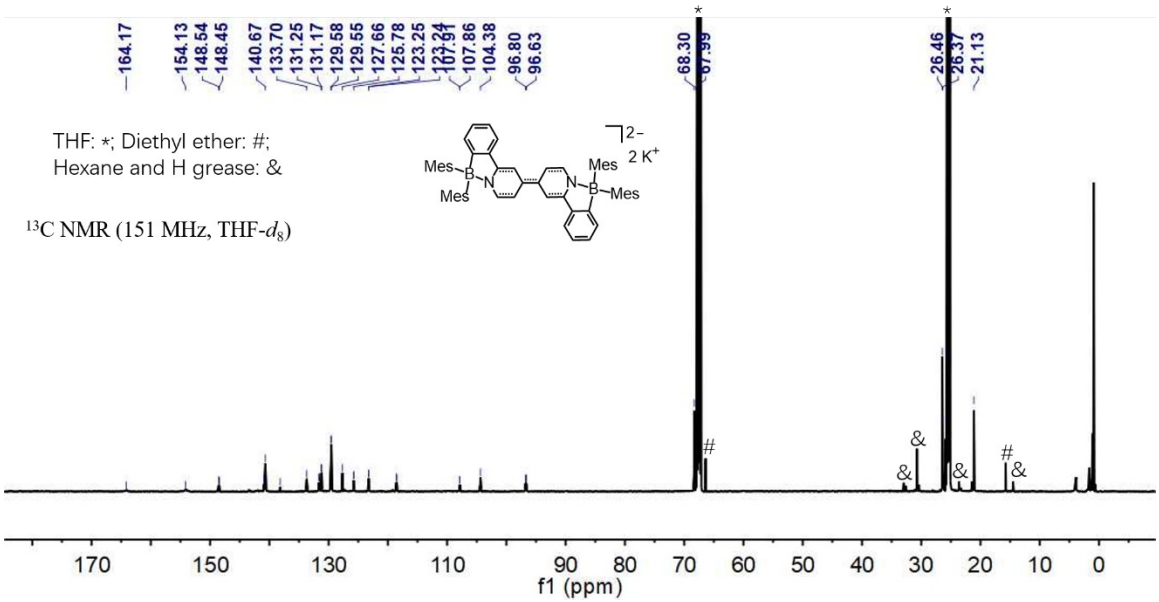

Figure S10. ^{13}C NMR spectrum of **BN2K2** in THF-d_8.

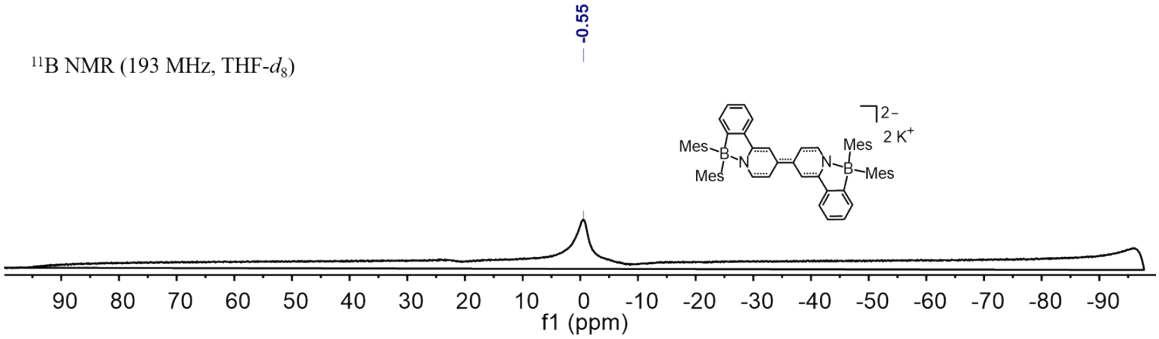

Figure S11. ^{11}B NMR spectrum of **BN2K2** in THF-d_8.

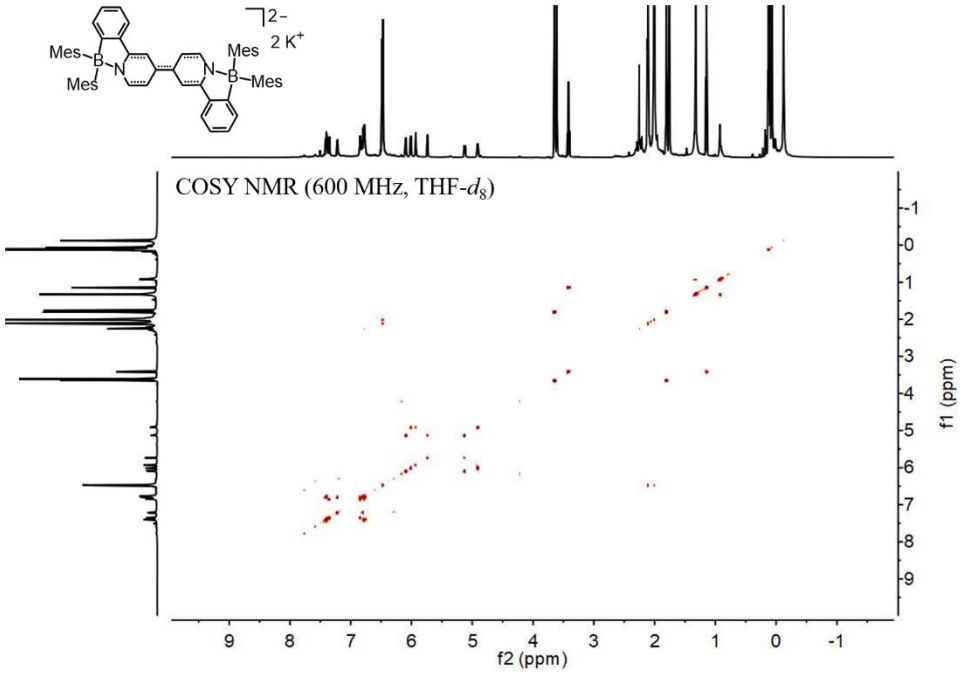

Figure S12. COSY NMR spectrum of **BN2K2** in THF-d_8.

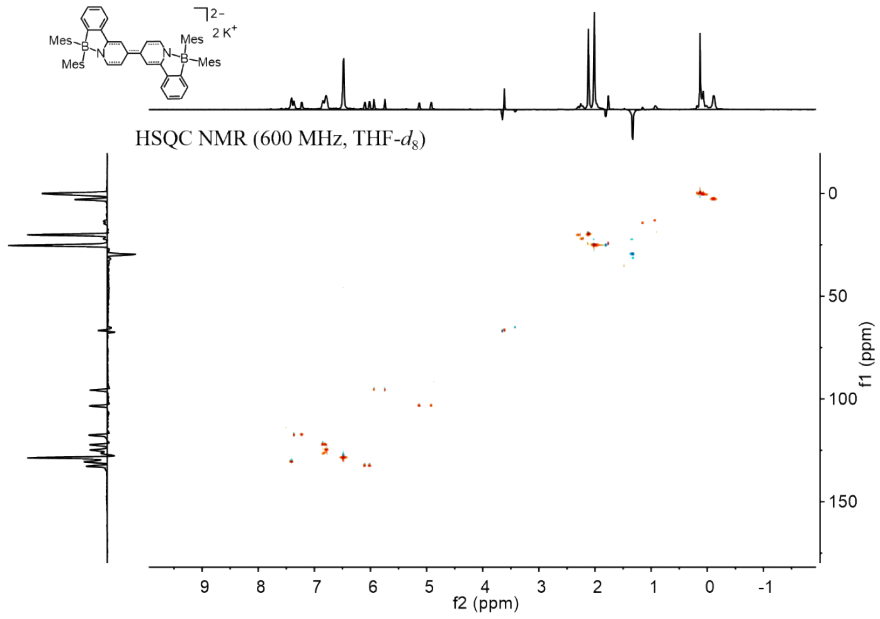

Figure S13. HSQC NMR spectrum of **BN2K2** in THF-d_8.

S3. Photochemical Reactivity Study

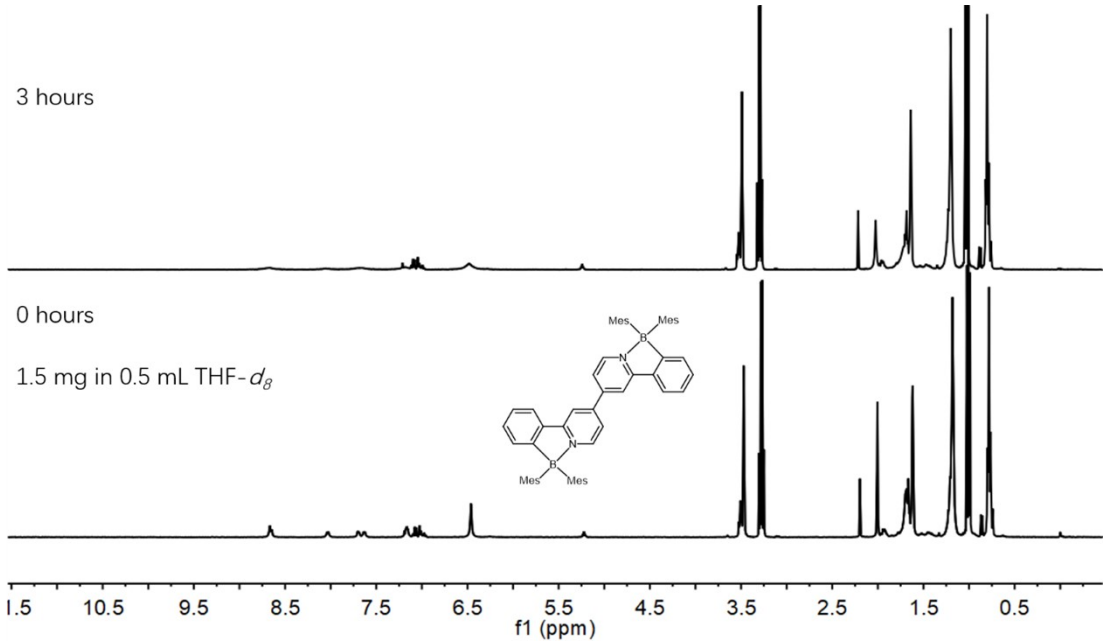

Figure S14. NMR tracking experiment of **BN2** in THF-d_8 upon UV light (300 nm) irradiation.

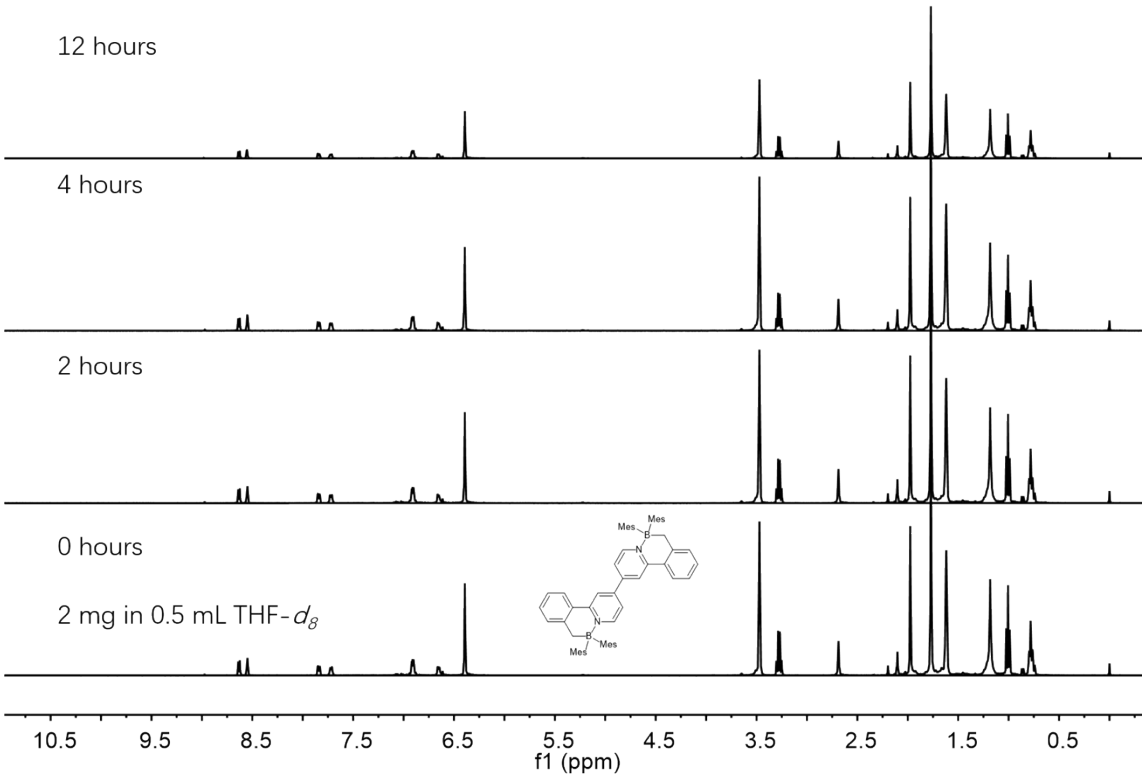

Figure S15. NMR tracking experiment of **BN4** in THF-d_8 upon UV light (300 nm) irradiation.

S4. Cyclic Votammetric Studies

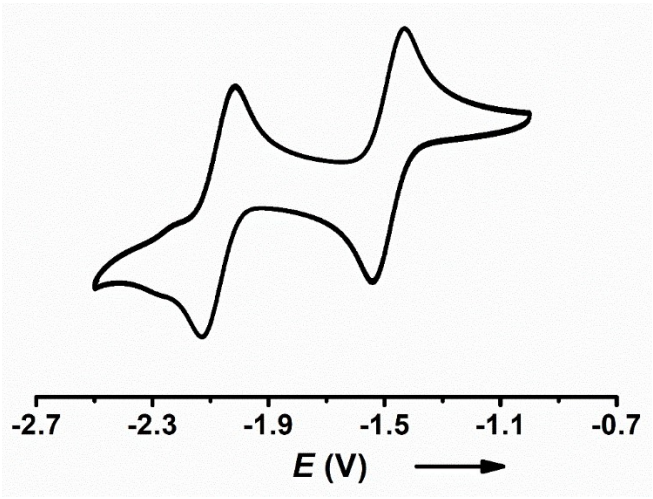

Figure S16. The cyclic voltammogram of compound **BN2** in THF at room temperature containing 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte (scan rate: 100 mV/s; $E_{1/2}(Fc^+/Fc)$ = 0.14 V).

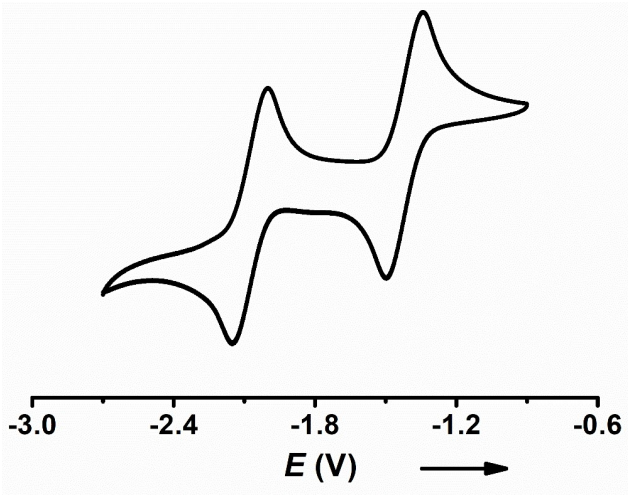

Figure S17. The cyclic voltammogram of compound **BN4** in THF at room temperature containing 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte (scan rate: 100 mV/s; $E_{1/2}(Fc^+/Fc)$ = 0.14 V).

S5. IR spectra

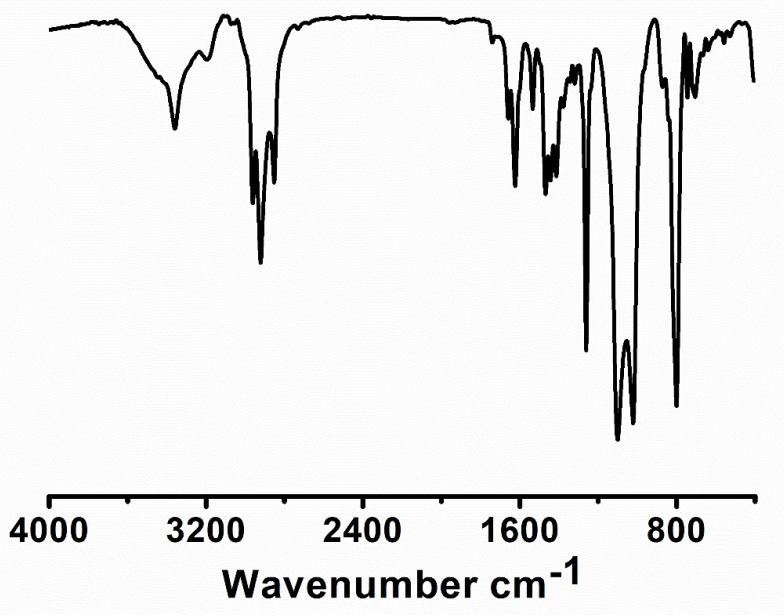

Figure S18. IR spectrum of **BN2**.

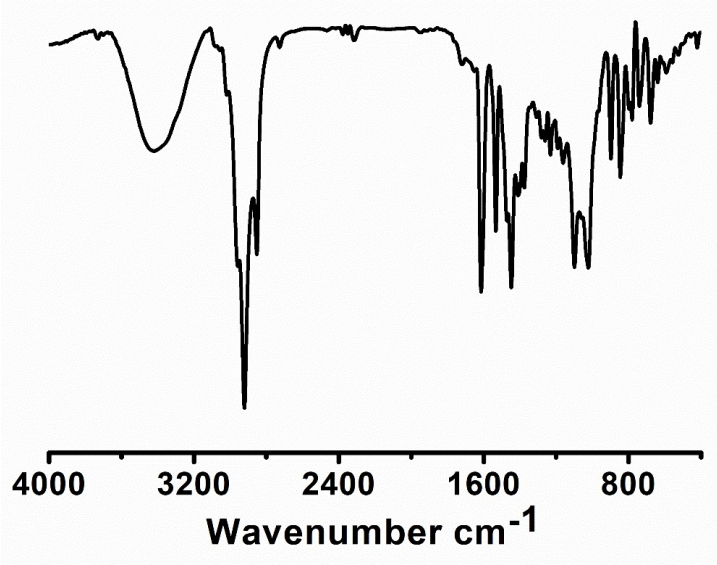

Figure S19. IR spectrum of **BN4**.

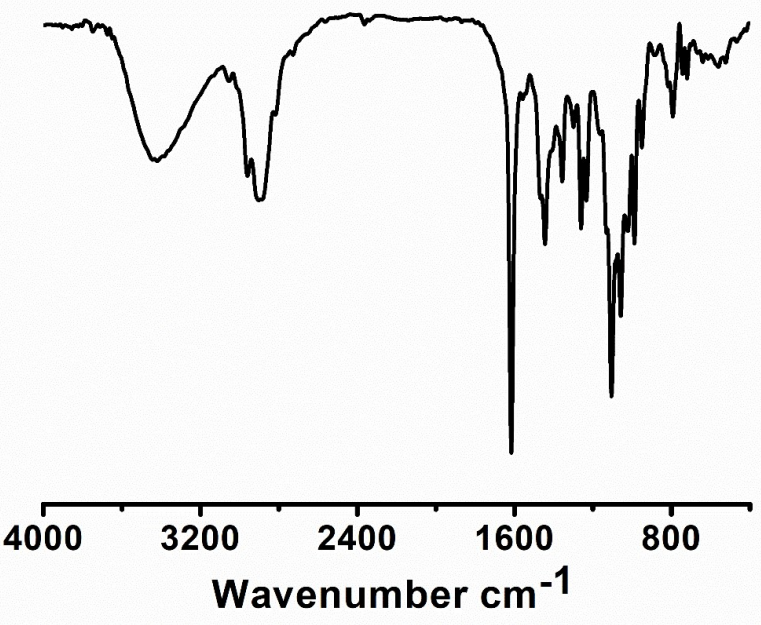

Figure S20. IR spectrum of **BN2K(crypt)**.

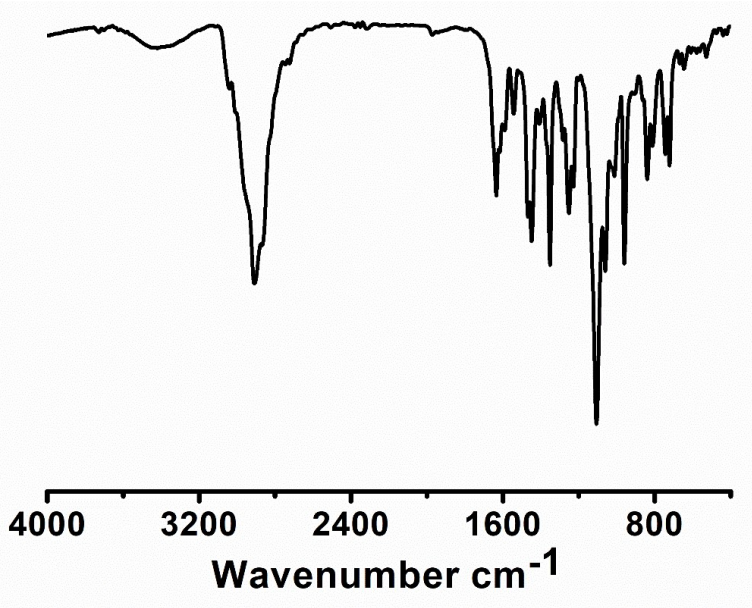

Figure S21. IR spectrum of **$BN2K_2(18c6)_2$**.

S6. TD-DFT Calculation Data, UV/Vis Absorption Spectra and Calculated transitions, Fluorescent Spectra

All calculations were performed with the Gaussian 16 program suite.[S3] All the geometry optimizations were performed with the PBE1PBE functional and def2svp basis set.

Frequency calculations were carried out to confirm that all optimized geometries correspond to energy minima, and no imaginary frequency was found. The absolute energy and frequency values were shown as follows. UV-Visible spectra were recorded on an Agilent Cary 60 UV-Vis spectrophotometer. The UV-Vis absorption spectra were calculated using the PBE1PBE functional and def2svp basis set and polarized continuum model (PCM) was adopted to consider solvent (THF) effects.

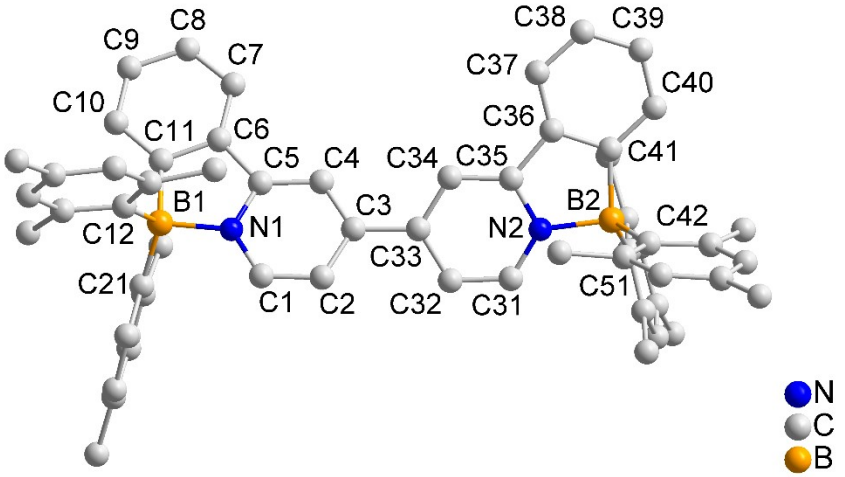

Figure S22. Structure of **BN2** calculated at the PBE1PBE/def2svp level of theory. H atoms are omitted for clarity.

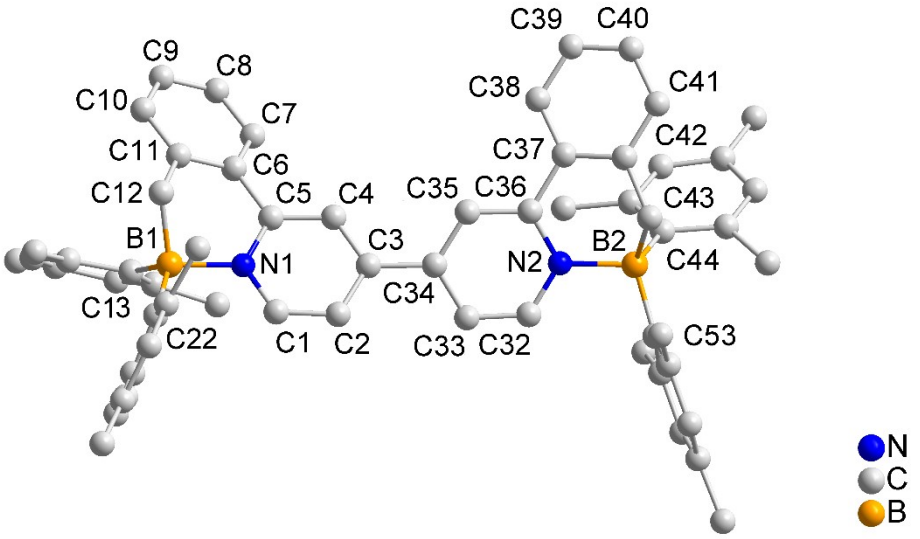

Figure S23. Structure of **BN4** calculated at the PBE1PBE/def2svp level of theory. H atoms are omitted for clarity.

Coordinates, absolute energy (E_a) and frequency values of the model molecules

BN2, Ea = -2399.99911 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.515518	-0.0174	-0.01976
2	7	0	-3.51526	0.064681	-0.03212
3	6	0	0.738963	0.035748	0.000789
4	6	0	-0.73853	0.05758	-0.00313
5	6	0	3.748759	-1.6774	1.567621
6	6	0	1.479196	0.924106	-0.8012
7	1	0	0.984652	1.673683	-1.41952
8	6	0	2.836585	-0.86275	0.790022
9	6	0	2.859541	0.874784	-0.76823
10	1	0	3.474574	1.566864	-1.34281
11	6	0	-1.46242	-0.13888	1.170585
12	1	0	-0.95465	-0.26801	2.126927
13	6	0	-2.85933	-0.12093	1.136987
14	6	0	5.956209	-0.91777	-1.02535
15	6	0	5.080203	-1.27246	1.33915
16	6	0	-1.45461	0.293968	-1.19114
17	1	0	-0.94014	0.452059	-2.13934
18	6	0	5.384656	-1.75749	-2.01239
19	6	0	1.439301	-0.8559	0.809738
20	1	0	0.9124	-1.56432	1.449772
21	6	0	5.567594	1.423134	0.429485
22	6	0	7.373356	-0.83232	-0.99324
23	6	0	-2.83584	0.298257	-1.15912
24	1	0	-3.4323	0.491653	-2.05031
25	6	0	5.520695	2.00857	1.721308
26	6	0	-3.79329	-0.25884	2.236559

27	6	0	3.404251	-2.7212	2.436776
28	1	0	2.361271	-3.01475	2.583181
29	6	0	6.194744	-2.39814	-2.95785
30	1	0	5.717678	-3.02712	-3.71677
31	6	0	5.905115	2.278176	-0.65245
32	6	0	-5.11358	-0.05587	1.784211
33	6	0	8.146411	-1.49998	-1.94948
34	1	0	9.23645	-1.40266	-1.90183
35	6	0	6.082197	-1.99482	1.999775
36	1	0	7.134185	-1.75804	1.829329
37	6	0	-5.52837	1.520118	-0.59757
38	6	0	5.754658	-3.02469	2.877321
39	1	0	6.552227	-3.56511	3.394258
40	6	0	7.582165	-2.27906	-2.95696
41	6	0	4.419725	-3.39066	3.103025
42	1	0	4.183479	-4.20816	3.787811
43	6	0	6.231427	3.622014	-0.41921
44	1	0	6.489912	4.2546	-1.27502
45	6	0	5.864805	3.350383	1.911646
46	1	0	5.824895	3.765454	2.924133
47	6	0	-3.47733	-0.54915	3.570542
48	1	0	-2.44224	-0.70634	3.885583
49	6	0	-5.97713	-1.21172	-0.31698
50	6	0	5.090359	1.242263	2.944366
51	1	0	4.101516	0.777759	2.816136
52	1	0	5.034605	1.906334	3.818679
53	1	0	5.783491	0.423831	3.187646
54	6	0	3.906565	-2.04123	-2.10288
55	1	0	3.513473	-2.45077	-1.16
56	1	0	3.706677	-2.78582	-2.88601
57	1	0	3.311055	-1.14889	-2.34925
58	6	0	-6.13517	-0.19966	2.731716

59	1	0	-7.18039	-0.09975	2.43281
60	6	0	6.239079	4.180044	0.855516
61	6	0	-5.42695	-2.49388	-0.56309
62	6	0	-5.46903	2.774601	0.06344
63	6	0	-5.84108	1.537144	-1.98236
64	6	0	8.142934	-0.0105	0.014164
65	1	0	8.29118	1.022973	-0.33926
66	1	0	9.139088	-0.44742	0.180464
67	1	0	7.641878	0.079977	0.984529
68	6	0	5.96459	1.842069	-2.09904
69	1	0	6.939572	1.39319	-2.3466
70	1	0	5.82216	2.708047	-2.76283
71	1	0	5.22509	1.077143	-2.36759
72	6	0	-5.83581	-0.47426	4.063243
73	1	0	-6.64797	-0.56614	4.789428
74	6	0	-6.13323	2.746927	-2.62886
75	1	0	-6.3736	2.725381	-3.69712
76	6	0	-6.1293	3.970075	-1.96543
77	6	0	-5.77863	3.956741	-0.61606
78	1	0	-5.73027	4.905128	-0.07087
79	6	0	-4.51092	-0.64576	4.490108
80	1	0	-4.2968	-0.86851	5.53776
81	6	0	-7.39092	-1.09564	-0.37314
82	6	0	-6.25134	-3.56314	-0.93285
83	1	0	-5.79086	-4.53784	-1.12534
84	6	0	-5.9085	0.306349	-2.85823
85	1	0	-5.1942	-0.47979	-2.58301
86	1	0	-5.73419	0.578848	-3.91003
87	1	0	-6.8971	-0.17636	-2.80191
88	6	0	-8.14093	0.185199	-0.09155
89	1	0	-7.63913	0.841328	0.628533
90	1	0	-9.14774	-0.03992	0.291305

91	1	0	-8.26352	0.788483	-1.00586
92	6	0	6.638067	5.60867	1.088606
93	1	0	6.527863	6.214524	0.177206
94	1	0	7.693517	5.677086	1.402244
95	1	0	6.0347	6.072635	1.883642
96	5	0	5.135772	-0.14154	0.170466
97	6	0	-7.6343	-3.43798	-1.04224
98	6	0	-5.06182	2.913144	1.506783
99	1	0	-5.77723	2.430847	2.188728
100	1	0	-4.9903	3.972975	1.789846
101	1	0	-4.08548	2.448657	1.709023
102	6	0	-3.95947	-2.80662	-0.41415
103	1	0	-3.32844	-2.26915	-1.13827
104	1	0	-3.7791	-3.8798	-0.56724
105	1	0	-3.59269	-2.55719	0.593164
106	6	0	-8.17961	-2.1941	-0.73386
107	1	0	-9.26693	-2.06738	-0.77216
108	5	0	-5.13821	0.117818	0.166644
109	6	0	8.435509	-3.00256	-3.95885
110	1	0	8.78146	-3.97141	-3.56002
111	1	0	9.332762	-2.42126	-4.21986
112	1	0	7.882096	-3.21054	-4.88656
113	6	0	-6.49207	5.248129	-2.66508
114	1	0	-6.36741	5.163723	-3.75467
115	1	0	-5.87671	6.090382	-2.31382
116	1	0	-7.5452	5.516298	-2.47529
117	6	0	-8.49629	-4.58884	-1.47509
118	1	0	-8.63362	-4.59185	-2.56993
119	1	0	-9.49805	-4.53613	-1.02295
120	1	0	-8.04846	-5.55583	-1.20122

BN4, Ea = -2478.45432 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.551478	0.191413	0.30792
2	7	0	-3.51453	0.411307	0.247298
3	6	0	0.758931	0.294017	0.260631
4	6	0	-0.71714	0.33866	0.251952
5	6	0	3.559219	-2.23276	0.546583
6	6	0	1.527923	1.452745	0.095455
7	1	0	1.067274	2.433891	-0.02446
8	6	0	2.839607	-0.95738	0.437914
9	6	0	2.906073	1.353437	0.14134
10	1	0	3.550457	2.23102	0.05669
11	6	0	-1.47025	-0.48662	1.084692
12	1	0	-0.97472	-1.14455	1.798239
13	6	0	-2.86903	-0.45926	1.067407
14	6	0	5.920301	-0.53193	-0.88241
15	6	0	4.837903	-2.23685	1.139923
16	6	0	-1.41658	1.217574	-0.58308
17	1	0	-0.90067	1.886716	-1.27255
18	6	0	5.293936	-0.96856	-2.07918
19	6	0	1.441333	-0.9077	0.439157
20	1	0	0.89071	-1.83879	0.571209
21	6	0	5.670797	1.728722	0.75312
22	6	0	7.307338	-0.8174	-0.76113
23	6	0	-2.79853	1.22429	-0.54182
24	1	0	-3.38603	1.908298	-1.15693
25	6	0	5.573236	2.301022	2.053737
26	6	0	-3.65619	-1.37113	1.907722
27	6	0	3.00393	-3.41661	0.040426
28	1	0	2.029773	-3.39938	-0.45501

29	6	0	6.000015	-1.72346	-3.02433
30	1	0	5.478427	-2.04493	-3.93213
31	6	0	6.197141	2.582425	-0.2599
32	6	0	-4.943	-0.97034	2.315208
33	6	0	7.97982	-1.56391	-1.73486
34	1	0	9.050623	-1.75385	-1.60152
35	6	0	5.529455	-3.44832	1.205789
36	1	0	6.525443	-3.46141	1.655156
37	6	0	-5.55044	1.979907	-0.45023
38	6	0	4.978754	-4.62143	0.69589
39	1	0	5.547099	-5.5537	0.746243
40	6	0	7.341352	-2.0606	-2.86745
41	6	0	3.711474	-4.61046	0.11118
42	1	0	3.283919	-5.52598	-0.30289
43	6	0	6.698498	3.852112	0.056044
44	1	0	7.105547	4.468337	-0.75224
45	6	0	6.084207	3.575566	2.32654
46	1	0	5.994981	3.969848	3.344255
47	6	0	-3.15564	-2.63005	2.272014
48	1	0	-2.17034	-2.95232	1.925921
49	6	0	-5.94949	-0.75713	-0.37972
50	6	0	4.88693	1.629356	3.218554
51	1	0	3.938012	1.154317	2.930614
52	1	0	4.658861	2.368417	3.999827
53	1	0	5.51371	0.85235	3.681549
54	6	0	3.877462	-0.62346	-2.47686
55	1	0	3.129683	-1.28402	-2.01018
56	1	0	3.755909	-0.73553	-3.56358
57	1	0	3.604492	0.411458	-2.2303
58	6	0	-5.70399	-1.86195	3.075135
59	1	0	-6.70905	-1.56408	3.38337
60	6	0	6.685881	4.363997	1.349779

61	6	0	-5.37803	-1.92839	-0.93714
62	6	0	-5.69463	3.213471	0.243581
63	6	0	-5.76666	2.03242	-1.85788
64	6	0	8.171567	-0.31927	0.375432
65	1	0	9.144955	0.016758	-0.01366
66	1	0	8.384231	-1.12153	1.102168
67	1	0	7.728066	0.521391	0.921187
68	6	0	6.226899	2.231771	-1.72688
69	1	0	7.034823	1.528897	-1.97581
70	1	0	6.373849	3.141647	-2.32709
71	1	0	5.296765	1.756373	-2.06301
72	6	0	-5.20885	-3.11485	3.425243
73	1	0	-5.82923	-3.80003	4.00853
74	6	0	-6.17602	3.215759	-2.48632
75	1	0	-6.33465	3.205412	-3.56966
76	6	0	-6.38251	4.40016	-1.78626
77	6	0	-6.11078	4.37357	-0.42104
78	1	0	-6.21713	5.297846	0.156252
79	6	0	-3.92819	-3.50294	3.027369
80	1	0	-3.54043	-4.48901	3.291413
81	6	0	-7.37019	-0.74182	-0.26649
82	6	0	-6.17546	-3.04281	-1.2369
83	1	0	-5.69348	-3.93197	-1.65739
84	6	0	-5.55797	0.856117	-2.77819
85	1	0	-4.65511	0.280649	-2.53598
86	1	0	-5.46429	1.19975	-3.8188
87	1	0	-6.39368	0.142396	-2.73147
88	6	0	-8.16168	0.497293	0.079852
89	1	0	-7.7333	1.096498	0.890812
90	1	0	-9.19244	0.233705	0.358359
91	1	0	-8.21351	1.172384	-0.78987
92	6	0	7.28089	5.703113	1.674179

93	1	0	7.236355	6.385951	0.812664
94	1	0	8.343043	5.60269	1.955121
95	1	0	6.765442	6.182197	2.52004
96	5	0	5.20555	0.175254	0.429723
97	6	0	-7.5503	-3.05865	-1.03415
98	6	0	-5.40063	3.391048	1.71218
99	1	0	-6.12927	2.872102	2.351917
100	1	0	-5.43266	4.456402	1.980653
101	1	0	-4.40355	3.014681	1.98369
102	6	0	-3.9223	-2.08198	-1.31633
103	1	0	-3.4651	-1.15002	-1.67076
104	1	0	-3.82628	-2.81307	-2.13205
105	1	0	-3.30757	-2.45902	-0.48442
106	6	0	-8.12726	-1.87608	-0.57377
107	1	0	-9.21559	-1.82561	-0.46182
108	5	0	-5.17542	0.545459	0.277937
109	6	0	8.063235	-2.91151	-3.87185
110	1	0	7.991711	-3.9807	-3.6084
111	1	0	9.13349	-2.66044	-3.92089
112	1	0	7.638788	-2.79678	-4.88057
113	6	0	-6.87519	5.644145	-2.46646
114	1	0	-6.58903	5.665876	-3.52851
115	1	0	-6.48158	6.552237	-1.98559
116	1	0	-7.97591	5.705314	-2.4242
117	6	0	-8.37711	-4.28269	-1.30278
118	1	0	-9.36604	-4.02226	-1.70994
119	1	0	-8.54968	-4.8551	-0.37532
120	1	0	-7.88161	-4.95827	-2.01583
121	6	0	5.372443	-0.93896	1.639777
122	1	0	4.784426	-0.66487	2.525932
123	1	0	6.408219	-1.05218	1.977799
124	6	0	-5.41324	0.38225	1.904848
125	1	0	-6.45931	0.518512	2.203666

126	1	0	-4.82287	1.116236	2.473111

BN2$^{\bullet-}$, Ea = -2400.08303 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.558305	0.100388	-0.00897
2	7	0	-3.55886	0.095045	-0.00633
3	6	0	0.715444	0.1545	0.034567
4	6	0	-0.71603	0.153073	0.034969
5	6	0	3.801549	-0.90033	2.058259
6	6	0	1.490164	0.729834	-1.02369
7	1	0	1.009808	1.222217	-1.86846
8	6	0	2.863744	-0.40669	1.054002
9	6	0	2.858932	0.694698	-1.00202
10	1	0	3.449165	1.155448	-1.79381
11	6	0	-1.48633	-0.40615	1.095213
12	1	0	-1.00258	-0.83004	1.974369
13	6	0	-2.86265	-0.41536	1.053929
14	6	0	5.939284	-1.16079	-0.69563
15	6	0	5.130779	-0.63282	1.671179
16	6	0	-1.49247	0.729886	-1.02122
17	1	0	-1.01352	1.225648	-1.86481
18	6	0	5.317496	-2.27224	-1.32114
19	6	0	1.487434	-0.39979	1.096187
20	1	0	1.00505	-0.82006	1.977825
21	6	0	5.660584	1.548493	-0.14603
22	6	0	7.358233	-1.13016	-0.71824
23	6	0	-2.86119	0.693037	-0.99834
24	1	0	-3.45267	1.155372	-1.78824
25	6	0	5.66493	2.555138	0.855311
26	6	0	-3.79883	-0.91649	2.05603

27	6	0	3.482487	-1.55211	3.253948
28	1	0	2.440744	-1.74949	3.521657
29	6	0	6.082263	-3.23876	-1.98507
30	1	0	5.563778	-4.07427	-2.46861
31	6	0	6.007368	1.958772	-1.4595
32	6	0	-5.12883	-0.65033	1.670732
33	6	0	8.088114	-2.12437	-1.38255
34	1	0	9.182344	-2.05948	-1.38469
35	6	0	6.144649	-1.08471	2.524487
36	1	0	7.193694	-0.94495	2.253565
37	6	0	-5.66169	1.543779	-0.12917
38	6	0	5.840833	-1.72222	3.726804
39	1	0	6.650587	-2.05331	4.383663
40	6	0	7.47372	-3.18627	-2.03959
41	6	0	4.511377	-1.95468	4.097677
42	1	0	4.283339	-2.46251	5.038491
43	6	0	6.404686	3.28012	-1.71522
44	1	0	6.666683	3.560053	-2.74181
45	6	0	6.077927	3.858978	0.563701
46	1	0	6.073856	4.604263	1.366865
47	6	0	-3.4779	-1.5744	3.247852
48	1	0	-2.43561	-1.77053	3.514372
49	6	0	-5.93963	-1.16058	-0.70107
50	6	0	5.202699	2.290671	2.263909
51	1	0	4.198854	1.842198	2.283977
52	1	0	5.166244	3.225522	2.842749
53	1	0	5.861114	1.587232	2.793929
54	6	0	3.82798	-2.50328	-1.29681
55	1	0	3.44163	-2.55262	-0.26801
56	1	0	3.579213	-3.45517	-1.7882
57	1	0	3.262134	-1.71077	-1.80828
58	6	0	-6.14146	-1.11048	2.521036

59	1	0	-7.19087	-0.97227	2.250669
60	6	0	6.471283	4.246233	-0.71685
61	6	0	-5.31807	-2.27147	-1.32761
62	6	0	-5.66613	2.542385	0.880364
63	6	0	-6.00927	1.964806	-1.43901
64	6	0	8.180615	-0.03251	-0.0836
65	1	0	8.355053	0.79736	-0.78835
66	1	0	9.165158	-0.42038	0.221482
67	1	0	7.701925	0.421292	0.790976
68	6	0	5.98991	1.043803	-2.66286
69	1	0	6.925961	0.469971	-2.75411
70	1	0	5.869126	1.632733	-3.58527
71	1	0	5.192225	0.291729	-2.62902
72	6	0	-5.83583	-1.75441	3.719469
73	1	0	-6.6446	-2.09211	4.374151
74	6	0	-6.40739	3.288037	-1.68376
75	1	0	-6.67002	3.576178	-2.70792
76	6	0	-6.47403	4.245917	-0.6776
77	6	0	-6.07991	3.848311	0.599563
78	1	0	-6.07587	4.586981	1.408813
79	6	0	-4.50568	-1.98497	4.089092
80	1	0	-4.2762	-2.49778	5.026846
81	6	0	-7.35861	-1.12862	-0.72626
82	6	0	-6.08233	-3.23279	-1.99991
83	1	0	-5.56431	-4.07131	-2.47861
84	6	0	-5.99267	1.060282	-2.65031
85	1	0	-5.19994	0.302956	-2.62027
86	1	0	-5.86526	1.656645	-3.56707
87	1	0	-6.93207	0.493232	-2.74976
88	6	0	-8.18128	-0.03849	-0.07911
89	1	0	-7.70245	0.406081	0.800123
90	1	0	-9.16536	-0.4305	0.22219

91	1	0	-8.35681	0.798832	-0.77468
92	6	0	6.940222	5.645522	-0.9994
93	1	0	6.901893	5.875428	-2.07489
94	1	0	7.982967	5.79273	-0.66875
95	1	0	6.327145	6.392073	-0.47021
96	5	0	5.150983	0.009605	0.165432
97	6	0	-7.47304	-3.17396	-2.06438
98	6	0	-5.20321	2.267212	2.286687
99	1	0	-5.8606	1.558854	2.811363
100	1	0	-5.1677	3.197522	2.872849
101	1	0	-4.1988	1.81987	2.302929
102	6	0	-3.83037	-2.51204	-1.28812
103	1	0	-3.25412	-1.7219	-1.79151
104	1	0	-3.58246	-3.46422	-1.77939
105	1	0	-3.45556	-2.5665	-0.25529
106	6	0	-8.08801	-2.11739	-1.39889
107	1	0	-9.18235	-2.05459	-1.3979
108	5	0	-5.15133	0.002311	0.169684
109	6	0	8.270954	-4.2578	-2.7286
110	1	0	8.402847	-5.14111	-2.07964
111	1	0	9.275663	-3.90118	-3.00238
112	1	0	7.772129	-4.60518	-3.64696
113	6	0	-6.94342	5.647371	-0.94837
114	1	0	-6.91139	5.884105	-2.02257
115	1	0	-6.32642	6.39	-0.41818
116	1	0	-7.98395	5.793413	-0.61033
117	6	0	-8.26714	-4.20029	-2.82209
118	1	0	-8.33083	-3.94738	-3.8949
119	1	0	-9.2982	-4.27394	-2.4436
120	1	0	-7.80795	-5.19887	-2.75362

$BN2^{2-}$, Ea = -2400.04697 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.58369	-0.10944	0.137518
2	6	0	-5.97574	1.159474	-0.46964
3	6	0	-6.07077	1.037186	2.772887
4	1	0	-7.12801	0.89084	2.535486
5	6	0	-5.08431	0.613244	1.875602
6	6	0	-7.39429	1.162105	-0.42375
7	6	0	-3.73917	0.884316	2.218867
8	6	0	-8.20362	0.064687	0.228894
9	1	0	-8.42523	-0.74761	-0.4839
10	1	0	-9.16608	0.460252	0.592736
11	1	0	-7.68467	-0.4143	1.066029
12	6	0	-5.70054	-1.55301	0.063285
13	6	0	-2.83147	0.423375	1.172398
14	6	0	-6.14269	3.253143	-1.73611
15	1	0	-5.63088	4.079089	-2.24444
16	6	0	-5.36457	2.26071	-1.12753
17	6	0	-5.73885	1.65594	3.980614
18	1	0	-6.53099	1.966096	4.669924
19	6	0	-8.13953	2.181389	-1.03322
20	1	0	-9.23453	2.140342	-0.97666
21	6	0	-4.39895	1.893713	4.306726
22	1	0	-4.14033	2.385047	5.24987
23	6	0	-3.39555	1.517807	3.418831
24	1	0	-2.3463	1.718349	3.654268
25	6	0	-5.65795	-2.56873	1.05621
26	6	0	-7.53681	3.238031	-1.70868
27	6	0	-6.12413	-1.95824	-1.22895
28	6	0	-2.88586	-0.71251	-0.87527
29	1	0	-3.48891	-1.23751	-1.6184
30	6	0	-6.11686	-3.86253	0.78876

31	1	0	-6.07481	-4.61169	1.588439
32	6	0	-1.46679	0.469876	1.151499
33	1	0	-0.96049	0.889034	2.022424
34	6	0	-6.59742	-4.23712	-0.46642
35	6	0	-6.56473	-3.27046	-1.46557
36	1	0	-6.88572	-3.54284	-2.47825
37	6	0	-5.07862	-2.32059	2.423587
38	1	0	-4.07597	-1.87437	2.352379
39	1	0	-4.99691	-3.26231	2.988462
40	1	0	-5.68273	-1.61542	3.012617
41	6	0	-6.13014	-1.04085	-2.43008
42	1	0	-7.03306	-0.41047	-2.46674
43	1	0	-6.09456	-1.63218	-3.35909
44	1	0	-5.28314	-0.34367	-2.43546
45	6	0	-1.52963	-0.6954	-0.96379
46	1	0	-1.07209	-1.22441	-1.80128
47	6	0	-3.87018	2.442022	-1.20134
48	1	0	-3.41339	2.484643	-0.20162
49	1	0	-3.62257	3.377922	-1.72561
50	1	0	-3.36451	1.616857	-1.7245
51	5	0	-5.13773	-0.02004	0.355928
52	6	0	-0.69359	-0.0453	0.040768
53	6	0	-8.34314	4.339985	-2.33848
54	1	0	-8.35353	5.248007	-1.70931
55	1	0	-9.39102	4.036833	-2.49122
56	1	0	-7.931	4.635251	-3.31735
57	6	0	-7.10769	-5.62783	-0.72327
58	1	0	-8.09551	-5.79091	-0.25672
59	1	0	-6.4292	-6.39182	-0.30908
60	1	0	-7.21727	-5.82406	-1.80117
61	7	0	3.583694	0.109443	-0.13753
62	6	0	5.97573	-1.15947	0.469647

63	6	0	6.070787	-1.03719	-2.77289
64	1	0	7.128023	-0.89081	-2.5355
65	6	0	5.084318	-0.61325	-1.87561
66	6	0	7.394278	-1.16212	0.423752
67	6	0	3.739183	-0.88435	-2.21886
68	6	0	8.20362	-0.06472	-0.22893
69	1	0	8.425331	0.747532	0.483885
70	1	0	9.166028	-0.46033	-0.59285
71	1	0	7.684635	0.414311	-1.066
72	6	0	5.700546	1.553011	-0.0633
73	6	0	2.831475	-0.4234	-1.1724
74	6	0	6.142666	-3.25311	1.736165
75	1	0	5.630845	-4.07904	2.244504
76	6	0	5.364558	-2.26069	1.127555
77	6	0	5.738871	-1.65597	-3.98061
78	1	0	6.531012	-1.96612	-4.66992
79	6	0	8.139512	-2.18139	1.03325
80	1	0	9.234516	-2.14035	0.976691
81	6	0	4.398973	-1.89377	-4.3067
82	1	0	4.140356	-2.38513	-5.24984
83	6	0	3.395566	-1.51787	-3.41881
84	1	0	2.346321	-1.71844	-3.65424
85	6	0	5.65796	2.568731	-1.05624
86	6	0	7.536789	-3.23801	1.708733
87	6	0	6.124142	1.958251	1.228933
88	6	0	2.885862	0.71253	0.875244
89	1	0	3.488914	1.237541	1.618366
90	6	0	6.116877	3.862529	-0.7888
91	1	0	6.074831	4.611678	-1.58848
92	6	0	1.466798	-0.4699	-1.1515
93	1	0	0.960502	-0.88908	-2.02242
94	6	0	6.597422	4.237126	0.466385

95	6	0	6.564742	3.270473	1.465536
96	1	0	6.885737	3.542865	2.478219
97	6	0	5.078643	2.320572	-2.42362
98	1	0	4.076001	1.874336	-2.35241
99	1	0	4.996913	3.262296	-2.98849
100	1	0	5.682773	1.615419	-3.01264
101	6	0	6.130153	1.040869	2.430067
102	1	0	7.033036	0.410428	2.466694
103	1	0	6.094642	1.632202	3.359076
104	1	0	5.283107	0.343738	2.43548
105	6	0	1.529632	0.69542	0.963767
106	1	0	1.072092	1.224443	1.801241
107	6	0	3.870159	-2.44198	1.201384
108	1	0	3.413364	-2.48461	0.201668
109	1	0	3.622548	-3.37787	1.725664
110	1	0	3.364502	-1.61681	1.724538
111	5	0	5.137733	0.020039	-0.35594
112	6	0	0.6936	0.045292	-0.04078
113	6	0	8.343108	-4.33995	2.338561
114	1	0	8.353458	-5.248	1.709444
115	1	0	9.390997	-4.03682	2.491257
116	1	0	7.930987	-4.63516	3.317466
117	6	0	7.107625	5.627857	0.72323
118	1	0	8.095105	5.791229	0.256049
119	1	0	6.428723	6.391835	0.30969
120	1	0	7.217895	5.823851	1.801105

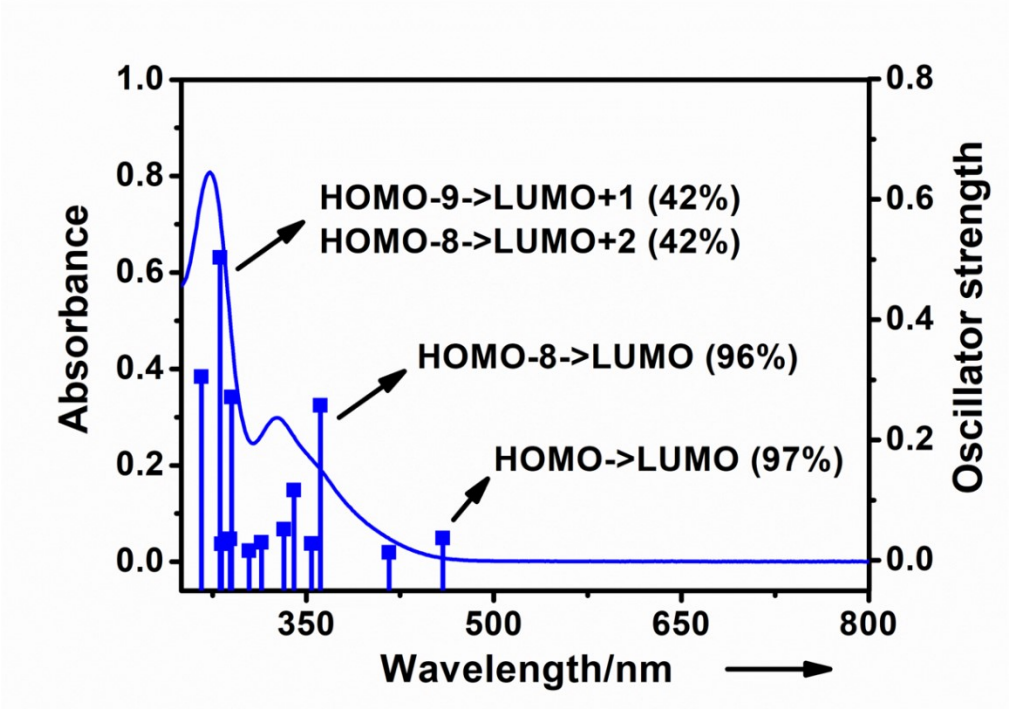

Figure S24. UV/Vis absorption spectrum of **BN2** in THF solution at room temperature along with transitions calculated at the PBE1PBE/def2svp level of theory.

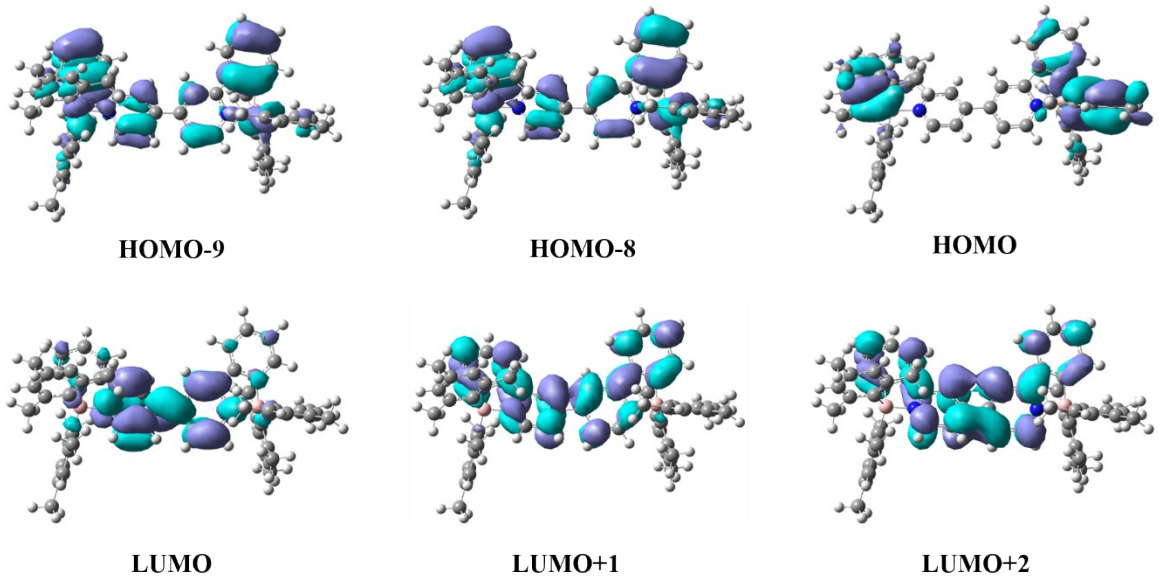

Figure S25. HOMO-9, HOMO-8, HOMO, LUMO, LUMO+1 and LUMO+2 of **BN2** (Isovalue = 0.02).

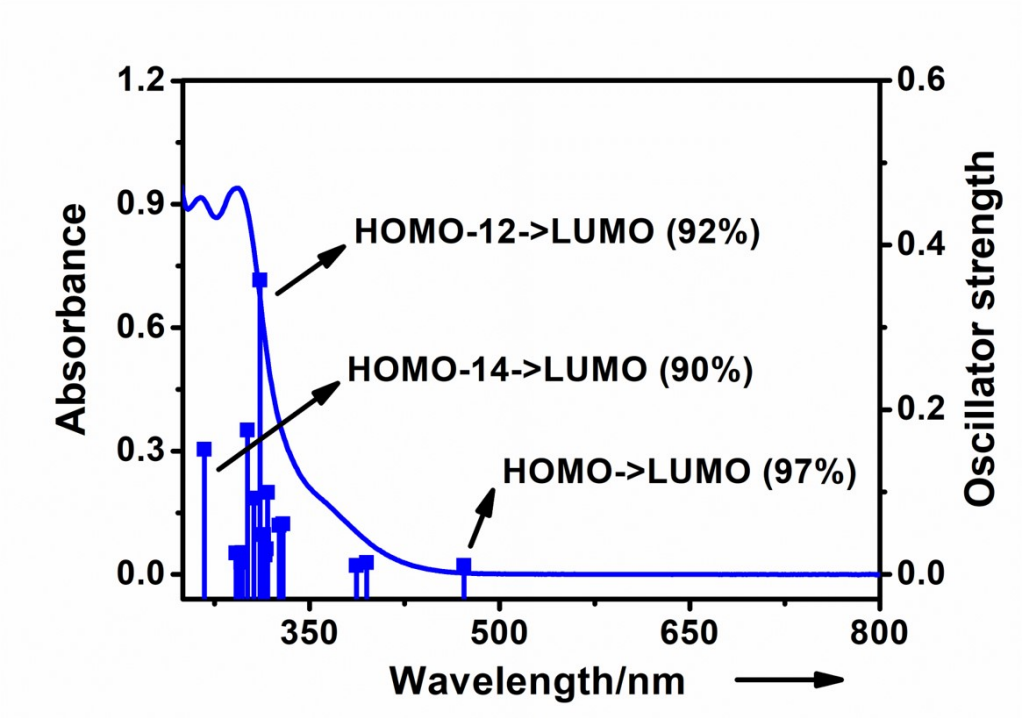

Figure S26. UV/Vis absorption spectrum of **BN4** in THF solution at room temperature along with transitions calculated at the PBE1PBE/def2svp level of theory.

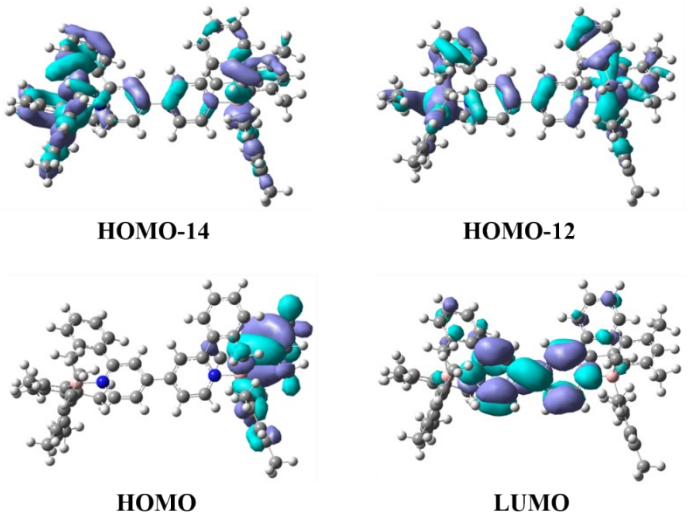

Figure S27. HOMO-14, HOMO-12, HOMO and LUMO of **BN4** (Isovalue = 0.02).

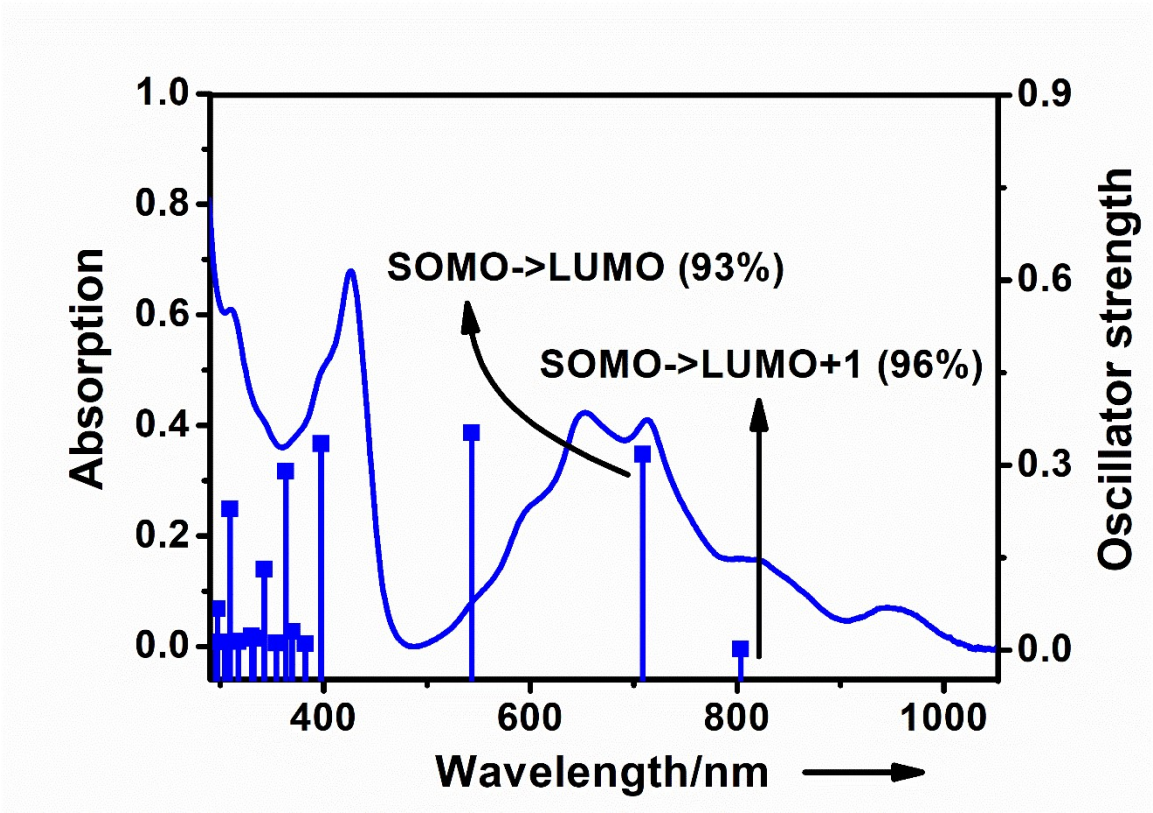

Figure S28. UV/Vis absorption spectrum of **BN2K(crypt)** in THF solution at room temperature along with transitions calculated at the UPBE1PBE/def2svp level of theory.

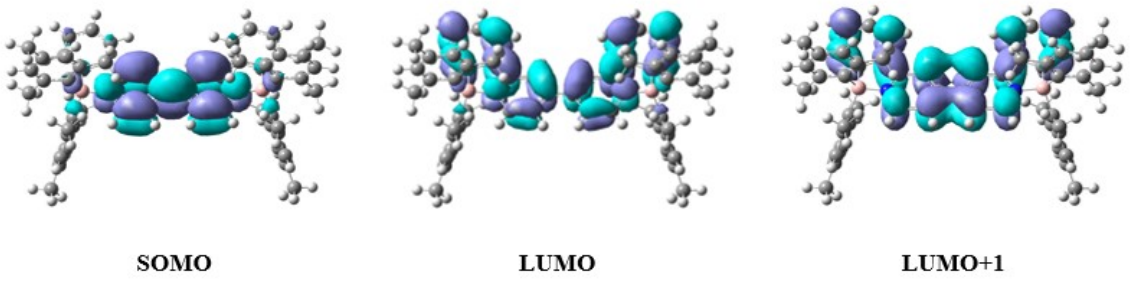

Figure S29. SOMO, LUMO and LUMO+1 of **BN2**$^{\bullet-}$ (Isovalue = 0.02).

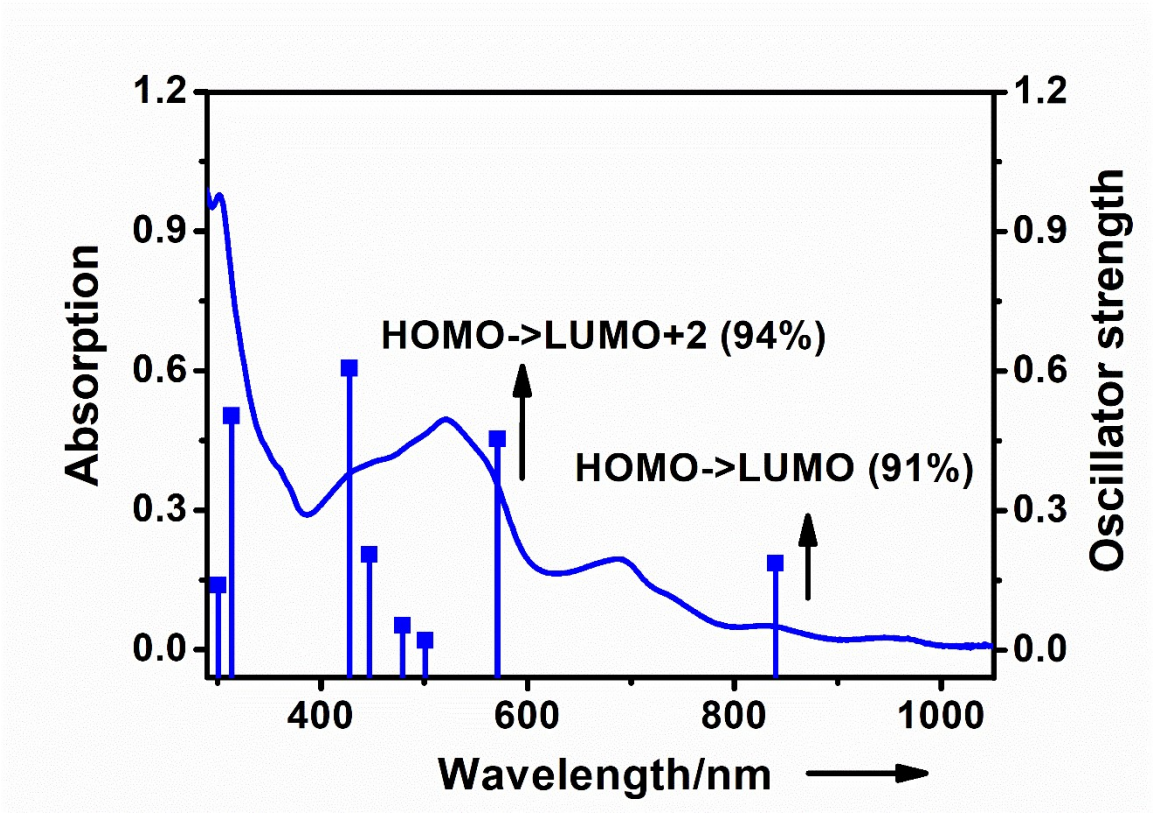

Figure S30. UV/Vis absorption spectrum of **$BN2K_2(18c6)_2$** in THF solution at room temperature along with transitions calculated at the PBE1PBE/def2svp level of theory.

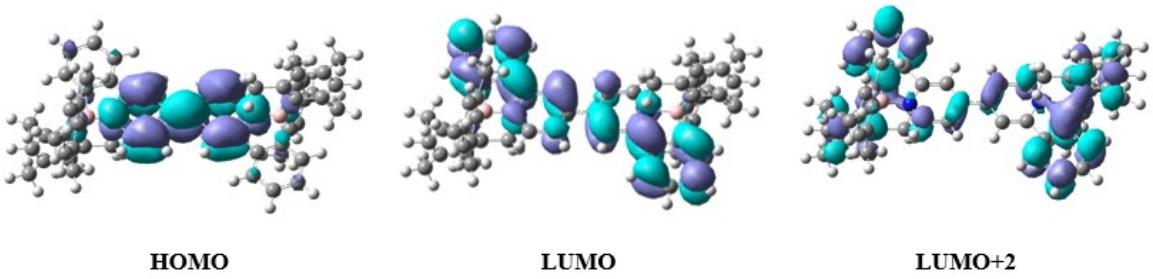

Figure S31. HOMO, LUMO and LUMO+2 of **$BN2^{2-}$** (Isovalue = 0.02).

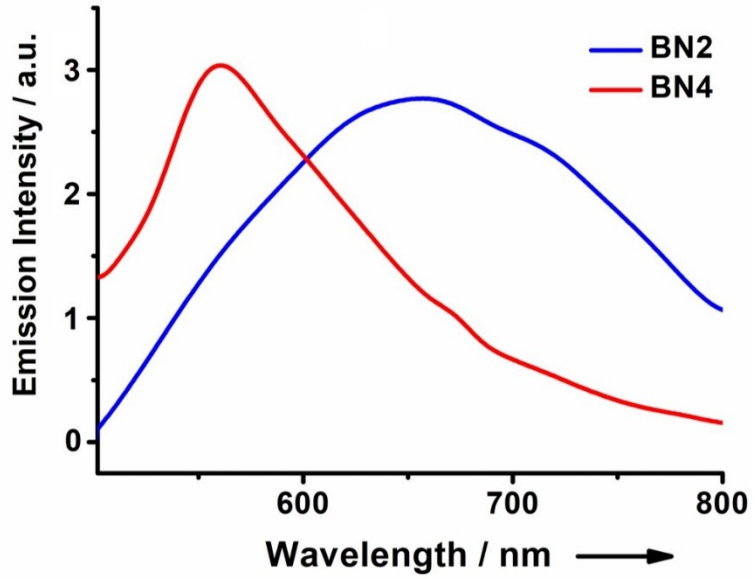

Figure S32. Fluorescent spectra of **BN2** and **BN4**.

S7. X-Ray Crystal Structure Data

	BN2K(crypt)	**$BN2K_2(18c6)_2$**
CCDC No.	2181040	2181041
Formula	$C_{80}H_{102}B_2KN_4O_7$	$C_{106}H_{154}B_2K_2N_2O_{18}$
Formula weight	1292.37	1844.12
Temp. (K)	180(2)	180(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	13.8912(4)	31.8072(17)
b (Å)	26.8301(7)	12.8637(7)
c (Å)	22.9414(6)	26.0895(14)
α(°)	90	90
β(°)	107.383(3)	99.889(6)
γ(°)	90	90
V [Å^3]	8159.8(4)	10516.1(10)
Z	4	4
ρ_{calcd}(g·cm^{-3})	1.052	1.165
μ(mm^{-1})	0.115	0.154
F(000)	2780	3984
Collected data	100990	77775
Unique data	16076 [R(int) = 0.0300]	9220 [R(int) = 0.0962]
GOF on F^2	1.036	1.059
Final R indexes [I > 2σ(I)]	R_1 = 0.0514 ωR_2 = 0.1406	R_1 = 0.0999 ωR_2 = 0.2527
R indexes (all data)	R_1 = 0.0632 ωR_2 = 0.1483	R_1 = 0.1535 ωR_2 = 0.2909
Completeness	0.999	0.994

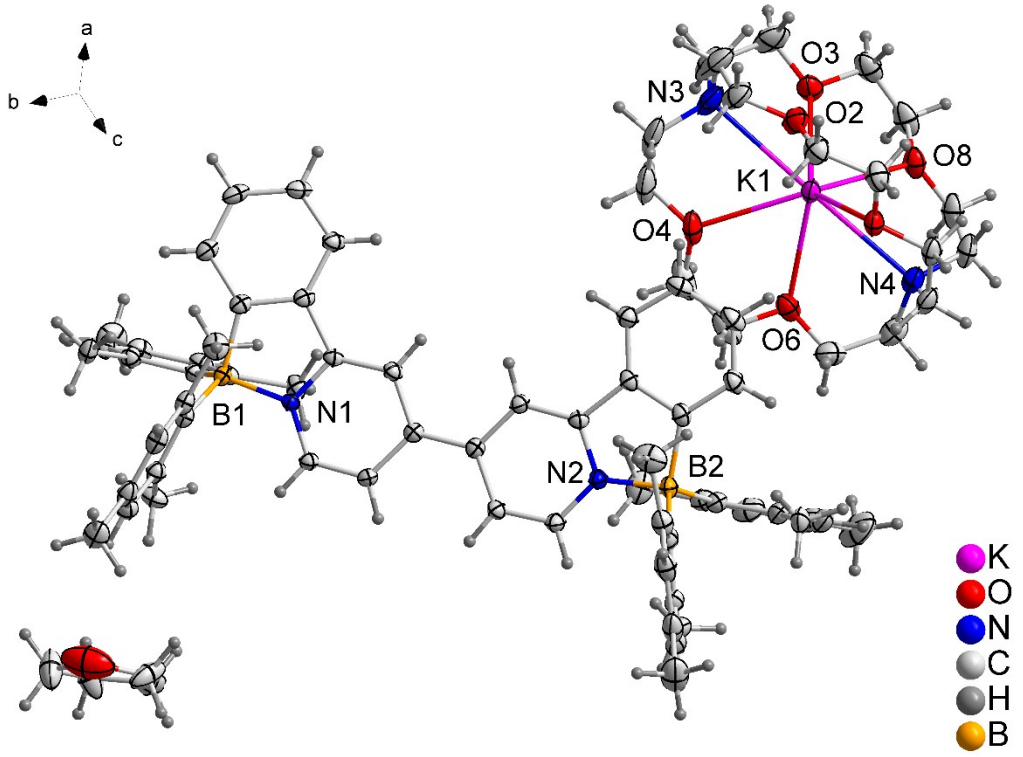

Figure S33. Structure of **BN2K(crypt)**.

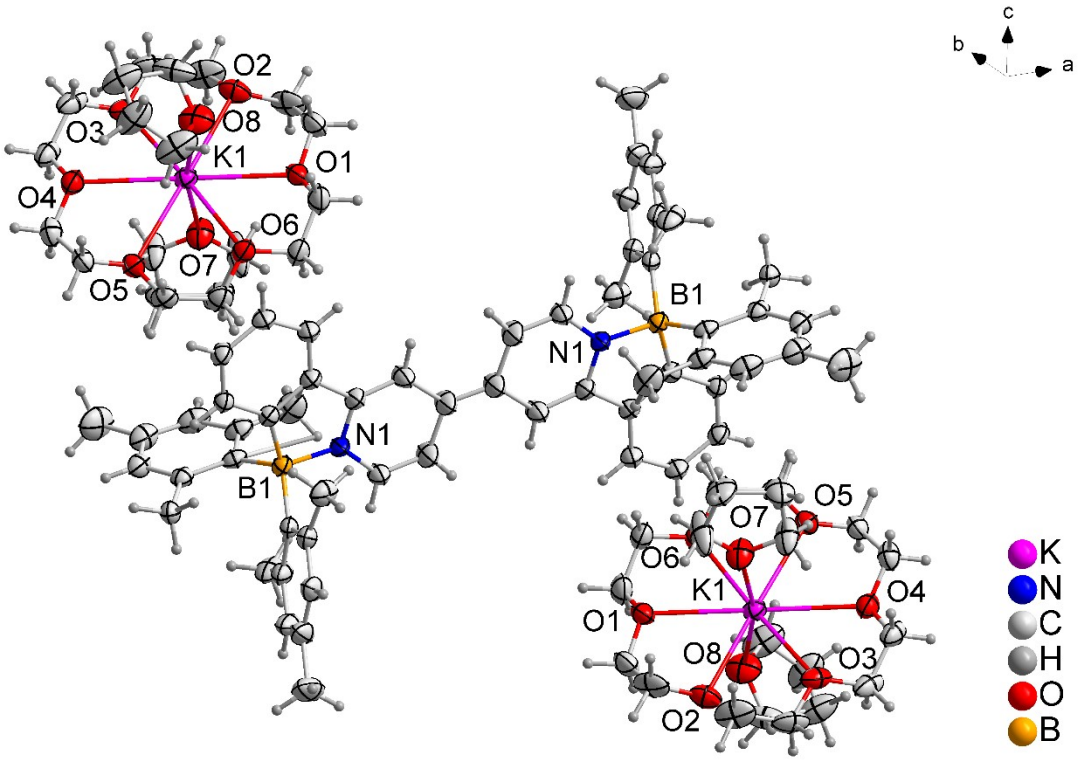

Figure S34. Structure of **$BN2K_2(18c6)_2$**.

S8. References

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