

## Supporting Information

# Orthogonal Steric Modulation to Suppress Concentration Quenching and Spectral Broadening in Multi-Resonance TADF Emitters

*Qiang Zhang*<sup>a</sup>, *Hanrui Su*<sup>a</sup>, *Hongbo Shao*<sup>a</sup>, *Shan Huang*<sup>a</sup>, *Haotian Yue*<sup>a</sup>, *Runda Guo*<sup>\*a</sup>, *Lei Wang*<sup>\*a, b</sup>

<sup>a</sup>*Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China.*

<sup>b</sup>*Shenzhen Huazhong University of Science and Technology Research Institute, Shenzhen, 518057, People's Republic of China.*

### Corresponding Author

\*Email: [wanglei@mail.hust.edu.cn](mailto:wanglei@mail.hust.edu.cn)

\*Email: [runda\\_guo@hust.edu.cn](mailto:runda_guo@hust.edu.cn)

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## Characterization.

The intermediates and final compounds were confirmed by  $^1\text{H}$  NMR or  $^{13}\text{C}$  NMR spectra on a Bruker Ascend<sup>TM</sup> 600MHz spectrometer. Mass spectra were recorded on Agilent 1100 LC-MS Trap XCT ion trap mass spectrometry. Thermogravimetric analysis (TGA) was undertaken using a PerkinElmer Instruments Pyris1 TGA at a heating rate of  $10^\circ\text{C min}^{-1}$  from 30 to  $600^\circ\text{C}$  under a nitrogen atmosphere. The thermal decomposition temperatures ( $T_d$ ) were corresponded to 5% weight loss temperatures. The UV-vis absorption spectra were measured on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) in the wavelength range of 190-1100 nm. The PL spectra and the transient photoluminescence spectra were recorded on an Edinburgh Instruments (FLS 920 spectrometer). The absolute photoluminescence quantum yields ( $\Phi_{\text{PL}}$ ) and time-resolved photoluminescence (TRPL) tests were conducted using a Horiba Fluorolog-QM spectrofluorometer, with the  $\Phi_{\text{PL}}$  test equipped with a calibrated integrating sphere. Cyclic voltammetry was recorded on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional three-electrode system, which consisted of a platinum wire counter electrode, Ag/AgNO<sub>3</sub> (0.1 M) reference electrode, and a glassy carbon working electrode of 2 mm diameter. A 0.10 M tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) solution in dry dichloromethane and *N,N*-dimethylformamide were employed as the supporting electrolyte, and ferrocene was added as a calibrant in the whole measurement. Finally, the dipole orientation was measured by RSQX-01 from Changchun RuoshuiTechnology Development Co., Ltd.

**Calculation Formulas for the Photophysical Parameters:** The evaluations of exciton dynamic rate constants were calculated by equations S1-S6:

$$k_p = 1/\tau_{\text{PF}} \quad \text{Equation S1}$$

$$k_d = 1/\tau_{\text{DF}} \quad \text{Equation S2}$$

$$k_F = \Phi_{\text{PF}}/\tau_{\text{PF}} \quad \text{Equation S3}$$

$$\Phi = k_F/(k_F + k_{\text{IC}}) \quad \text{Equation S4}$$

$$\Phi_{\text{PF}} = k_F/(k_F + k_{\text{IC}} + k_{\text{ISC}}) \quad \text{Equation S5}$$

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The total PLQY of the emitter-doped *m*CBP films is high enough. And phosphorescence was not observed at room temperature. Therefore, it is reasonably assumed that 1)  $k_r^S \gg k_{nr}^S, k_r^T, k_{nr}^T$  and 2)  $k_{RISC} \gg k_r^T, k_{nr}^T$ . Where  $k_r^S$  and  $k_{nr}^S$  are the rate constants for radiative and non-radiative decay from  $S_1$ ,  $k_r^T$  and  $k_{nr}^T$  are the rate constants of radiative and non-radiative decay from  $T_1$ , respectively. It is experimentally observed that  $k_p \gg k_d$ , then  $k_p \approx k_r + k_{ISC} + k_{RISC}$  and  $k_p k_d \approx k_r k_{RISC}$ . When  $k_{ISC} \gg k_{RISC}$ ,  $k_p$  can be expressed as  $k_p \approx k_r + k_{ISC}$ , and  $k_{RISC}$  is obtained as:

$$k_{RISC} = k_p k_d / (k_p - k_{ISC}) \quad \text{Equation S6}$$

### Device fabrication and measurements.

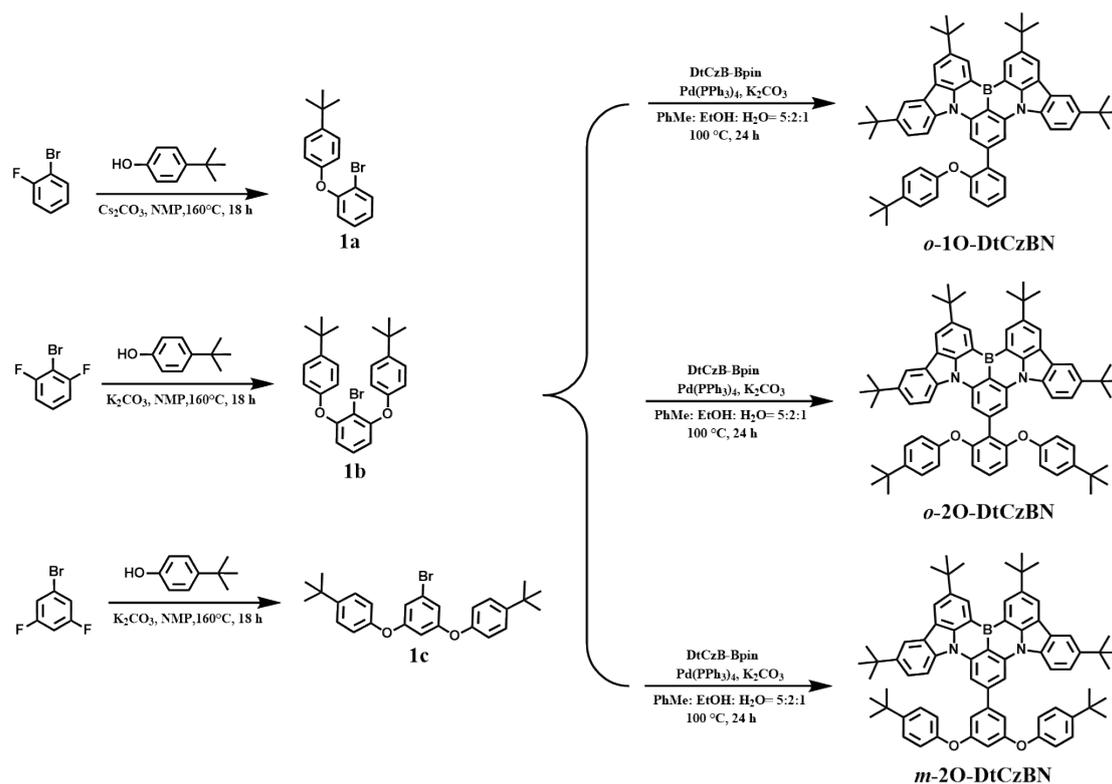
The used ITO glass substrates, MoO<sub>3</sub>, LiF, TAPC, TCTA, *m*CBP, PPF, TmPyPB, and Al were commercially available. The devices were fabricated by evaporating organic layers on ITO (20 Ω square<sup>-1</sup>), which were precleaned carefully and treated with oxygen plasma for 25 min. The organic layers were deposited onto the substrate in a vacuum chamber under a high vacuum (<10<sup>-4</sup> Pa). For all of the OLEDs, the emitting areas were determined by the overlap of two electrodes as 0.06 cm<sup>2</sup>. The *J-V-L* of the devices was measured using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The EL spectra were measured using a PR655 spectrometer. All measurements were carried out at room temperature under ambient conditions.

### Calculation details

The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were employed to optimize the ground state and excited state geometries and electronic properties, which were carried out with the B3LYP hybrid functional at the basis set level of 6-31G(d,p) by Gaussian 09.<sup>1,2</sup> The noncovalent interactions were analysed through RDG using Multiwfn (version 3.8). Natural transition orbitals (NTO)

were also performed by the Multiwfn program and drawn by VMD software (version 1.9.3).<sup>3</sup> The calculations of RMSD were also completed by the VMD software.<sup>4</sup> The spin-orbit coupling matrix elements (SOCME) were calculated by the ORCA program and also under the TD-DFT method, and it was carried out with the B3LYP hybrid functional at the basis set level of def2-TZVP.<sup>5</sup>

## Material synthesis



**Scheme S1.** The synthetic routes of *o*-10-DtCzBN, *o*-20-DtCzBN, and *m*-20-DtCzBN.

**Synthesis of DtCzB-Bpin:** The synthetic process was referred to the reported literature.<sup>6</sup>

**Synthesis of 1a:** 1-bromo-2-fluorobenzene (6.0 g, 35.0 mmol), 4-(*tert*-butyl)phenol (5.78 g, 38.5 mmol), and cesium carbonate (22.8 g, 70.0 mmol) were taken sequentially and added to a 250 ml three-necked round-bottomed flask. Then 100 ml of anhydrous NMP was added, and then the nitrogen was pumped out for ten minutes and replaced three times with nitrogen. Subsequently, the temperature was increased to 160°C under a nitrogen atmosphere, the condensate was adjusted to keep the reaction reflux rate appropriate, and the reaction was continued to be stirred for 18 h. The

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resulting solution was extracted with ethyl acetate/water, and the organic layer was concentrated under vacuum. The product was purified by column chromatography using a mixture eluent of dichloromethane: petroleum ether (1:10), resulting in a white solid (8.30 g, 78% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.24 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 6.99 (td, *J* = 7.6, 1.5 Hz, 1H), 6.95 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.95 – 6.89 (m, 2H), 1.33 (s, 9H). HRMS (APCI): Theoretical value: C<sub>16</sub>H<sub>17</sub>BrO, 304.05; Experimental value: 305.06, [M+H]<sup>+</sup>.

**Synthesis of 1b:** 2-bromo-1,3-difluorobenzene (2.87 g, 15.0 mmol), 4-(*tert*-butyl)phenol (4.95 g, 33.0 mmol), and potassium carbonate (8.30 g, 60.0 mmol) were taken sequentially and added to a 250 ml three-necked round-bottomed flask. Then 100 ml of anhydrous NMP was added, and then the nitrogen was pumped out for ten minutes and replaced three times with nitrogen. Subsequently, the temperature was increased to 160°C under a nitrogen atmosphere, the condensate was adjusted to keep the reaction reflux rate appropriate, and the reaction was continued to be stirred for 18 h. The resulting solution was extracted with ethyl acetate/water, and the organic layer was concentrated under vacuum. The product was purified by column chromatography using a mixture eluent of dichloromethane: petroleum ether (1:10), resulting in a white solid (5.76 g, 85% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 4H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.00 – 6.93 (m, 4H), 6.67 (d, *J* = 8.2 Hz, 2H), 1.33 (s, 18H). HRMS (APCI): Theoretical value: C<sub>26</sub>H<sub>29</sub>BrO<sub>2</sub>, 452.14; Experimental value: 453.14, [M+H]<sup>+</sup>.

**Synthesis of 1c:** The synthetic pathway of **1c** is the same as that of **1b**. Only replace 2-bromo-1,3-difluorobenzene with an equimolar amount of 1-bromo-3,5-difluorobenzene. The experimental operation and post-treatment were consistent with the same column chromatographic separation using dichloromethane: petroleum ether (1:10) as eluent to give a white solid (5.15 g, 76% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 4H), 6.99 – 6.93 (m, 4H), 6.80 (d, *J* = 2.2 Hz, 2H), 6.58 (t, *J* = 2.2 Hz, 1H), 1.33 (s, 18H). HRMS (APCI): Theoretical value: C<sub>26</sub>H<sub>29</sub>BrO<sub>2</sub>, 452.14; Experimental value: 453.14, [M+H]<sup>+</sup>.

#### Synthesis of *o*-10-DtCzBN

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**DtCzB-Bpin** (2.30 g, 3.0 mmol), compound (**1a**) (1.10 g, 3.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (173 mg, 0.15 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.5 mmol) were added to a mixture of toluene (30 mL), ethanol (12 mL), and water (6 mL). The mixture was bubbled with nitrogen for 15 minutes and refluxed for 24 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and water, and the combined organic layer was condensed in vacuum, and then the crude product was purified by column chromatography with a mixture eluent of dichloromethane: petroleum ether (1:5), resulting in a yellow solid (2.0 g, 78% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 1.9 Hz, 1H), 8.63 (s, 1H), 8.47 (d, *J* = 1.8 Hz, 1H), 8.39 (d, *J* = 8.7 Hz, 1H), 8.26 (d, *J* = 2.0 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.18 – 7.10 (m, 1H), 1.69 (s, 7H), 1.56 (dd, *J* = 11.5, 5.1 Hz, 2H), 1.53 (s, 9H), 1.31 (s, 5H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 145.15, 144.56, 144.05, 141.77, 138.33, 131.55, 129.80, 129.43, 126.99, 126.70, 124.28, 123.99, 123.64, 120.62, 119.85, 118.35, 117.20, 114.22, 109.33, 35.20, 34.78, 32.23, 31.87, 31.55. HRMS (APCI): Theoretical value: C<sub>62</sub>H<sub>65</sub>BN<sub>2</sub>O, 864.52; Experimental value: 865.52, [M+H]<sup>+</sup>.

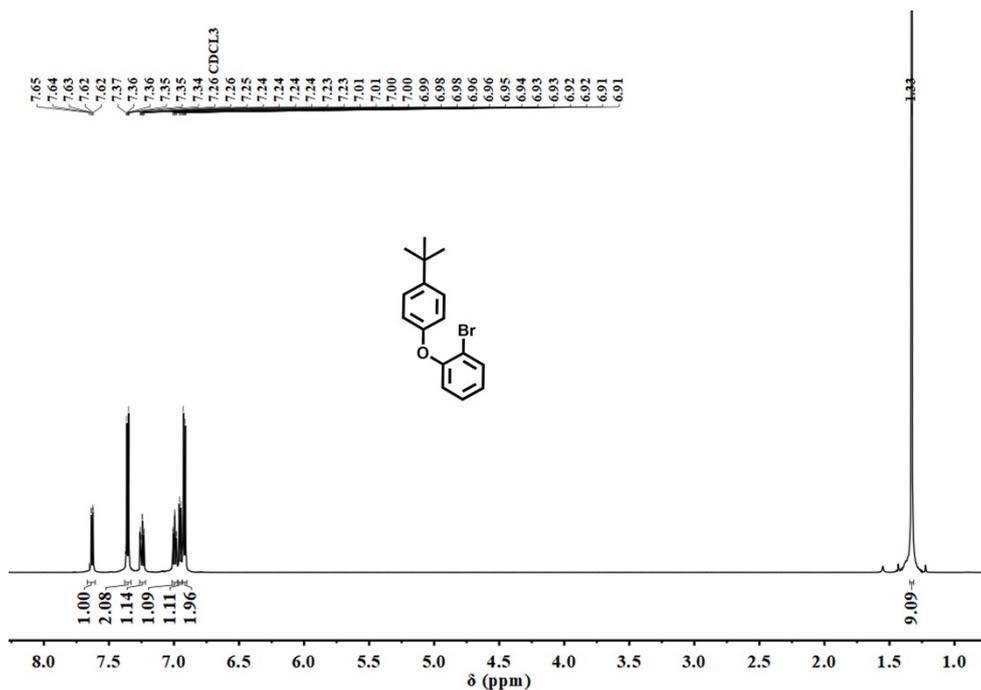
#### Synthesis of *o*-2O-DtCzBN

The synthetic pathway of *o*-2O-DtCzBN is the same as that of *o*-1O-DtCzBN. Only replace **1a** with an equimolar amount of **1b**. The experimental operation and post-treatment were consistent with the same column chromatographic separation using dichloromethane: petroleum ether (1:5) as eluent to give a yellow solid (1.8 g, 61% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.09 (d, *J* = 1.9 Hz, 2H), 8.48 (s, 2H), 8.44 (d, *J* = 1.8 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 2.1 Hz, 2H), 7.48 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.38 (t, *J* = 8.3 Hz, 1H), 7.28 – 7.23 (m, 5H), 6.98 (dd, *J* = 8.6, 3.0 Hz, 6H), 1.66 (s, 17H), 1.52 (s, 17H), 1.19 (s, 16H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 156.11, 155.20, 145.86, 144.92, 144.41, 143.39, 141.67, 138.34, 129.73, 129.28, 126.88, 126.48, 124.09, 123.56, 120.48, 117.99, 117.08, 114.98, 114.19, 110.79, 35.16, 34.76, 34.19, 32.22, 31.88, 31.41. HRMS (APCI): Theoretical value: C<sub>72</sub>H<sub>77</sub>BN<sub>2</sub>O<sub>2</sub>, 1012.61; Experimental value: 1013.61, [M+H]<sup>+</sup>.

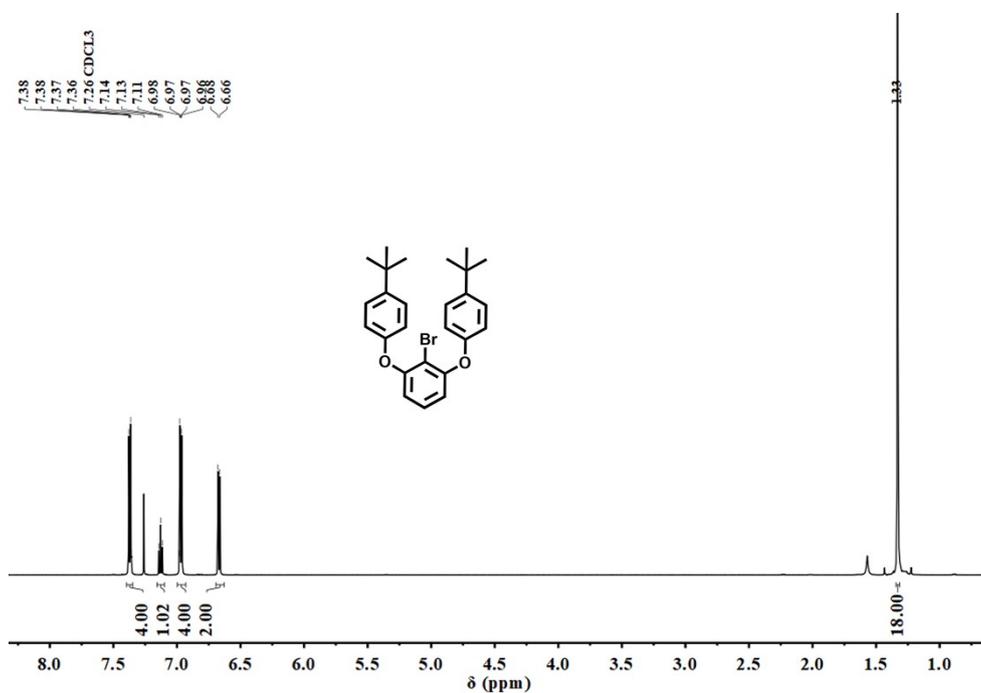
#### Synthesis of *m*-2O-DtCzBN

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The synthetic pathway of ***m*-2O-DtCzBN** is the same as that of ***o*-1O-DtCzBN**. Only replace **1a** with an equimolar amount of **1c**. The experimental operation and post-treatment were consistent with the same column chromatographic separation using dichloromethane: petroleum ether (1:5) as eluent to give a yellow solid (2.6 g, 87% yield). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 1.9 Hz, 2H), 8.46 (d, *J* = 1.8 Hz, 2H), 8.43 (s, 2H), 8.35 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 2.0 Hz, 2H), 7.67 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.28 (d, *J* = 2.2 Hz, 3H), 7.18 – 7.12 (m, 4H), 6.80 (t, *J* = 2.2 Hz, 1H), 1.67 (s, 18H), 1.55 (s, 19H), 1.33 (s, 18H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 156.11, 155.20, 145.86, 144.92, 144.41, 143.39, 141.67, 138.34, 129.73, 129.28, 126.88, 126.48, 124.09, 123.56, 120.48, 117.99, 117.08, 114.98, 114.19, 110.79, 35.16, 34.76, 34.19, 32.22, 31.88, 31.41. HRMS (APCI): Theoretical value: C<sub>72</sub>H<sub>77</sub>BN<sub>2</sub>O<sub>2</sub>, 1012.61; Experimental value: 1013.61, [M+H]<sup>+</sup>.



**Figure S1.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .



**Figure S2.**  $^1\text{H}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .

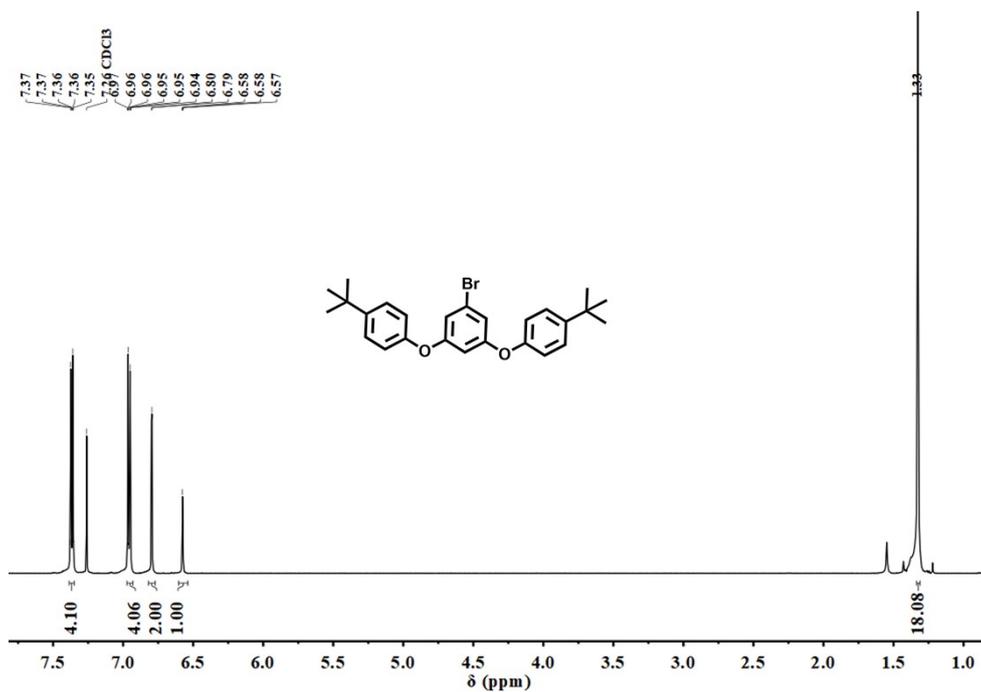


Figure S3. <sup>1</sup>H NMR spectrum of **1c** in CDCl<sub>3</sub>.

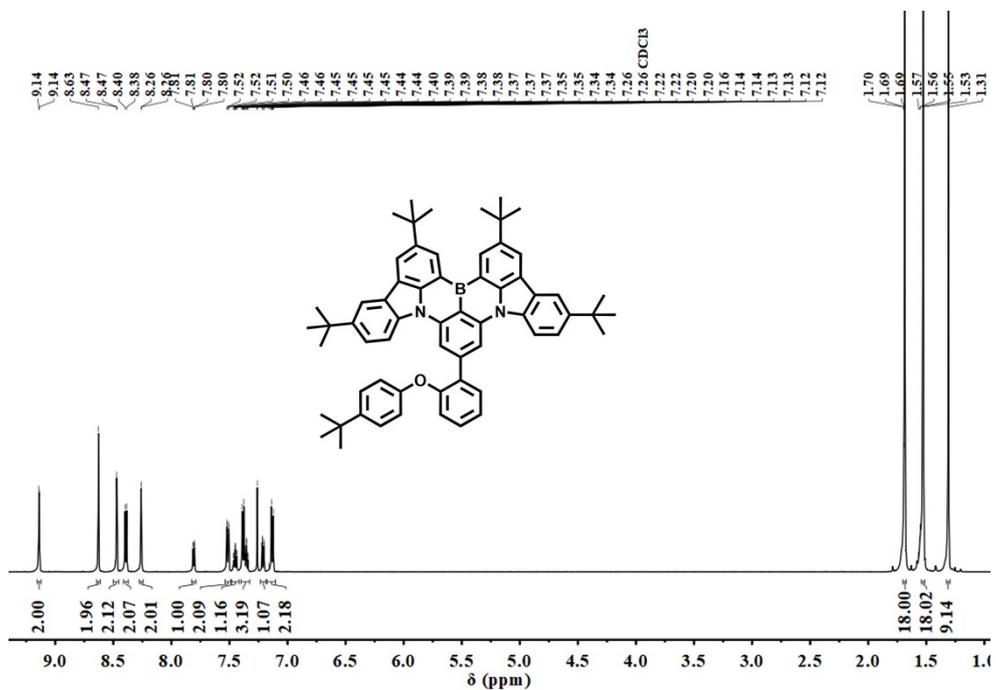


Figure S4. <sup>1</sup>H NMR spectrum of **o-10-DtCzBN** in CDCl<sub>3</sub>.

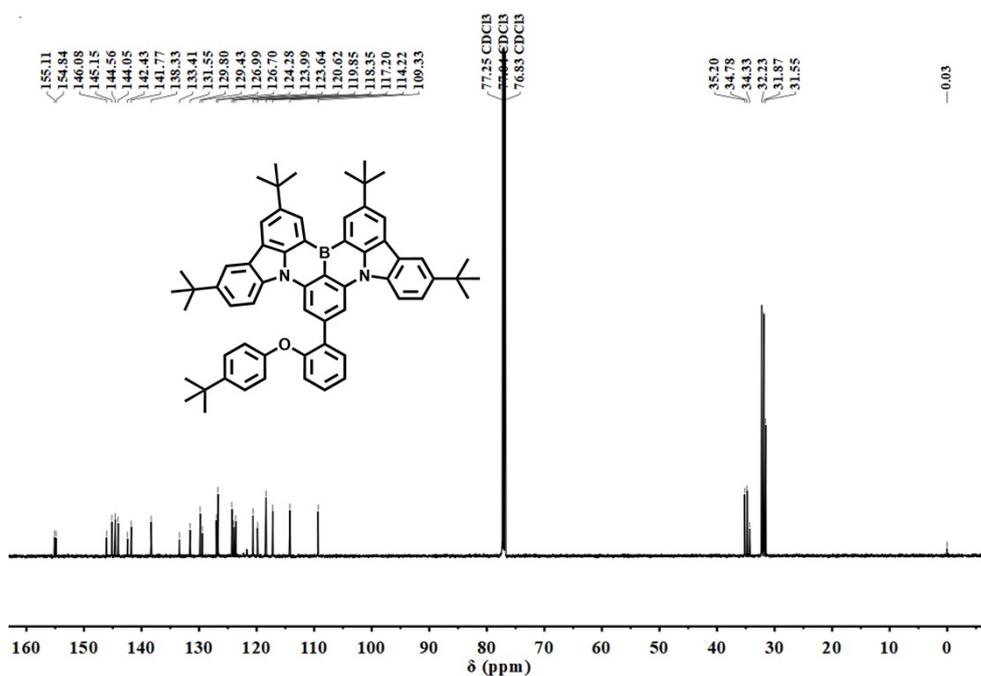


Figure S5. <sup>13</sup>C NMR spectrum of *o*-10-DtCzBN in CDCl<sub>3</sub>.

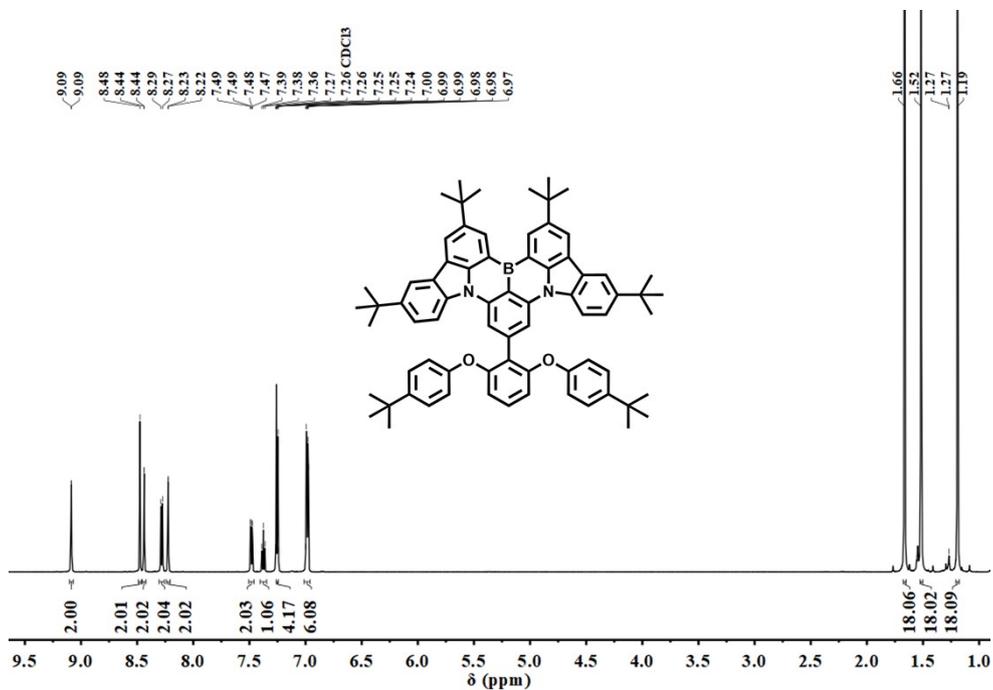


Figure S6. <sup>1</sup>H NMR spectrum of *o*-20-DtCzBN in CDCl<sub>3</sub>.

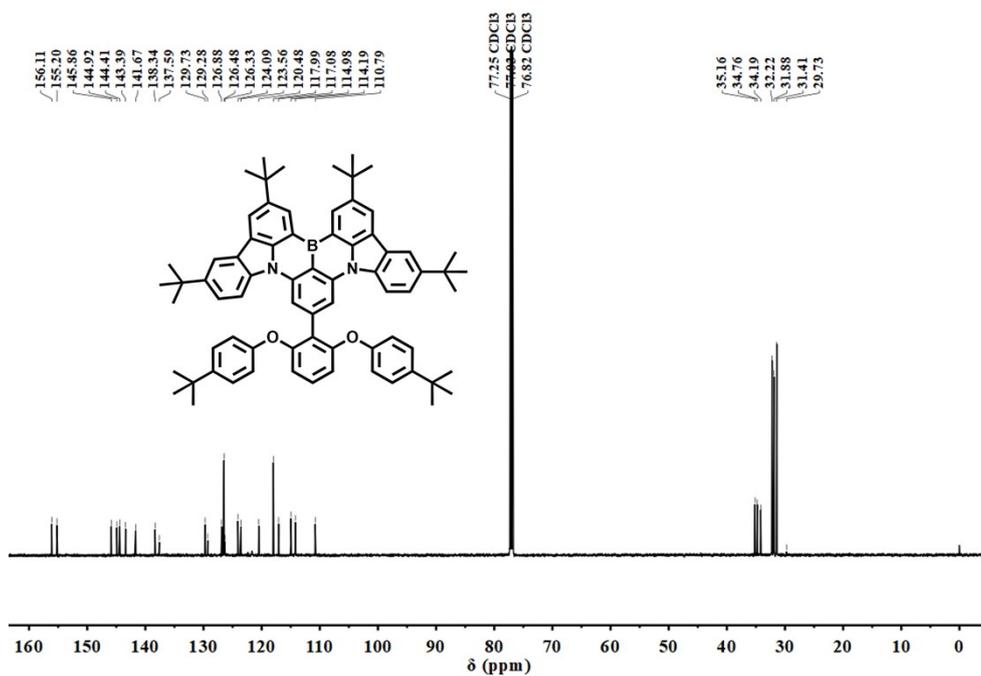


Figure S7. <sup>13</sup>C NMR spectrum of *o*-2O-DtCzBN in CDCl<sub>3</sub>.

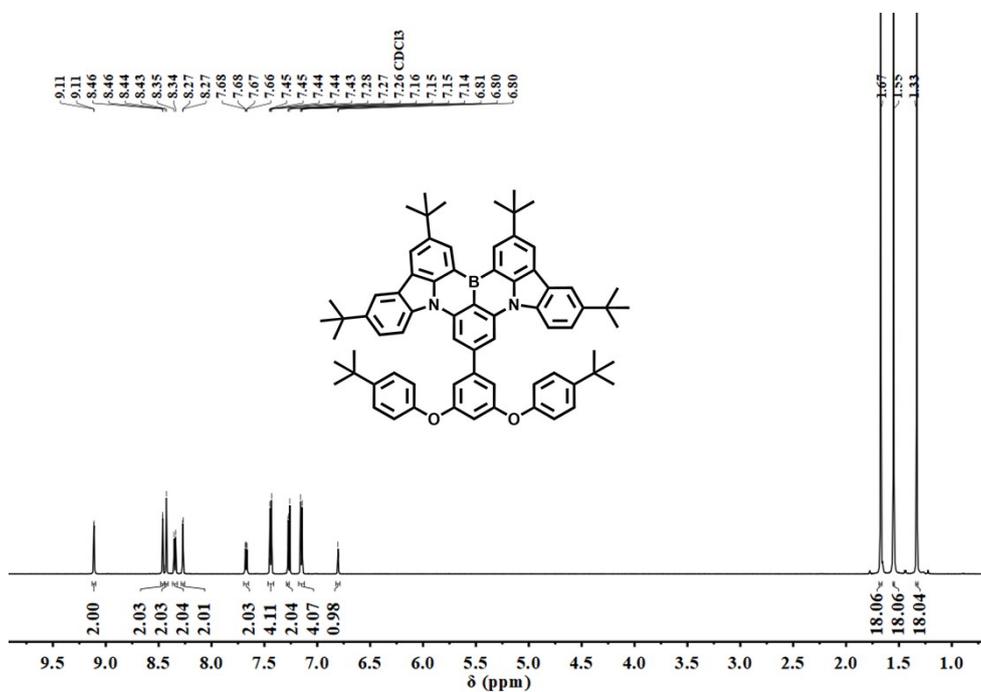


Figure S8. <sup>1</sup>H NMR spectrum of *m*-2O-DtCzBN in CDCl<sub>3</sub>.

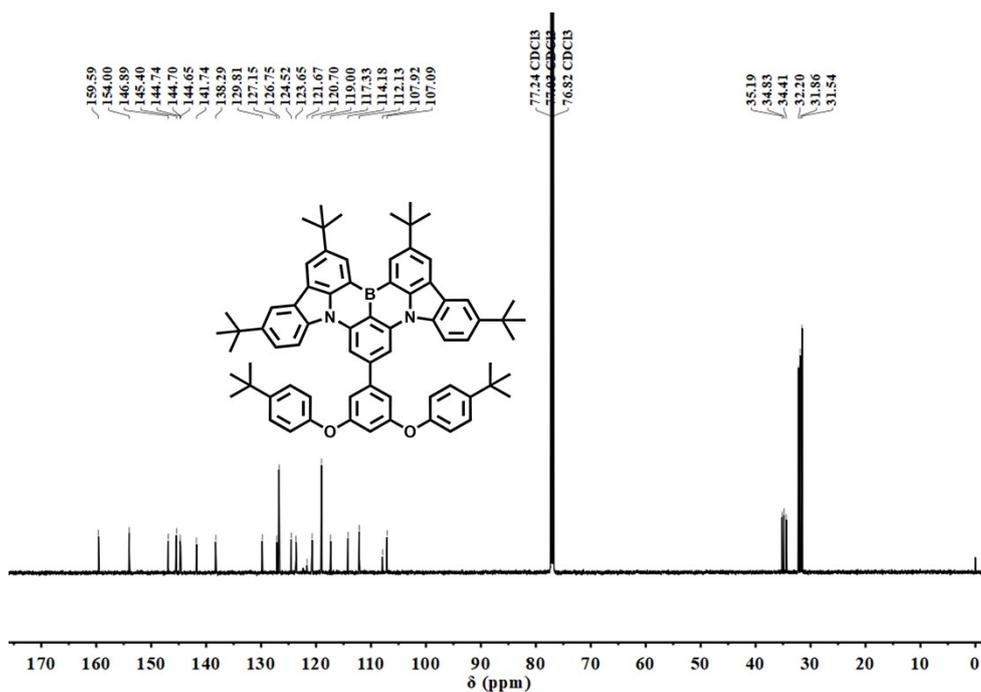


Figure S9.  $^{13}\text{C}$  NMR spectrum of *m*-2O-DtCzBN in  $\text{CDCl}_3$ .

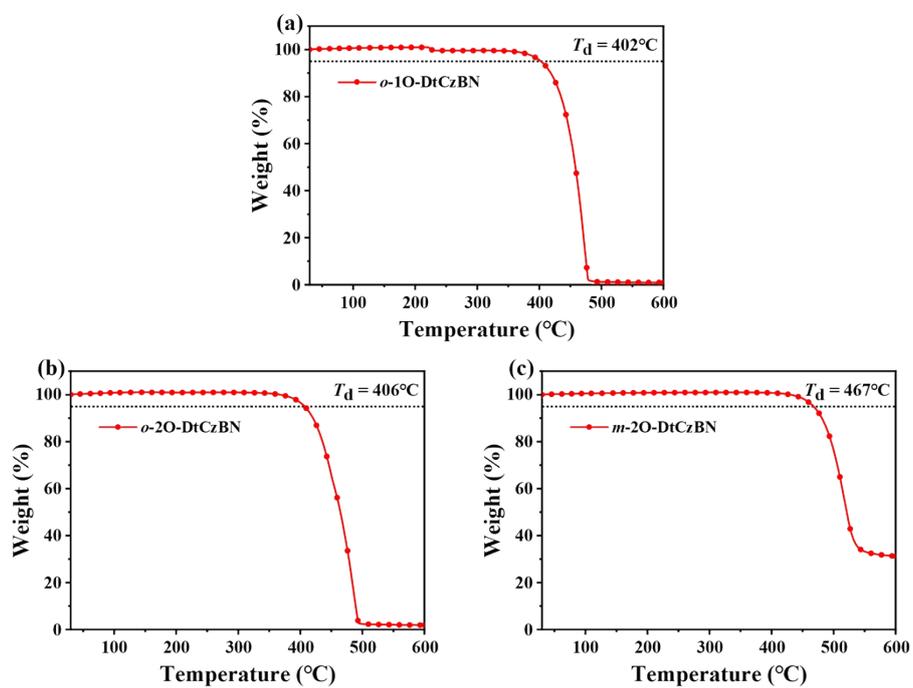
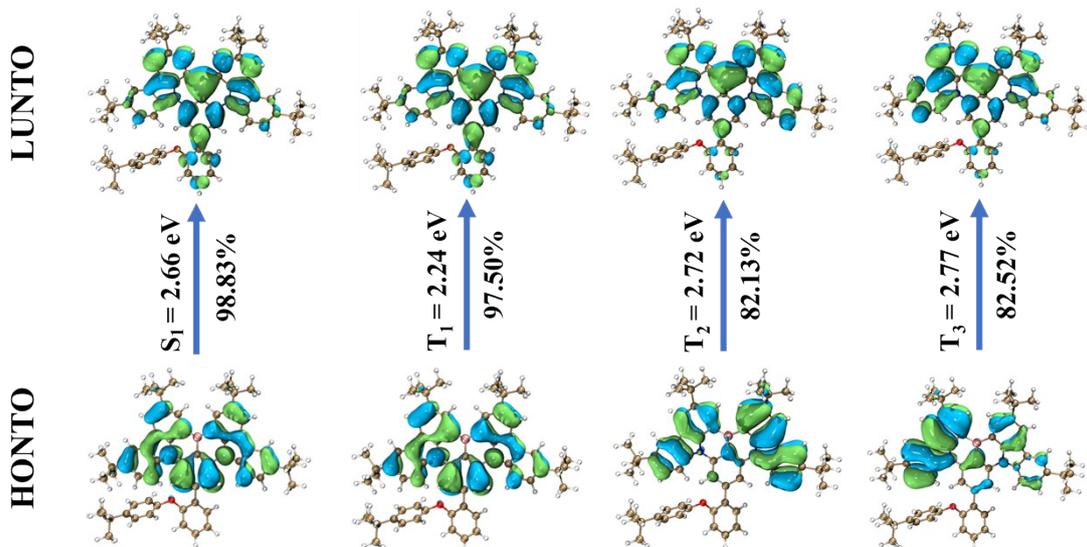
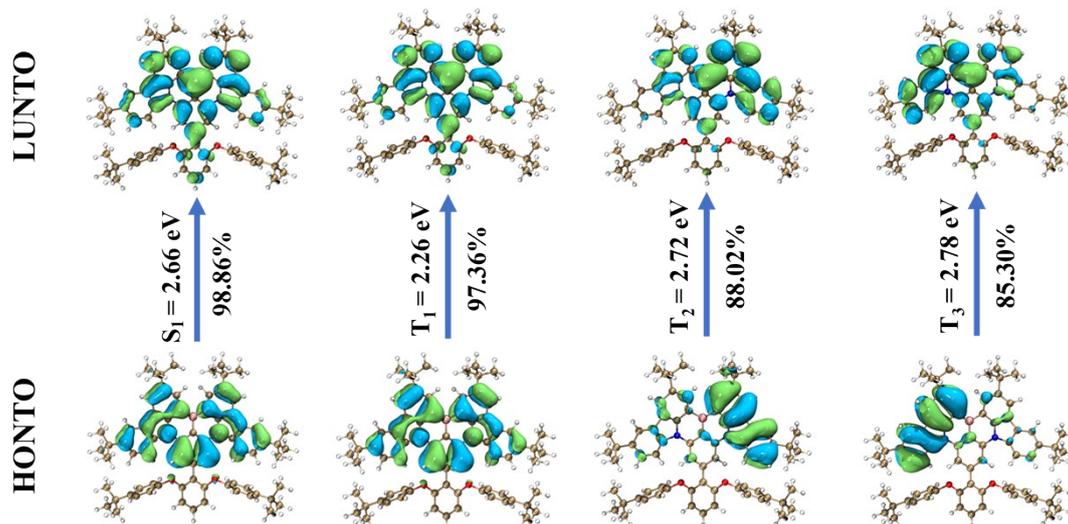


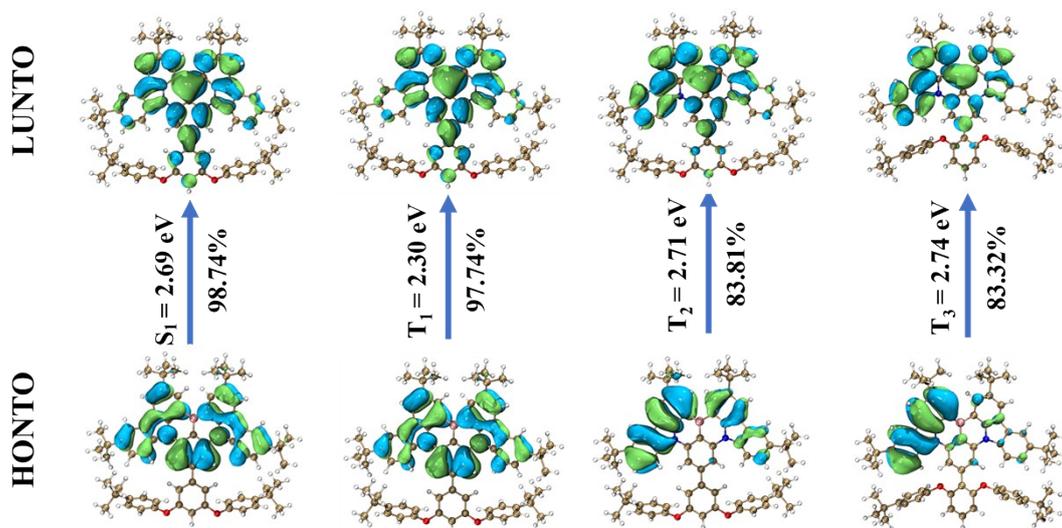
Figure S10. TGA curves of (a) *o*-1O-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN.



**Figure S11.** Natural transition orbitals (NTOs) describing the excitation characters of the S<sub>1</sub>, T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub> states in *o*-10-DtCzBN; the weights of the hole-electron contributions to the excitations are included.



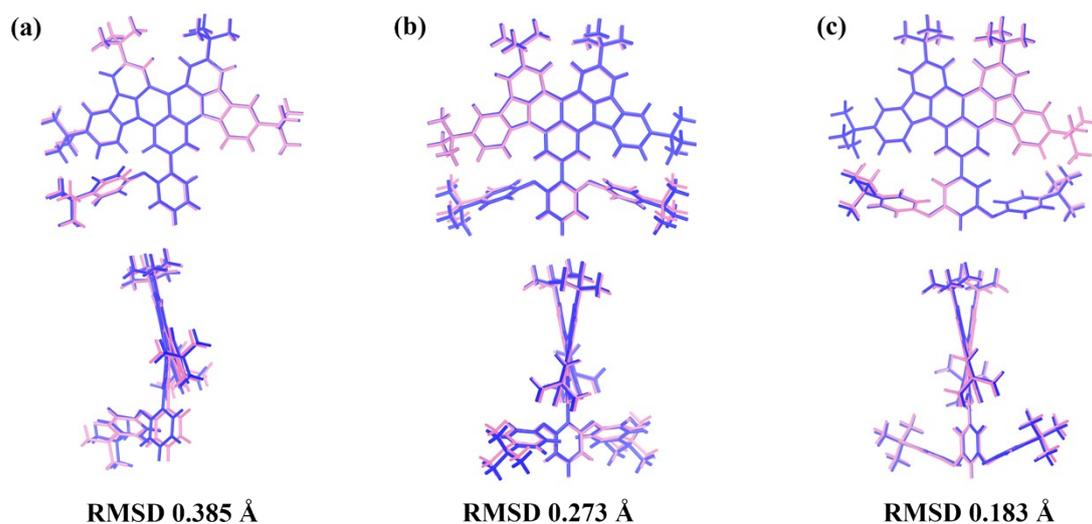
**Figure S12.** Natural transition orbitals (NTOs) describing the excitation characters of the S<sub>1</sub>, T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub> states in *o*-20-DtCzBN; the weights of the hole-electron contributions to the excitations are included.



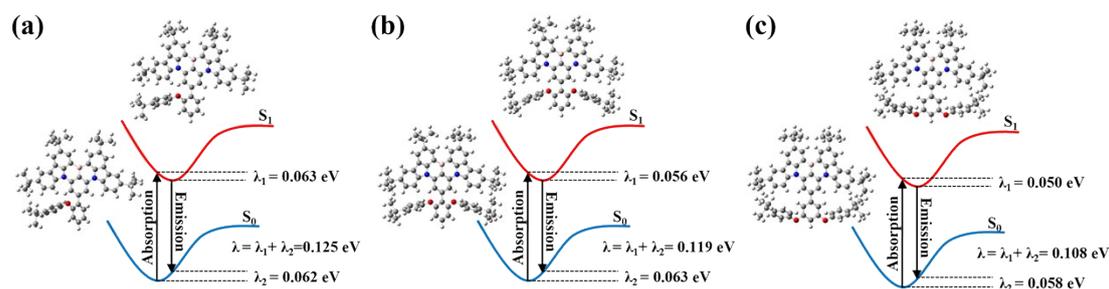
**Figure S13.** Natural transition orbitals (NTOs) describing the excitation characters of the  $S_1$ ,  $T_1$ ,  $T_2$ , and  $T_3$  states in *m*-2O-DtCzBN; the weights of the hole-electron contributions to the excitations are included.

**Table S1.** Spin-orbit coupling (SOC) matrix elements between the low-lying singlet and triplet excited states of the fluorophores with all values reported in  $\text{cm}^{-1}$

SOC	<i>o</i> -1O-DtCzBN	<i>o</i> -2O-DtCzBN	<i>m</i> -2O-DtCzBN
$S_1$ - $T_1$	0.043	0.020	0.028
$S_1$ - $T_2$	0.083	0.061	0.050
$S_1$ - $T_3$	0.128	0.108	0.124



**Figure S14.** The root mean squared displacement (RMSD) of (a) *o*-10-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN between optimized S<sub>0</sub> (blue) and S<sub>1</sub> (pink) geometries.



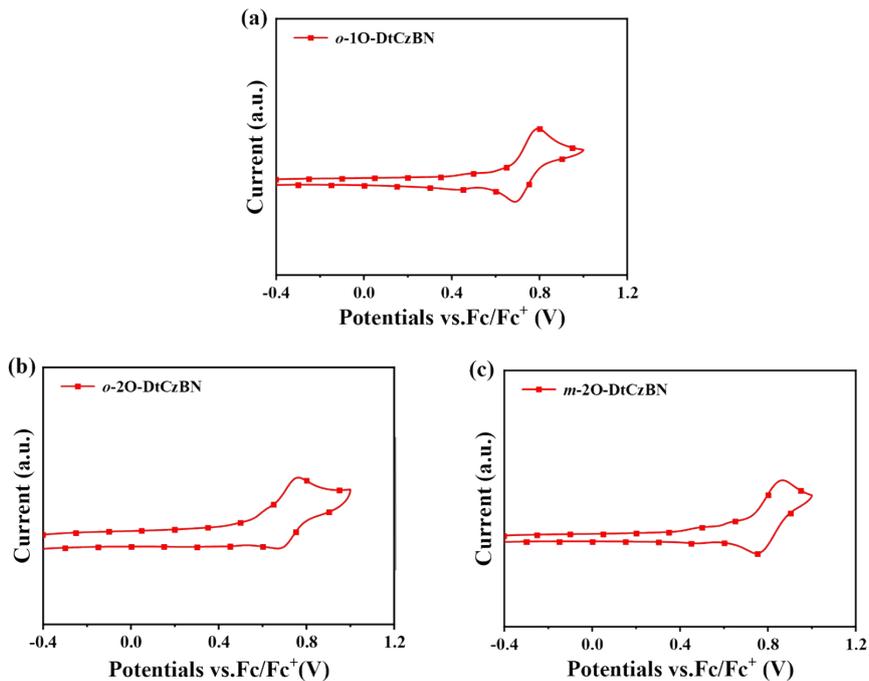
**Figure S15.** The reorganization energies with optimized S<sub>0</sub> and S<sub>1</sub> geometries of (a) *o*-10-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN.

**Table S2.** Summary of the physical properties of *o*-10-DtCzBN, *o*-2O-DtCzBN, and *m*-2O-DtCzBN.

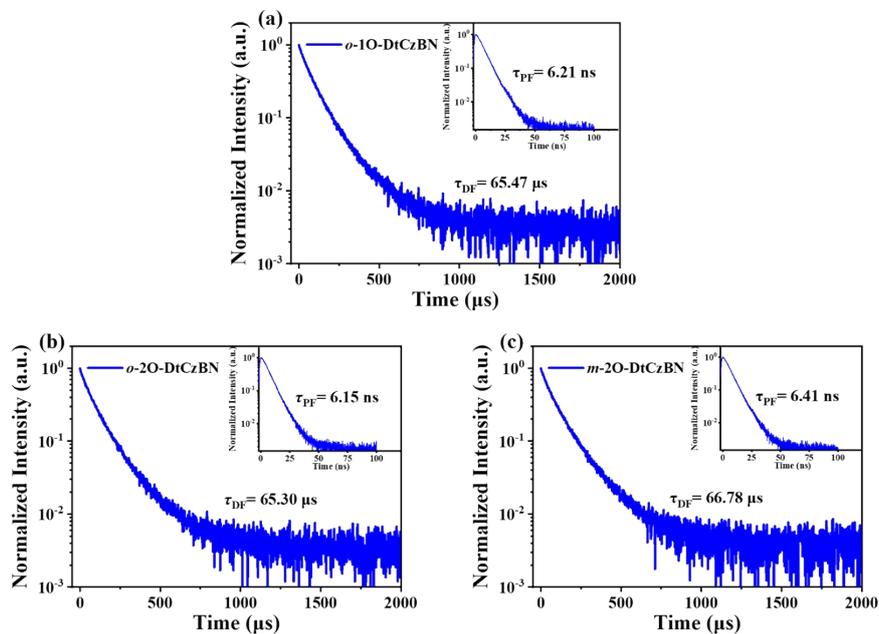
Emitter	$E_{S1}^{a)}$ (eV)	$E_{T1}^{b)}$ (eV)	$\Delta E_{ST}^{c)}$ (eV)	$E_g^{d)}$ (eV)	HOMO <sup>e)</sup> (eV)	LUMO <sup>f)</sup> (eV)
<i>o</i> -10-DtCzBN	2.39	2.26	0.13	2.52	-5.37	-2.85
<i>o</i> -2O-DtCzBN	2.39	2.26	0.13	2.51	-5.28	-2.77
<i>m</i> -2O-DtCzBN	2.40	2.27	0.13	2.52	-5.39	-2.86

<sup>a)</sup> Singlet energy estimated from the onset of the fluorescence spectrum ( $10^{-5}$  M, 300 K). <sup>b)</sup> Triplet energy estimated from the onset of the phosphorescence spectrum in a frozen toluene matrix ( $10^{-5}$  M, 77 K). <sup>c)</sup>  $\Delta E_{ST} = E_{S1} - E_{T1}$ .

<sup>d)</sup> Optical band gap estimated from the absorption edge of the UV-vis spectrum. <sup>e)</sup> Determined from cyclic voltammetry using the formula:  $E_{HOMO} = -(E_{ox} + 4.8)$  eV. <sup>f)</sup>  $E_{LUMO} = E_{HOMO} + E_g$ .



**Figure S16.** Cyclic Voltammetry (CV) curves of (a) *o*-1O-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN.

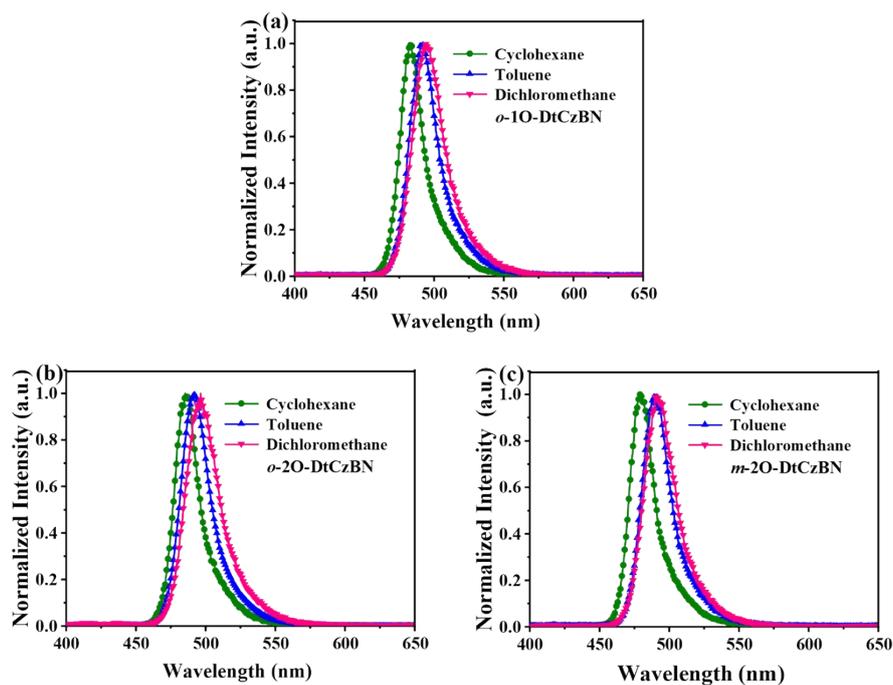


**Figure S17.** Transient photoluminescence decay profiles of (a) *o*-1O-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN in oxygen-free toluene ( $10^{-5}$  M).

**Table S3.** Summary of the photophysical properties of *o*-10-DtCzBN, *o*-20-DtCzBN, and *m*-20-DtCzBN in oxygen-free toluene ( $1.0 \times 10^{-5}$  M).

Emitter	$\Phi_{\text{PL}}^{\text{a}}$ [%]	$\Phi_{\text{P}}^{\text{a}}$ [%]	$\Phi_{\text{D}}^{\text{a}}$ [%]	$\tau_{\text{p}}^{\text{b}}$ (ns)	$\tau_{\text{d}}^{\text{b}}$ ( $\mu\text{s}$ )	$k_{\text{F}}^{\text{c}}$ ( $10^8 \text{ s}^{-1}$ )	$k_{\text{IC}}^{\text{c}}$ ( $10^5 \text{ s}^{-1}$ )	$k_{\text{ISC}}^{\text{c}}$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{RISC}}^{\text{c}}$ ( $10^4 \text{ s}^{-1}$ )
<i>o</i> -10-DtCzBN	99.6	73.5	26.1	6.21	65.47	1.18	4.75	4.22	2.07
<i>o</i> -20-DtCzBN	99.3	75.6	23.7	6.15	65.30	1.23	8.67	3.88	2.01
<i>m</i> -20-DtCzBN	98.8	76.2	22.6	6.41	66.78	1.19	14.4	3.57	1.94

<sup>a)</sup> The total photoluminescence quantum yield ( $\Phi_{\text{PL}}$ ), prompt ( $\Phi_{\text{P}}$ ) and delayed ( $\Phi_{\text{D}}$ ) fluorescent component of  $\Phi$ ; <sup>b)</sup> The lifetime of prompt fluorescence ( $\tau_{\text{p}}$ ) and delayed fluorescence ( $\tau_{\text{d}}$ ); <sup>c)</sup> The rate constant of radiative decay ( $k_{\text{F}}$ ), internal conversion ( $k_{\text{IC}}$ ), intersystem crossing ( $k_{\text{ISC}}$ ) and reverse intersystem crossing ( $k_{\text{RISC}}$ ).

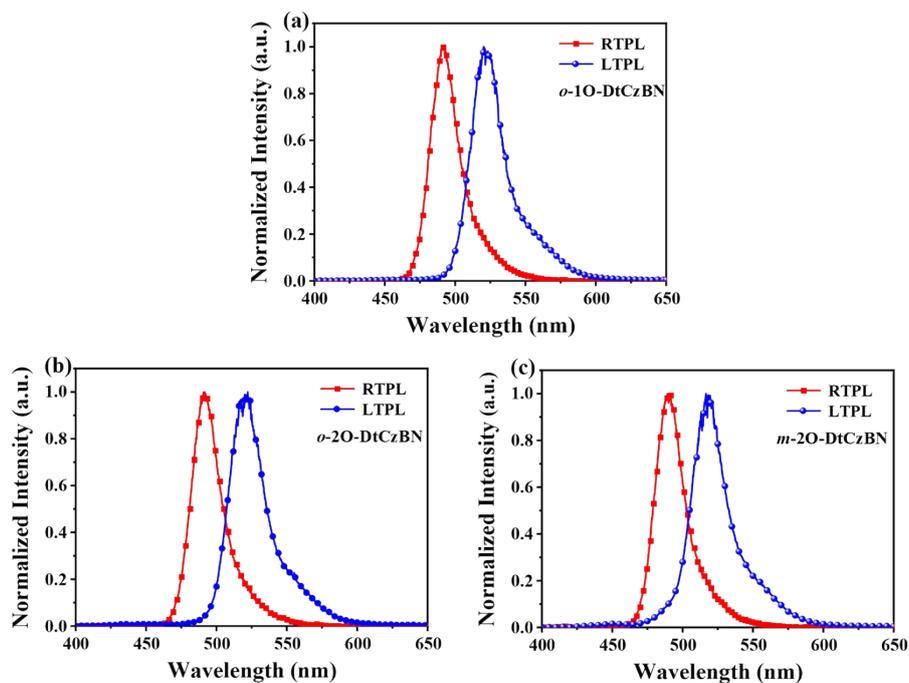


**Figure S18.** The fluorescence (FL, room temperature) spectra of (a) *o*-10-DtCzBN, (b) *o*-20-DtCzBN, and (c) *m*-20-DtCzBN in different solvents ( $1.0 \times 10^{-5}$  M).

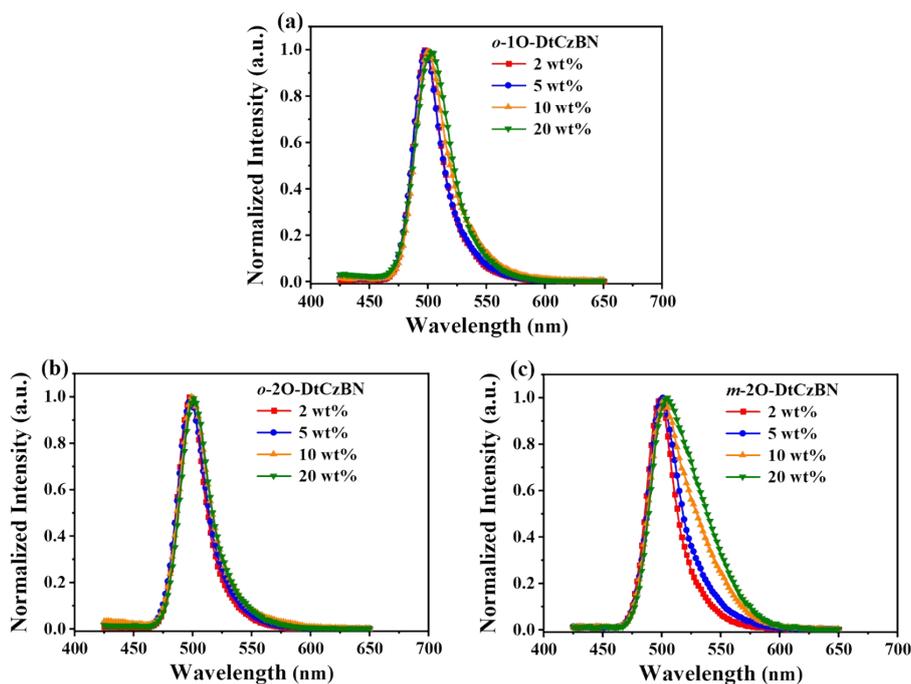
**Table S4.** The photophysical data of *o*-10-DtCzBN, *o*-20-DtCzBN, and *m*-20-DtCzBN in different solvents ( $1.0 \times 10^{-5}$  M).

Emitter	Fluorescence	Cyclohexane	Toluene	Dichloromethane
<i>o</i> -10-DtCzBN	$\lambda^a_{em}$ (nm)	483	491	494
	FWHM <sup>b</sup> (nm)	20	24	27
<i>o</i> -20-DtCzBN	$\lambda^a_{em}$ (nm)	485	492	496
	FWHM <sup>b</sup> (nm)	20	24	27
<i>m</i> -10-DtCzBN	$\lambda^a_{em}$ (nm)	479	491	492
	FWHM <sup>b</sup> (nm)	21	24	26

<sup>a</sup>) The peak wavelength of the PL spectrum. <sup>b</sup>) Full width at half maximum.



**Figure S19.** Normalized room temperature photoluminescence (RTPL) and low temperature phosphorescence (LTPL) in toluene solution for (a) *o*-10-DtCzBN, (b) *o*-20-DtCzBN, and (c) *m*-20-DtCzBN.

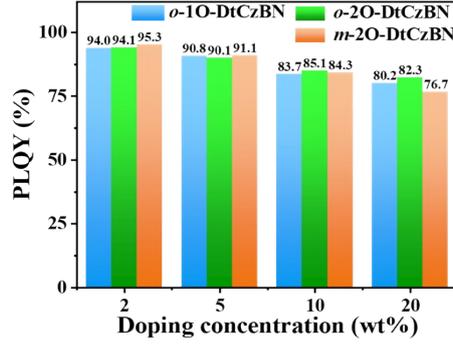


**Figure S20.** Photoluminescence spectra of (a) *o*-1O-DtCzBN, (b) *o*-2O-DtCzBN, and (c) *m*-2O-DtCzBN in the different doping concentrations.

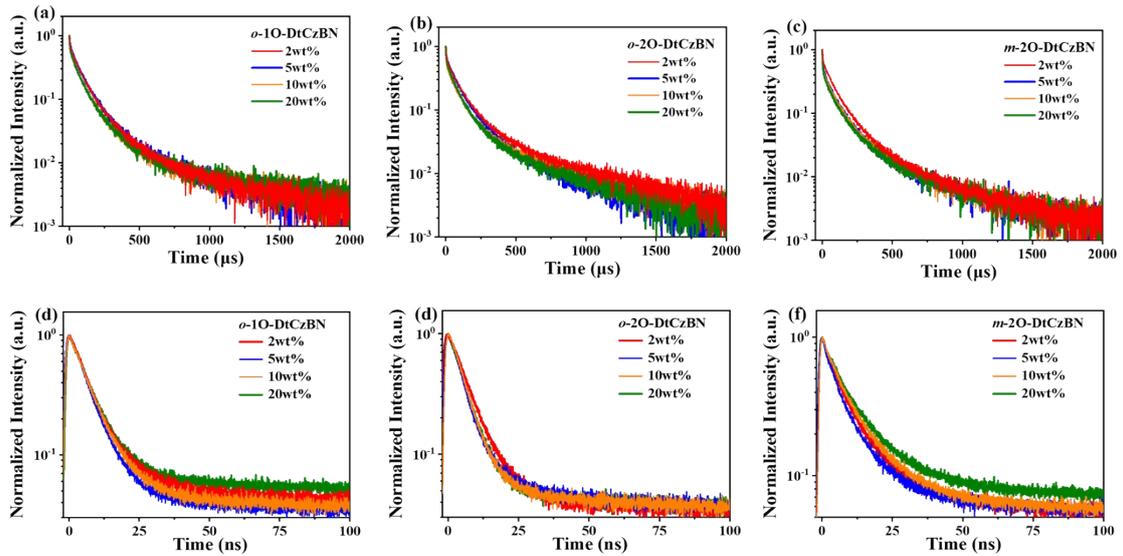
**Table S5.** Summary of the photophysical properties of *o*-1O-DtCzBN, *o*-2O-DtCzBN, and *m*-2O-DtCzBN in different doping concentrations.

Emitter	doping (wt%)	$\lambda_{em}^a$ (nm)	FWHM <sup>b</sup> (nm)	$\Phi_{PL}^c$ (%)	$\tau_p^c$ (ns)	$\tau_d^c$ ( $\mu$ s)	$k_F^c$ ( $10^7 s^{-1}$ )	$k_{IC}^c$ ( $10^6 s^{-1}$ )	$k_{ISC}^c$ ( $10^7 s^{-1}$ )	$k_{RISC}^c$ ( $10^4 s^{-1}$ )
<b><i>o</i>-1O-DtCzBN</b>	2	497	28	94.0	6.60	78.41	10.2	6.48	4.35	1.79
	5	498	29	90.8	6.49	75.22	11.8	12.0	2.41	1.58
	10	500	31	83.7	6.44	74.38	10.9	21.3	2.49	1.60
	20	502	34	80.2	6.60	71.87	9.39	23.2	3.44	1.80
<b><i>o</i>-2O-DtCzBN</b>	2	497	27	94.1	6.48	79.03	10.2	6.40	4.59	1.80
	5	498	27	90.1	5.16	78.79	13.9	15.2	3.98	1.60
	10	499	29	85.1	5.17	74.29	13.3	23.3	3.73	1.67
	20	500	29	82.3	5.40	72.61	11.1	23.9	5.00	1.89
<b><i>m</i>-2O-DtCzBN</b>	2	498	27	95.3	8.50	86.57	8.13	4.01	3.23	1.59
	5	501	31	91.1	7.53	83.58	9.54	9.32	2.81	1.52
	10	502	42	84.3	9.27	81.90	7.39	13.8	2.02	1.50
	20	505	50	76.7	10.22	77.15	5.57	16.9	2.53	1.75

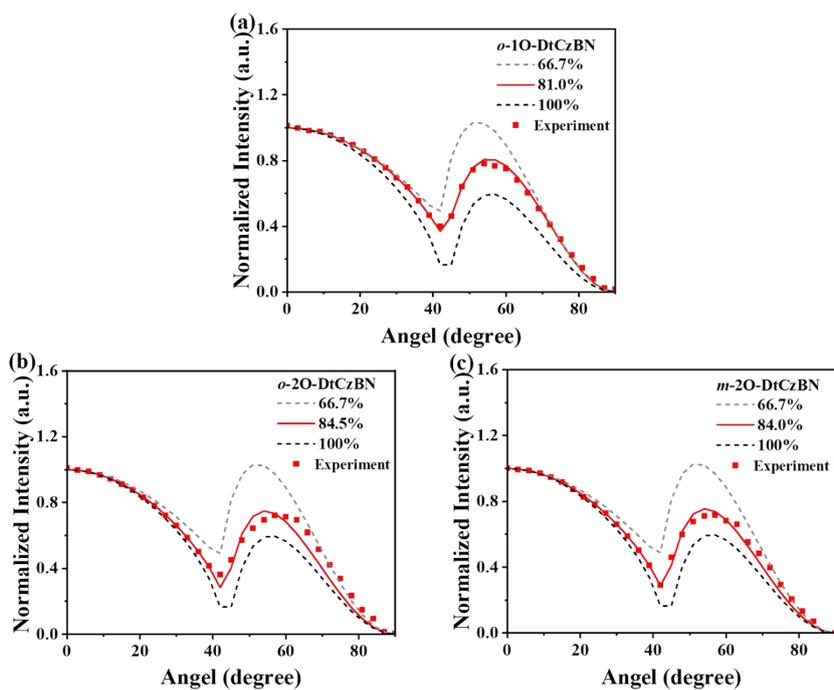
<sup>a</sup>) Peak of PL spectra measured in mCBP host-blended film; <sup>b</sup>) Full width at half maximum of the PL spectra measured in the mCBP host-blended film; <sup>c</sup>) The total photoluminescence quantum yield ( $\Phi_{PL}$ ), the lifetime of prompt fluorescence ( $\tau_p$ ) and delayed fluorescence ( $\tau_d$ ) and the rate constant of radiative decay ( $k_F$ ), internal conversion ( $k_{IC}$ ), intersystem crossing ( $k_{ISC}$ ) and reverse intersystem crossing ( $k_{RISC}$ ) measured in mCBP film.



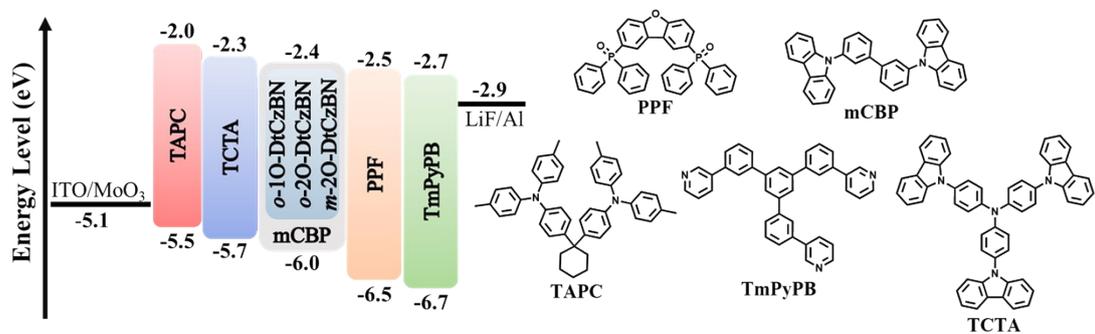
**Figure S21.**  $\Phi_{\text{PL}}$  values of *o*-1O-DtCzBN, *o*-2O-DtCzBN, and *m*-2O-DtCzBN doped films (2-20 wt% in *m*CBP) versus doping concentration.



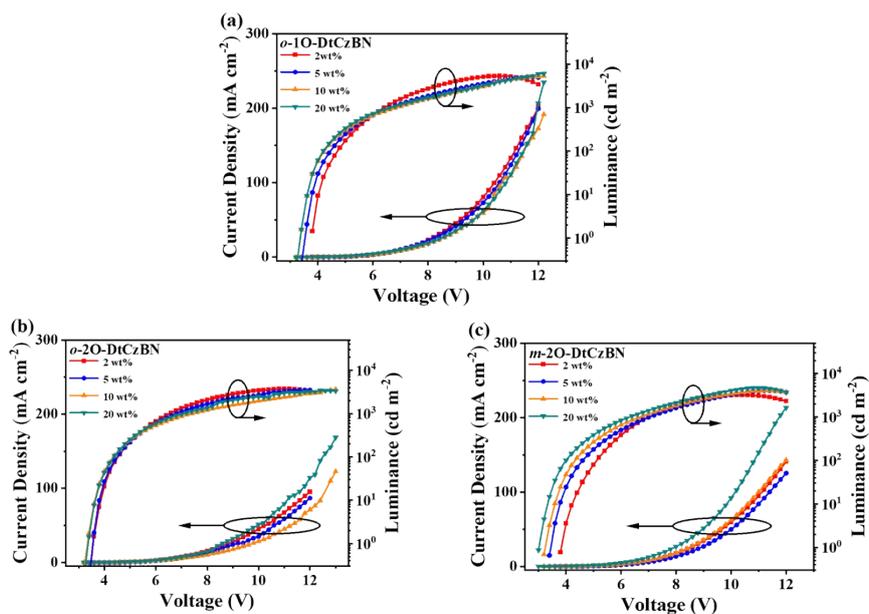
**Figure S22.** Transient PL decay curves of *o*-1O-DtCzBN, *o*-2O-DtCzBN, and *m*-2O-DtCzBN doped films at different doping concentrations (2-20 wt% in *m*CBP): (a-c) delayed fluorescence (DF) at microsecond scale, (d-f) prompt fluorescence (PF) decay at nanosecond scale.



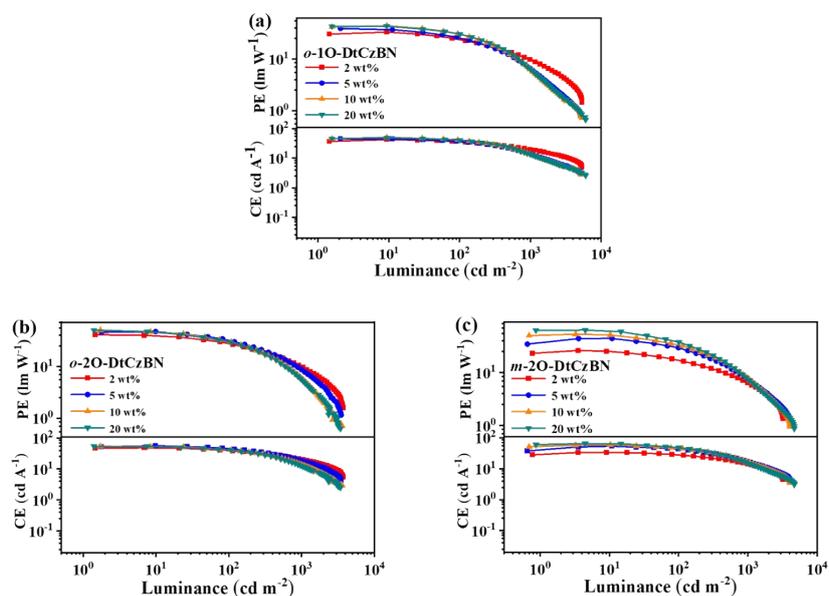
**Figure S23.** Angle-dependent PL spectra of the three emitters in 5wt% *m*CBP host films.



**Figure S24.** The device configuration of the investigated OLEDs and the materials used in the device.



**Figure S25.**  $J$ - $V$ - $L$  curves of devices with the configuration of [ITO/MoO<sub>3</sub> (5 nm)/TAPC (30 nm)/TCTA (10 nm)/mCBP: $x$  wt% (a) *o*-10-DtCzBN, (b) *o*-20-DtCzBN, and (c) *m*-20-DtCzBN (20 nm)/PPF (10 nm)/TmPyPB (30 nm)/LiF (1 nm)/Al (100 nm)] ( $x$  = 2, 5, 10, 20)].



**Figure S26.** CE- $L$  and PE- $L$  curves of devices with the configuration of [ITO/MoO<sub>3</sub> (5 nm)/TAPC (30 nm)/TCTA (10 nm)/mCBP: $x$  wt% (a) *o*-10-DtCzBN, (b) *o*-20-DtCzBN, and (c) *m*-20-DtCzBN (20 nm)/PPF (10 nm)/TmPyPB (30 nm)/LiF (1 nm)/Al (100 nm)] ( $x$  = 2, 5, 10, 20)].

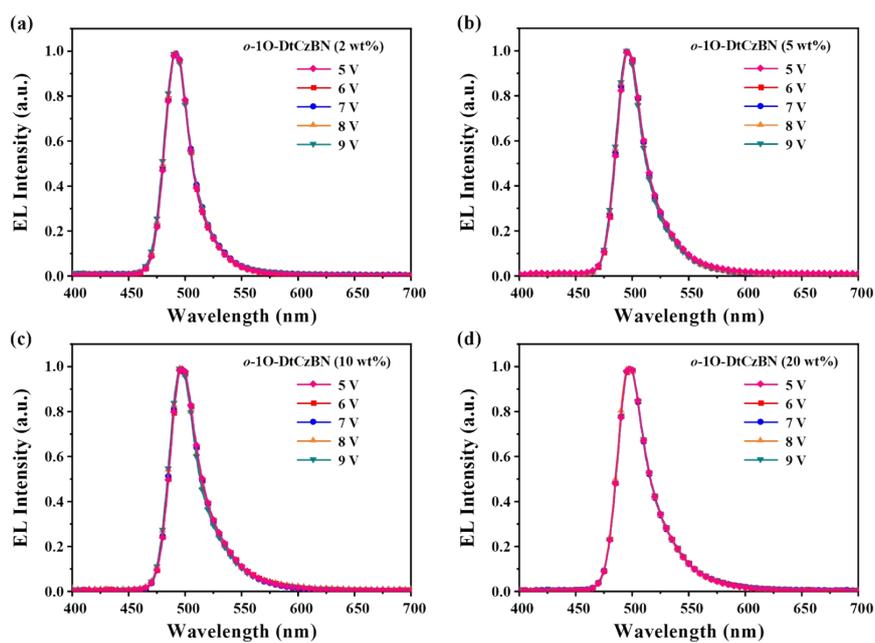


Figure S27. EL spectra of devices based on *o*-10-DtCzBN taken at various voltages from 5 to 9 V.

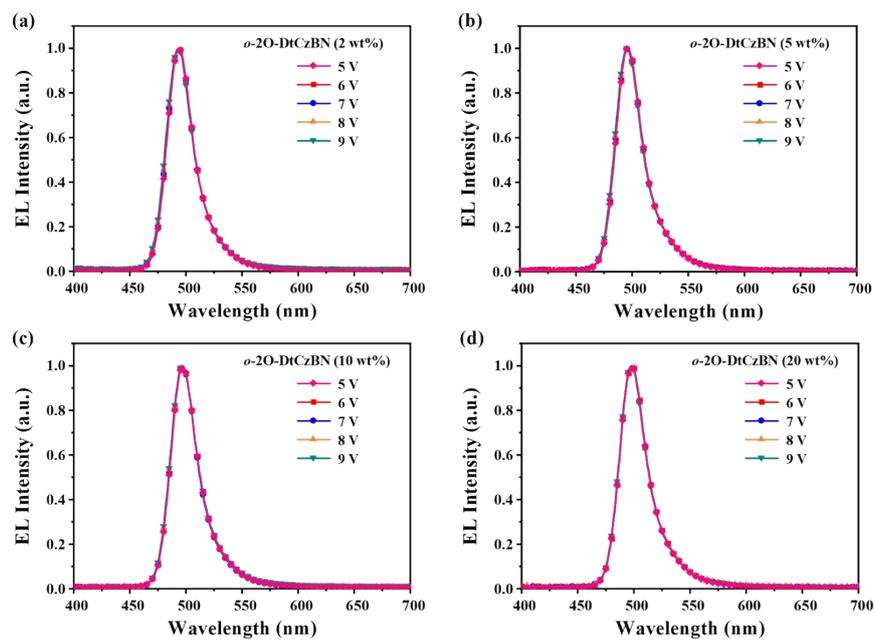
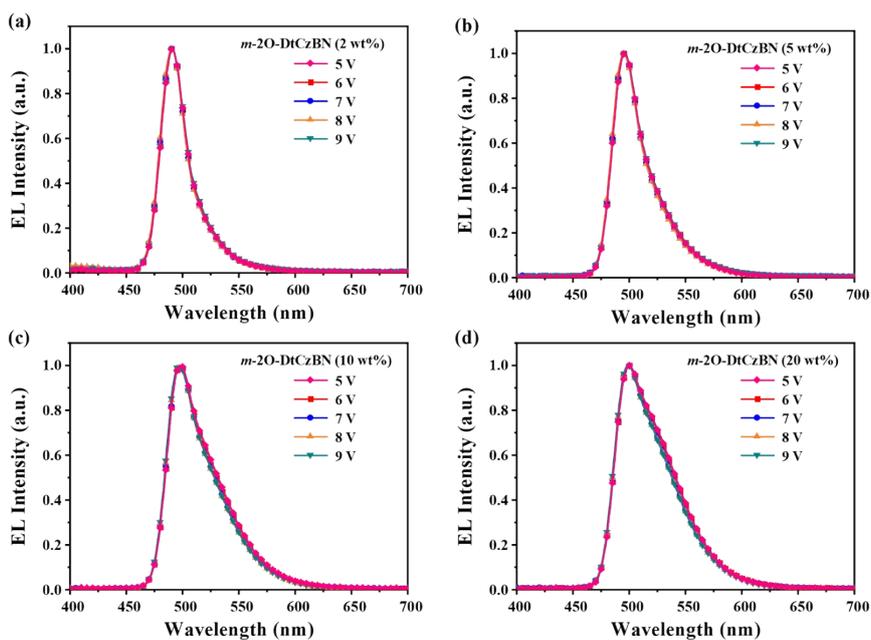


Figure S28. EL spectra of devices based on *o*-20-DtCzBN taken at various voltages from 5 to 9 V.



**Figure S29.** EL spectra of devices based on *m*-2O-DtCzBN taken at various voltages from 5 to 9 V.

**Table S6.** Cartesian coordinates of *o*-10-DtCzBN at the optimized  $S_0$  geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	-0.317465	0.080187	-0.754101
C	-0.953522	-1.159116	-0.866145
C	-0.212089	-2.339201	-0.768723
C	1.173684	-2.275748	-0.593343
C	1.820220	-1.040394	-0.472526
C	1.081317	0.183008	-0.474420
B	1.723753	1.522843	-0.043197
C	-4.507871	1.215493	-2.383917
C	-4.888463	2.545252	-2.108261
C	-3.955406	3.360964	-1.462823
C	-2.708271	2.854756	-1.087993
C	-2.371370	1.500462	-1.331684
C	-3.273868	0.682426	-2.017654
C	-1.544612	3.482990	-0.492672
C	-0.548156	2.487411	-0.410152
N	-1.052653	1.271476	-0.864971
C	-1.252425	4.765448	-0.046887
C	0.023986	5.064233	0.472067
C	0.985754	4.044533	0.501415

C	0.751706	2.723010	0.052740
N	3.210968	-0.974156	-0.288841
C	4.208557	-1.975553	-0.416061
C	4.170918	-3.284178	-0.899144
C	5.353606	-4.028728	-0.921340
C	6.589850	-3.517653	-0.490613
C	6.618316	-2.186347	-0.054124
C	5.455724	-1.419378	-0.025154
C	5.219172	-0.027377	0.301695
C	6.038199	1.023842	0.707489
C	5.494726	2.305500	0.895653
C	4.119468	2.486204	0.663835
C	3.237882	1.458519	0.269488
C	3.845150	0.204859	0.104065
C	0.310603	6.493588	0.975589
C	0.115947	7.499353	-0.184225
C	1.746537	6.656229	1.508666
C	-0.666792	6.841644	2.123473
C	6.353324	3.508872	1.336201
C	6.290324	4.616685	0.258026
C	7.832301	3.129550	1.542128
C	5.813159	4.066926	2.674421
C	7.886489	-4.349181	-0.500772
C	8.451706	-4.436497	0.936765
C	7.659191	-5.784354	-1.012477
C	8.929732	-3.671151	-1.420231
C	-6.280632	3.045133	-2.536154
C	-7.369155	2.202606	-1.829717
C	-6.436765	2.901044	-4.068870
C	-6.507608	4.523535	-2.169086
C	-2.009944	-4.030160	-0.142302
C	-2.571061	-5.305322	-0.255597
C	-2.009529	-6.240060	-1.123473
C	-0.879800	-5.911125	-1.871426
C	-0.318235	-4.642879	-1.739463
C	-0.863121	-3.673888	-0.882260
C	-4.871281	-3.140464	0.263381
C	-6.175182	-3.053431	0.742090
C	-6.461841	-2.918637	2.112068
C	-5.369646	-2.875895	2.988572
C	-4.054504	-2.970704	2.529068
C	-3.805813	-3.104346	1.167001
O	-2.483778	-3.097951	0.756165

C	-7.923452	-2.820842	2.586391
C	-8.691776	-4.094635	2.161346
C	-8.032059	-2.684638	4.116716
C	-8.591457	-1.582308	1.943110
H	-2.024720	-1.221519	-0.959322
H	1.715166	-3.197163	-0.455668
H	-5.196019	0.564593	-2.914449
H	-4.178196	4.401480	-1.256391
H	-3.033063	-0.330998	-2.305297
H	-2.015491	5.536747	-0.097558
H	1.964095	4.277253	0.896240
H	3.271283	-3.735178	-1.290582
H	5.292079	-5.042921	-1.297460
H	7.554313	-1.730964	0.255773
H	7.095046	0.842568	0.866496
H	3.717393	3.484399	0.781634
H	0.312180	8.521693	0.158642
H	0.800398	7.280456	-1.010235
H	-0.903380	7.473166	-0.580626
H	1.944767	5.990908	2.355331
H	2.494126	6.458707	0.733335
H	1.896286	7.683839	1.855281
H	-0.544131	6.150766	2.963901
H	-0.482379	7.858340	2.488967
H	-1.710712	6.789756	1.800192
H	6.671793	4.251935	-0.701159
H	5.267938	4.970481	0.095840
H	6.895939	5.478830	0.560093
H	8.290736	2.756697	0.620214
H	8.398346	4.012255	1.856695
H	7.954051	2.367182	2.318708
H	4.775573	4.402039	2.586501
H	5.851288	3.305032	3.459748
H	6.413035	4.923909	3.001544
H	8.674616	-3.447177	1.347102
H	7.736976	-4.922324	1.608989
H	9.380158	-5.018788	0.948506
H	7.293827	-5.796695	-2.044556
H	8.604204	-6.336582	-0.991666
H	6.944041	-6.330639	-0.388870
H	8.557273	-3.598421	-2.447208
H	9.174022	-2.659655	-1.082630
H	9.860048	-4.250301	-1.435634

H	-7.293289	2.299158	-0.741768
H	-8.368190	2.536686	-2.132540
H	-7.284159	1.140097	-2.075791
H	-5.681675	3.493265	-4.595923
H	-6.331219	1.861951	-4.394228
H	-7.425938	3.249381	-4.387090
H	-6.435947	4.689670	-1.089213
H	-5.787777	5.182078	-2.666145
H	-7.509217	4.833139	-2.484412
H	-3.437009	-5.561428	0.343889
H	-2.455466	-7.226872	-1.205568
H	-0.440944	-6.632003	-2.553931
H	0.551689	-4.373690	-2.330953
H	-4.679405	-3.236941	-0.800151
H	-6.987274	-3.082671	0.021856
H	-5.529056	-2.770038	4.055121
H	-3.216173	-2.933693	3.216701
H	-8.689216	-4.229429	1.075635
H	-8.246513	-4.988655	2.609984
H	-9.736733	-4.035959	2.486168
H	-7.536604	-1.779277	4.482110
H	-9.085651	-2.623674	4.407538
H	-7.597134	-3.545951	4.634292
H	-8.589505	-1.639881	0.850578
H	-9.634045	-1.497721	2.269704
H	-8.069480	-0.663512	2.229043

**Table S7.** Cartesian coordinates of *o*-10-DtCzBN at the optimized S<sub>1</sub> geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	0.263298	0.025267	0.590595
C	0.897636	-1.233032	0.585716
C	0.156260	-2.419632	0.468182
C	-1.237798	-2.304909	0.369345
C	-1.872434	-1.045287	0.365621
C	-1.135454	0.171791	0.370501
B	-1.783092	1.534934	0.034702
C	4.513081	0.974050	2.147354
C	4.912057	2.309700	1.923310

C	3.974190	3.184215	1.358850
C	2.702415	2.732371	1.005031
C	2.350523	1.366820	1.184171
C	3.253012	0.493437	1.801087
C	1.530249	3.418872	0.498816
C	0.515658	2.455801	0.387618
N	1.021978	1.190238	0.744043
C	1.245881	4.747314	0.167935
C	-0.053559	5.092705	-0.253920
C	-1.038804	4.092530	-0.320594
C	-0.807863	2.728400	0.003210
N	-3.264045	-0.961906	0.267136
C	-4.254051	-1.951993	0.444279
C	-4.198121	-3.239780	0.979224
C	-5.373652	-3.992727	1.044473
C	-6.616649	-3.495798	0.612835
C	-6.662373	-2.174921	0.132467
C	-5.509185	-1.400463	0.058964
C	-5.279699	-0.015144	-0.301831
C	-6.113187	1.032114	-0.720348
C	-5.557364	2.301233	-0.943136
C	-4.176053	2.493992	-0.724734
C	-3.288502	1.476911	-0.297919
C	-3.910806	0.226111	-0.127183
C	-0.349728	6.561902	-0.616781
C	-0.081840	7.461596	0.613597
C	-1.808623	6.784384	-1.058679
C	0.572284	6.999291	-1.780333
C	-6.414369	3.495129	-1.408997
C	-6.343530	4.626612	-0.355520
C	-7.895676	3.118112	-1.601758
C	-5.876101	4.020276	-2.761562
C	-7.909530	-4.329025	0.672155
C	-8.500506	-4.458437	-0.752415
C	-7.670120	-5.748025	1.221511
C	-8.937358	-3.624689	1.590110
C	6.330021	2.755448	2.321181
C	7.368673	1.917179	1.537468
C	6.536764	2.536673	3.839388
C	6.584845	4.242982	2.013456
C	1.985247	-4.048100	-0.231233
C	2.520103	-5.337789	-0.244854
C	1.886477	-6.367618	0.448975

C	0.708655	-6.110375	1.151051
C	0.175088	-4.825173	1.148698
C	0.787579	-3.759189	0.462429
C	4.855732	-3.167720	-0.212033
C	6.205786	-3.012893	-0.512798
C	6.650236	-2.653982	-1.797576
C	5.668061	-2.457125	-2.777269
C	4.309290	-2.616546	-2.498761
C	3.903650	-2.973330	-1.216702
O	2.541045	-3.025412	-0.974354
C	8.156374	-2.494279	-2.073976
C	8.875898	-3.835998	-1.798486
C	8.441772	-2.087080	-3.531745
C	8.739187	-1.401921	-1.146163
H	1.972950	-1.291176	0.605688
H	-1.819109	-3.197154	0.190699
H	5.202617	0.283099	2.621087
H	4.218188	4.228256	1.201568
H	2.991824	-0.525061	2.053424
H	2.022374	5.501634	0.242525
H	-2.036245	4.374418	-0.624209
H	-3.286142	-3.658588	1.382143
H	-5.305262	-4.990552	1.459663
H	-7.607986	-1.738736	-0.174750
H	-7.171413	0.851287	-0.862829
H	-3.772633	3.485229	-0.888258
H	-0.282537	8.511480	0.370461
H	-0.726151	7.177405	1.451890
H	0.955716	7.391027	0.952684
H	-2.059258	6.194977	-1.946529
H	-2.518050	6.528100	-0.265178
H	-1.960315	7.839582	-1.308601
H	0.398309	6.383015	-2.668370
H	0.379970	8.044690	-2.048269
H	1.630412	6.912186	-1.517147
H	-6.726633	4.283925	0.611225
H	-5.319061	4.976705	-0.201697
H	-6.945806	5.484571	-0.675990
H	-8.351894	2.769545	-0.669394
H	-8.459068	3.995250	-1.936319
H	-8.021573	2.336706	-2.358389
H	-4.835871	4.348857	-2.686173
H	-5.924041	3.241167	-3.529362

H	-6.472779	4.873519	-3.104366
H	-8.733691	-3.482150	-1.187042
H	-7.797808	-4.962924	-1.423428
H	-9.427377	-5.042625	-0.728375
H	-7.287377	-5.729729	2.247155
H	-8.614182	-6.301974	1.233234
H	-6.964836	-6.311295	0.601812
H	-8.547807	-3.523143	2.608176
H	-9.189301	-2.623693	1.228277
H	-9.865837	-4.204883	1.637131
H	7.254200	2.063341	0.458476
H	8.386256	2.214214	1.815507
H	7.265702	0.847368	1.740799
H	5.816812	3.122026	4.420318
H	6.417492	1.486568	4.121303
H	7.545281	2.847601	4.134536
H	6.478653	4.462054	0.946037
H	5.903075	4.896494	2.567342
H	7.605692	4.509730	2.305048
H	3.424637	-5.529972	-0.810593
H	2.312881	-7.365959	0.433171
H	0.212904	-6.901994	1.704061
H	-0.725765	-4.620998	1.719322
H	4.542135	-3.441874	0.789762
H	6.927752	-3.170494	0.282940
H	5.950553	-2.176389	-3.785013
H	3.557538	-2.459401	-3.265012
H	8.745979	-4.162424	-0.762341
H	8.490064	-4.627926	-2.448660
H	9.951451	-3.737931	-1.983867
H	7.981164	-1.126495	-3.784383
H	9.521297	-1.984099	-3.680959
H	8.081546	-2.837580	-4.242935
H	8.610822	-1.653851	-0.089264
H	9.812389	-1.278083	-1.329661
H	8.250487	-0.438006	-1.320826

**Table S8.** Cartesian coordinates of *o*-2O-DtCzBN at the optimized S<sub>0</sub> geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	-1.163619	0.480719	0.335874

C	-1.130435	-0.916291	0.391704
C	0.016477	-1.608232	-0.003363
C	1.156579	-0.904247	-0.398267
C	1.176702	0.492616	-0.340994
C	0.002803	1.233806	-0.001772
B	-0.004980	2.777325	0.000722
C	-5.624216	-0.639128	0.992255
C	-6.406561	0.413075	1.511031
C	-5.787598	1.655868	1.670820
C	-4.437282	1.822965	1.353068
C	-3.659682	0.733087	0.887523
C	-4.275136	-0.503252	0.672389
C	-3.582523	2.994696	1.337466
C	-2.326029	2.566209	0.862393
N	-2.339278	1.189834	0.640771
C	-3.760773	4.338043	1.645542
C	-2.703375	5.256740	1.478350
C	-1.486452	4.783850	0.965963
C	-1.254542	3.432126	0.621931
N	2.345895	1.213062	-0.645520
C	3.668755	0.768883	-0.898357
C	4.296838	-0.462061	-0.687875
C	5.645638	-0.584639	-1.013369
C	6.415733	0.476217	-1.533522
C	5.784750	1.713328	-1.688806
C	4.433847	1.867621	-1.365272
C	3.567963	3.030315	-1.344795
C	3.736255	4.379066	-1.655637
C	2.673431	5.282945	-1.482444
C	1.460019	4.794722	-0.963124
C	1.238962	3.446015	-0.620248
C	2.320269	2.589729	-0.866276
C	-2.931306	6.735567	1.850919
C	-4.080659	7.314183	0.991665
C	-1.679729	7.602424	1.616423
C	-3.309482	6.840130	3.347715
C	2.801121	6.779766	-1.831995
C	1.748874	7.152614	-2.903158
C	4.192675	7.135691	-2.389354
C	2.564025	7.631755	-0.562593
C	7.897123	0.243528	-1.883369
C	8.664472	-0.221447	-0.622824
C	8.002242	-0.846925	-2.975906

C	8.579254	1.518834	-2.412784
C	-7.887068	0.166155	1.854666
C	-7.986347	-0.926630	2.945384
C	-8.645082	-0.304182	0.590510
C	-8.583083	1.434450	2.382935
C	-0.919929	-3.844872	-0.739459
C	-0.910968	-5.242011	-0.755152
C	0.039177	-5.924652	-0.001290
C	0.982189	-5.231151	0.751678
C	0.976596	-3.834027	0.734288
C	0.024370	-3.101299	-0.003025
C	-3.886820	-4.122891	-0.774047
C	-5.210476	-4.457206	-1.073162
C	-5.763325	-4.239612	-2.342236
C	-4.921771	-3.668009	-3.312750
C	-3.599691	-3.333897	-3.038199
C	-3.079010	-3.562882	-1.763811
O	-1.789476	-3.123028	-1.529654
C	-7.217899	-4.597754	-2.697552
C	-7.986329	-5.179390	-1.496111
C	-7.962522	-3.328271	-3.174454
C	-7.225557	-5.651047	-3.830875
C	3.643305	-3.295062	3.040323
C	4.966835	-3.617896	3.321461
C	5.817285	-4.184575	2.355876
C	5.272106	-4.408872	1.084672
C	3.947228	-4.085719	0.778926
C	3.130430	-3.530633	1.764033
O	1.838407	-3.101599	1.522957
C	7.273258	-4.529660	2.718245
C	8.006342	-3.251578	3.190056
C	7.285398	-5.576186	3.857780
C	8.050139	-5.112599	1.522866
H	-1.974196	-1.476070	0.759602
H	2.005900	-1.455523	-0.766063
H	-6.080148	-1.607620	0.811575
H	-6.347147	2.512627	2.028597
H	-3.761767	-1.339793	0.221933
H	-4.722505	4.676717	2.019875
H	-0.668077	5.480139	0.836644
H	3.793166	-1.304075	-0.236538
H	6.111756	-1.548940	-0.836233
H	6.334874	2.575825	-2.047464

H	4.693444	4.720192	-2.033358
H	0.639271	5.490953	-0.829505
H	-4.256451	8.365803	1.245567
H	-3.837982	7.257489	-0.074450
H	-5.019319	6.774380	1.147907
H	-0.829948	7.262728	2.217259
H	-1.376724	7.604926	0.564133
H	-1.891132	8.638668	1.899640
H	-2.507636	6.447567	3.981427
H	-3.482877	7.885780	3.626545
H	-4.220668	6.280358	3.579099
H	1.898763	6.569305	-3.817542
H	0.728769	6.967403	-2.554583
H	1.825114	8.215180	-3.161236
H	4.416460	6.587112	-3.310309
H	4.232620	8.204059	-2.624999
H	4.988113	6.929164	-1.665592
H	1.569177	7.464234	-0.139491
H	3.299826	7.391808	0.211905
H	2.650496	8.699224	-0.795786
H	8.608768	0.532425	0.169100
H	8.261455	-1.156182	-0.221443
H	9.721424	-0.390165	-0.858878
H	7.481262	-0.537764	-3.887880
H	9.051847	-1.034676	-3.230129
H	7.564004	-1.793938	-2.647302
H	8.098733	1.888647	-3.324406
H	8.570203	2.323316	-1.670150
H	9.625371	1.304968	-2.654561
H	-7.471481	-0.614113	3.859681
H	-9.035156	-1.124061	3.195491
H	-7.538505	-1.869236	2.617058
H	-8.593324	0.451193	-0.200240
H	-8.231914	-1.234676	0.189537
H	-9.701297	-0.482972	0.822304
H	-8.110181	1.807379	3.297295
H	-8.578282	2.240049	1.641461
H	-9.628241	1.210679	2.619787
H	-1.636488	-5.777406	-1.355723
H	0.044890	-7.010416	-0.000601
H	1.713266	-5.758280	1.352795
H	-3.488765	-4.303203	0.218858
H	-5.811925	-4.894395	-0.284549

H	-5.301250	-3.477221	-4.311998
H	-2.961643	-2.888865	-3.794354
H	-7.532962	-6.106508	-1.130305
H	-8.036899	-4.470476	-0.663036
H	-9.013993	-5.411498	-1.793093
H	-7.976587	-2.563867	-2.390697
H	-7.494499	-2.887172	-4.059380
H	-8.999567	-3.569645	-3.433273
H	-6.716925	-6.568246	-3.516384
H	-8.254385	-5.909766	-4.105688
H	-6.723485	-5.283359	-4.730650
H	2.998251	-2.853776	3.792716
H	5.340370	-3.422071	4.321971
H	5.880700	-4.842553	0.299641
H	3.555185	-4.270791	-0.215502
H	8.017705	-2.492058	2.401524
H	7.531240	-2.808576	4.070268
H	9.044139	-3.483431	3.454504
H	6.785319	-6.499342	3.547016
H	8.315366	-5.824878	4.137525
H	6.777396	-5.207428	4.753772
H	7.604423	-6.044842	1.160671
H	8.098967	-4.408057	0.686008
H	9.078281	-5.335962	1.824875

**Table S9.** Cartesian coordinates of *o*-2O-DtCzBN at the optimized S<sub>1</sub> geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	-1.161896	0.600593	0.309195
C	-1.123395	-0.802267	0.388920
C	0.016791	-1.522604	-0.000665
C	1.146815	-0.791460	-0.390245
C	1.168247	0.613303	-0.315521
C	-0.002076	1.369791	-0.005337
B	-0.011346	2.904108	-0.006380
C	-5.611014	-0.573990	0.853470
C	-6.410402	0.468298	1.377333
C	-5.811355	1.718035	1.562065
C	-4.458504	1.909156	1.268054
C	-3.662428	0.823495	0.808193
C	-4.261122	-0.416664	0.558544

C	-3.620184	3.089778	1.268896
C	-2.356423	2.682467	0.817465
N	-2.348613	1.294090	0.595856
C	-3.834512	4.440570	1.559767
C	-2.778764	5.368007	1.380989
C	-1.548813	4.914057	0.890777
C	-1.280297	3.552280	0.567310
N	2.346035	1.319980	-0.601390
C	3.666635	0.863435	-0.812374
C	4.279079	-0.369194	-0.560885
C	5.631578	-0.511308	-0.854047
C	6.419121	0.539181	-1.376925
C	5.805292	1.782081	-1.563428
C	4.450217	1.957186	-1.271591
C	3.597839	3.128252	-1.273820
C	3.801822	4.482526	-1.569163
C	2.741615	5.394452	-1.394262
C	1.510463	4.925033	-0.902788
C	1.252479	3.568492	-0.578245
C	2.339480	2.707991	-0.823796
C	-3.031770	6.848825	1.725352
C	-4.188897	7.390667	0.851876
C	-1.796744	7.736512	1.481476
C	-3.418741	6.969416	3.219048
C	2.899047	6.893743	-1.719646
C	1.879005	7.292727	-2.812832
C	4.308613	7.241534	-2.235574
C	2.638080	7.731767	-0.445268
C	7.905525	0.289777	-1.688198
C	8.641585	-0.138202	-0.395823
C	8.026365	-0.836826	-2.742167
C	8.606279	1.543293	-2.244851
C	-7.893137	0.201200	1.690786
C	-7.998878	-0.926879	2.744838
C	-8.625926	-0.235442	0.399414
C	-8.607957	1.446208	2.248622
C	-1.011708	-3.758481	-0.600890
C	-1.005396	-5.154446	-0.615992
C	0.037386	-5.837509	0.003202
C	1.073699	-5.143513	0.621105
C	1.067176	-3.747563	0.603400
C	0.024203	-3.007165	0.000544
C	-4.027789	-4.140767	-0.516503

C	-5.314451	-4.585867	-0.829145
C	-5.842481	-4.475767	-2.123513
C	-5.016186	-3.897170	-3.102246
C	-3.728629	-3.454428	-2.812703
C	-3.233138	-3.578115	-1.515062
O	-1.987901	-3.030589	-1.252962
C	-7.257082	-4.956165	-2.495911
C	-8.009846	-5.547347	-1.289225
C	-8.080467	-3.765113	-3.040890
C	-7.158100	-6.050187	-3.585622
C	3.783545	-3.415224	2.811969
C	5.075724	-3.845121	3.100253
C	5.906346	-4.416556	2.120978
C	5.377775	-4.532888	0.827380
C	4.086445	-4.100630	0.515987
C	3.287604	-3.544907	1.515076
O	2.036754	-3.009852	1.254129
C	7.326045	-4.882800	2.491981
C	8.138765	-3.683082	3.033960
C	7.239225	-5.976088	3.583458
C	8.082668	-5.468547	1.285051
H	-1.971872	-1.345615	0.771424
H	2.002429	-1.325419	-0.769892
H	-6.056886	-1.541375	0.646653
H	-6.389895	2.561607	1.920035
H	-3.729503	-1.235517	0.096263
H	-4.805147	4.771474	1.913939
H	-0.743617	5.623622	0.759165
H	3.756756	-1.194036	-0.098681
H	6.087886	-1.473670	-0.646423
H	6.374400	2.632275	-1.920871
H	4.770180	4.814607	-1.922331
H	0.702056	5.635478	-0.774270
H	-4.385013	8.442723	1.088808
H	-3.939241	7.322385	-0.211911
H	-5.117422	6.835220	1.012145
H	-0.944135	7.425231	2.093294
H	-1.487878	7.723987	0.431255
H	-2.031606	8.773246	1.744028
H	-2.612842	6.600176	3.861531
H	-3.609918	8.016594	3.480372
H	-4.320706	6.397253	3.454527
H	2.047329	6.720540	-3.731038

H	0.848864	7.112676	-2.493435
H	1.974476	8.357942	-3.053302
H	4.549306	6.702907	-3.157947
H	4.366758	8.312688	-2.454539
H	5.081755	7.014502	-1.494181
H	1.630750	7.571356	-0.051307
H	3.349981	7.472351	0.345144
H	2.745713	8.800675	-0.662929
H	8.577114	0.643512	0.367848
H	8.219882	-1.054121	0.028769
H	9.701287	-0.324327	-0.604372
H	7.523408	-0.556563	-3.673347
H	9.079873	-1.034622	-2.970568
H	7.579858	-1.771633	-2.390887
H	8.144812	1.887384	-3.176152
H	8.590610	2.370994	-1.528397
H	9.654899	1.314558	-2.460568
H	-7.498150	-0.640581	3.675380
H	-9.049618	-1.137370	2.974570
H	-7.541613	-1.856240	2.392959
H	-8.571956	0.547062	-0.364256
H	-8.194038	-1.146248	-0.025927
H	-9.683000	-0.434193	0.609596
H	-8.149044	1.795806	3.179138
H	-8.603508	2.273990	1.532101
H	-9.653376	1.204903	2.466138
H	-1.801867	-5.692568	-1.114680
H	0.042507	-6.923140	0.004181
H	1.875224	-5.673213	1.120729
H	-3.644251	-4.236579	0.493977
H	-5.906860	-5.022680	-0.033655
H	-5.379280	-3.787661	-4.119559
H	-3.101828	-3.005401	-3.575858
H	-7.494526	-6.419333	-0.873343
H	-8.139401	-4.811526	-0.488726
H	-9.007344	-5.872795	-1.600899
H	-8.173603	-2.975330	-2.288212
H	-7.621082	-3.323998	-3.930211
H	-9.089142	-4.093138	-3.315788
H	-6.587152	-6.911984	-3.224963
H	-8.157737	-6.398807	-3.868197
H	-6.667366	-5.680050	-4.490559
H	3.153372	-2.971637	3.575531

H	5.439055	-3.731118	4.116990
H	5.973433	-4.964539	0.031500
H	3.702609	-4.201017	-0.493935
H	8.223320	-2.893619	2.279933
H	7.676382	-3.244992	3.923226
H	9.150907	-4.001024	3.307967
H	6.676051	-6.843874	3.224939
H	8.242589	-6.314659	3.865043
H	6.746318	-5.609354	4.488600
H	7.575000	-6.345933	0.871110
H	8.204160	-4.732667	0.483350
H	9.083630	-5.784138	1.595764

**Table S10.** Cartesian coordinates of *m*-2O-DtCzBN at the optimized S<sub>0</sub> geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	1.162172	0.603843	0.333607
C	1.119307	-0.793525	0.376397
C	-0.025165	-1.479780	-0.042580
C	-1.154932	-0.762188	-0.449041
C	-1.167703	0.634735	-0.381850
C	0.005426	1.367315	-0.018589
B	0.022473	2.909821	-0.008126
C	5.597222	-0.562953	1.132120
C	6.371522	0.485282	1.658460
C	5.756528	1.738154	1.787298
C	4.421651	1.918012	1.432240
C	3.645156	0.828970	0.952496
C	4.254654	-0.412976	0.772739
C	3.577033	3.096367	1.392689
C	2.331457	2.677988	0.891536
N	2.335619	1.299893	0.669951
C	3.764813	4.440854	1.708538
C	2.720944	5.364041	1.520899
C	1.507900	4.897445	0.982772
C	1.269221	3.553480	0.631646
N	-2.326466	1.361687	-0.703996
C	-3.647681	0.925385	-0.985960
C	-4.284294	-0.308242	-0.818480

C	-5.628840	-0.418168	-1.167302
C	-6.387079	0.657959	-1.672744
C	-5.747822	1.894789	-1.790871
C	-4.401781	2.035663	-1.443160
C	-3.531762	3.194215	-1.393382
C	-3.691132	4.547193	-1.689587
C	-2.626161	5.444013	-1.494246
C	-1.421025	4.943650	-0.968123
C	-1.210228	3.590096	-0.637268
C	-2.292500	2.741986	-0.905453
C	2.869212	6.857271	1.877446
C	1.813360	7.241855	2.940881
C	2.656800	7.718114	0.609693
C	4.261524	7.188736	2.447752
C	-2.742232	6.945205	-1.828617
C	-1.681093	7.321968	-2.889576
C	-4.128255	7.315838	-2.390115
C	-2.507191	7.782162	-0.548885
C	-7.864389	0.441281	-2.049089
C	-8.653908	-0.030732	-0.805059
C	-7.961476	-0.635880	-3.155462
C	-8.526876	1.728363	-2.574972
C	7.845576	0.308450	2.070155
C	8.005697	0.659207	3.568414
C	8.343850	-1.133898	1.860773
C	8.735799	1.251322	1.226231
C	1.120269	-3.679957	-0.393063
C	1.093781	-5.076278	-0.405570
C	-0.068219	-5.775837	-0.080246
C	-1.215740	-5.059258	0.256932
C	-1.214887	-3.662355	0.268831
C	-0.040433	-2.967060	-0.055670
O	2.192200	-5.857560	-0.688325
O	-2.332391	-5.821781	0.520328
C	3.309640	-5.314352	-1.303139
C	4.534282	-5.422733	-0.645737
C	5.692536	-4.967707	-1.270854
C	5.666855	-4.388419	-2.551209
C	4.419508	-4.296767	-3.185142
C	3.249420	-4.757863	-2.578941
C	6.973476	-3.894967	-3.199143
C	6.737369	-3.263272	-4.583917
C	7.943746	-5.087727	-3.371558

C	7.630910	-2.828807	-2.290383
C	-3.413314	-5.289474	1.204387
C	-3.286789	-4.740107	2.478731
C	-4.424768	-4.290881	3.151424
C	-5.704685	-4.387439	2.587131
C	-5.796809	-4.960530	1.307163
C	-4.672221	-5.403417	0.615865
C	-6.976954	-3.903872	3.306820
C	-7.934283	-5.100376	3.520290
C	-6.669825	-3.282786	4.682521
C	-7.683879	-2.832194	2.442670
H	1.943357	-1.358017	0.780441
H	-1.990976	-1.301807	-0.862561
H	6.041139	-1.539596	0.981624
H	6.319242	2.590598	2.156388
H	3.743445	-1.255312	0.330794
H	4.721610	4.764155	2.102521
H	0.700237	5.607032	0.841107
H	-3.787643	-1.167670	-0.392974
H	-6.101178	-1.385585	-1.027884
H	-6.287747	2.767056	-2.141096
H	-4.642296	4.896973	-2.074390
H	-0.598209	5.634230	-0.819872
H	1.945753	6.652320	3.853933
H	1.904153	8.301863	3.204343
H	0.793596	7.074544	2.582256
H	3.395411	7.470549	-0.159681
H	1.663079	7.568308	0.177253
H	2.757420	8.782981	0.848535
H	5.059705	6.969761	1.730689
H	4.317246	8.255885	2.685264
H	4.467788	6.635525	3.370016
H	-1.829389	6.749352	-3.810923
H	-1.748824	8.387588	-3.136863
H	-0.664264	7.126469	-2.536963
H	-4.349522	6.779596	-3.318877
H	-4.929366	7.105796	-1.673648
H	-4.160396	8.386996	-2.613692
H	-3.248220	7.538518	0.219407
H	-1.515367	7.604549	-0.122532
H	-2.585946	8.852395	-0.771302
H	-8.263067	-0.970996	-0.405236
H	-8.606631	0.715947	-0.005745

H	-9.707979	-0.190527	-1.059287
H	-7.422446	-0.322018	-4.055235
H	-7.539525	-1.591631	-2.831099
H	-9.008530	-0.809343	-3.428963
H	-8.026690	2.105775	-3.472818
H	-9.569717	1.525190	-2.838670
H	-8.526448	2.523531	-1.822276
H	7.707390	1.690608	3.777623
H	7.391234	0.001734	4.191949
H	9.050425	0.544415	3.879214
H	9.389626	-1.211529	2.175444
H	7.767436	-1.853788	2.450947
H	8.293218	-1.433766	0.808920
H	8.464100	2.301788	1.366120
H	9.788427	1.139606	1.510105
H	8.645396	1.022973	0.159268
H	2.021460	-3.151794	-0.674760
H	-0.078882	-6.858975	-0.089425
H	-2.106014	-3.121923	0.559422
H	4.565645	-5.868938	0.342830
H	6.635635	-5.068210	-0.742257
H	4.342252	-3.865861	-4.176275
H	2.296391	-4.686620	-3.092774
H	6.074000	-2.394091	-4.527923
H	7.691047	-2.924400	-5.000948
H	6.306094	-3.979374	-5.290993
H	7.508948	-5.855449	-4.019707
H	8.883996	-4.752918	-3.824196
H	8.184285	-5.557477	-2.413270
H	6.962773	-1.974609	-2.139835
H	7.883682	-3.234263	-1.305864
H	8.557843	-2.460468	-2.744025
H	-2.307840	-4.663978	2.940260
H	-4.295129	-3.864628	4.139158
H	-6.767024	-5.064766	0.831011
H	-4.755254	-5.844291	-0.372101
H	-8.223166	-5.564445	2.572628
H	-7.465369	-5.871548	4.139962
H	-8.850590	-4.770673	4.022891
H	-6.013515	-2.410491	4.598578
H	-7.600958	-2.950946	5.152847
H	-6.198712	-4.003093	5.359238
H	-7.027633	-1.973691	2.266855

H	-7.984827	-3.229151	1.468291
H	-8.587798	-2.471984	2.946334

**Table S11.** Cartesian coordinates of *m*-2O-DtCzBN at the optimized S<sub>1</sub> geometry

Atom	Coordinates (Angstroms)		
	x	y	z
C	1.165797	0.668605	0.327879
C	1.104239	-0.732403	0.392344
C	-0.039567	-1.437427	-0.023516
C	-1.152668	-0.679171	-0.426250
C	-1.153387	0.722636	-0.344063
C	0.023405	1.461348	-0.005439
B	0.057772	2.990093	-0.000970
C	5.583406	-0.593710	1.027701
C	6.379936	0.433953	1.566371
C	5.793796	1.700757	1.716829
C	4.461000	1.915702	1.379102
C	3.658270	0.841637	0.900315
C	4.242698	-0.408015	0.683793
C	3.643098	3.112276	1.350649
C	2.386229	2.726586	0.866355
N	2.356923	1.339665	0.647596
C	3.877879	4.458573	1.651290
C	2.848929	5.400490	1.450133
C	1.617111	4.964896	0.927603
C	1.329865	3.618538	0.596121
N	-2.314415	1.448873	-0.653143
C	-3.636991	1.014282	-0.899959
C	-4.277834	-0.211569	-0.683752
C	-5.624224	-0.328054	-1.014465
C	-6.380601	0.741922	-1.544175
C	-5.741128	1.976490	-1.696592
C	-4.392328	2.125084	-1.366310
C	-3.521720	3.282334	-1.338199
C	-3.696987	4.641015	-1.628646
C	-2.625245	5.534444	-1.426955
C	-1.412458	5.040628	-0.914117
C	-1.184877	3.678858	-0.592373
C	-2.280812	2.837978	-0.864304

C	3.039865	6.894110	1.780897
C	2.005494	7.319581	2.850580
C	2.831303	7.739304	0.501462
C	4.446140	7.202743	2.329674
C	-2.750873	7.037695	-1.746436
C	-1.703968	7.424556	-2.818475
C	-4.144672	7.412642	-2.285620
C	-2.498819	7.863635	-0.462337
C	-7.860884	0.521831	-1.902306
C	-8.643516	0.101409	-0.635179
C	-7.969978	-0.596732	-2.966198
C	-8.519967	1.791474	-2.473249
C	7.852528	0.223202	1.962951
C	8.033247	0.566686	3.461054
C	8.317423	-1.229191	1.746330
C	8.754348	1.150201	1.113225
C	1.116910	-3.646605	-0.242749
C	1.080100	-5.040588	-0.259401
C	-0.114411	-5.735822	-0.068942
C	-1.284634	-5.004743	0.135893
C	-1.275334	-3.609931	0.149416
C	-0.067053	-2.912737	-0.038597
O	2.208427	-5.821008	-0.405333
O	-2.439672	-5.749364	0.259611
C	3.322543	-5.336782	-1.068722
C	4.561231	-5.483741	-0.444766
C	5.719120	-5.091768	-1.111812
C	5.681992	-4.538609	-2.403401
C	4.421334	-4.405057	-3.002341
C	3.250436	-4.801788	-2.353972
C	6.989153	-4.116536	-3.099135
C	6.740401	-3.516087	-4.495583
C	7.907895	-5.350805	-3.260977
C	7.711546	-3.051550	-2.239856
C	-3.525703	-5.265857	0.967273
C	-3.410973	-4.747593	2.256382
C	-4.559480	-4.354506	2.946055
C	-5.838962	-4.475216	2.385891
C	-5.918796	-5.011191	1.088964
C	-4.784501	-5.399165	0.381007
C	-7.121929	-4.056574	3.127140
C	-8.045004	-5.286831	3.294708
C	-6.827768	-3.482728	4.525928

C	-7.860953	-2.971471	2.308235
H	1.930701	-1.288445	0.805539
H	-2.003465	-1.193347	-0.844926
H	6.008796	-1.573906	0.851584
H	6.381605	2.534795	2.087899
H	3.712769	-1.226714	0.218858
H	4.845322	4.763183	2.030584
H	0.832310	5.697756	0.781121
H	-3.780740	-1.055645	-0.227661
H	-6.102071	-1.286092	-0.837943
H	-6.285709	2.840098	-2.059752
H	-4.651825	4.991660	-2.000089
H	-0.594466	5.736080	-0.766635
H	2.136666	6.742692	3.771832
H	2.124748	8.381509	3.094239
H	0.978404	7.168485	2.507187
H	3.553617	7.461367	-0.272969
H	1.829098	7.607040	0.084496
H	2.962890	8.804498	0.723244
H	5.230000	6.954746	1.606471
H	4.528471	8.271812	2.550418
H	4.650139	6.658330	3.257454
H	-1.864884	6.860256	-3.742810
H	-1.777241	8.492361	-3.054621
H	-0.682910	7.225814	-2.481333
H	-4.377340	6.884765	-3.216202
H	-4.935109	7.194139	-1.560085
H	-4.180517	8.485966	-2.498093
H	-3.229565	7.612983	0.313508
H	-1.501801	7.683154	-0.050950
H	-2.583048	8.935312	-0.675908
H	-8.253644	-0.824267	-0.202193
H	-8.588901	0.878665	0.133913
H	-9.699425	-0.063396	-0.877622
H	-7.432728	-0.321832	-3.879616
H	-7.554654	-1.542823	-2.607241
H	-9.019549	-0.771344	-3.228334
H	-8.022844	2.132396	-3.387231
H	-9.564872	1.582854	-2.723912
H	-8.513342	2.614618	-1.751371
H	7.759614	1.603344	3.677674
H	7.412138	-0.080335	4.088838
H	9.078520	0.428813	3.759625

H	9.362204	-1.330838	2.056842
H	7.726977	-1.937689	2.336370
H	8.256962	-1.524640	0.693898
H	8.505583	2.205553	1.257890
H	9.806273	1.015395	1.389107
H	8.651114	0.926208	0.046599
H	2.053631	-3.137016	-0.426644
H	-0.133011	-6.818474	-0.080773
H	-2.195285	-3.073515	0.342354
H	4.602277	-5.910545	0.551982
H	6.671626	-5.221795	-0.606702
H	4.332959	-3.991620	-4.000112
H	2.287966	-4.696954	-2.843442
H	6.113923	-2.619391	-4.448404
H	7.694625	-3.228046	-4.948082
H	6.261066	-4.234275	-5.168715
H	7.426320	-6.118945	-3.874623
H	8.847936	-5.066638	-3.747258
H	8.155908	-5.802631	-2.295952
H	7.083304	-2.164958	-2.104393
H	7.967617	-3.436378	-1.247977
H	8.643196	-2.737854	-2.723971
H	-2.433734	-4.653118	2.717704
H	-4.437700	-3.954570	3.945856
H	-6.887181	-5.130486	0.612175
H	-4.858640	-5.812840	-0.619356
H	-8.325710	-5.719483	2.329865
H	-7.551194	-6.069387	3.879756
H	-8.967699	-5.004537	3.814172
H	-6.197194	-2.589057	4.475949
H	-7.766127	-3.196992	5.011845
H	-6.333144	-4.215730	5.171486
H	-7.231792	-2.085315	2.174609
H	-8.144694	-3.334895	1.315797
H	-8.777952	-2.662455	2.822339

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