Supporting Information

Peripheral Carbazole Units-Decorated MR Emitter Containing B-N Covalent Bond for Highly Efficient Green OLEDs with Low Roll-off

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1. Experimental Section

1.1 General Information. Reagents for the reactions, purification, and measurements were procured from Shanghai Bide Medical Technology Co. Ltd. Materials for device fabrication were obtained from Jilin Optical and Electronic Materials Co. Ltd., all used without further purification. Other reagents and solvents were obtained from commercial sources without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature in deuterated dichloromethane or deuterated chloroform, with tetramethylsilane as the internal standard. MALDI-TOF-MS data was acquired on a Shimadzu AXIMA Performance MALDI-TOF instrument in positive detection mode. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were conducted on a Netzsch STA 449 F3 thermal analyzer at a heating rate of 10 °C min^{-1} under N_2 flow. UV-vis absorption and PL spectra were measured using UV-2600 (Shimadzu) and FluoroMax-4P (Horiba) instruments, respectively. The photoluminescence quantum yields (PLQYs) were obtained with an absolute photoluminescence quantum yield measurement system, Hamamatsu C9920-03G, in an integrating sphere.

1.2 Computational methods. The calculations were performed with the Gaussian 09 package, using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method with the B3LYP hybrid functional.[1-3] The structures were optimized using DFT or TD-DFT (S_1 state) methods with a 6-31G(d,p) basis set.

The calculations were performed with the Gaussian 09 package, using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method with the B3LYP hybrid functional.[1-3] The structures were optimized using TD-DFT (S_1 state) methods with a 6-31G(d,p) basis set. Natural transition orbital analyses[4] were also performed to examine the nature of the excited states. Electron-hole analysis was carried out using the Multiwfn software.[5] The RMSDs of the optimized structures at S_0 and S_1 states were analyzed by VMD software.[6]

1.3 Measurement of absorption and emission characteristics. 1×10^{-5} M solutions were prepared by stepwise dilution for solution measurements. Thin films for photophysical characterization were prepared by thermal evaporation on quartz substrates at 1-2 Å s^{-1} in a vacuum chamber with a base pressure of < 10^{-5} torr. UV-vis absorption and PL spectra were measured using UV-2600 (Shimadzu) and FluoroMax-4P (Horiba) instruments at 77 and 298

K. The PLQYs were obtained with an absolute photoluminescence quantum yield measurement system Hamamatsu C9920-03G in an integrating sphere. The solution sample was bubbled with nitrogen for 10 minutes before measurement while the films were measured in air. The transient spectra were collected on an Edinburgh Fluorescence Spectroscopy FLS1000.

1.4 Electrochemical measurements. Cyclic voltammetry was performed on a CHI 660 instrument, using a platinum (Pt) electrode as the working electrode, a Pt wire as the auxiliary electrode and an Ag/Ag^+ electrode as the reference electrode. The oxidation/reduction potentials were measured in dry dichloromethane/DMF solutions with 0.1 M of $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

$$E_{HOMO} = -(E_{[onset,ox\ vs.\ Fc^+/Fc]} + 4.8)\ (eV) \qquad E_{LUMO} = -(E_{[onset,red\ vs.\ Fc^+/Fc]} + 4.8)\ (eV)$$

1.5 The rate constants calculation. The prompt fluorescence and delayed fluorescence quantum yield ratio (Φ_{PF} and Φ_{DF}) were determined from the total PL quantum efficiency (Φ_{PL}) and the proportion of the integrated area of each component in the transient spectra to the total integrated area, r_{PF} and r_{DF} are individual component ratio for prompt and delayed fluorescence. The quantum efficiencies and rate constants were determined using the following equations according to Adachi's method.[7]

(1) $\Phi_{PF} = \Phi_{PL} r_{PF}$ $\qquad r_{PF} = \tau_1 A_1/(\tau_1 A_1 + \tau_2 A_2)$

(2) $\Phi_{DF} = \Phi_{PL} r_{DF}$ $\qquad r_{DF} = \tau_2 A_2/(\tau_1 A_1 + \tau_2 A_2)$

(3) $k_r = \Phi_{PF}/\tau_{PF}$

(4) $k_{ISC} = 1 - \Phi_{PF}/\tau_{PF}$

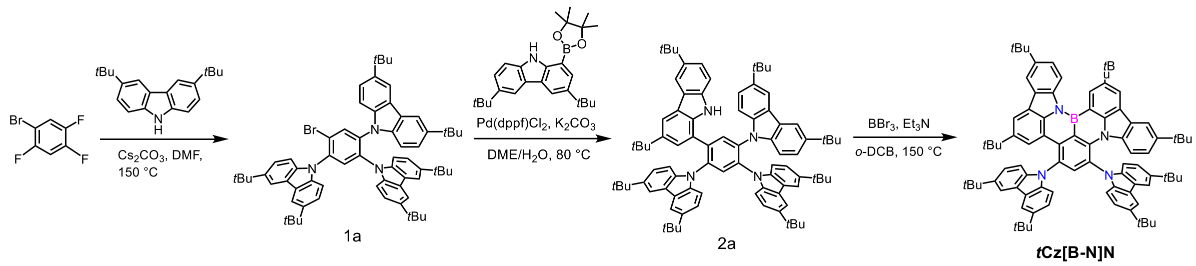
(5) $k_{RISC} = \Phi_{DF}/k_{ISC} \,.\, \tau_{PF} \,.\, \tau_{DF} \,.\, \Phi_{PF}$

1.6 Device fabrication and measurement of EL characteristics. All compounds were subjected to temperature-gradient sublimation under a high vacuum before use. The device architecture comprised layers of Indium tin oxide (ITO)/ HATCN (1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile, 5 nm)/NPB (N4,N4'-di(naphthalen-1-yl)-N4,N4'-diphenyl-[1,1'-biphenyl]-4,4'-diamine, 30 nm)/ TCTA (tris(4-(9H-carbazol-9-yl)phenyl)amine), 10 nm)/ mCPBC (9-(3-(9H-carbazol-9-yl)phenyl)-9H-3,9'-bicarbazole): 3CTF (2,4,6-tris((r)-2-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-(trifluoromethyl)phenyl)-1,3,5-triazine): x wt% emitter, (30 nm)/ CzPhPy (4,6-bis(3-(9H-carbazol-9-yl)phenyl)pyrimidine), (10 nm)/ DPPyA (9,10-

bis(6-phenylpyridin-3-yl)anthracene, 30 nm)/ LiF (0.5 nm)/ Al (150 nm).

OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode. Before device fabrication, the ITO glass substrates were pre-cleaned carefully. All material layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of 10^{-6} torr. The deposition system permits the fabrication of the complete device structure in a single vacuum pump-down without breaking vacuum. The deposition rate of organic layers was kept at 0.1~0.2 nm s^{-1}. The doping was conducted by co-evaporation from separate evaporation sources with different evaporation rates. The current density, voltage, luminance, external quantum efficiency, electroluminescent spectra and other characteristics were measured with a Keithley 2400 source meter and an absolute EQE measurement system in an integrating sphere at the same time. The EQE measurement system is Hamamatsu C9920-12, which is equipped with Hamamatsu PMA-12 Photonic multichannel analyzer C10027-02 whose longest detection wavelength is 1100 nm.

2. Synthesis and characterization



Scheme. S1. The synthetic route of compound ***t*Cz[B-N]N**.

*Synthesis of **1a***: 3,6-di-*t*-butylcarbazole (19.87 g, 71.1 mmol), 1-bromo-2,4,5-trifluorobenzene (5.0 g, 23.7 mmol), and Cesium carbonate (Cs_2CO_3) (46.33 g, 142.2 mmol) were dissolved in dry dimethylformamide (DMF, 100 mL) in a 250 mL Schlenk flask at room temperature. The resulting mixture was stirred at 150 ºC for 18 hours. After cooling to room temperature, the reaction mixture was poured into water. The precipitates were filtered and then purified by recrystallization from methanol to afford **1a** as a white solid (20.96 g, 89.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 1H), 8.19 (d, J = 1.9 Hz, 2H), 7.92 (s, 1H), 7.69 (s, 2H), 7.63 (d, J = 1.8 Hz, 2H), 7.56 (dd, J = 8.6, 1.9 Hz, 2H), 7.32 (s, 1H), 7.30 (s, 1H), 7.03 (s, 4H), 6.96 (dd, J = 8.6, 1.9 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 1.50 (s, 18H), 1.36 (s, 18H), 1.32 (s, 18H).

*Synthesis of **2a***: In a 250 mL Schlenk flask, 3,6-di-tert-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.41 g, 1.0 mmol) and **1a** (1.0 g, 1.0 mmol) were added. Following the addition of 20 mL dimethoxyethane (DME) and 5 mL aqueous K_2CO_3 (0.70 g, 5.1 mmol) solution, the mixture was degassed for 30 minutes. Subsequently, Pd(dppf)Cl_2 (0.04 g, 0.05 mmol) was added, and the mixture was heated to 80 °C and stirred for 18 hours. The reaction mixture was then poured into water and extracted with CH_2Cl_2 three times. After drying the organic phase over Na_2SO_4 and evaporating the solvent under vacuum, the crude product was purified by flash chromatography on silica gel using petroleum ether / CH_2Cl_2 (5:1, v/v) to give **2a** as a white solid (0.99 g, 82.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 1H), 8.18 (s, 1H), 7.91 (dd, J = 8.9, 1.8 Hz, 3H), 7.83 (s, 1H), 7.77 – 7.68 (m, 5H), 7.36 (dd, J = 8.5, 1.9 Hz, 1H), 7.25 (d, J = 1.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.04 – 6.99 (m, 6H), 1.41 – 1.33 (m, 63H), 1.02 (s, 9H).

*Synthesis of **tCz[B-N]N***: A mixture of **2a** (0.95 g, 0.8 mmol), triethylamine (Et_3N) (0.56 mL, 4.0 mmol) in dry 1,2-dichlorobenzene (*o*-DCB) (15 mL) was stirred at room temperature for 10 minutes. Then, BBr_3 (0.19 mL, 2.0 mmol) was added dropwise to the reaction mixture. The reaction mixture was heated to 150 ºC for 16 hours. After removing the solvent under vacuum, the crude product was washed with hexane and collected by filtration. The obtained solid was sonicated with methanol and collected by filtration to give the title compound ***tCz[B-N]N*** as a blight yellow solid (0.90 g, 94% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm): 9.21 (s, 2H), 8.50 (d, J = 1.7 Hz, 1H), 8.45 (d, J = 1.7 Hz, 1H), 8.39 (s, 1H), 8.21 – 8.06 (m, 3H), 7.98 (s, 1H), 7.94 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.31 (s, 1H), 7.21 – 6.96 (m, 3H), 6.83 (s, 1H), 6.65 – 6.58 (m, 2H), 6.49 (dd, J = 8.8, 2.0 Hz, 1H), 1.72 (d, J = 2.1 Hz, 18H), 1.46 (d, J = 4.3 Hz, 18H), 1.33 (s, 9H), 1.22 (d, J = 13.2 Hz, 18H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2) (ppm): 145.85, 145.47, 145.27, 143.84, 143.56, 143.38, 143.21, 143.07, 142.97, 140.66, 139.69, 139.56, 138.55, 138.10, 137.71, 135.78, 130.16, 130.01, 126.18, 125.37, 125.21, 125.08, 124.75, 124.65, 124.54, 124.27, 124.19, 123.80, 123.26, 123.05, 122.56, 122.35, 122.05, 121.99, 117.20, 116.87, 116.78, 116.35, 116.23, 115.77, 115.07, 113.98, 110.63, 109.36, 35.78, 35.21, 35.17, 35.05, 34.89, 34.84, 34.82, 32.54, 32.53, 32.33, 32.30, 32.17, 31.93, 31.80. MALDI-TOF: Calculated: 1194.7650, Found: 1194.7668.

3. Supplementary figures and tables

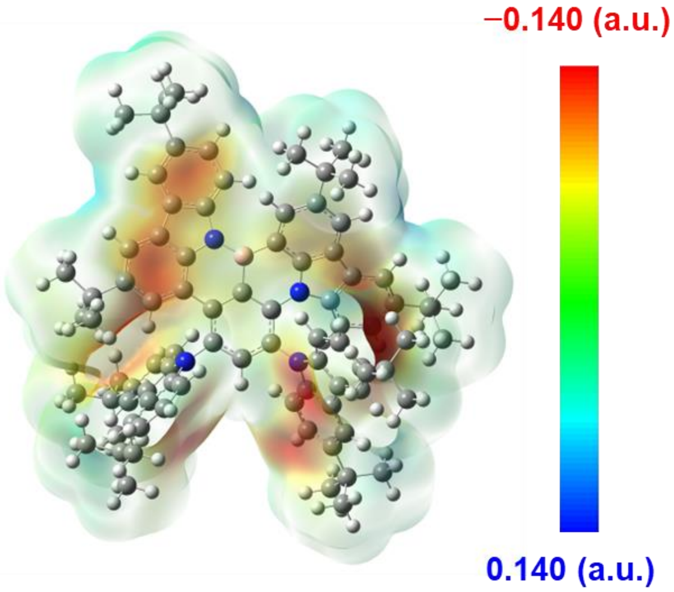
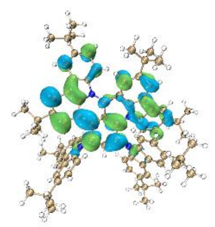
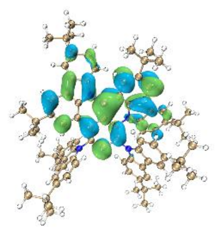
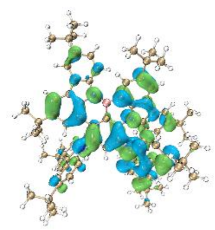
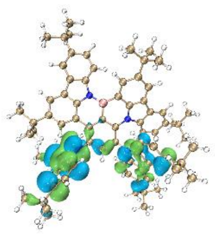
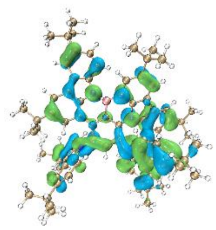
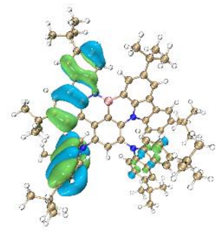
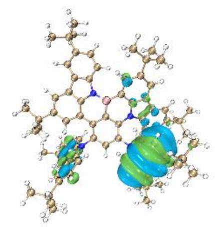
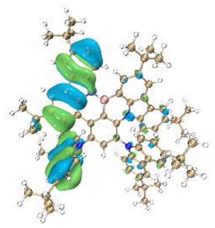
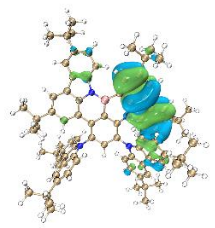


Figure S1. The molecular surface electrostatic potentials (ESP) of ***t*Cz[B-N]N** in S_0 state (measuring scale (a.u.), blue and red color indicate negative and positive electrostatic potentials, respectively).

Table S1. Primary orbitals which contribute to the calculated transitions of ***t*Cz[B-N]N** (iso = 0.02).

		
LUMO+1	LUMO	HOMO
		
HOMO-1	HOMO-2	HOMO-3
		
HOMO-4	HOMO-5	HOMO-6

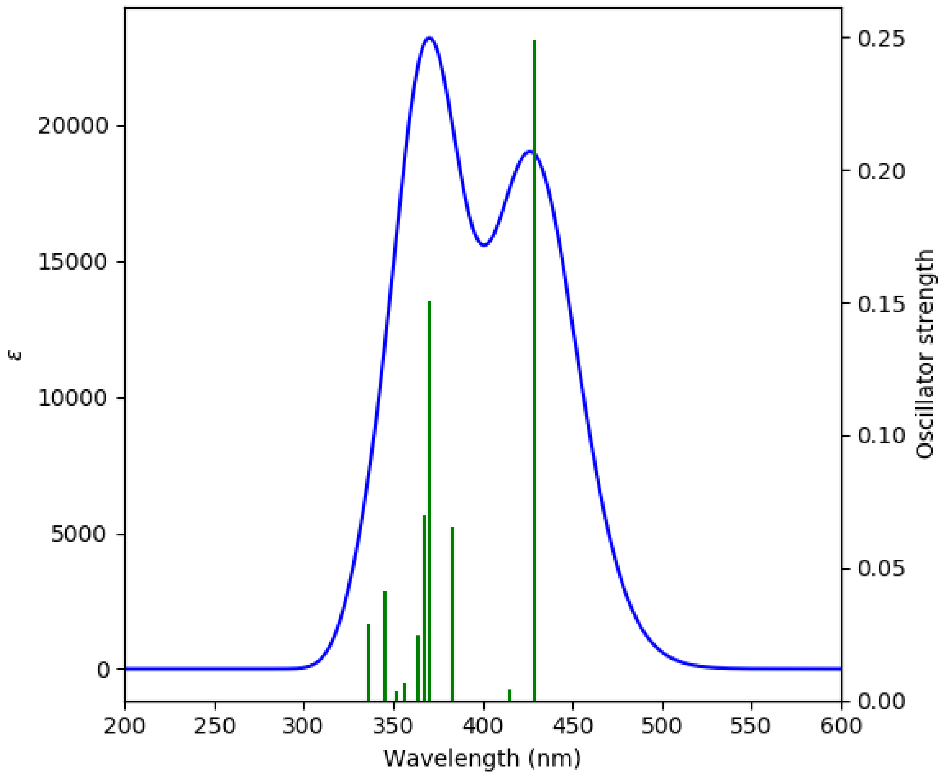


Figure S2. Predicted UV/Vis spectra of ***t*Cz[B-N]N** based on TD-DFT calculation.

Table S2. Summary of TD-DFT calculation for ***t*Cz[B-N]N** at the S_0 and S_1 structures at the B3LYP/6-31G(d, p) level.

Compound	**Optimized Structure**	**Transition**	**Wavelength (nm)**	**Energy (eV)**	**Oscillator Strength**
***t*Cz[B-N]N**	S_0	$S_0 \rightarrow S_1$	429.08	2.8896	0.2491
		$S_0 \rightarrow T_1$	494.28	2.5084	0
	S_1	$S_1 \rightarrow S_0$	475.32	2.6085	0.1890

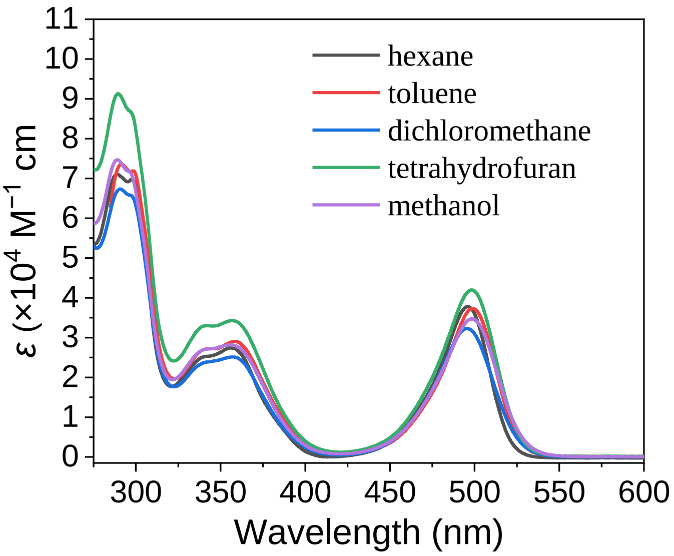


Figure S3. The solvent polarity-dependent UV-vis absorption spectra range from hexane to methanol.

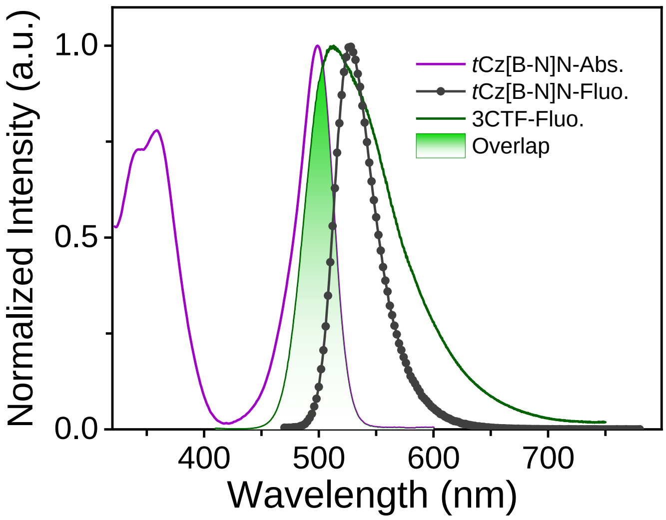
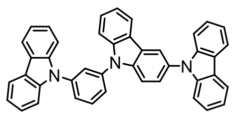
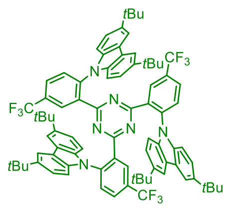


Figure S4. UV-vis spectra of ***t*Cz[B-N]N** in toluene solution and PL spectra of both ***t*Cz[B-N]N** and 3CTF in doped film.

Table S3. The basic material parameters and chemical structures of mCPBC and 3CTF.

Name	Structure	HOMO [eV]	LUMO [eV]
mCPBC		−5.7	−1.7

3CTF		−5.69	−2.87

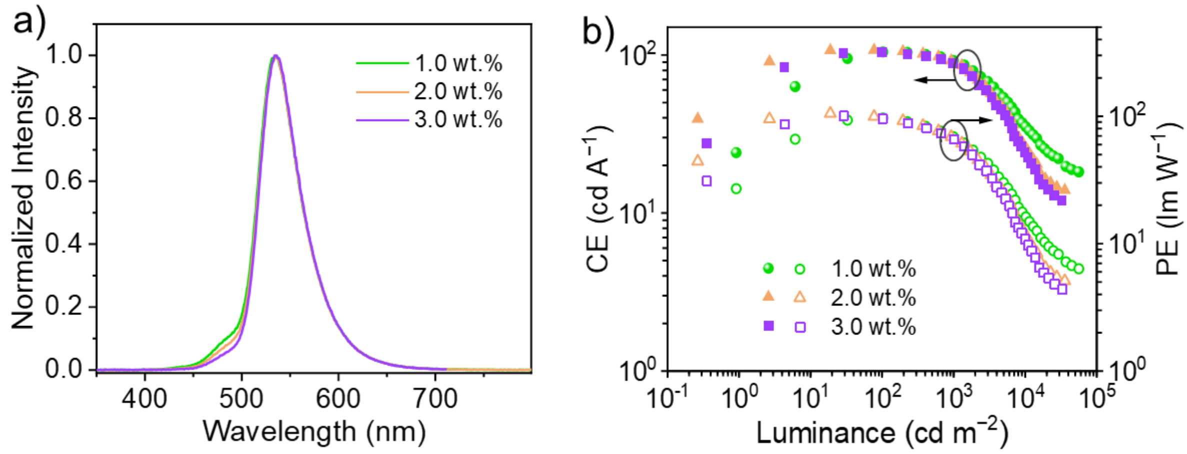


Figure S5. The EL spectra (a) and EQE curves (b) under different concentration of ***t*Cz[B-N]N**.

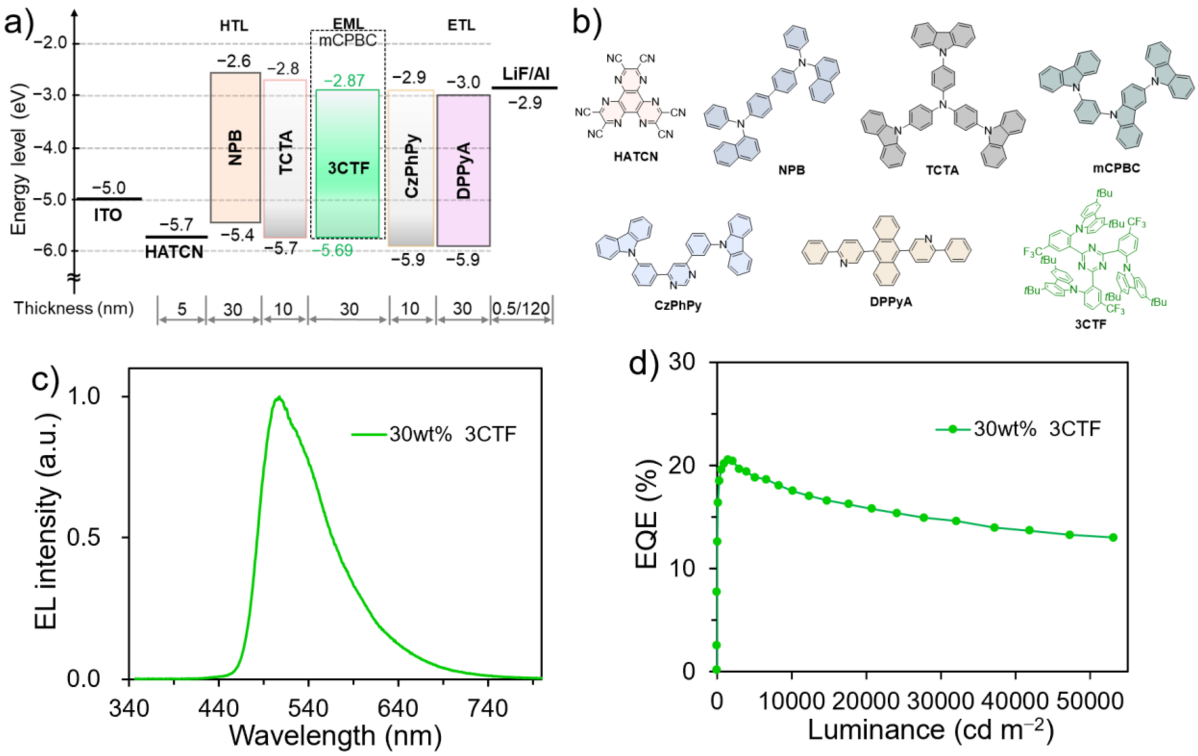
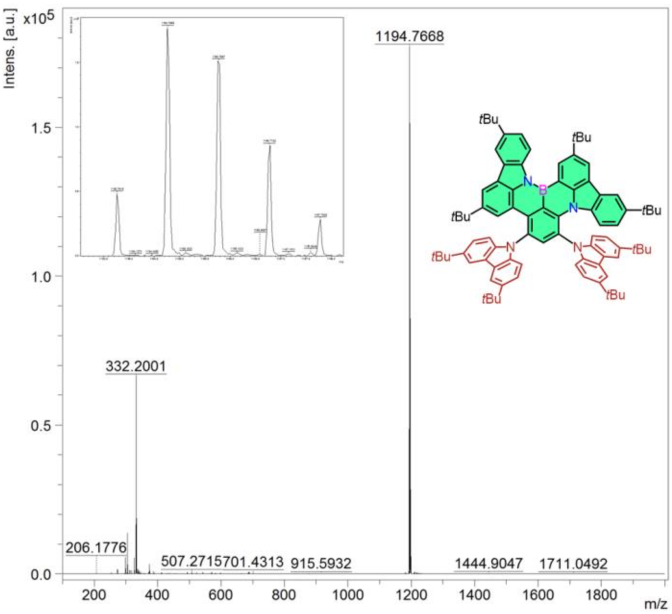


Figure S6. (a) The OLED architecture, and (b) structures of each layer's functional materials. (c) The EL spectra under 1000 cd cm^{-2}. (d) The plots of EQE versus luminance at 30 wt% doping concentration.



m/z	S/N	Intens.	Area
1194.7668	13872	177391	14946
1195.7697	11838	151379	13466
1196.7728	6705	85746	6866
332.2001	5466	66441	2357
1193.7619	3805	48662	3632
1197.7825	2211	28278	2152
333.1983	1540	18723	558
304.2928	1147	13665	365
332.3231	855	10394	437
1198.7822	452	5790	406
298.3383	466	5554	194
326.3683	446	5425	170
374.2017	264	3223	124
305.2976	253	3014	79.4
1197.5848	184	2357	149
333.3272	176	2149	87.4
1195.1230	167	2138	218
1196.1333	165	2119	235
334.1974	160	1947	65.8
299.3431	150	1789	45.2
338.2791	131	1609	48.7
273.1257	146	1586	38.7
1197.1513	113	1445	141
1198.5973	109	1400	120
312.3170	101	1224	45.3
327.3744	100	1216	36.2
318.2728	99	1204	34.4
340.3472	98	1203	33.5
331.1872	95	1159	35.1
375.2049	87	1051	35.5
1192.7651	75	964	70.4
507.2715	90	953	48.3
346.3031	77	951	32.4
1196.5867	74	946	68.6
1199.7812	74	936	62.5
1195.3378	68	874	133
1196.3333	62	803	88.1
386.2721	66	799	30.3
688.4131	73	754	42.4
372.2363	56	685	21.6

Target

Target type	0209519
Target serial number	1005031
Position	P12

Laser

Laser beam attenuation	80
Laser beam focus	86
Laser repetition rate	10000 Hz
Number of shots	1000

Spectrometer

positive voltage polarity	POS
PIE delay	100 ns
Ion source voltage 1	20 kV
Ion source voltage 2	17.39 kV
Lens voltage	11.25 kV
Linear detector voltage	0 kV
Deflection on	deflection
Deflection mass	79.942
Reflector voltage 1	20.84 kV
Reflector voltage 2	1.085 kV
Reflector voltage 3	8.65 kV
Reflector detector volt.	1.983 kV

Instrument

Instrument type	rapifleX
Instrument serial	1846003.10201
Name of computer	FLEX-PC
Operator ID or name	admin
flexControl version	4.0.48.0_905_885
flexAnalysis version	

Figure S6. Mass spectrometry of ***t*Cz[B-N]N**.

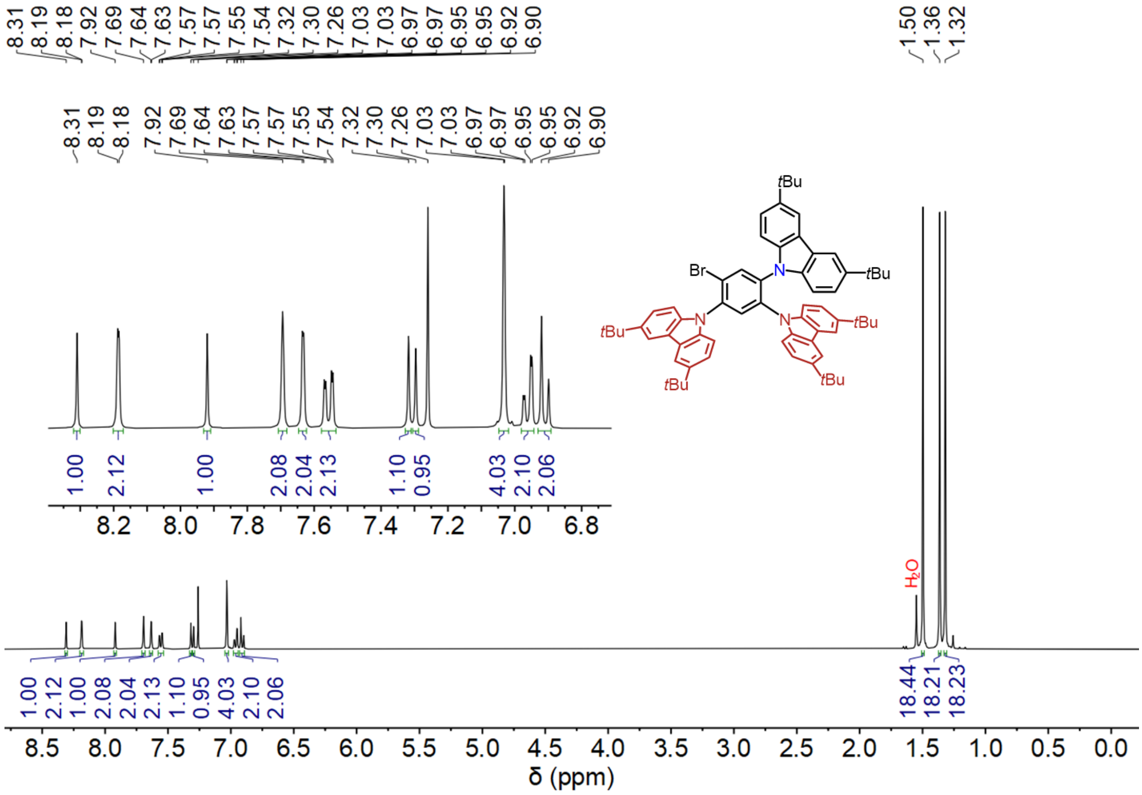


Figure S7. [1]H NMR spectrum of **1a** in $CDCl_3$.

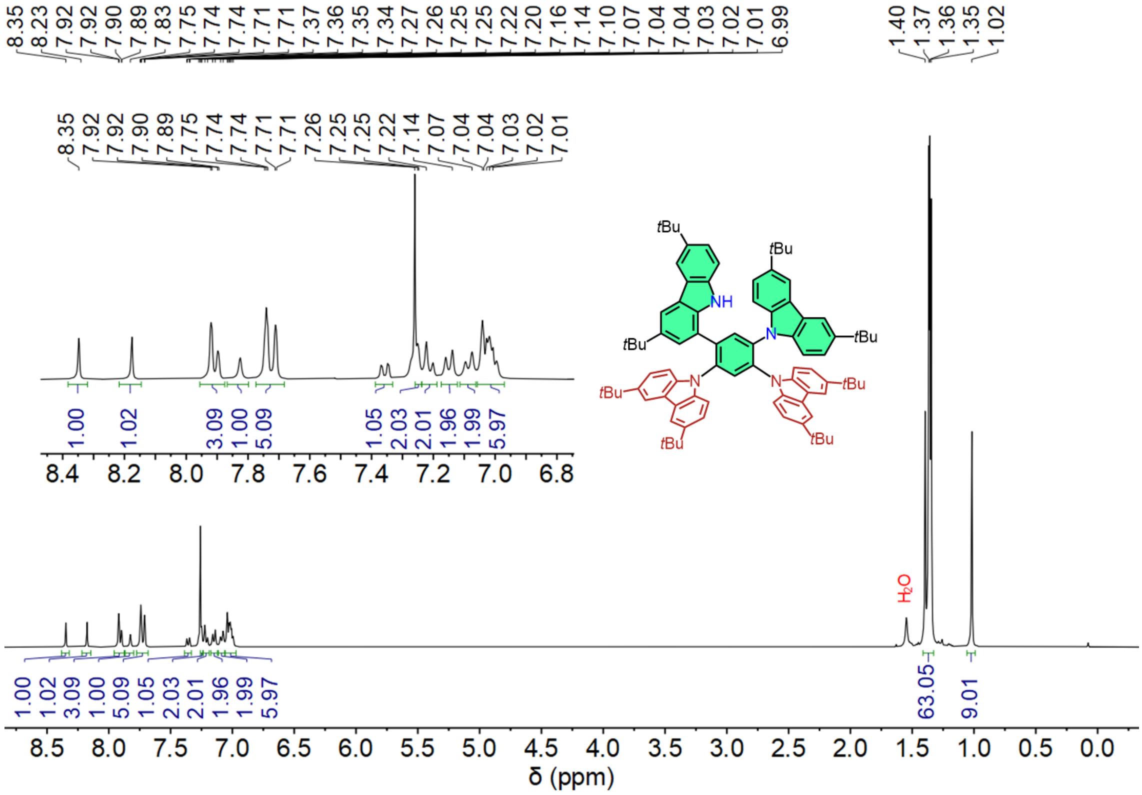


Figure S8. [1]H NMR spectrum of **2a** in $CDCl_3$.

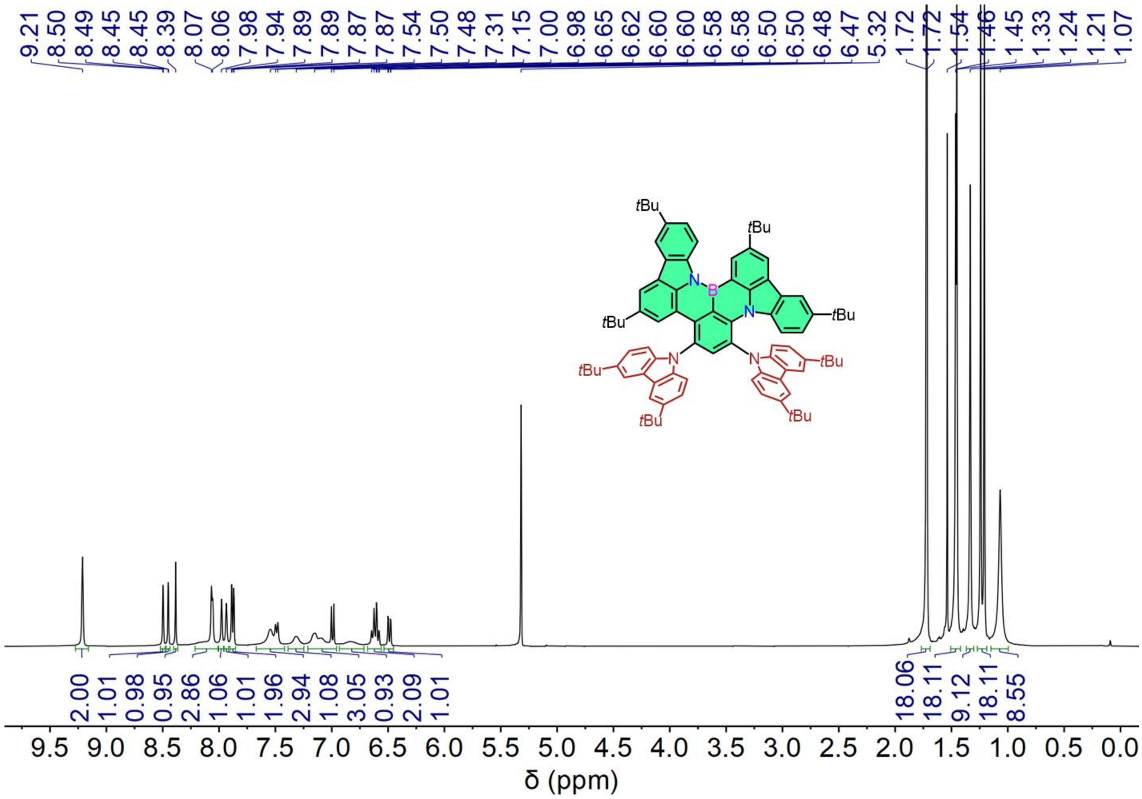


Figure S9. [1]H NMR spectrum of ***t*Cz[B-N]N** in CD_2Cl_2.

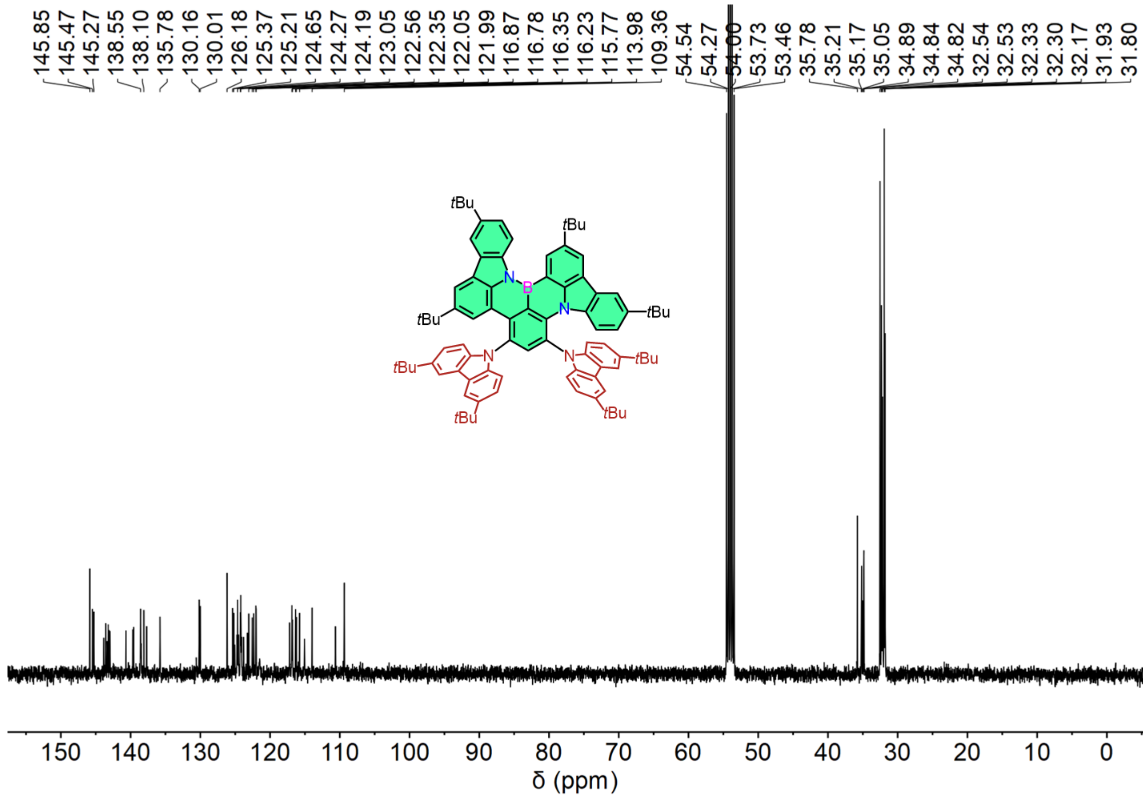


Figure S10. ^{13}C NMR spectrum of ***t*Cz[B-N]N** in CD_2Cl_2.

Table S4. Cartesian coordinates of optimized structure of ***t*Cz[B-N]N**.

	S_0				S_1		
Atom	X	Y	Z	Atom	X	Y	Z
C	0.606	-1.3747	-1.0475	C	-0.03487	-1.61768	0.00175
C	-4.8387	2.2512	-0.1448	C	-5.28306	2.59155	1.55314
C	-5.536	1.164	-0.5244	C	-5.84209	1.53186	2.27337
C	-4.8308	0.0252	-0.667	C	-5.03312	0.39798	2.5003
C	-3.496	-0.0251	-0.528	C	-3.73584	0.27649	2.00802
C	-0.3898	3.1816	0.7308	C	-0.70056	3.50418	-0.14025
C	-0.4929	4.474	1.073	C	-0.90332	4.82326	-0.6099
C	-1.6846	5.1046	1.1086	C	-2.15072	5.46404	-0.59231
C	-2.7729	4.378	0.7782	C	-3.2517	4.77699	-0.03521
C	-1.456	2.48	0.3478	C	-1.85787	2.83959	0.26604
C	-2.6373	3.1028	0.3937	C	-3.11365	3.46614	0.40373
C	-3.5082	2.1786	-0.0111	C	-3.98142	2.49849	1.05281
C	-2.7775	1.0807	-0.2721	C	-3.22443	1.31761	1.23667
N	-1.5145	1.2909	-0.1271	N	-1.94042	1.50225	0.65652
B	0.9277	2.3011	0.8023	B	0.58532	2.67247	0.0499

C	3.9203	4.2945	3.5269	C	4.75534	5.44792	0.17041
C	3.1475	5.1429	4.2365	C	4.21671	6.6862	0.53105
C	1.8153	4.9205	4.235	C	2.83081	6.74647	0.79914
C	1.2418	3.9246	3.5394	C	1.98815	5.64314	0.68694
C	3.3506	3.3038	2.8303	C	3.93047	4.32349	0.05873
C	2.0213	3.1322	2.795	C	2.53947	4.42905	0.27686
N	1.7166	2.1297	2.0665	N	1.93926	3.15346	0.12343
C	1.7664	0.0207	0.2975	C	1.5222	0.24716	-0.0381
C	0.6819	0.8287	0.2444	C	0.40629	1.12741	0.14327
C	-0.4901	0.5366	-0.3639	C	-0.91119	0.59966	0.3418
C	-0.4545	-0.5498	-1.1853	C	-1.14172	-0.77994	0.12677
C	1.6887	-1.2096	-0.2622	C	1.27298	-1.14831	-0.01818
C	5.1021	1.9729	1.7321	C	5.36989	2.21088	-0.50285
C	3.8602	2.3251	2.0745	C	4.21112	2.92234	-0.20207
C	2.8039	1.6408	1.6269	C	2.98044	2.24865	-0.09981
C	2.8977	0.5989	0.7859	C	2.85458	0.8567	-0.23493
C	5.2719	0.9257	0.8998	C	5.29826	0.82441	-0.69626
C	4.1679	0.2907	0.443	C	4.05412	0.18329	-0.54952
N	-1.3232	-0.8335	-2.0967	N	-2.4287	-1.34871	-0.059
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C	-2.7862	-0.5088	-3.6742	C	-4.36689	-1.95812	-1.13039
C	-3.5824	0.1839	-4.4989	C	-5.37825	-1.84327	-2.09177
C	-3.5346	1.5293	-4.5087	C	-5.3419	-0.81732	-3.03937
C	-1.7222	-1.9769	-2.5395	C	-2.90252	-2.51736	0.55409
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C	-3.2296	-2.8381	-4.1526	C	-4.79326	-4.03814	0.39677
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C	-2.6961	6.6448	2.8059	C	-2.80139	7.82065	0.03165
C	-7.0563	1.1667	-0.7157	C	-7.27386	1.57071	2.83857
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C	-7.4097	0.5594	-2.0932	C	-8.0921	0.40089	2.24144

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C	-5.1331	3.4726	-4.5486	C	-7.09159	0.7489	-3.95999
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C	3.7268	6.3098	5.0463	C	5.07251	7.95948	0.66654
C	5.2609	6.4557	4.9236	C	6.55559	7.7055	0.33633
C	3.1019	7.6333	4.5494	C	4.5439	9.04133	-0.3054
C	3.4012	6.1091	6.5425	C	4.98841	8.49044	2.11758
C	6.6638	0.4883	0.4182	C	6.53975	-0.02047	-1.05071
C	7.8273	1.2049	1.1418	C	7.79944	0.84729	-1.2386
C	6.8557	-1.0257	0.6598	C	6.82058	-1.03141	0.08643
C	6.7945	0.791	-1.0901	C	6.29096	-0.78758	-2.37139
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C	3.2426	-2.3652	0.931	C	2.98214	-2.62664	1.06756
C	4.0693	-3.4102	0.7864	C	3.74979	-3.758	0.69458
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C	2.943	-3.0394	-0.9919	C	2.57835	-2.98921	-1.13147
C	3.8692	-3.8503	-0.456	C	3.4924	-3.98974	-0.71537
C	2.6704	-3.2688	-2.2896	C	2.1225	-2.93565	-2.44695
C	3.2258	-4.3001	-2.9501	C	2.58856	-3.90047	-3.34051
C	4.1064	-5.1429	-2.3778	C	3.49765	-4.91296	-2.9663
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C	4.7558	-6.3165	-3.1202	C	4.00839	-5.97508	-3.96058
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C	5.7942	-3.8116	4.0779	C	5.4488	-4.67672	4.01253
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H	3.8197	5.1463	6.9148	H	5.36444	7.74628	2.82886
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H	2.3081	6.1011	6.7472	H	3.96051	8.73594	2.40432
H	8.8155	0.8292	0.7919	H	8.64877	0.20818	-1.50492
H	7.8344	2.3007	0.9457	H	7.67421	1.58221	-2.04239
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H	6.051	0.2351	-1.7032	H	5.43801	-1.46935	-2.29899
H	3.8879	-1.8003	4.1306	H	3.79536	-2.44119	4.32387
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H	4.4795	-5.6213	-5.2084	H	3.68116	-4.82366	-5.80487
H	6.7873	-6.913	-3.7487	H	5.92939	-6.63402	-4.77431
H	6.7574	-6.0521	-2.187	H	6.03889	-6.04495	-3.10871
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H	7.9534	-4.1484	4.3996	H	7.56541	-5.16103	4.28158

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