Electronic Supporting Information

High-efficiency narrowband multi-resonance TADF emitter via the introduction of bulky adamantane unit

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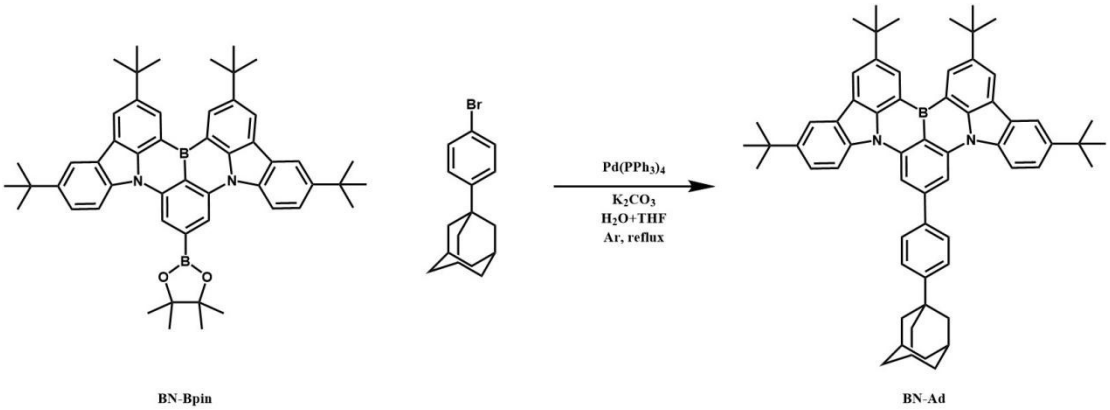
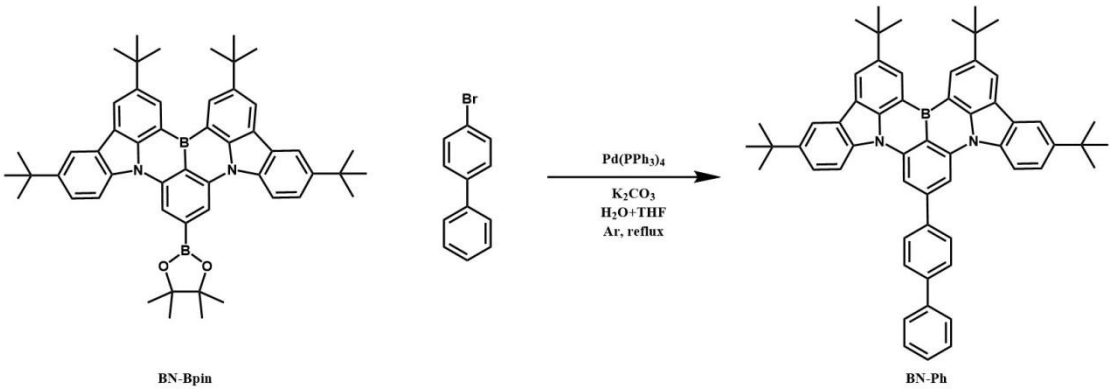
Synthesis



BN-Bpin BN-Ad

A mixture of 1-(4-bromophenyl)adamantane (291 mg, 1 mmol) and BN-Bpin (767 mg, 1 mmol) in mixed solution of THF and 4 M K_2CO_3 (5:1, v/v) was degassed before $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) was added. And the mixture was refluxed under Ar for 1 day. After the reaction was finished, the organic layer was separated, washed with water, dried with Na_2SO_4, filtered and moved out with rotary evaporator. The residue was chromatographically purified on silica gel column with DCM/PE (1:15, v/v) to give **BN-Ad** as a yellow solid (366 mg, 43%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.07 (2H, s), 8.37-8.48 (6H, m), 8.24 (2H, s), 7.85-7.89 (2H, m), 7.65 (2H, d, J = 8.6 Hz), 7.62 (2H, d, J = 8.6 Hz) 2.19 (3H, s), 2.05 (6H, s), 1.81-1.89 (6H, t, J=18.0Hz), 1.66 (18H, s), 1.54 (18H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.58, 145.99, 145.20, 145.18, 144.63, 144.53, 141.76, 138.97, 138.33, 129.75, 127.57, 127.10, 125.68, 124.38, 123.57, 121.70, 120.53, 117.23, 114.22, 107.02, 43.29, 36.86, 36.29, 35.15, 34.79, 32.20, 31.85, 29.02. ^{11}B NMR ($CDCl_3$, 193 MHz) δ (ppm): 45.26. Mass (HRMS): m/z, calcd. for $C_{62}H_{68}BN_2^+$: 851.5480; found: 851.5476.



Synthesis procedure for **BN-Ph** was similar to **BN-Ad** but replacement of the reactant. Yellow solid, yield: 57%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.07 (1H, s), 8.32-8.53 (7H, m), 8.23 (2H, s), 7.88-7.97 (2H, m), 7.75-7.81 (2H, m), 7.70-7.74 (2H, d, J = 6.0Hz), 7.61-7.66 (2H, d, J = 6.0Hz), 7.50-7.58 (2H, m), 7.42 (1H, m), 1.66 (18H, s), 1.57 (18H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.25, 144.65, 144.54, 141.74, 140.62, 138.28, 129.73, 128.91, 128.11, 127.75, 127.54, 127.13, 124.38, 123.95, 123.58, 120.58, 117.26, 114.15, 106.85, 35.16, 34.79, 32.19, 31.84. ^{11}B NMR ($CDCl_3$, 193 MHz) δ (ppm): 44.90. Mass (HRMS): m/z, calcd. for $C_{58}H_{58}BN_2^+$: 793.4697; found: 793.4693.

Quantum Chemical Calculations

All of the simulation calculations were carried out with Gaussian 09 program package. The ground state geometries were optimized via density functional theory (DFT) calculations in vacuum using the B3LYP hybrid functional and the 6-31G(d,p) basis set. Excited state analysis by time-dependent DFT (TD-DFT) were performed at the B3LYP/6-31G(d,p) level on the basis of optimized ground-state geometries.

Thermal and Electrochemical Characterization

Thermogravimetric analysis (TGA) was performed on TGA Q50 (TA instrument)

under nitrogen flow (10 mL min^{-1}) at a heating rate of 10 ^{o}C min^{-1} from 50 to 800 ^{o}C.

Cyclic voltammograms (CV) were acquired in dichloromethane at room temperature with a CHI600 electrochemical analyzer (Chenhua, China) at 25 ^{o}C and a sweep speed of 100 mV s^{-1}. Tetrabutylammonium hexafluorophosphate (0.1 M) was applied as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode and an Ag/Ag^{+} reference electrode with ferroceniumferrocene (Fc^{+} /Fc) as the internal standard. The HOMO energy levels of the compounds were calculated according to the formula: E_{HOMO} (eV) = -[4.8 + ($E_{1/2(ox/red)}$ - $E_{1/2(Fc+/Fc)}$)] eV. The LUMO energy levels of the compounds were then deduced from the HOMO levels and the UV-Vis absorption on-sets of the longer wavelength.

Photophysical Characterization

UV-vis absorption spectra were acquired from a Shimadzu UV-2700 spectrophotometer (Shimadzu, Japan) at 25 ^{o}C. Photoluminescence (PL) spectra were recorded on an Edingburgh FS5 fluorescence spectrophotometer (Edingburgh, England) at 25 ^{o}C. Phosphorescence spectra were conducted at 77 K on a Hitachi F-4600 fluorescence spectrophotometer (Hitachi, Japan). The transient PL decay curves were obtained by Edingburgh FLS980 (Edingburgh, England) with a Picosecond Pulsed UV-LASTER (LASTER365) as the excitation source.

Single Crystal X-ray Crystallographic Data

X-ray single crystal data of **BN-Ad** and **BN-Ph** were collected on a Bruker D8 Venture diffractometer using GaK (λ = 1.34139) and MoK radiation (λ = 0.71073)

source. The selected crystal was kept at 150.0 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization. Selected crystal data and experimental details are listed in Table S2 and S3. All crystallographic information in CIF format have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number 2265333 for **BN-Ad** and 2265334 for **BN-Ph**.

Analysis of Rate Constants

The rate constants of radiative decay (k_r) and nonradiative decay (k_{nr}), the rate constants of intersystem crossing (k_{ISC}) and reverse intersystem crossing (k_{RISC}) could be estimated using the following equations.[4-6]

$$k_r = \Phi_p k_p + \Phi_d k_d \approx \Phi_p k_p \quad \text{Eq.(1)}$$

$$k_{nr} = \frac{1 - \Phi_{PL}}{\Phi_{PL}} k_r \quad \text{Eq.(2)}$$

$$k_{ISC} = k_p - k_r - k_{nr} \quad \text{Eq.(3)}$$

$$k_{RISC} = (k_p k_d \Phi_d)/(k_{ISC} \Phi_p) \quad \text{Eq.(4)}$$

Where k_p and k_d represent the decay rate constants for prompt and delayed fluorescence, respectively, which are in reciprocal relationship with the decay time constants (τ_p and τ_d) experimentally determined from transient PL characteristics. Φ_p and Φ_d indicate prompt and delayed fluorescence components and can be distinguished from the total Φ_{PL} by comparing the integrated intensities of prompt (r_p) and delayed components (r_d) in the transient PL spectra. r_p and r_d were determined using τ_p and τ_d

and fitting parameter (A_p, A_d) as follows.

$$I(t) = A_p e^{-\frac{1}{\tau_p}} + A_d e^{-\frac{1}{\tau_d}} \quad \text{Eq.(5)}$$

$$r_p = A_p\tau_p/(A_p\tau_p + A_d\tau_d) \quad \text{Eq.(6)}$$

$$r_d = A_d\tau_d/(A_p\tau_p + A_d\tau_d) \quad \text{Eq.(7)}$$

Device Fabrication and Measurement

The ITO coated glass substrates with a sheet resistance of 15 Ω square^{-1} were consecutively ultrasonicated with acetone/ethanol and dried with nitrogen gas flow, followed by 20 min ultraviolet light-ozone (UVO) treatment in a UV-ozone surface processor (PL16 series, Sen Lights Corporation). Then the sample was transferred to the deposition system. Both 8-hydroxyquinolinolato-lithium (Liq) as electron injection layer and aluminum (Al) as cathode layer were deposited by thermal evaporation at 5×10^{-5} Pa. Additionally, the organic layers were deposited at the rates of 0.2-3 Å/s. After the organic film deposition, Liq and Al layer were deposited with rates of 0.1 and 3 Å/s, respectively. The emitting area of the device is about 0.09 cm^2. The current density-voltage-luminance (*J-V-L*), *L-EQE* curves and electroluminescence spectra were measured using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

Figures, Tables and Schemes

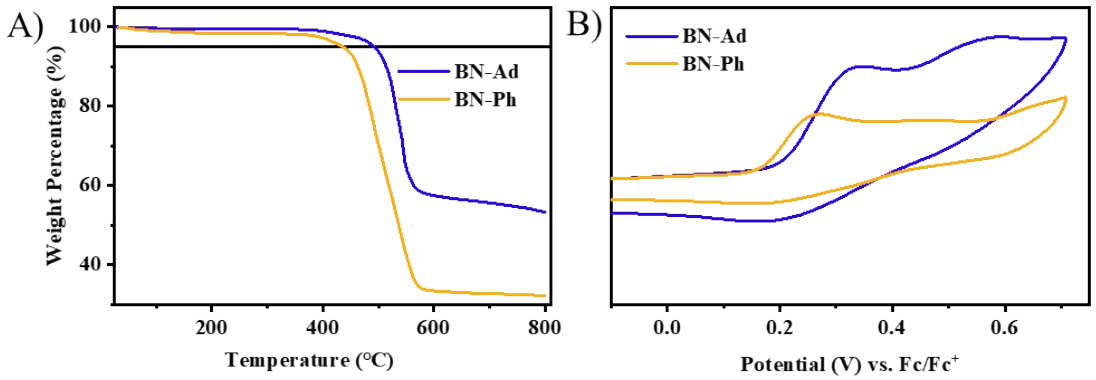


Fig. S1. A) Thermal gravimetric analysis (TGA) curves of **BN-Ad** and **BN-Ph** at a heating rate of 10 °C min^{-1}; B) cyclic voltammograms (CV, oxidation) of **BN-Ad** and **BN-Ph**.

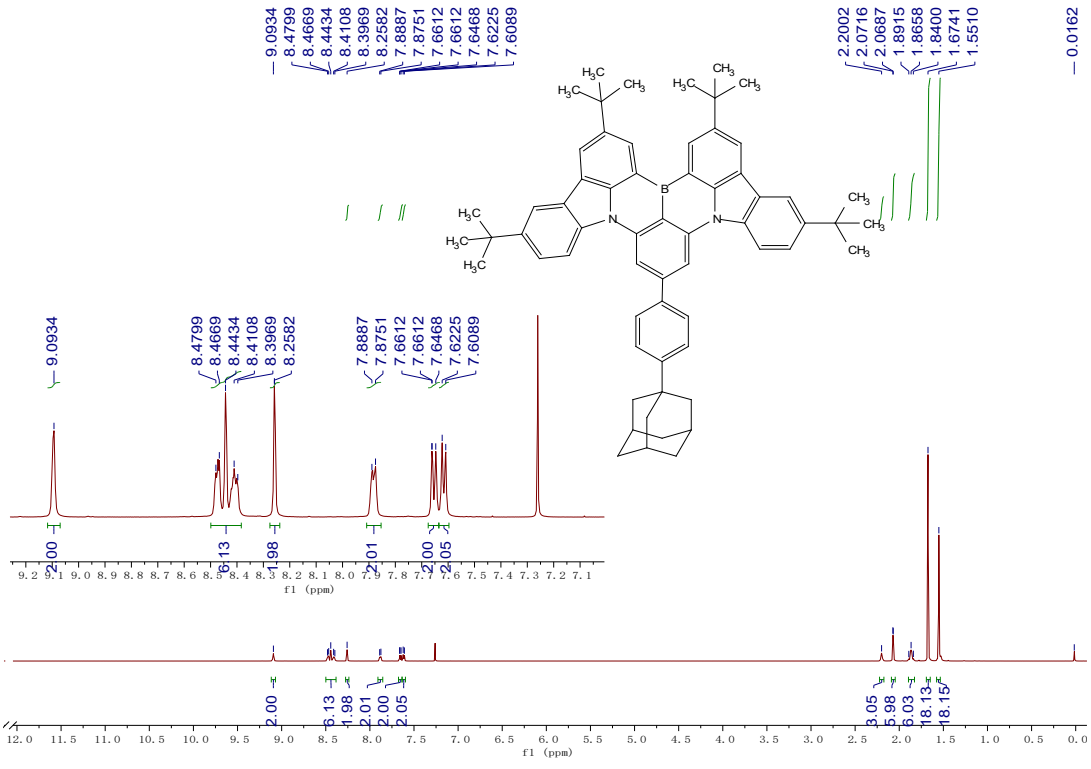


Fig. S2. ^{1}H NMR spectrum of **BN-Ad** in $CDCl_3$ (600 MHz, 25 °C).

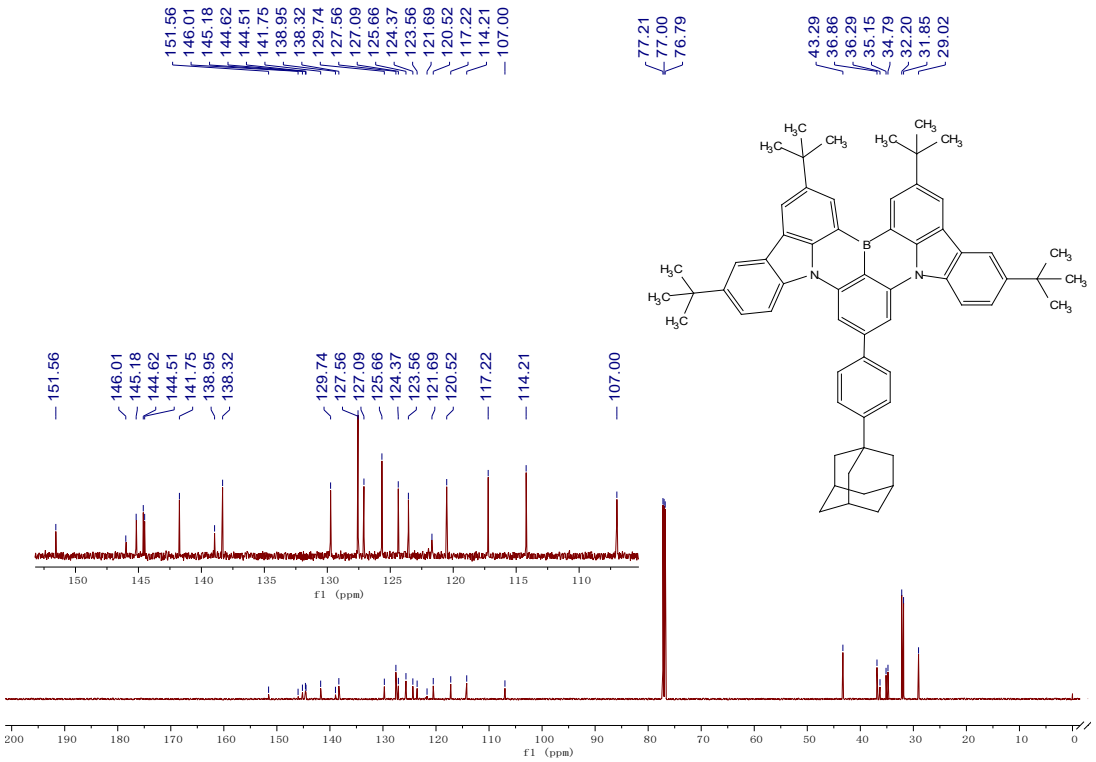


Fig. S3. ^{13}C NMR spectrum of **BN-Ad** in $CDCl_3$ (151 MHz, 25 °C).

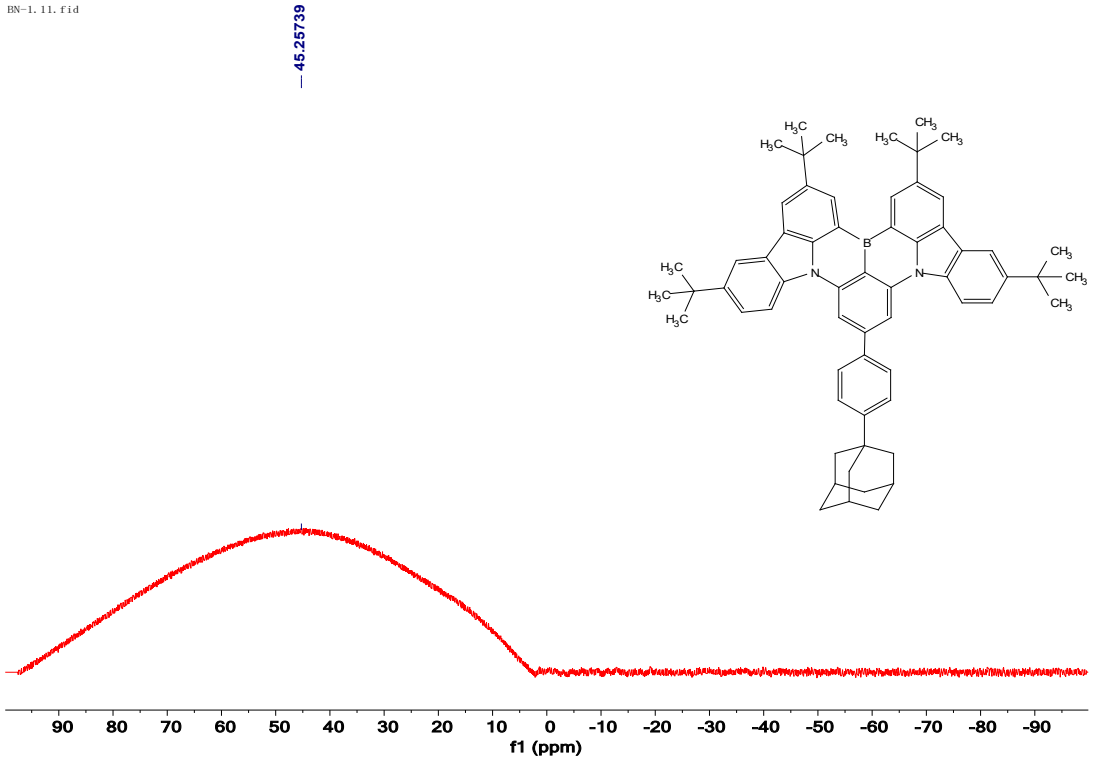


Fig. S4. ^{11}B NMR spectrum of **BN-Ad** in $CDCl_3$ (193 MHz, 25 °C).

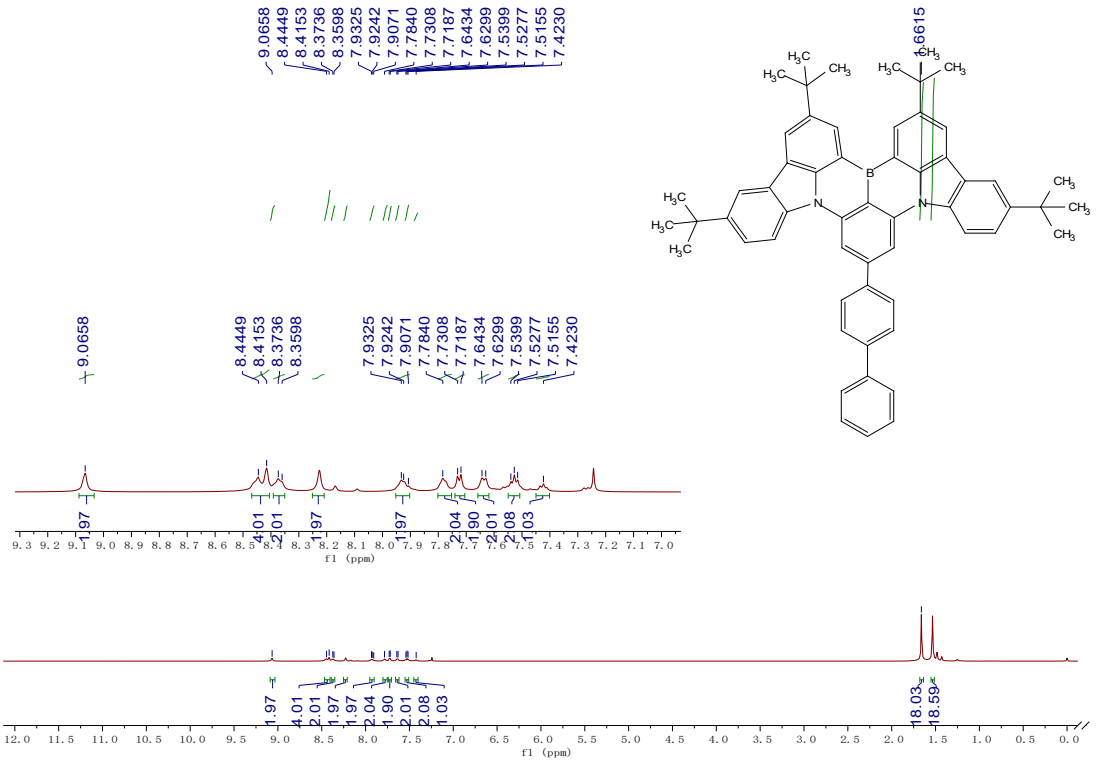


Fig. S5. ^{1}H NMR spectrum of **BN-Ph** in $CDCl_3$ (600 MHz, 25 °C).

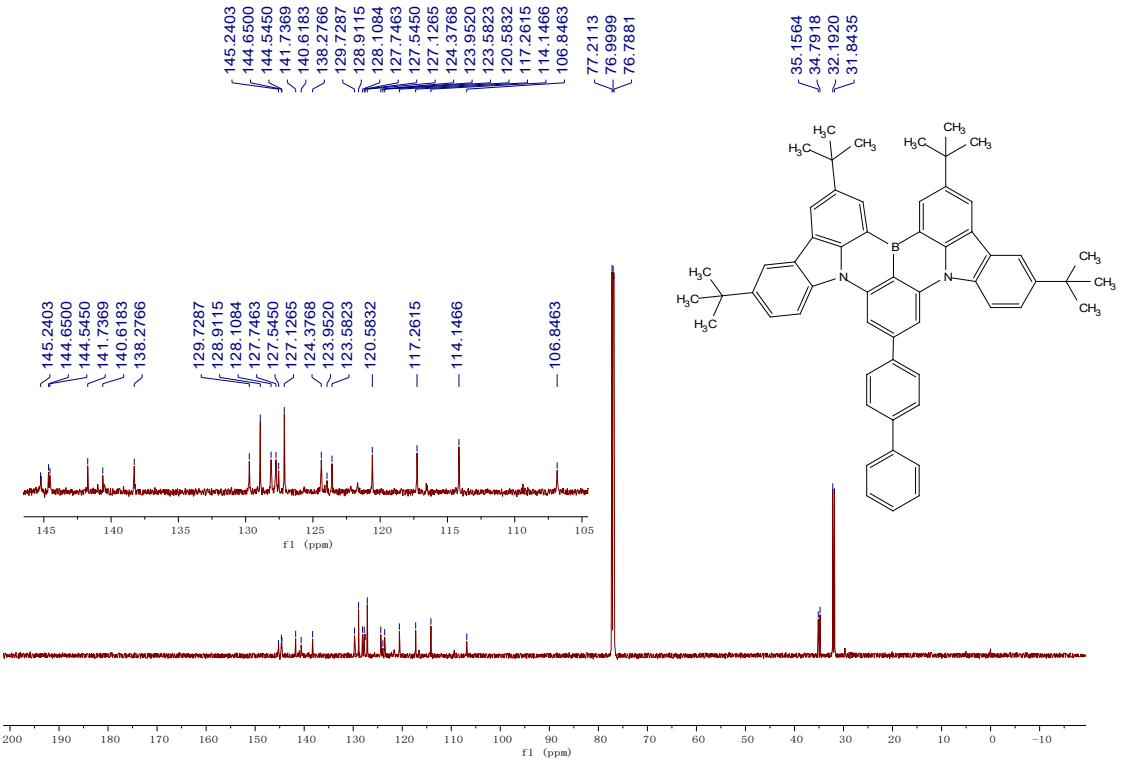


Fig. S6. ^{13}C NMR spectrum of **BN-Ph** in $CDCl_3$ (151 MHz, 25 °C).

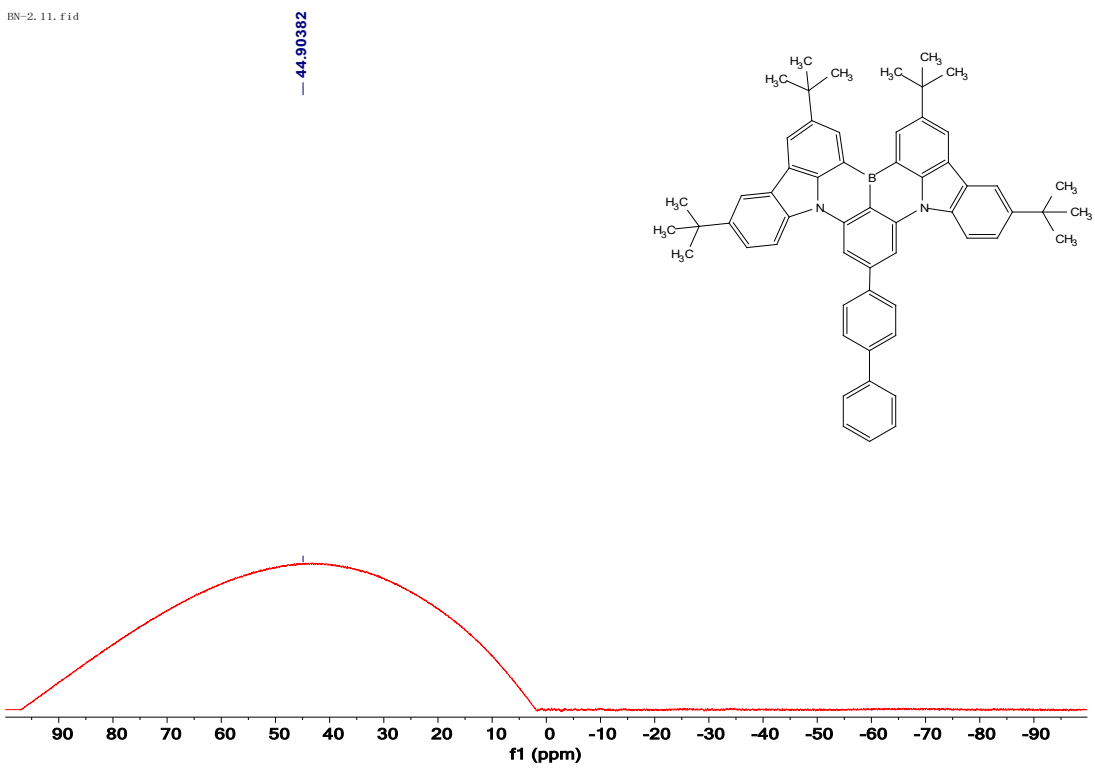


Fig. S7. ^{11}B NMR spectrum of **BN-Ph** in $CDCl_3$ (193 MHz, 25 ^{o}C).

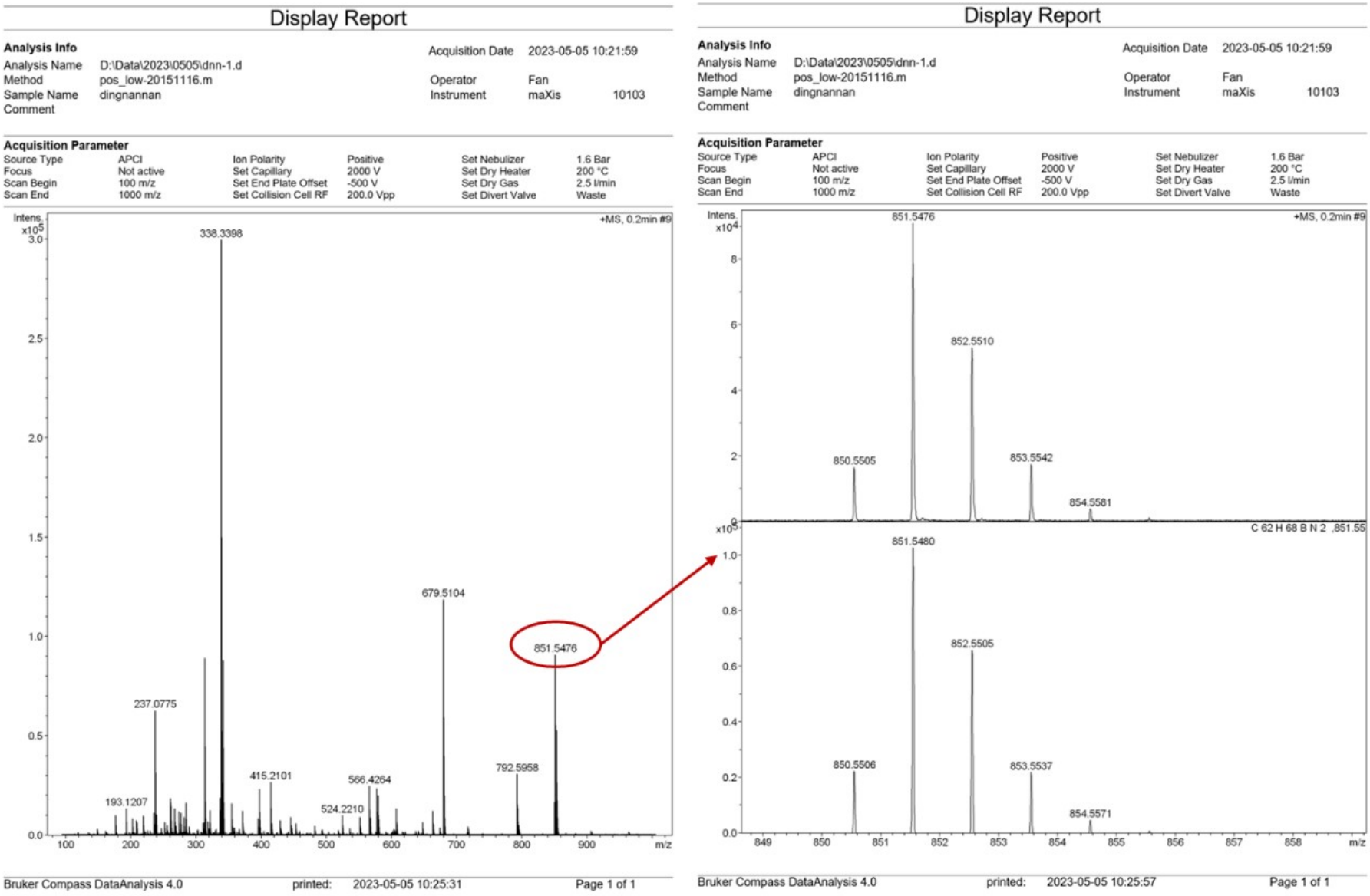


Fig. S8. HR-MS spectrum of **BN-Ad**.

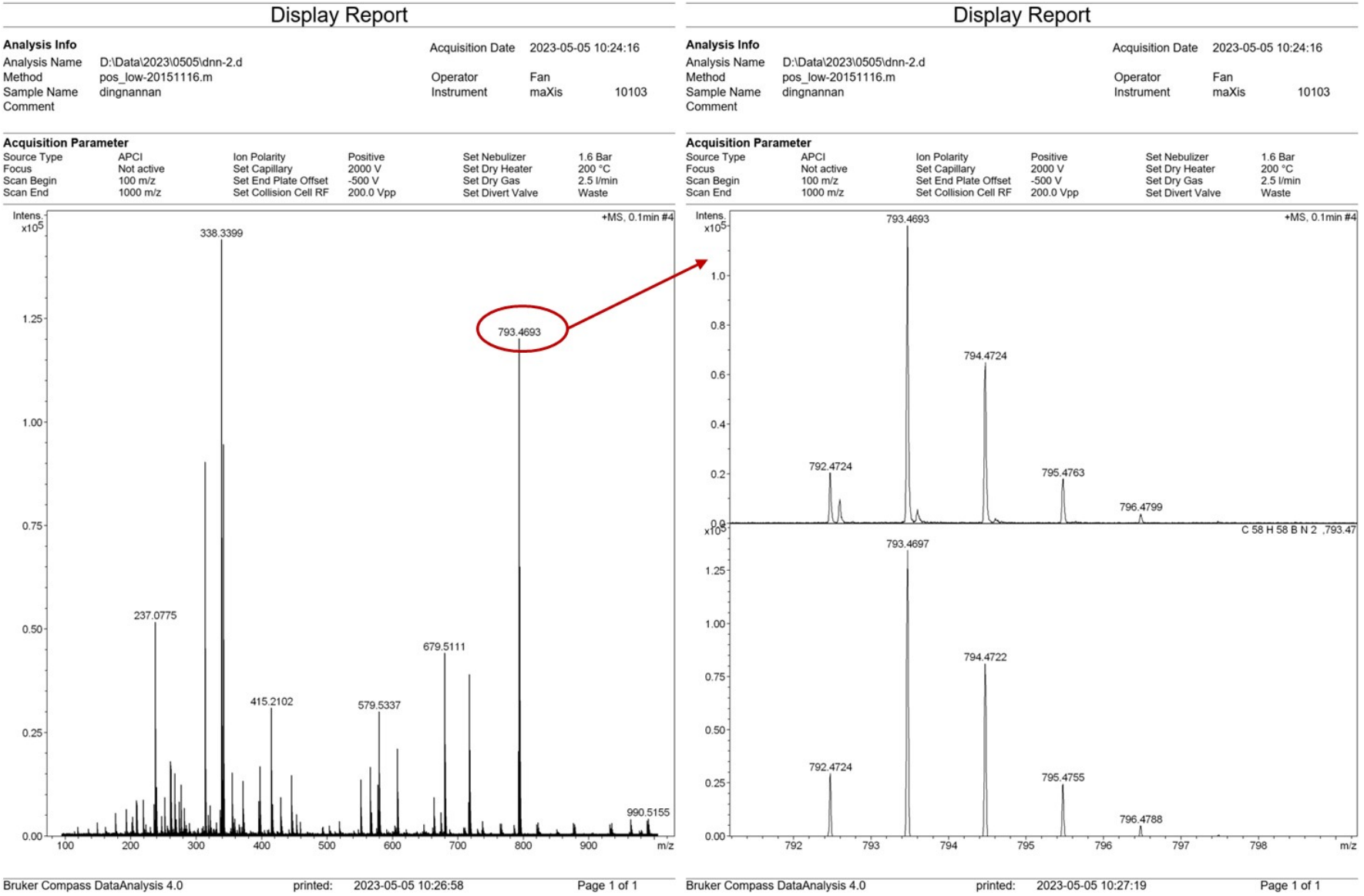


Fig. S9. HR-MS spectrum of **BN-Ph**.

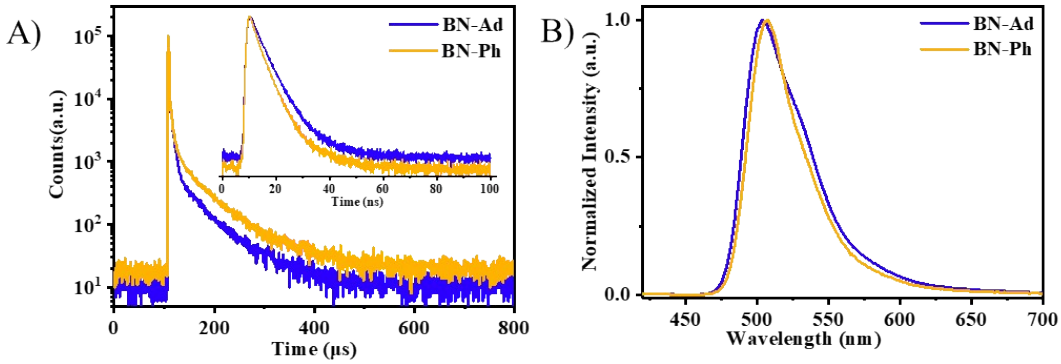


Fig. S10. A) transient photoluminescence decay curves of 6 wt% emitters doped in mCBP films; B) photoluminescence curves of **BN-Ad** and **BN-Ph** 6 wt% doped in mCBP films.

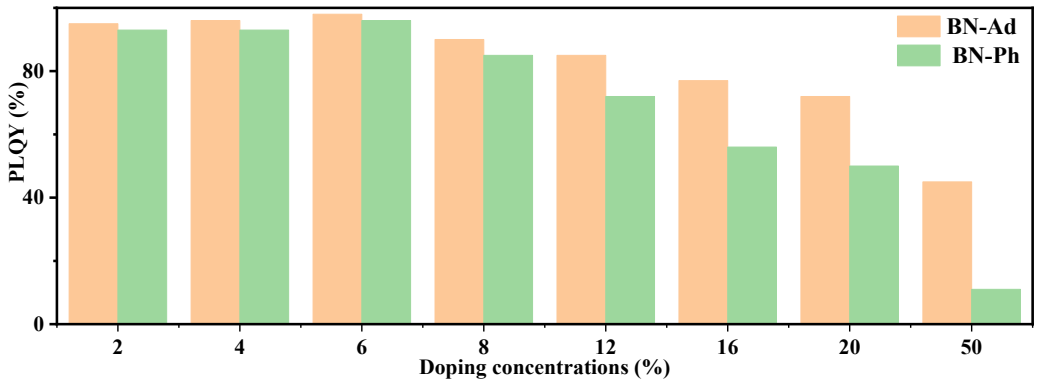


Fig. S11. PLQY of **BN-Ad** and **BN-Ph** doped in mCBP versus doping concentrations.

Table S1. Thermal and electrochemical properties of **BN-Ad** and **BN-Ph**.

Compound	T_d [a] (°C)	E_{HOMO} [b] (eV)	E_{LUMO} [c] (eV)	E_g [d] (eV)
BN- Ad	493	-5.01	-2.48	2.53
BN-Ph	436	-4.97	-2.44	2.53

[a] Obtained from thermal gravimetric analysis (TGA) measurements; [b] determined from the onset of the oxidation potentials by cyclic voltammetry (CV); [c] calculated by using HOMO levels and E_gs, where $E_{LUMO} = E_{HOMO} + E_g$; [d] estimated from the onset of the absorption spectra.

Table S2. Crystal data and structure refinement for **BN-Ad**.

Identification code	230317LU_LGPZ085847_0m

Empirical formula	$C_{63}H_{69}BCl_2N_2$
Formula weight	935.91
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	11.7271(8)
b/Å	15.7392(10)
c/Å	17.3908(11)
α/°	66.260(3)
β/°	72.704(4)
γ/°	75.147(4)
Volume/Å^3	2770.9(3)
Z	2
ρ_{calc}g/cm^3	1.122
μ/mm^{-1}	0.881
F(000)	1000.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.95 to 120.708
Index ranges	$-14 \leq h \leq 15$, $-18 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected	31407
Independent reflections	12120 [R_{int} = 0.0746, R_{sigma} = 0.0918]
Data/restraints/parameters	12120/378/717
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0769, wR_2 = 0.2042
Final R indexes [all data]	R_1 = 0.1473, wR_2 = 0.2523
Largest diff. peak/hole / e Å^{-3}	0.39/-0.52

Table S3. Crystal data and structure refinement for **BN-Ph**.

Identification code	cu_230511_WQANGZ_061145_0m
Empirical formula	$C_{58}H_{57}BN_2$
Formula weight	792.86
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	5.7146(2)
b/Å	17.2543(5)
c/Å	22.4781(8)
α/°	101.701(2)
β/°	93.212(2)
γ/°	90.068(2)
Volume/Å^3	2166.73(13)
Z	2
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	0.521
F(000)	848.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.02 to 159.906
Index ranges	$-6 \le h \le 7$, $-20 \le k \le 21$, $-28 \le l \le 28$
Reflections collected	24575
Independent reflections	8507 [R_{int} = 0.0558, R_{sigma} = 0.0564]
Data/restraints/parameters	8507/0/563
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1946
Final R indexes [all data]	R_1 = 0.0975, wR_2 = 0.2190
Largest diff. peak/hole / e Å^{-3}	0.74/-0.23

Table S4. Cartesian coordinates of **BN-Ad** at the optimized S_0 geometry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.809396	-4.640047	0.086627
2	6	0	1.630712	-6.024577	0.032959
3	6	0	0.378500	-6.569133	-0.263749
4	6	0	-0.672457	-5.668264	-0.530035
5	6	0	-0.524291	-4.283648	-0.478862
6	6	0	0.723959	-3.755613	-0.135384
7	7	0	1.195626	-2.421055	-0.023824
8	6	0	2.574489	-2.482501	0.181315
9	6	0	2.990900	-3.824460	0.291490
10	6	0	3.450854	-1.394694	0.240874
11	6	0	4.800958	-1.725410	0.499700
12	6	0	5.262623	-3.040515	0.654678
13	6	0	4.332996	-4.094103	0.531224
14	6	0	0.534969	1.237960	0.013225
15	6	0	-0.862697	1.247664	-0.036460
16	6	0	-1.581613	0.048871	0.017454
17	6	0	-0.897417	-1.169950	0.064959
18	6	0	0.499875	-1.199899	0.004456
19	6	0	1.265192	0.008120	0.005779
20	7	0	1.265203	2.439110	0.037062
21	5	0	2.808009	-0.014649	0.000559
22	6	0	0.832497	3.786107	0.150374
23	6	0	1.942345	4.638353	-0.079309
24	6	0	3.097442	3.788907	-0.291751
25	6	0	2.644029	2.462459	-0.178314
26	6	0	-0.397839	4.350625	0.501042

27	6	0	-0.505265	5.738831	0.552212
28	6	0	0.570231	6.608515	0.278930
29	6	0	1.804028	6.027857	-0.025353
30	6	0	4.448411	4.025014	-0.542573
31	6	0	5.342228	2.947902	-0.671582
32	6	0	4.841258	1.642627	-0.511603
33	6	0	3.489581	1.347504	-0.243840
34	6	0	6.840752	3.154309	-0.973491
35	6	0	0.355425	8.131936	0.343927
36	6	0	-0.727288	8.543007	-0.682026
37	6	0	-0.108568	8.531342	1.764865
38	6	0	1.641464	8.916254	0.022726
39	6	0	7.211773	4.643294	-1.110894
40	6	0	7.689896	2.555236	0.172719
41	6	0	7.201943	2.447410	-2.301519
42	6	0	6.739505	-3.375498	0.945536
43	6	0	7.620906	-2.116398	1.048648
44	6	0	6.840370	-4.140048	2.287051
45	6	0	7.302881	-4.261211	-0.191287
46	6	0	0.119168	-8.085616	-0.328088
47	6	0	1.383256	-8.906988	-0.012314
48	6	0	-0.970779	-8.465362	0.702263
49	6	0	-0.362046	-8.470764	-1.747230
50	6	0	-9.616139	1.195305	0.829608
51	6	0	-10.108482	-0.153125	1.391015
52	6	0	-9.529869	-1.299882	0.539484
53	6	0	-10.003015	-1.145808	-0.920455
54	6	0	-9.518393	0.207580	-1.479622
55	6	0	-10.097190	1.352870	-0.626271
56	6	0	-7.989286	-1.249673	0.589208

57	6	0	-8.074702	1.241642	0.872913
58	6	0	-7.977710	0.260768	-1.434025
59	6	0	-7.456636	0.100718	0.025002
60	6	0	-5.923943	0.111534	0.041374
61	6	0	-5.203737	-0.860066	-0.675599
62	6	0	-3.813538	-0.883513	-0.685345
63	6	0	-3.065901	0.070413	0.024982
64	6	0	-3.778231	1.041771	0.741210
65	6	0	-5.172860	1.060449	0.748742
66	1	0	2.485324	-6.666396	0.213682
67	1	0	-1.650356	-6.056140	-0.797901
68	1	0	-1.365956	-3.661167	-0.744132
69	1	0	5.505504	-0.910065	0.597668
70	1	0	4.662051	-5.124716	0.627515
71	1	0	-1.405174	2.168717	-0.172940
72	1	0	-1.464714	-2.075154	0.206690
73	1	0	-1.255730	3.753201	0.772037
74	1	0	-1.469736	6.155261	0.825852
75	1	0	2.675830	6.644398	-0.211875
76	1	0	4.798526	5.046190	-0.640506
77	1	0	5.529572	0.810855	-0.613939
78	1	0	-0.898038	9.624954	-0.645165
79	1	0	-0.420717	8.281532	-1.700019
80	1	0	-1.683084	8.048619	-0.485041
81	1	0	-0.269665	9.613757	1.823942
82	1	0	0.642826	8.258049	2.512769
83	1	0	-1.046782	8.041103	2.040836
84	1	0	2.011079	8.697156	-0.984365
85	1	0	1.440587	9.991173	0.073720
86	1	0	2.441777	8.696825	0.737044

87	1	0	8.280824	4.738027	-1.326702
88	1	0	6.667026	5.125831	-1.929082
89	1	0	7.011900	5.200720	-0.189774
90	1	0	8.758107	2.693761	-0.029691
91	1	0	7.511994	1.482786	0.294418
92	1	0	7.458742	3.041422	1.126137
93	1	0	7.002858	1.372714	-2.258405
94	1	0	6.622472	2.859740	-3.133943
95	1	0	8.265898	2.580425	-2.528704
96	1	0	8.655247	-2.407628	1.258045
97	1	0	7.623403	-1.543218	0.115614
98	1	0	7.294541	-1.454646	1.857432
99	1	0	7.883997	-4.392725	2.506469
100	1	0	6.270136	-5.073581	2.268252
101	1	0	6.456727	-3.532223	3.112874
102	1	0	7.251645	-3.741487	-1.153568
103	1	0	8.351383	-4.513408	0.004018
104	1	0	6.749711	-5.199904	-0.290408
105	1	0	1.150916	-9.975593	-0.061924
106	1	0	2.186386	-8.711316	-0.730373
107	1	0	1.763606	-8.698478	0.993040
108	1	0	-1.173010	-9.541856	0.665767
109	1	0	-1.912674	-7.943432	0.509392
110	1	0	-0.652581	-8.213335	1.719066
111	1	0	-1.286858	-7.953511	-2.019111
112	1	0	0.393792	-8.218959	-2.498184
113	1	0	-0.554575	-9.548033	-1.805961
114	1	0	-10.013286	2.016130	1.440186
115	1	0	-9.795304	-0.264482	2.437397
116	1	0	-11.205654	-0.188768	1.380654

117	1	0	-9.869909	-2.264414	0.937718
118	1	0	-11.098104	-1.204341	-0.970348
119	1	0	-9.612114	-1.969135	-1.532911
120	1	0	-9.849981	0.317113	-2.520076
121	1	0	-9.776020	2.322820	-1.028098
122	1	0	-11.194197	1.338564	-0.665408
123	1	0	-7.637369	-1.374110	1.621385
124	1	0	-7.574078	-2.085588	0.013894
125	1	0	-7.727991	2.213814	0.499406
126	1	0	-7.736032	1.158693	1.913695
127	1	0	-7.617331	1.213030	-1.843964
128	1	0	-7.562367	-0.530586	-2.069093
129	1	0	-5.736961	-1.612397	-1.249211
130	1	0	-3.296920	-1.633340	-1.277368
131	1	0	-3.235105	1.776786	1.328101
132	1	0	-5.671392	1.828498	1.328484

Table S5. Cartesian coordinates of **BN-Ph** at the optimized S_0 geometry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.624961	-4.480575	-0.084710
2	6	0	-1.618331	-5.876527	-0.031087
3	6	0	-0.444242	-6.571207	0.271511
4	6	0	0.708230	-5.806597	0.543869
5	6	0	0.731887	-4.414224	0.492523
6	6	0	-0.440009	-3.736582	0.142926
7	7	0	-0.743318	-2.353912	0.029380
8	6	0	-2.118474	-2.245331	-0.181957

9	6	0	-2.696256	-3.525836	-0.294572
10	6	0	-2.854117	-1.058069	-0.244846
11	6	0	-4.233592	-1.220158	-0.509362
12	6	0	-4.852838	-2.468444	-0.666805
13	6	0	-4.060293	-3.628384	-0.540114
14	6	0	0.362139	1.196191	-0.009739
15	6	0	1.750439	1.034424	0.044175
16	6	0	2.316167	-0.244079	-0.002892
17	6	0	1.488079	-1.370095	-0.050587
18	6	0	0.097269	-1.227937	0.003217
19	6	0	-0.513323	0.065175	-0.002800
20	7	0	-0.214916	2.477517	-0.036463
21	5	0	-2.047586	0.232334	-0.001845
22	6	0	0.380158	3.761275	-0.149358
23	6	0	-0.616438	4.743233	0.081122
24	6	0	-1.867353	4.042160	0.292856
25	6	0	-1.580620	2.670163	0.178280
26	6	0	1.670176	4.170295	-0.501090
27	6	0	1.947421	5.534838	-0.552332
28	6	0	0.987262	6.529960	-0.277350
29	6	0	-0.308287	6.105144	0.027824
30	6	0	-3.179047	4.442355	0.543866
31	6	0	-4.198748	3.483249	0.671323
32	6	0	-3.862225	2.126502	0.509524
33	6	0	-2.556863	1.667675	0.242195
34	6	0	-5.660573	3.872249	0.973082
35	6	0	1.387035	8.015616	-0.342411
36	6	0	2.518353	8.289515	0.676851
37	6	0	1.887392	8.356913	-1.766115
38	6	0	0.208950	8.951230	-0.012024

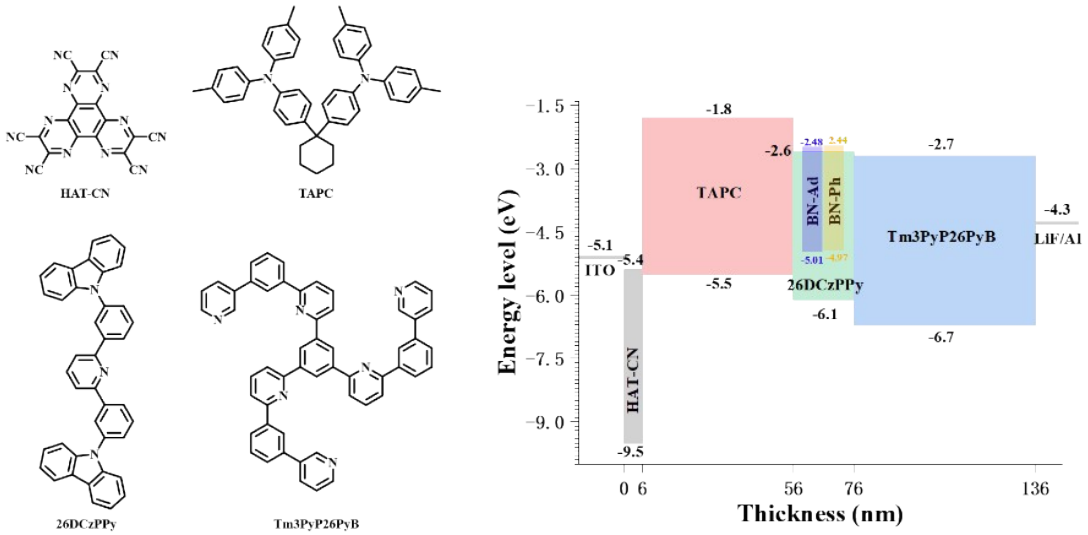
39	6	0	-5.844546	5.395176	1.116441
40	6	0	-6.575672	3.387486	-0.176420
41	6	0	-6.108252	3.210269	2.297875
42	6	0	-6.358436	-2.618965	-0.964208
43	6	0	-7.077782	-1.260741	-1.067860
44	6	0	-6.546909	-3.362786	-2.307882
45	6	0	-7.031321	-3.430580	0.168336
46	6	0	-0.374188	-8.108115	0.335751
47	6	0	-1.727684	-8.767352	0.010364
48	6	0	0.667480	-8.618884	-0.687897
49	6	0	0.046404	-8.549930	1.757619
50	6	0	8.097191	-0.873259	0.004606
51	6	0	6.621711	-0.713072	0.002083
52	6	0	5.792655	-1.592341	0.718656
53	6	0	4.409747	-1.442363	0.715942
54	6	0	3.791625	-0.405063	-0.001751
55	6	0	4.620289	0.474670	-0.717653
56	6	0	6.003078	0.323578	-0.716665
57	6	0	8.945488	0.247087	0.018214
58	6	0	10.331065	0.096933	0.020182
59	6	0	10.900457	-1.177439	0.009952
60	6	0	10.071017	-2.300024	-0.002968
61	6	0	8.685479	-2.149488	-0.006285
62	1	0	-2.544473	-6.408190	-0.216735
63	1	0	1.629475	-6.311788	0.816959
64	1	0	1.642387	-3.900180	0.762738
65	1	0	-4.832061	-0.324367	-0.609969
66	1	0	-4.513204	-4.610698	-0.638222
67	1	0	2.401087	1.882553	0.181156
68	1	0	1.940369	-2.338528	-0.188170

69	1	0	2.447722	3.471930	-0.773354
70	1	0	2.955363	5.829641	-0.827385
71	1	0	-1.097441	6.824060	0.215578
72	1	0	-3.400892	5.498711	0.643090
73	1	0	-4.647638	1.385559	0.610250
74	1	0	2.819403	9.342630	0.639981
75	1	0	2.188748	8.065516	1.696569
76	1	0	3.405645	7.682949	0.473128
77	1	0	2.179877	9.411387	-1.825743
78	1	0	1.103376	8.178898	-2.509249
79	1	0	2.756391	7.755314	-2.048260
80	1	0	-0.179355	8.776085	0.996641
81	1	0	0.540374	9.993380	-0.061615
82	1	0	-0.616185	8.834464	-0.722245
83	1	0	-6.893568	5.620600	1.333556
84	1	0	-5.243949	5.803428	1.935978
85	1	0	-5.577789	5.927316	0.197304
86	1	0	-7.618718	3.656911	0.025215
87	1	0	-6.532190	2.301698	-0.301963
88	1	0	-6.284298	3.844653	-1.127682
89	1	0	-6.043177	2.119395	2.250890
90	1	0	-5.483852	3.544970	3.132633
91	1	0	-7.148077	3.472545	2.524180
92	1	0	-8.139344	-1.422032	-1.281341
93	1	0	-7.013132	-0.693026	-0.133712
94	1	0	-6.669548	-0.642965	-1.874247
95	1	0	-7.612773	-3.484605	-2.531936
96	1	0	-6.096071	-4.359476	-2.289012
97	1	0	-6.087966	-2.805311	-3.130800
98	1	0	-6.920764	-2.922829	1.132019

99	1	0	-8.101998	-3.551457	-0.031885
100	1	0	-6.598428	-4.430439	0.267619
101	1	0	-1.628752	-9.856450	0.059391
102	1	0	-2.505465	-8.475402	0.723631
103	1	0	-2.072832	-8.512470	-0.997009
104	1	0	0.734647	-9.712135	-0.651810
105	1	0	1.665426	-8.217846	-0.487861
106	1	0	0.389866	-8.328646	-1.706390
107	1	0	1.025982	-8.150369	2.035913
108	1	0	-0.677628	-8.207168	2.503881
109	1	0	0.104567	-9.642691	1.816515
110	1	0	6.240573	-2.381808	1.314550
111	1	0	3.799735	-2.114359	1.312072
112	1	0	4.170739	1.262282	-1.314848
113	1	0	6.611924	0.998095	-1.311049
114	1	0	8.513442	1.242656	0.054382
115	1	0	10.966996	0.977367	0.039170
116	1	0	11.980065	-1.294590	0.012046
117	1	0	10.503372	-3.296376	-0.019872
118	1	0	8.050043	-3.029207	-0.044406

Table S6. Summary of photoluminescence data of **BN-Ad** and **BN-Ph** in solutions.

	BN-Ad		**BN-Ph**	
	λ_{em} (nm)	FWHM (nm)	λ_{em} (nm)	FWHM (nm)
Hexane (Hex.)	478	19	480	21
Toluene (Tol.)	486	21	486	24
Dichloromethane (DCM)	488	26	488	26
Tetrahydrofuran (THF)	488	26	488	27



Scheme S1. Device architecture for the MR-TADF OLEDs with energy level alignment of the relevant materials.

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