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Molecular engineering of carbazole-acrylonitrile fluorophore: substituent-dependent optical properties and mechanochromism

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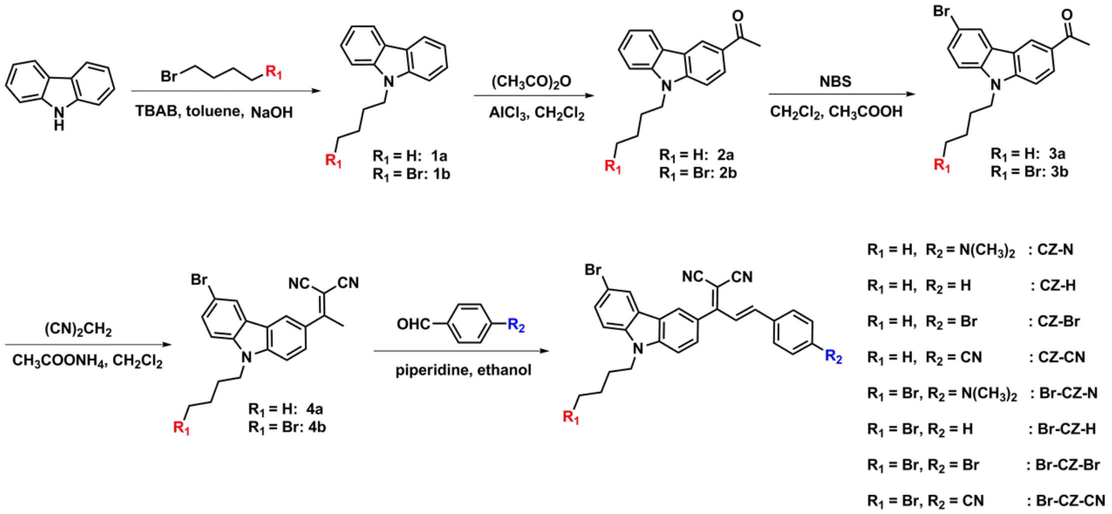


Characterization:

1a: Carbazole (16.7 g, 100 mmol) and NaOH (5.59 g, 150 mmol) were dissolved in 100 mL acetone. *n*-Butyl bromide (12 mL, 100 mmol) and 0.15 g TBAB were added to the above mixture. The mxiture was refluxed for 4 h, then the solvent was evaporated to dryness and the residue was added to 200 mL of water to get precipitation. The solid was filtered out, and the residue was washed with a large amount of water and recrystallized with ethanol/water at 50 ℃. After drying, a white needle-like solid was obtained (18.2 g). Go directly to the next step.

1b: Similar to **1a**, except that 1,4-dibromobutane was required a large excess (the stoichiometric ratio of carbazole and 1,4-dibromobutane is 1:8), and obtained white powder (yield: 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.87-1.94 (m, 2H), 2.02-2.09 (m, 2H), 3.37 (t, 2H, J = 6.84 Hz), 4.34 (t, 2H, J = 6.96 Hz), 7.21-7.25 (m, 2H), 7.39 (d, 2H, J = 8.16 Hz), 7.44-7.48 (m, 2H), 8.09 (d, 2H, J = 7.76 Hz).

2a: **1a** was added into the anhydrous CH_2Cl_2 (30 mL) under ice-bath. Then the anhydrous $AlCl_3$ (2.65 g, 19.85 mmol) was quickly added. 5 min later, the acetic anhydride (1.11 g, 10.92 mmol) was dropped into the above mixture and stired at room temperature overnight. The crude product was washed by water and extracted by CH_2Cl_2, then dried with anhydrous Na_2SO_4. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel with CH_2Cl_2/petroleum ether (1/2, v/v) as eluent. The pure product was a white solid (16.20 g, yield: 75%).

2b: Similar to **2a**. White powder (yield: 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.89-1.96 (m, 2H), 2.05-2.12 (m, 2H), 2.73 (s, 3H), 3.39 (t, 2H, J = 6.84 Hz), 4.39 (t, 2H, J = 6.96 Hz), 7.32 (t, 1H, J = 7.16 Hz), 7.40-7.45 (m, 2H), 7.53 (t, 1H, J = 7.32 Hz), 8.13 (d, 1H, J = 8.68 Hz), 8.16 (d, 1H, J = 8.16 Hz), 8.75 (s, 1H).

3a: **2a** (2.00 g, 7.54 mmol) and *N*-bromosuccinimide (1.74 g, 9.80 mmol) were dissolved in 40 mL chloroform/acetic acid (1/1, v/v), and stired at room temperature for 20 h. The reactant was dropped into 200 mL water and the pH value was adjusted to neutral by NaOH aqueous solution. After that, the crude product was extracted by CH_2Cl_2 and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel with CH_2Cl_2/petroleum ether (1/2, v/v) as eluent. The pure product was a white solid (1.95 g, yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.28 Hz, 3H), 1.32-1.42 (m, 2H), 1.80-1.88 (m, 2H), 2.72 (s, 3H), 4.30 (t, J = 7.12 Hz, 2H), 7.31 (d, J = 8.68 Hz, 1H), 7.40 (d, J = 8.72 Hz, 1H), 7.58 (dd, J_1= 8.64 Hz, J_2= 1.88 Hz, 1H), 8.14 (dd, J_1= 8.68 Hz, J_2= 1.56 Hz, 1H), 8.26 (d, J = 1.88 Hz, 1H), 8.67 (d, J = 1.56 Hz, 1H).

3b: Similar to **3a**. White powder (yield: 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.87-1.94 (m, 2H), 2.03-2.10 (m, 2H), 2.72 (s, 3H), 3.39 (t, 2H, J = 6.36 Hz), 4.36 (t, 2H, J = 7.08 Hz), 7.32 (d, 1H, J = 8.68 Hz), 7.42 (d, 1H, J = 8.68 Hz), 7.60 (dd, 1H, J_1 = 8.64 Hz, J_2 = 1.88 Hz), 8.16 (d, 1H, J = 8.68 Hz), 8.27 (s, 1H), 8.68 (s, 1H).

4a: **3a** (1.50 g, 4.37 mmol), malononitrile (0.375 g, 5.68 mmol) and ammonium acetate (0.438 g 5.68 mmol) were dissolved in 18 mL CH_2Cl_2/MeOH (2/1, v/v), and stired at room temperature for 20 h. The crude product was purified by silica gel with CH_2Cl_2/petroleum ether (1/4, v/v) as eluent. The pure product was a white solid (0.95 g, yield: 56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ:0.96 (t, J = 7.38 Hz, 3H), 1.35-1.42 (m,2H), 1.82-1.87 (m, 2H), 2.75 (s, 3H), 4.28 (t, J = 7.20Hz, 2H), 7.31 (d, J = 8.70 Hz, 1H), 7.45 (d, J = 8.70 Hz, 1H), 7.60 (d, J= 8.70 Hz, 1H), 7.80 (d, J =8.70 Hz, 1H), 8.23 (s, 1H), 8.32 (s, 1H).

4b: Similar to **4a**. Primrose-yellow powder (yield: 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88-1.95 (m, 2H), 2.03-2.11 (m, 2H), 2.77 (s, 3H), 3.40 (t, 2H, J = 6.32 Hz), 4.36 (t, 2H, J = 7.12 Hz), 7.33 (d, 1H, J = 8.68 Hz), 7.47 (d, 1H, J = 8.68 Hz), 7.63 (d, 1H, J_1 = 8.72 Hz, J_2 = 1.88 Hz), 7.81 (d, 1H, J = 8.72 Hz), 8.25 (s, 1H), 8.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.3, 27.5, 30.0, 32.7, 42.7, 81.8, 109.3, 110.7, 113.4, 113.6, 114.1, 121.1, 122.2, 123.6, 124.3, 126.3, 126.8, 129.9, 139.6, 142.6, 174.8.

CZ-N: **4a** (0.30 g, 0.74 mmol) and 4-(dimethylamino)benzaldehyde (0.14 g, 0.96 mmol) were dissolved in ethanol (15 mL), then the catalytic amount of piperidine was added. The reaction mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel with CH_2Cl_2 and petroleum ether (1/1, v/v) as the eluent to afford pure **CZ-N** as a red powder 174 mg (yield: 44%). m. p. 254.0-265.4 ℃. FT-IR (KBr, cm^{-1}): 2216, 1578, 1530, 1472, 1357, 1289, 1167, 969, 815. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, J = 7.32 Hz, 3H), 1.39-1.49 (m, 2H), 1.85-1.92 (m, 2H), 3.07 (s, 6H), 4.32 (t, J = 7.16 Hz, 2H), 6.63 (d, J = 8.92 Hz, 2H), 6.87 (d, J = 15.16 Hz, 1H), 7.32 (d, J = 8.68 Hz, 1H), 7.42 (d, J = 8.92 Hz, 2H), 7.46 (d, J = 15.16 Hz, 1H), 7.51 (m, 2H), 7.58 (dd, J_1 = 8.68 Hz, J_2 = 1.92 Hz, 1H), 8.06 (s, 1H), 8.17 (d, J = 1.76 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.1, 40.1, 43.3, 109.2, 110.6, 111.8, 112.5, 114.6, 115.4, 119.8, 121.8, 122.2, 122.5, 123.5, 124.2, 124.6, 127.6, 129.2, 131.3, 139.6, 142.0, 150.3, 152.7, 172.3. MS (APCI) m/z: calcd for $C_{30}H_{27}N_4Br$: 522.14, found 523.15 $[M + H]^+$.

CZ-H: Similar to **CZ-N**. Yellow powder (yield: 48%). m. p. 221.5-224.3 ℃. FT-IR (KBr, cm^{-1}): 2220, 1607, 1530, 1470, 1444, 1350, 1287, 1281, 1149, 971, 800. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (t, J = 7.28 Hz, 3H), 1.40-1.51 (m, 2H), 1.85-1.93 (m, 2H), 4.33 (t, J = 7.20 Hz, 2H), 6.97 (d, J = 15.52 Hz, 1H), 7.34-7.45 (m, 4H), 7.52-7.62 (m, 5H), 7.67 (d, J = 15.52 Hz, 1H), 8.11 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.1, 43.4, 81.0, 109.5, 110.8, 112.8, 113.5, 114.3, 122.0, 122.4, 123.5, 123.8, 124.1, 125.4, 127.6, 128.8, 129.2, 129.5, 131.5, 134.5, 139.7, 142.3, 149.3, 171.8. MS (APCI) m/z calcd for $C_{28}H_{22}N_3Br$: 479.10, found 480.10 $[M + H]^+$.

CZ-Br: Similar to **CZ-N**. Yellow powder (yield: 62%). m. p. 208.1-212.2 ℃. FT-IR (KBr, cm^{-1}): 2220, 1607, 1585, 1522, 1486, 1441, 1332, 1218, 1150, 1006, 977, 800. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (t, J = 7.32 Hz, 3H), 1.39-1.48 (m, 2H), 1.85-1.93 (m, 2H), 4.33 (t, J = 7.20 Hz, 2H), 6.89 (d, J = 15.56 Hz, 1H), 7.34-7.40 (m, 3H), 7.53-7.55 (m, 4H), 7.60 (dd, J_1 = 8.68 Hz, J_2 = 1.84 Hz, 1H), 7.64 (d, J = 15.56

Hz, 1H), 8.09 (s, 1H), 8.22 (d, *J* = 1.76 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.1, 43.4, 81.5, 109.5, 110.8, 112.8, 112.9, 113.4, 114.2, 122.1, 122.3, 123.5, 124.1, 125.9, 126.0, 127.5, 129.6, 130.0, 132.5, 133.4, 139.7, 142.3, 147.7, 171.4. MS (APCI) m/z calcd for $C_{28}H_{21}N_3Br_2$: 557.01 , found 559.02 $[M + 2H]^+$.

CZ-CN: Similar to **CZ-N**. Bright-yellow powder (yield: 37%). m. p. 254.6-258.3 ℃. FT-IR (KBr, cm^{-1}): 2220, 1607, 1596, 1522, 1481, 1441, 1338, 1212, 1155, 1069, 960, 830. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (t, *J* = 7.28 Hz, 3H), 1.40-1.50 (m, 2H), 1.86-1.93 (m, 2H), 4.34 (t, *J* = 7.16 Hz, 2H), 6.95 (d, *J* = 15.60 Hz, 1H), 7.35 (d, *J* = 8.76 Hz, 1H), 7.55-7.70 (m, 7H), 7.76 (d, *J* = 15.60 Hz, 1H), 8.11 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.6, 31.1, 43.4, 83.1, 109.6, 110.9, 113.0, 113.1, 113.8, 114.2, 118.1, 122.2, 122.3, 123.2, 123.5, 124.0, 127.4, 128.5, 128.9, 129.7, 132.8, 138.5, 139.8, 142.4, 146.1, 170.6. MS (APCI) m/z calcd for $C_{29}H_{21}N_4Br$: 504.10, found 505.10 $[M + H]^+$.

Br-CZ-N: Similar to **CZ-N**. Red powder (yield: 45%). m. p. 232.0-241.7 ℃. FT-IR (KBr, cm^{-1}): 2210, 1607, 1521, 1460, 1351, 1165, 1091, 976, 806. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-2.00 (m, 2H), 2.06-2.13 (m, 2H), 3.07 (s, 6H), 3.43 (t, 2H, *J* = 6.28 Hz), 4.37 (t, 2H, *J* = 6.92 Hz), 6.64 (d, 2H, *J* = 8.72 Hz), 6.88 (d, 1H, *J* = 15.12 Hz), 7.33 (d, 1H, *J* = 8.68 Hz), 7.41-7.51 (m, 5H), 7.60 (d, 1H, *J* = 8.82 Hz), 8.07 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 30.1, 32.8, 40.1, 42.7, 109.1, 110.5, 111.9, 112.8, 114.5, 115.3, 119.9, 122.0, 122.2, 122.5, 123.6, 124.3, 125.0, 127.7, 129.4, 131.3, 131.5, 139.5, 141.8, 150.2, 152.8, 172.1. MALDI-TOF calcd for $C_{30}H_{26}Br_2N_4$, 602.05, found, 602.22.

Br-CZ-H: Similar to **CZ-N**. Yellow powder (yield: 39%). m. p. 205.3-209.4 ℃. FT-IR (KBr, cm^{-1}): 2213, 1608, 1592, 1502, 1481, 1448, 1383, 1351, 1334, 1204, 1156, 873, 803, 765, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-2.00 (m, 2H), 2.07-2.15 (m, 2H), 3.43 (t, 2H, *J* = 6.32 Hz), 4.39 (t, 2H, *J* = 6.96 Hz), 6.98 (d, 1H, *J* = 15.56 Hz), 7.35 (d, 1H, *J* = 8.68 Hz), 7.39-7.45 (m, 3H), 7.53-7.58 (m, 4H), 7.62 (d, 1H, *J* = 8.72 Hz), 7.70 (d, 1H, *J* = 15.56 Hz), 8.12 (s, 1H), 8.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 30.1, 32.8, 42.7, 81.3, 109.4, 110.6, 113.1, 113.4, 114.2, 122.2, 112.4, 123.7, 124.1, 124.2, 125.4, 127.7, 128.8, 129.2, 129.7, 131.6, 134.5, 139.6, 142.1, 149.3, 171.7. MALDI-TOF calcd for $C_{28}H_{21}Br_2N_3$, 559.01, found, 559.57.

Br-CZ-Br: Similar to **CZ-N**. Orange powder (yield: 60%). m. p. 201.8-214.5 ℃. FT-IR (KBr, cm^{-1}): 2220, 1613, 1585, 1506, 1478, 1444, 1399, 1348, 1332, 1287, 1230, 1157, 1073, 1011, 983, 867, 800. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-2.00 (m, 2H), 2.07-2.14 (m, 2H), 3.43 (t, 2H, J = 6.28 Hz), 4.39 (t, 2H, J = 7.00 Hz), 6.90 (d, 1H, J = 15.56 Hz), 7.34-7.40 (m, 3H), 7.53-7.55 (m, 4H), 7.63 (d, 1H, J = 8.72 Hz), 7.67 (d, 1H, J = 15.56 Hz), 8.10 (s, 1H), 8.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 30.0, 32.8, 42.7, 81.8, 109.4, 110.6, 113.1, 113.3, 114.1, 122.2, 122.3, 123.7, 123.8, 124.2, 125.9, 126.1, 127.6, 129.8, 130.0, 132.5, 133.4, 139.6, 142.1, 147.7, 171.3. MALDI-TOF calcd for $C_{28}H_{20}Br_3N_3$, 636.92, found, 636.19.

Br-CZ-CN: Similar to **CZ-N**. Bright-yellow powder (yield: 44%). m. p. 212.7-217.3 ℃. FT-IR (KBr, cm^{-1}): 2219, 1617, 1591, 1511, 1482, 1437, 1373, 1328, 1287, 1226, 1181, 1155, 1024, 979, 874, 825, 560. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-2.00 (m, 2H), 2.07-2.15 (m, 2H), 3.44 (t, 2H, J = 6.28 Hz), 4.39 (t, 2H, J = 7.20 Hz), 6.96 (d, 1H, J = 15.52 Hz), 7.36 (d, 1H, J = 8.68 Hz), 7.61-7.65 (m, 3H), 7.69 (d, 2H, J = 8.36 Hz), 7.74 (d, 1H, J = 15.52 Hz), 8.11 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.6, 30.1, 32.9, 42.8, 109.6, 110.8, 113.0, 113.3, 113.8, 114.3, 118.2, 122.4, 123.5, 123.7, 124.2, 127.6, 128.5, 128.9, 130.0, 132.9, 138.6, 139.7, 142.3, 146.2, 170.6. MALDI-TOF calcd for $C_{29}H_{20}Br_2N_4$, 584.01, found, 584.31.

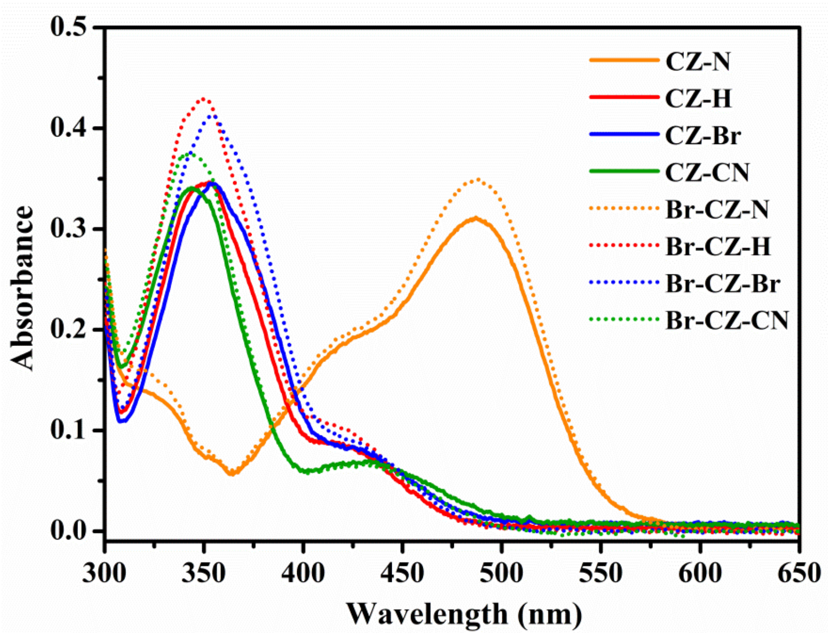


Fig. S1 The UV-vis absorption spectra of these compounds in THF (1.0×10^{-5} M).

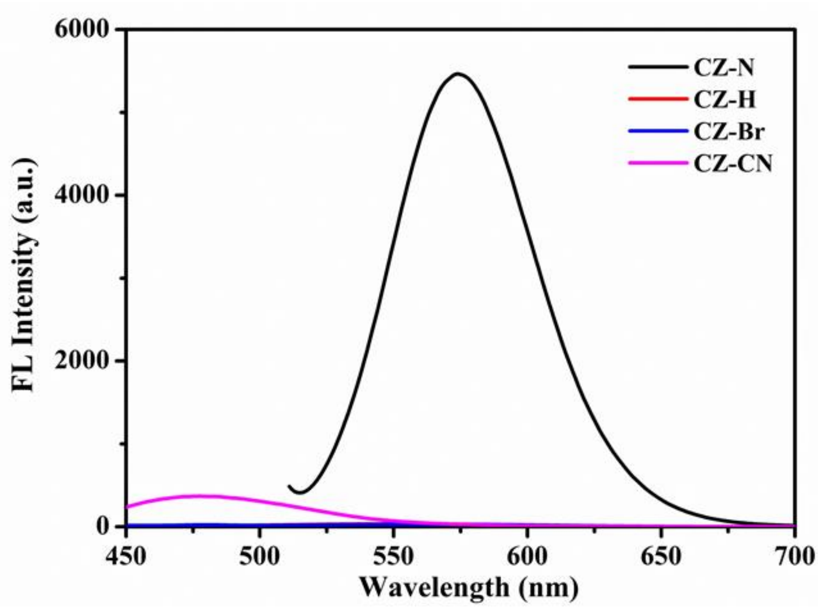


Fig. S2 The flourescence spectra of the compounds **CZ-N ~ CZ-CN** in THF (1.0×10^{-5} M).

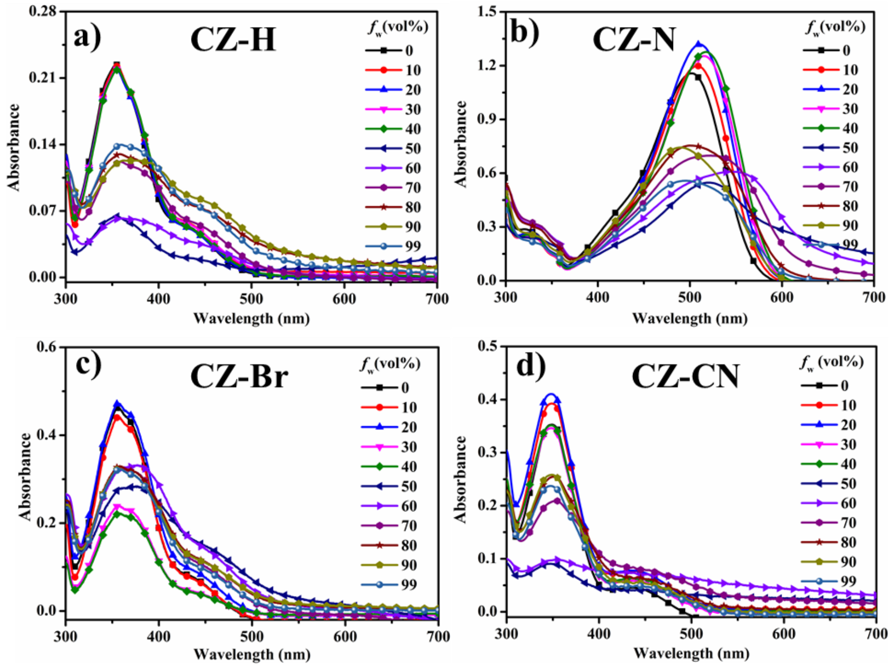


Fig. S3 The UV-vis absorption spectra of compounds **CZ-H**, **CZ-N**, **CZ-Br**, and **CZ-CN** in the DMF/H_2O system with different water fraction.

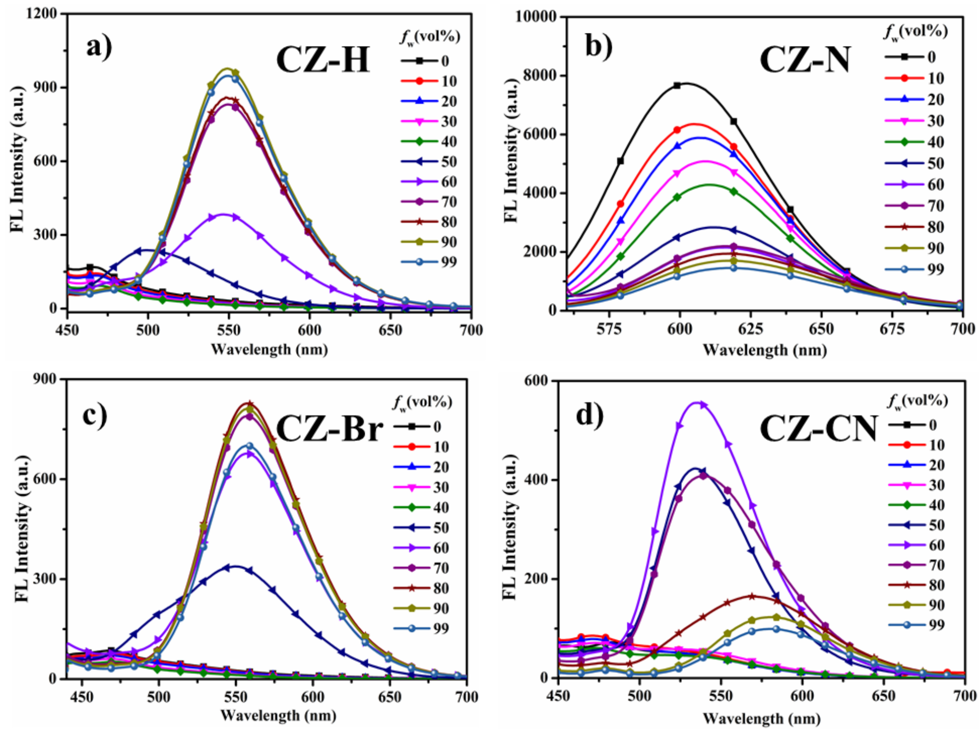


Fig. S4 The fluorescence spectra of compounds **CZ-H**, **CZ-N**, **CZ-Br**, and **CZ-CN** in the DMF/H_2O system with different water fraction.

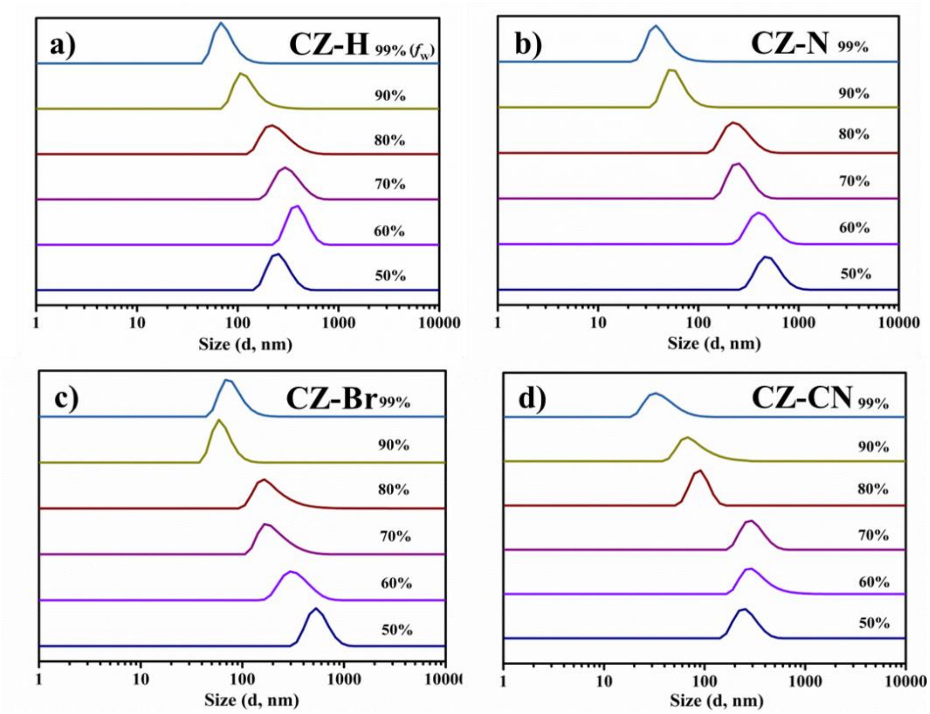


Fig. S5 The dynamic light scattering of compounds **CZ-H**, **CZ-N**, **CZ-Br**, and **CZ-CN** in the DMF/H_2O system with different water fraction.

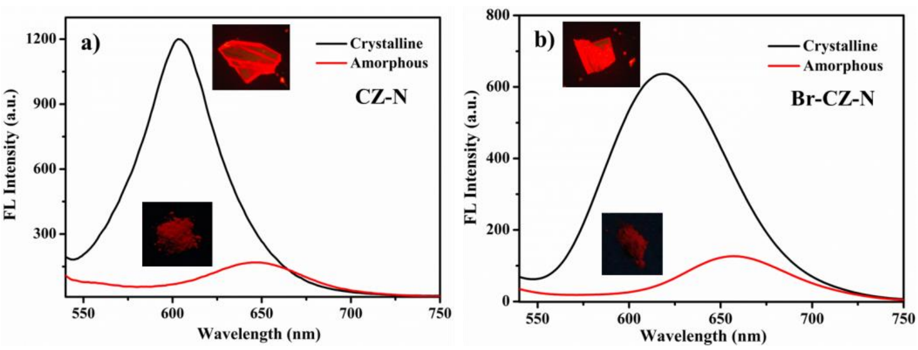


Fig. S6 The fluorescence spectra of **CZ-N** (a) and **Br-CZ-N** (b) in the crystalline state and amorphous state. Inset: the photographs in the crystalline state and amorphous state under the 365 nm UV lamp.

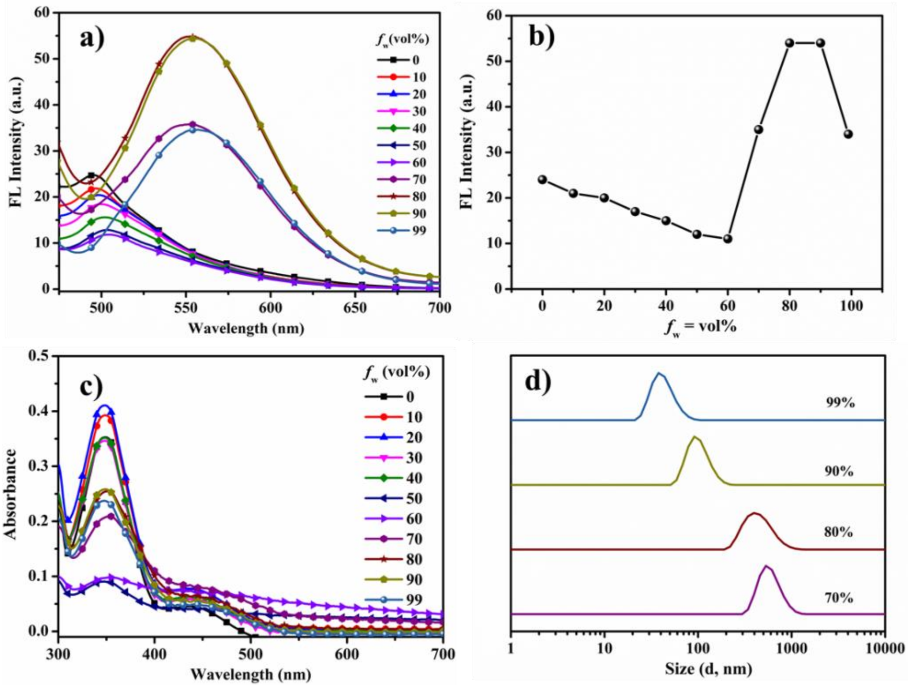


Fig. S7 The photophysical properties of compound **Br-CZ-H** in the DMF/H_2O system with different water fraction. The fluorescence spectra (a), the plots of fluorescence intensity vs. water fraction (b), the UV-vis absorption spectra (c), and the dynamic light scattering (d).

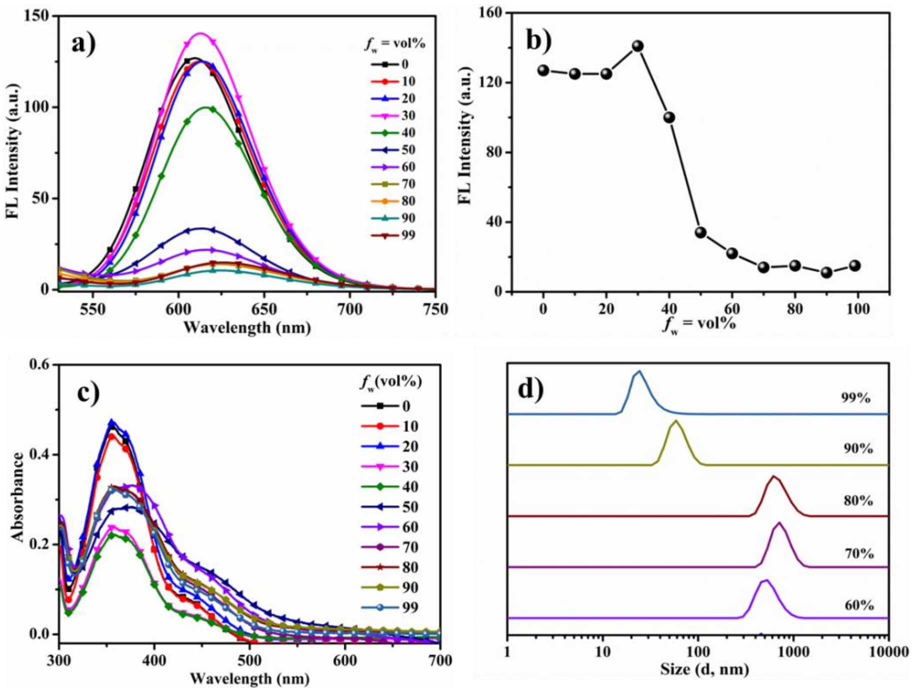


Fig. S8 The photophysical properties of compound **Br-CZ-N** in the DMF/H_2O system with different water fraction. The fluorescence spectra (a), the plots of fluorescence intensity vs. water fraction (b), the UV-vis absorption spectra (c), and the dynamic light scattering (d).

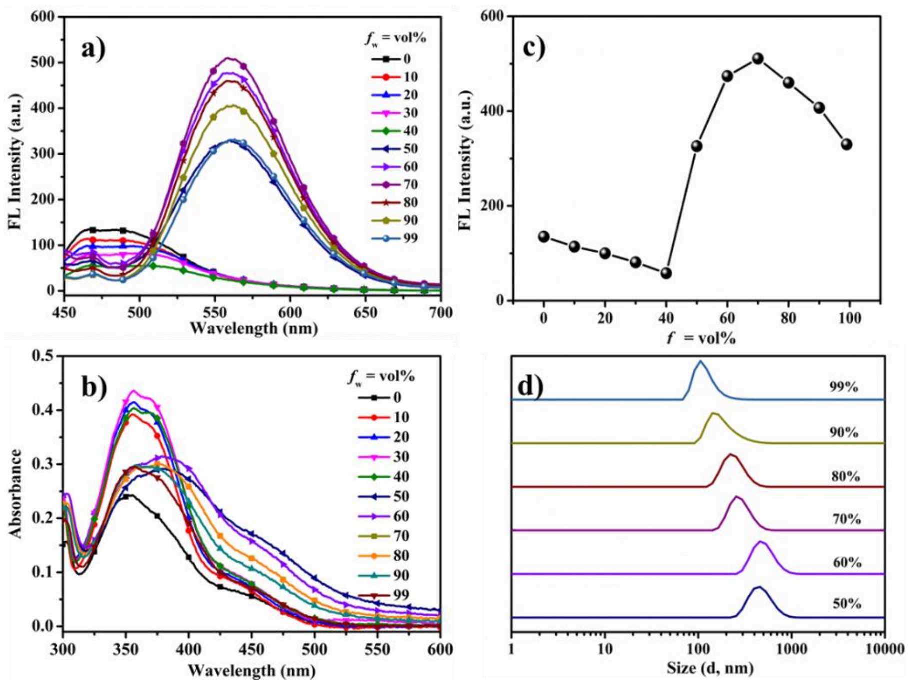


Fig. S9 The photophysical properties of compound **Br-CZ-Br** in the DMF/H_2O system with different water fraction. The fluorescence spectra (a), the plots of fluorescence intensity vs. water fraction (b), the UV-vis absorption spectra (c), and the dynamic light scattering (d).

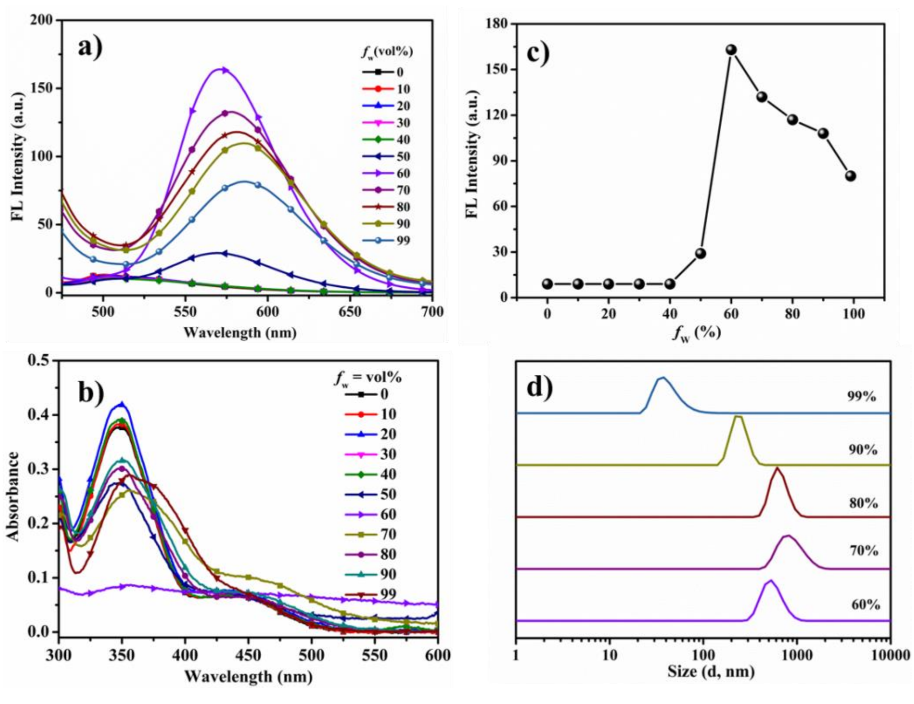


Fig. S10 The photophysical properties of compound **Br-CZ-CN** in the DMF/H_2O system with different water fraction. The fluorescence spectra (a), the plots of fluorescence intensity vs. water fraction (b), the UV-vis absorption spectra (c), and the dynamic light scattering (d).

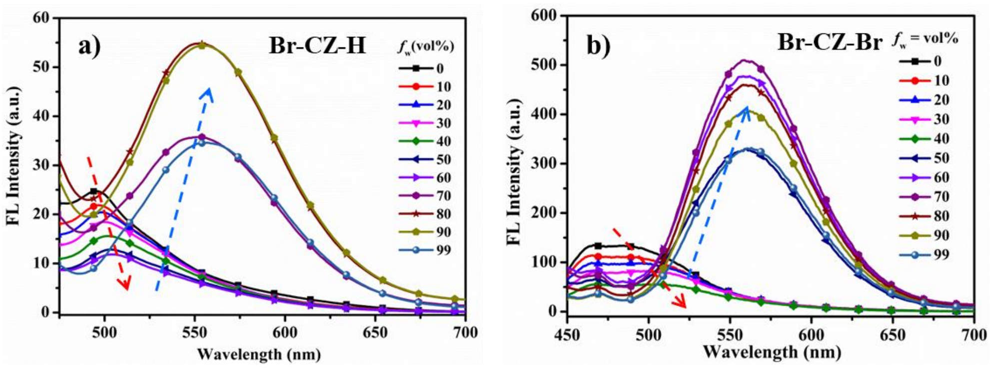


Fig. S11 The fluorescence spectra of compound **Br-CZ-H** and **Br-CZ-Br** in the DMF/H_2O system with different water fraction.

Table S1 The crystallographic data and structure refinement details for **CZ-N**, **CZ-H**, **CZ-Br**, **Br-CZ-N**, and **Br-CZ-Br**.

Compound	**CZ-N**	**CZ-H**	**CZ-Br**	**Br-CZ-N**	**Br-CZ-Br**
CCDC No:	1540851	1541386	1534287	2015185	2015186
formula	$C_{30}H_{27}BrN_4$	$C_{28}H_{22}BrN_3$	$C_{28}H_{21}Br_2N_3$	$C_{30}H_{26}Br_2N_4$	$C_{28}H_{20}Br_3N_3$
Weight (M_r)	523.47	480.39	559.30	602.37	638.20
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	17.509(9)	16.251(3)	8.0137(9)	17.292(4)	7.3087(4)
b (Å)	12.679(7)	12.879(2)	11.6967(13)	13.172(3)	11.5980(7)
c (Å)	12.592(7)	12.557(2)	13.9362(15)	12.572(3)	14.7149(8)
α (deg)	90	90	72.1240(10)	90	98.253(5)
β (deg)	105.956(7)	111.379(2)	81.6730(10)	106.655(2)	101.593(3)
γ (deg)	90	90	78.3640(10)	90	100.037(5)
V	2688(2)	2447.4(7)	1212.9(2)	2743.3(9)	1210.18(12)
Z	4	4	2	4	1
ρ (calad) (mg m^{-3})	1.294	1.304	1.531	1.458	1.751
reflns collected	18523	17052	8697	18768	10044
Goodness-of-fit on F^2	1.039	1.070	1.049	1.104	1.071
Final *R* [I>2σ(I)]	R_1 = 0.0701 wR_2 = 0.2071	R_1 = 0.0779, wR_2 = 0.2291	R_1 = 0.0347 wR_2 = 0.0873	R_1 = 0.0573 wR_2 = 0.1714	R_1 = 0.0361 wR_2 = 0.0887
R indices (all data)	R_1 = 0.0933 wR_2 = 0.2285	R_1 = 0.1040, wR_2 = 0.2508	R_1 = 0.0462 wR_2 = 0.0932	R_1 = 0.0861 wR_2 = 0.1866	R_1 = 0.0481 wR_2 = 0.0940

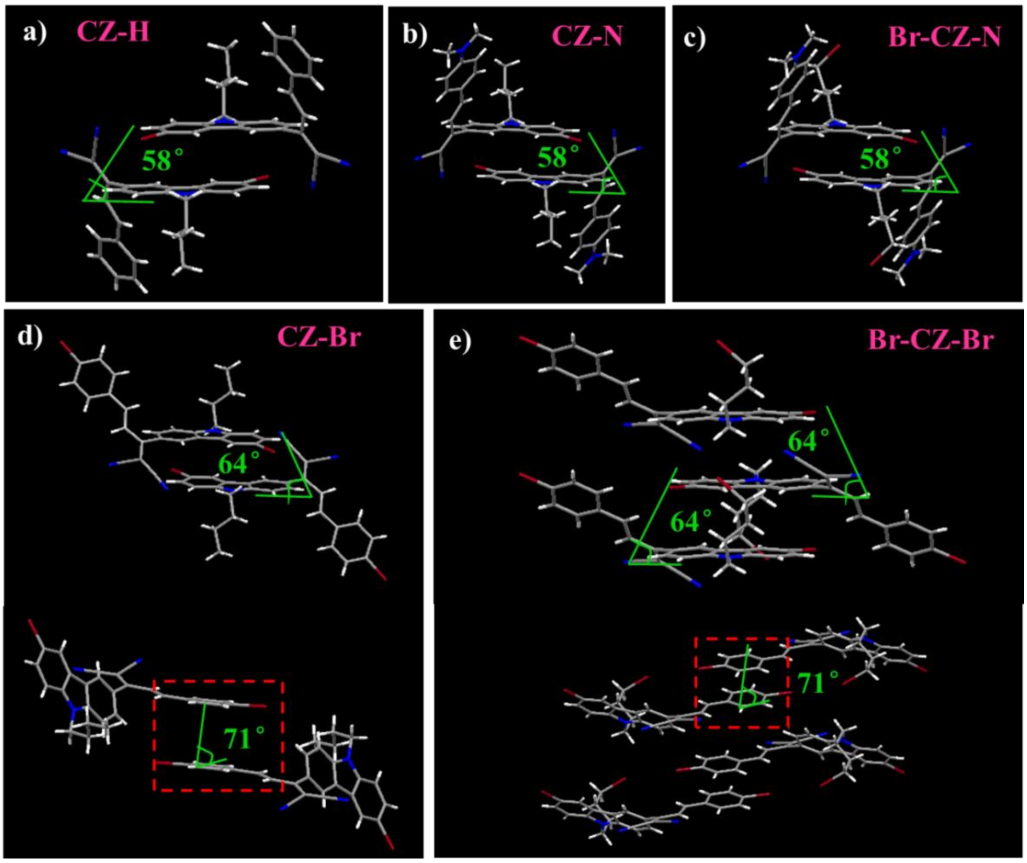


Fig. S12 The space-filling model of these dimers.

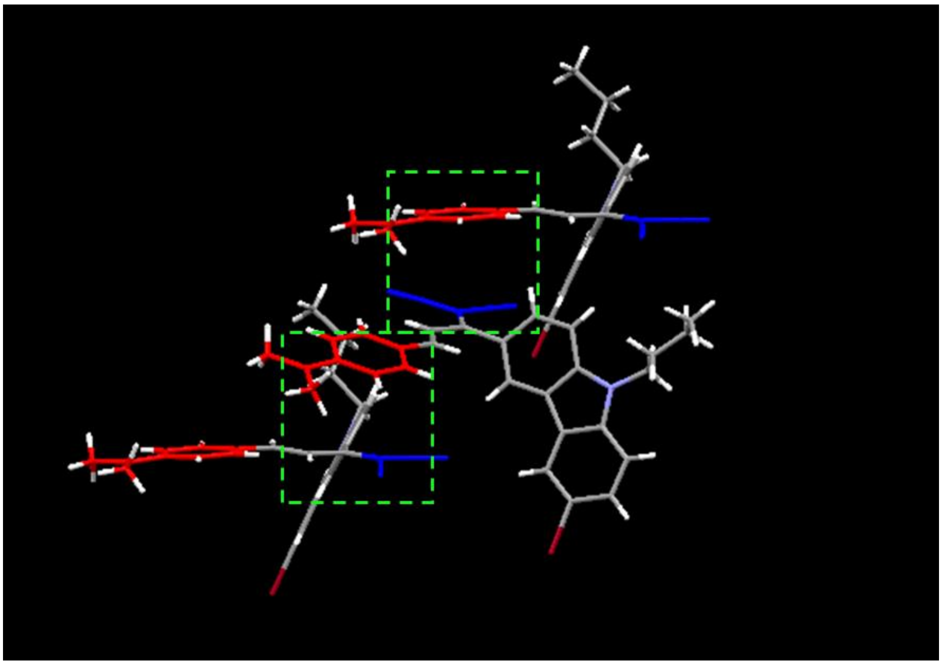


Fig. S13 The D-A stacking model of **CZ-N** molecules.

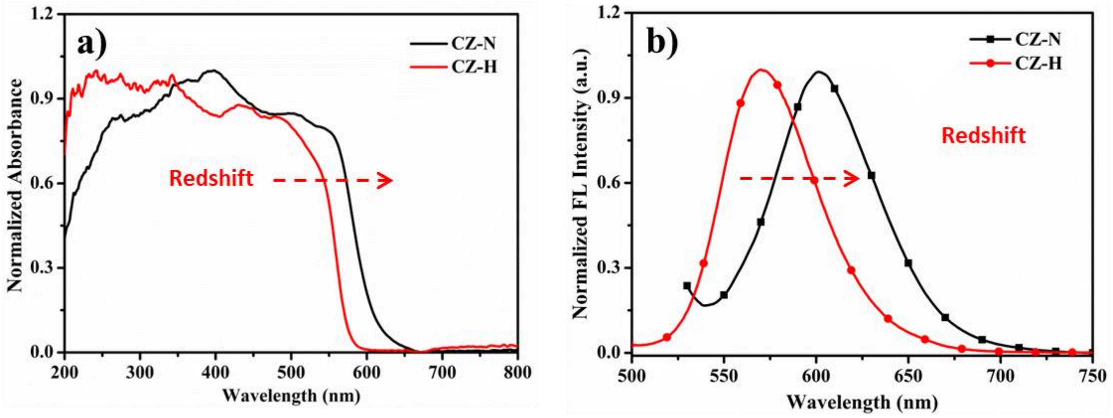


Fig. S14 The absorption and emission spectra of **CZ-N** and **CZ-H** in the solid state.

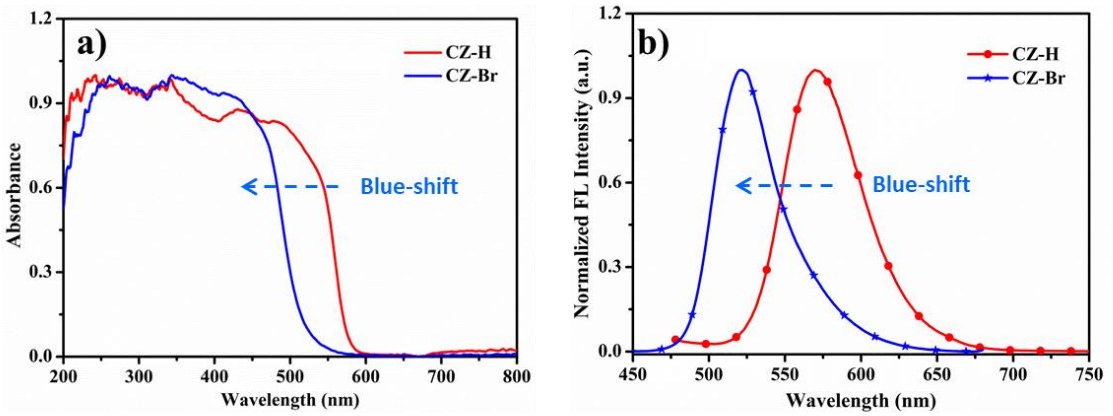


Fig. S15 The absorption and emission spectra of **CZ-H** and **CZ-Br** in the solid state.

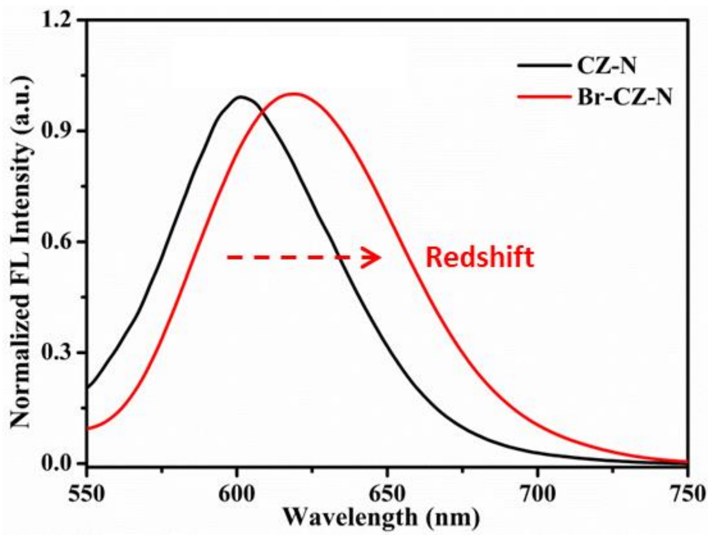


Fig. S16 The flourescence emission spectra of **CZ-N** and **Br-CZ-N** in the solid state.

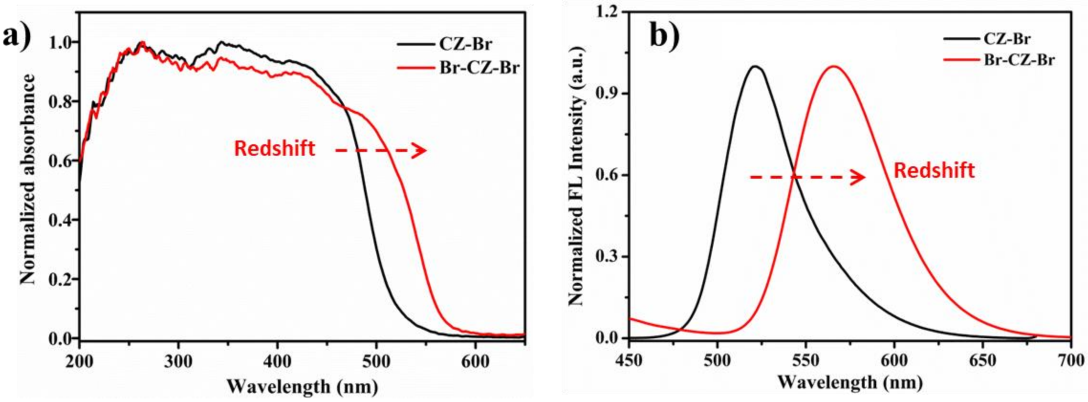


Fig. S17 The absorption and emission spectra of **CZ-Br** and **Br-CZ-Br** in the solid state.

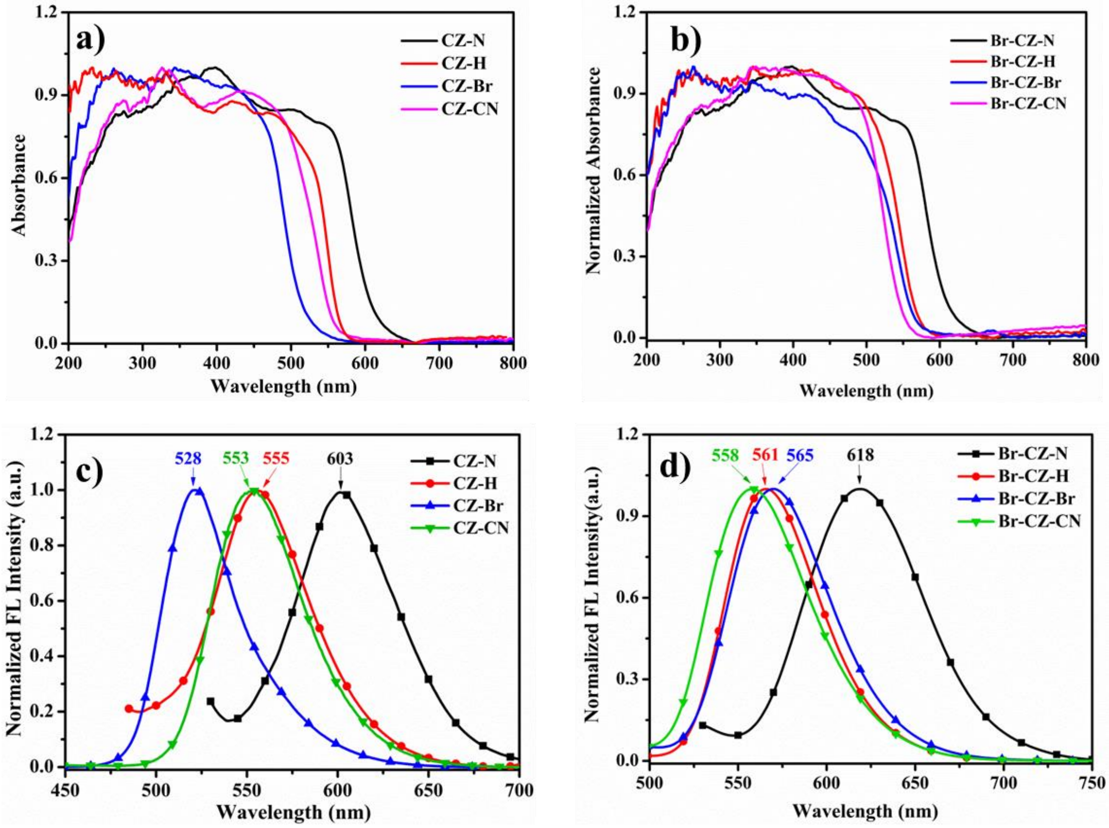


Fig. S18 The absorption and emission spectra of **CZ-N** ~ **Br-CZ-CN** in the solid state.

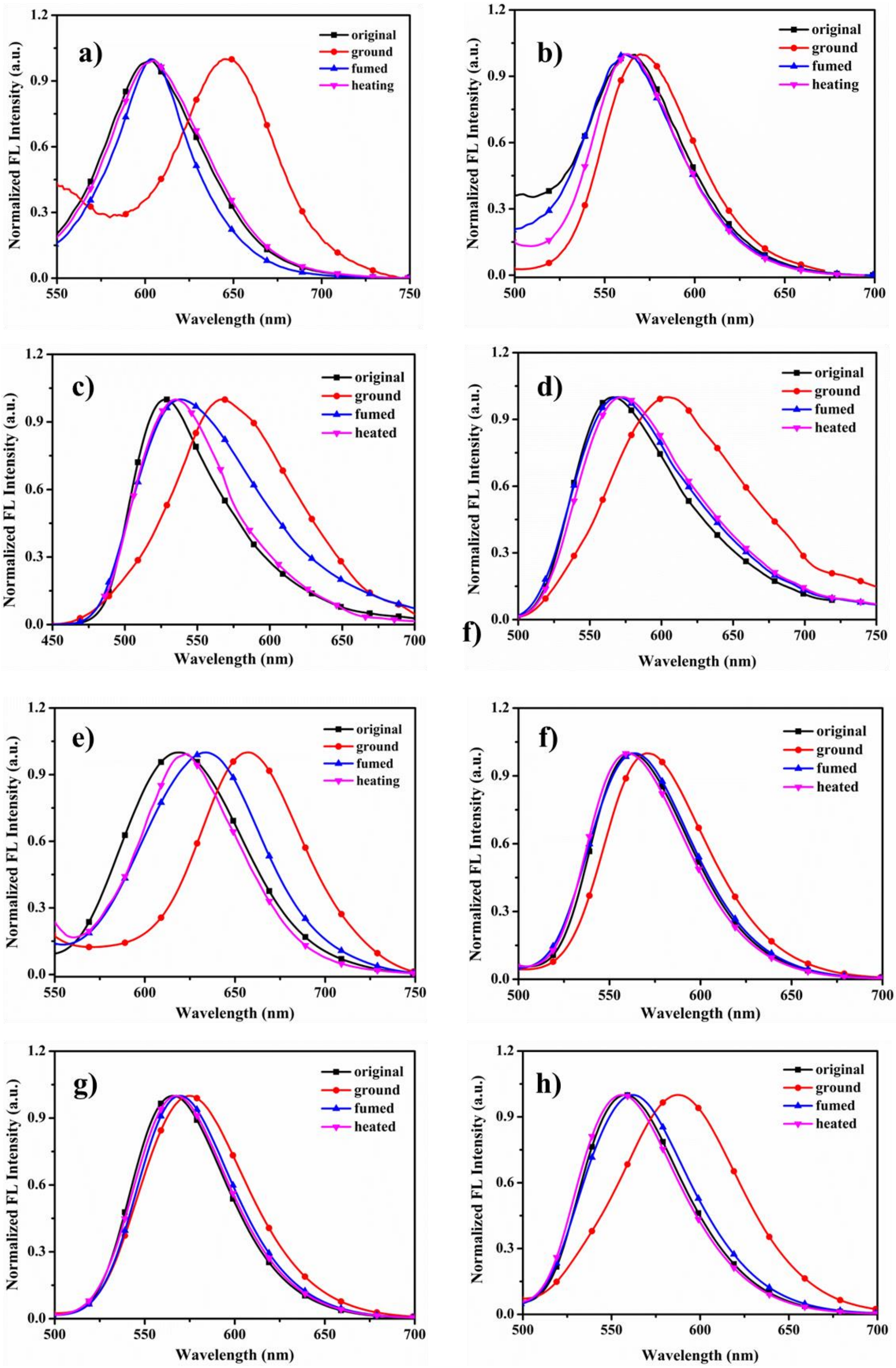


Fig. S19 The fluorescence spectra of compounds **CZ-N~Br-CZ-CN** (a-h) under different treatments.

Table S2 The fluorescence properties of these compounds in different solid states.

Compounds	**CZ-N**	**CZ-H**	**CZ-Br**	**CZ-CN**	**Br-CZ-N**	**Br-CZ-H**	**Br-CZ-Br**	**Br-CZ-CN**
λ_{em}[a] (nm)	603	568	528	553	618	561	565	558
λ_{em}[b] (nm)	647	565	580	605	658	570	575	588
λ_{em}[c] (nm)	603	566	538	553	634	561	569	558
λ_{em}[d] (nm)	603	566	536	554	625	561	568	558
$\Delta\lambda_{em}$[e] (nm)	44	9	52	52	40	9	10	30

The maximum emission peaks of original samples[a], ground samples[b], fumed samples[c] and heated samples[d]; $\Delta\lambda_{em}$[e] = λ_{em}[b] - λ_{em}[a].

Table S3 The fluorescence lifetime of these compounds in different states.

Compounds	**τ_1 [a] (ns)**	**τ_2 [a] (ns)**	**τ_3 [a] (ns)**	**A_1 [b]**	**A_2 [b]**	**A_3 [b]**	χ^2	**<τ> [c] (ns)**
$CZ\text{-}N_{original}$	0.41	1.16	2.66	0.70	0.27	0.03	1.02	0.67
$CZ\text{-}N_{ground}$	1.51	0.21	4.52	0.26	0.69	0.05	1.73	0.77
$CZ\text{-}H_{origina}$	0.11	0.75	-	0.97	0.03	-	1.27	0.13
$CZ\text{-}H_{ground}$	0.26	0.68	2.28	0.74	0.25	0.02	1.44	0.39
$CZ\text{-}Br_{original}$	0.33	1.56	4.06	0.61	0.35	0.04	1.13	0.91
$CZ\text{-}Br_{ground}$	0.70	1.53	7.57	0.62	0.37	0.01	1.17	1.07
$CZ\text{-}CN_{original}$	2.40	0.38	5.31	0.28	0.68	0.04	1.54	1.14
$CZ\text{-}CN_{ground}$	0.83	2.17	10.84	0.07	0.92	0.01	1.38	2.16

[a] Fluorescence lifetime. [b] Proportion. [c] Average life time $<\tau> = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$.

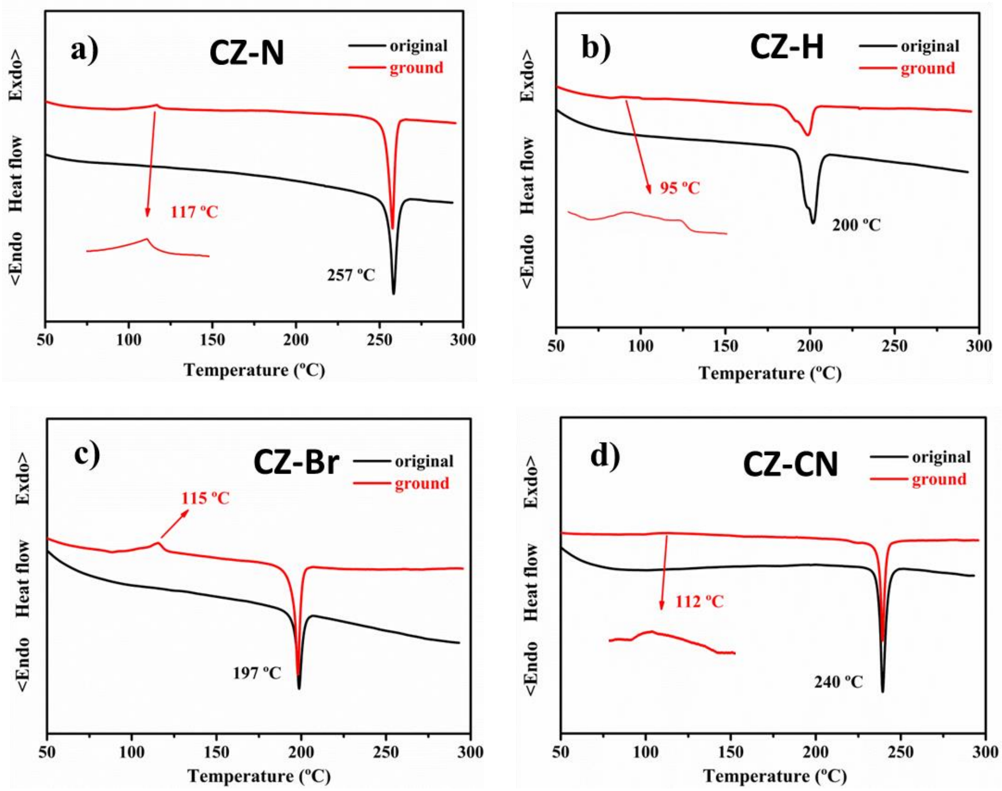
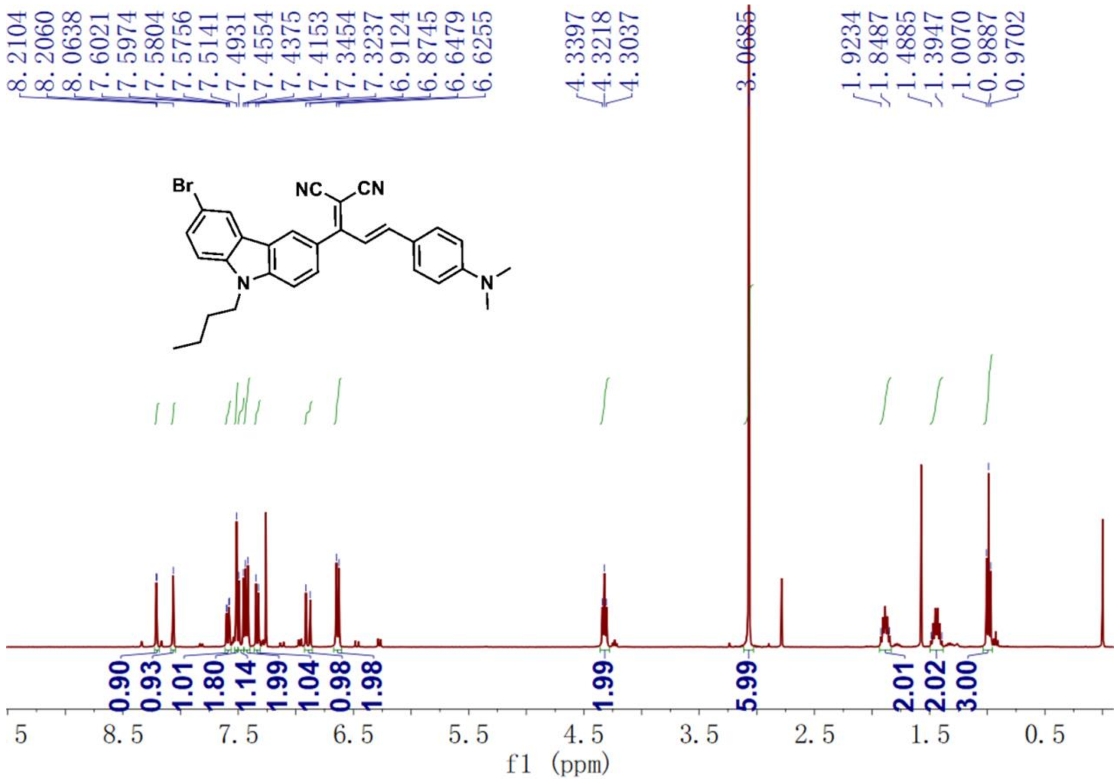
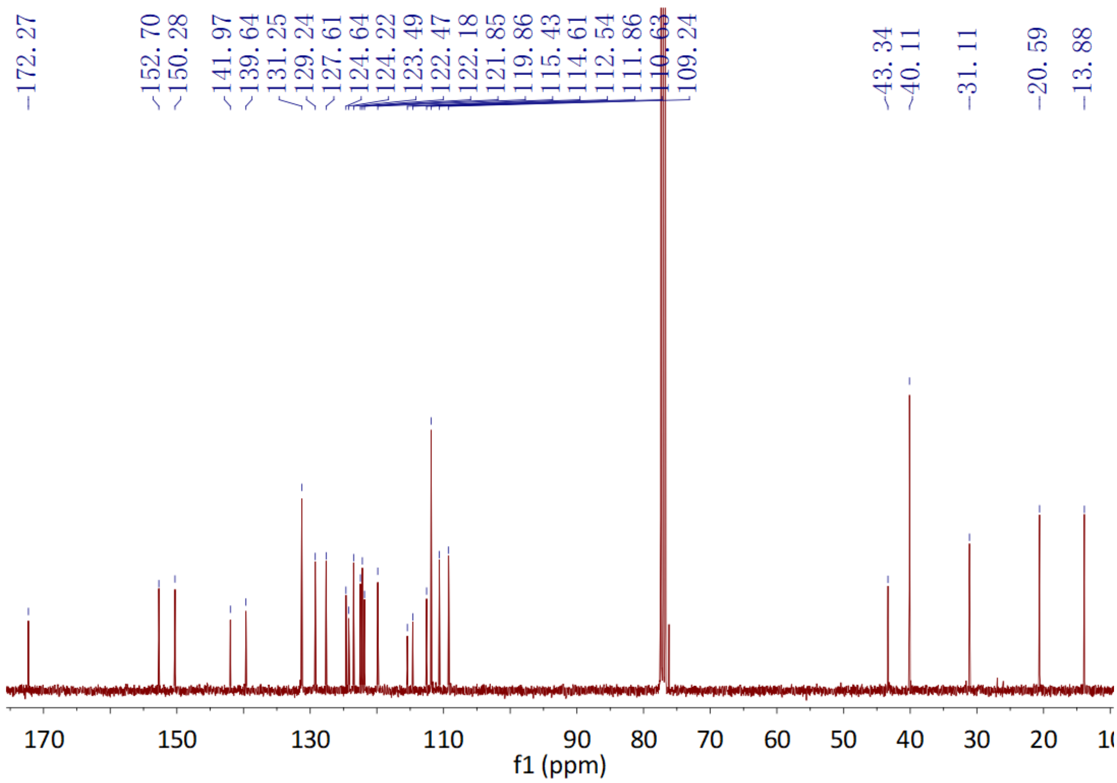


Fig. S20 DSC curves of compounds **CZ-N** ~ **CZ-CN** in the original and ground states.

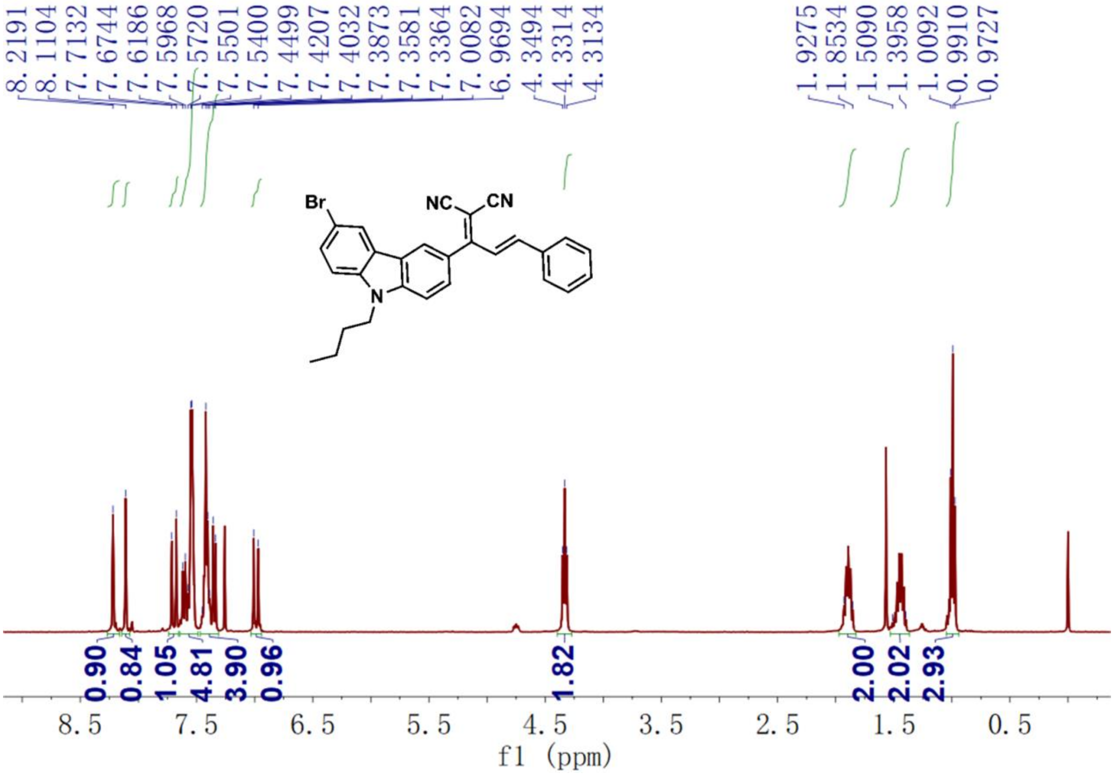
^{1}H NMR data of compound **CZ-N**



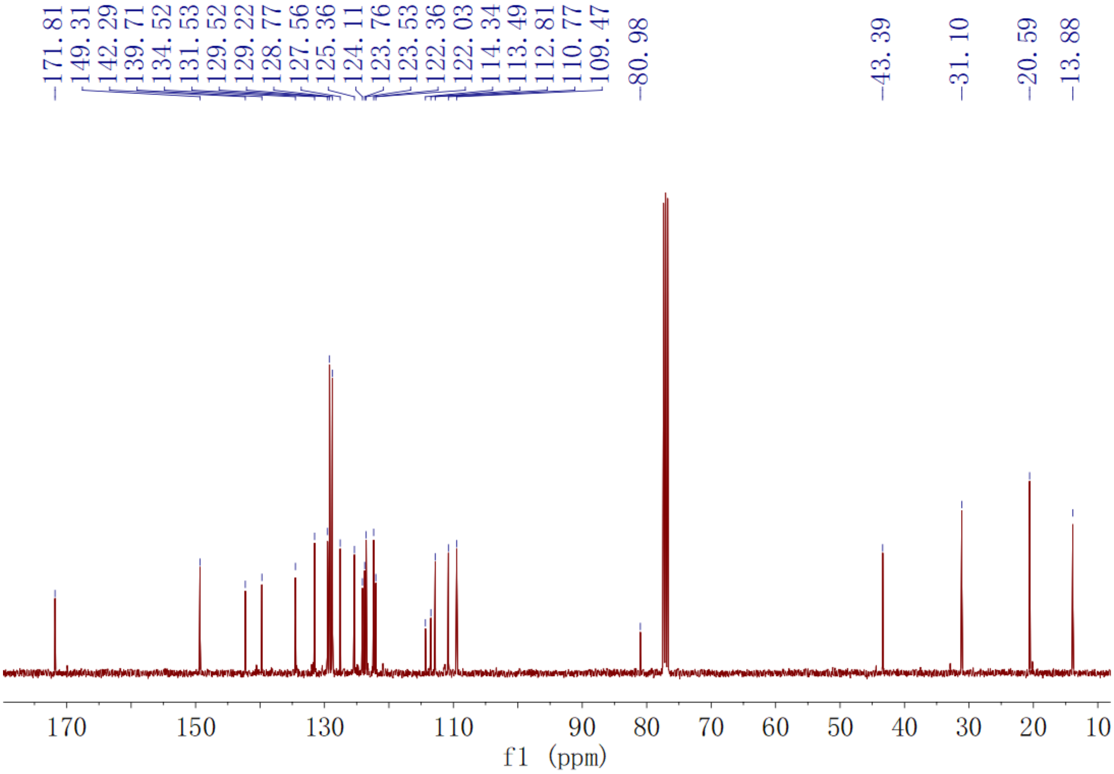
^{13}C NMR data of compound **CZ-N**



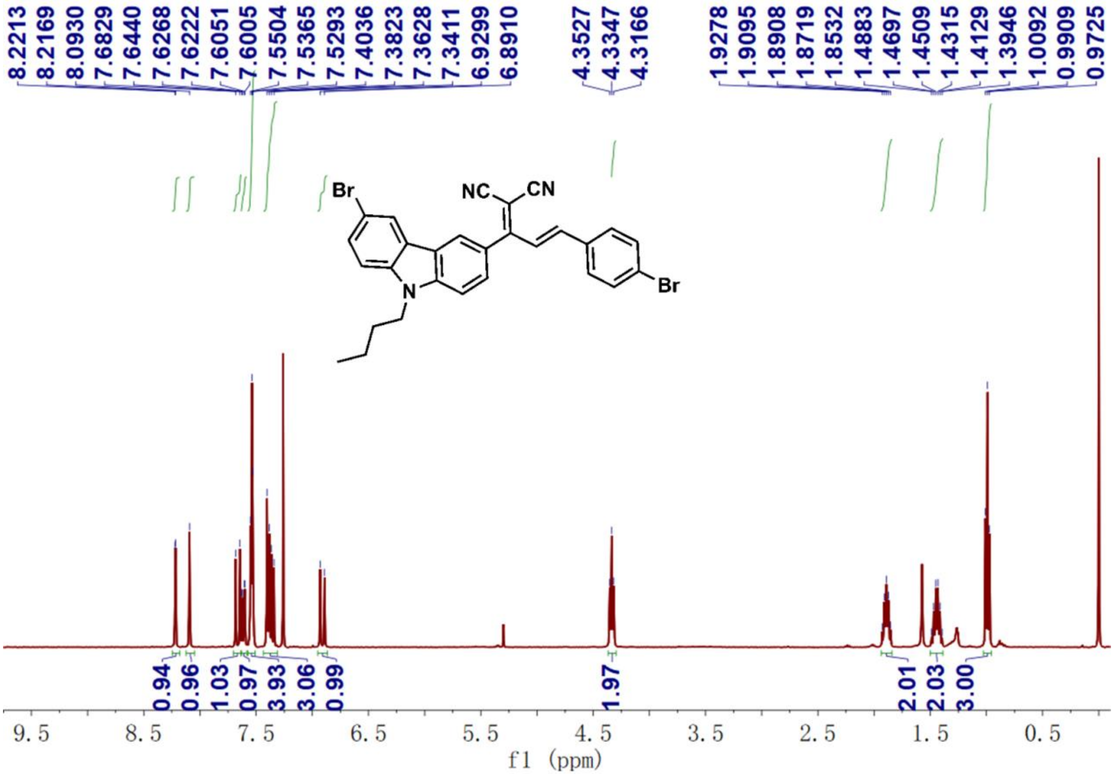
[1]H NMR data of compound **CZ-H**



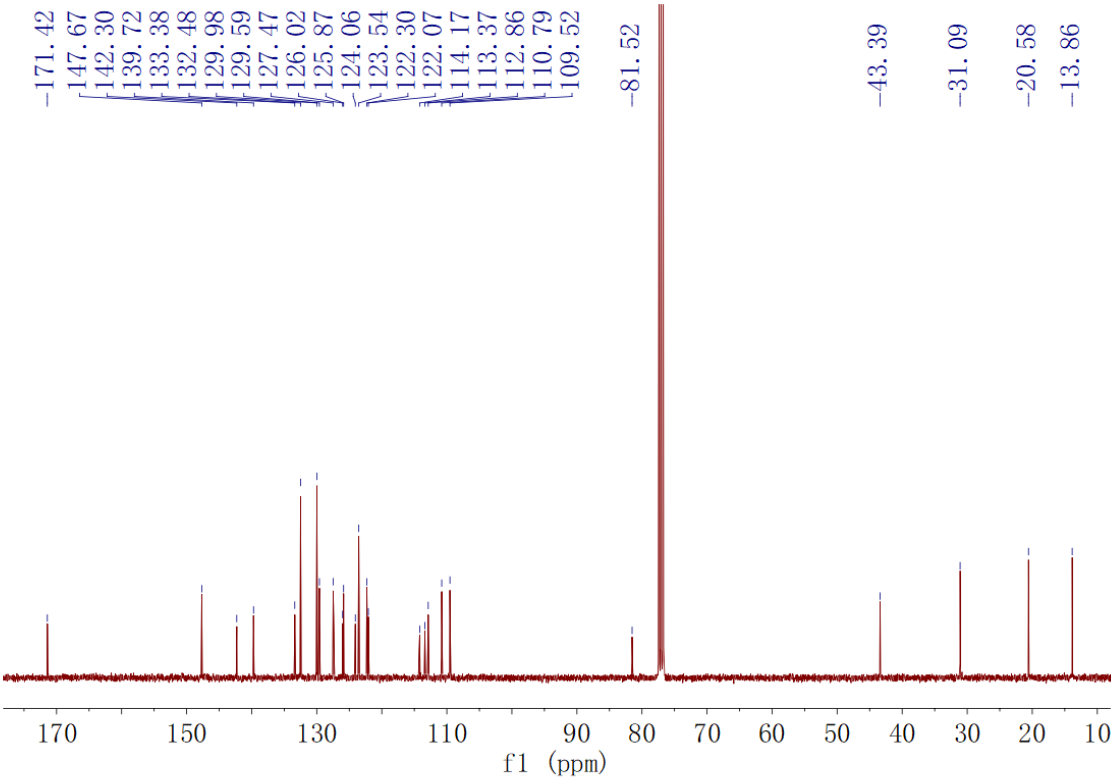
[13]C NMR data of compound **CZ-H**



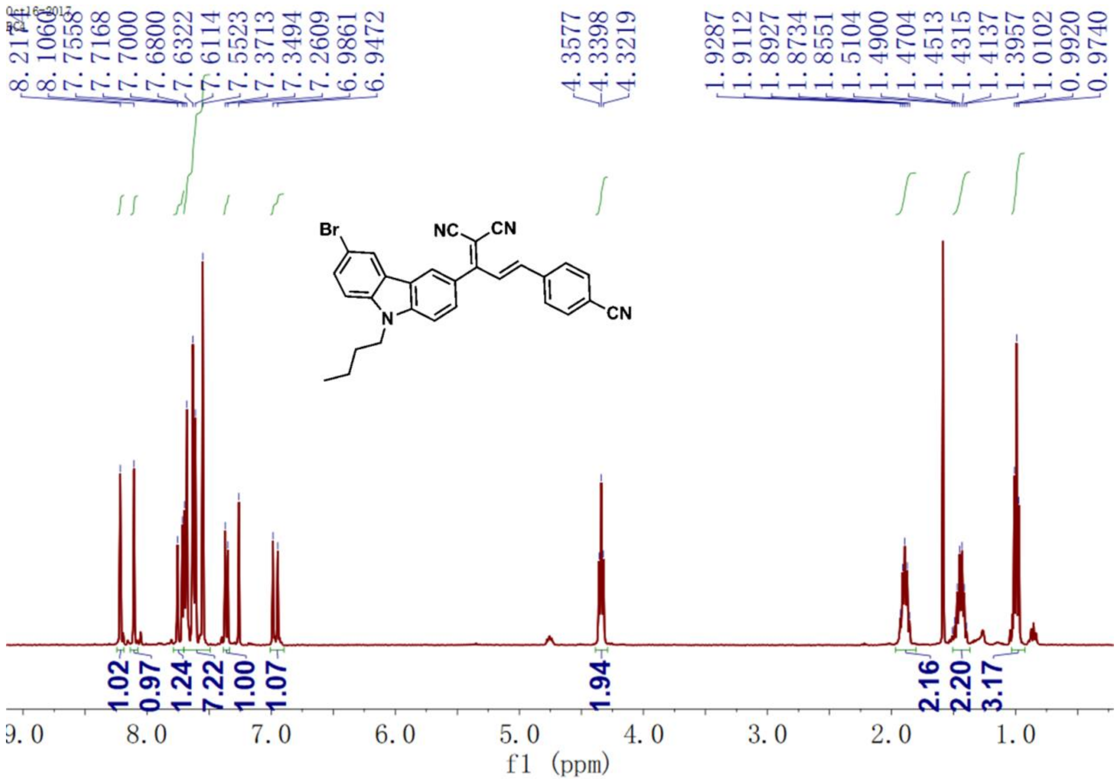
[1]H NMR data of compound **CZ-Br**



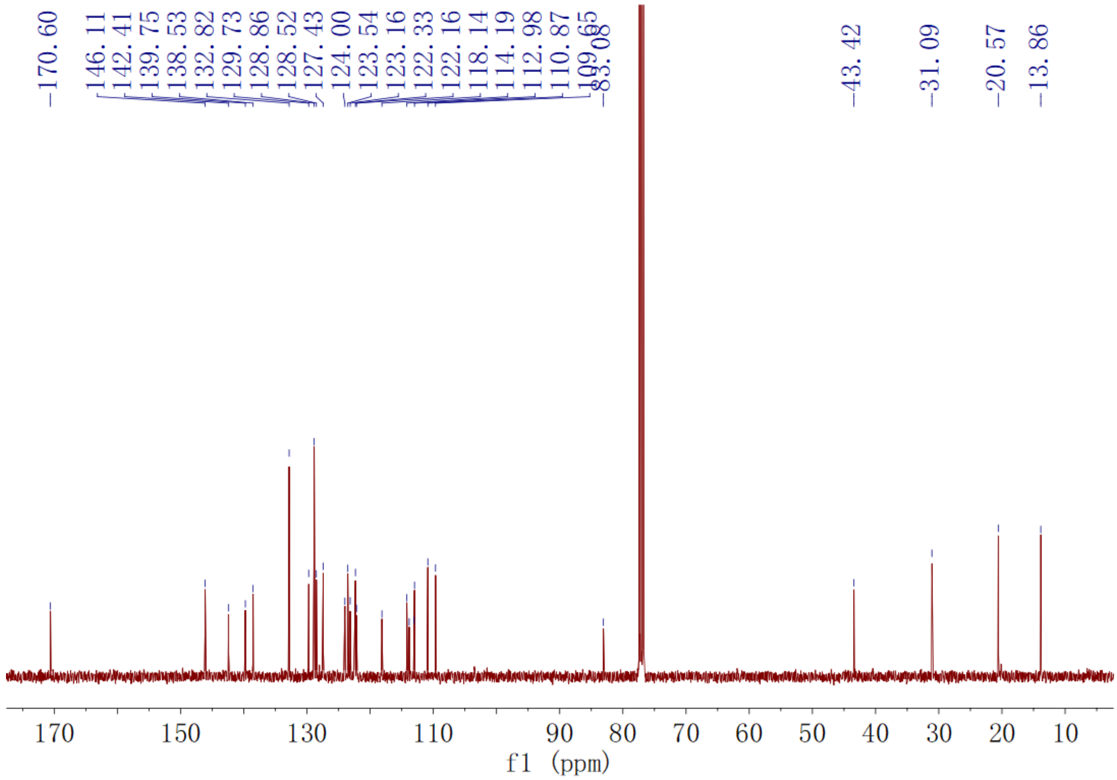
[13]C NMR data of compound **CZ-Br**



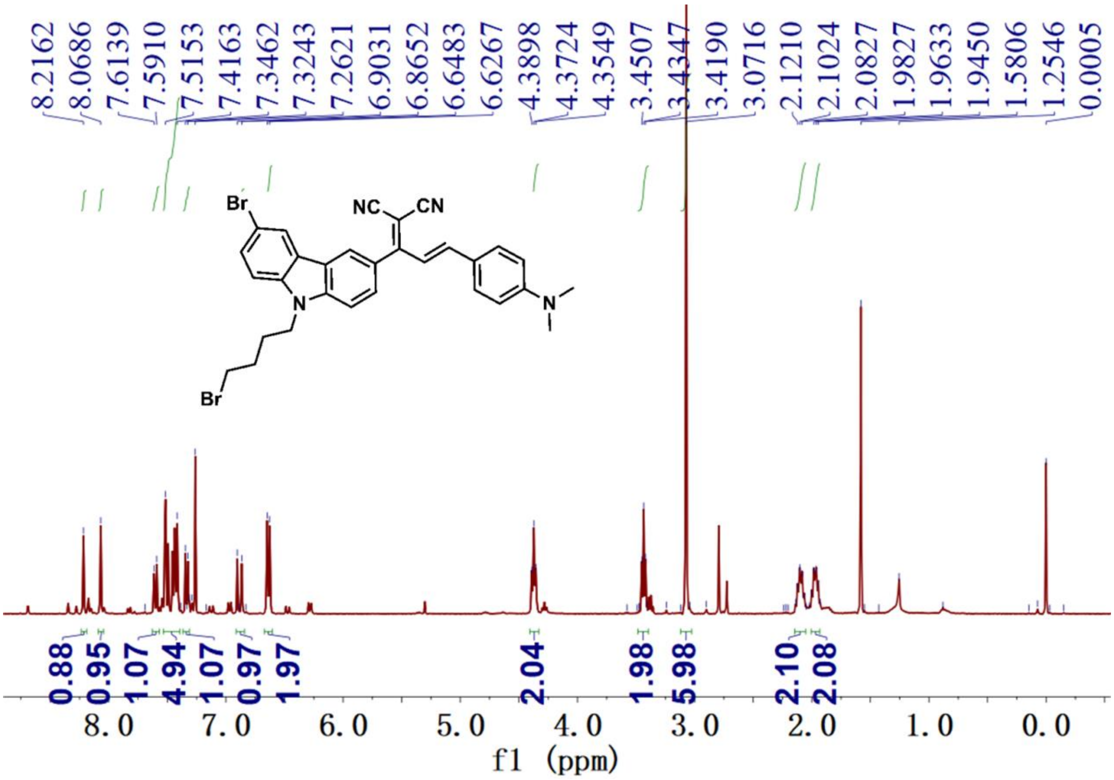
^{1}H NMR data of compound **CZ-CN**



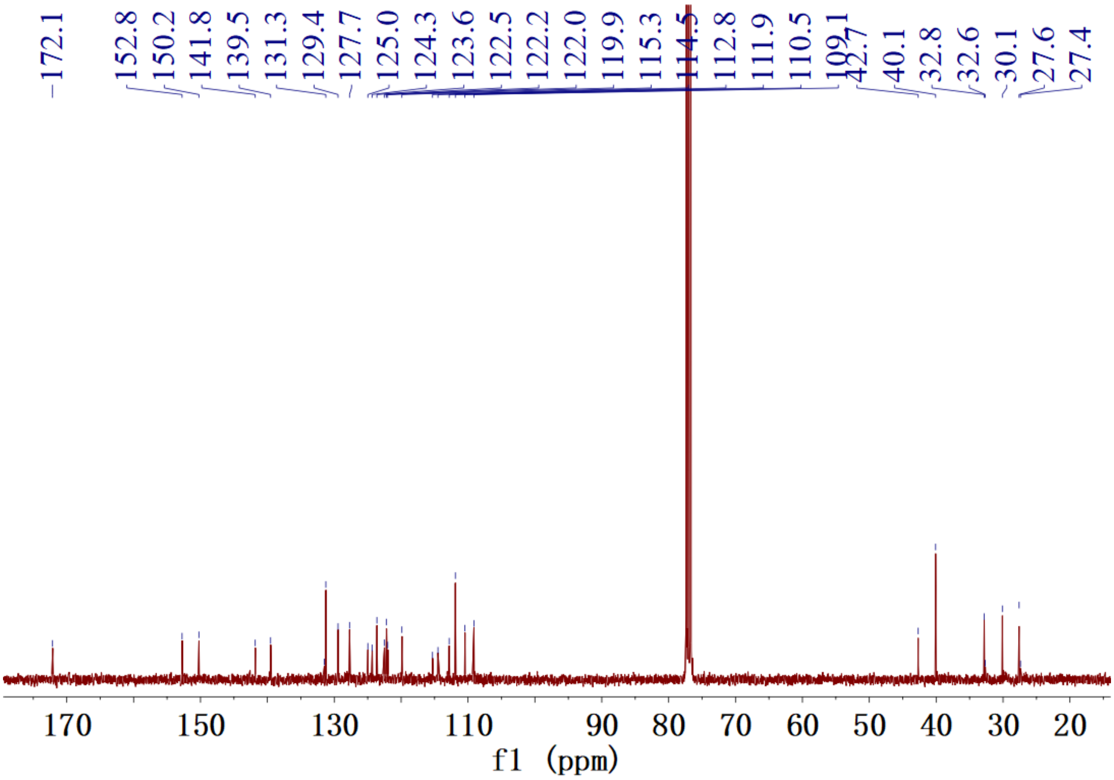
^{13}C NMR data of compound **CZ-CN**



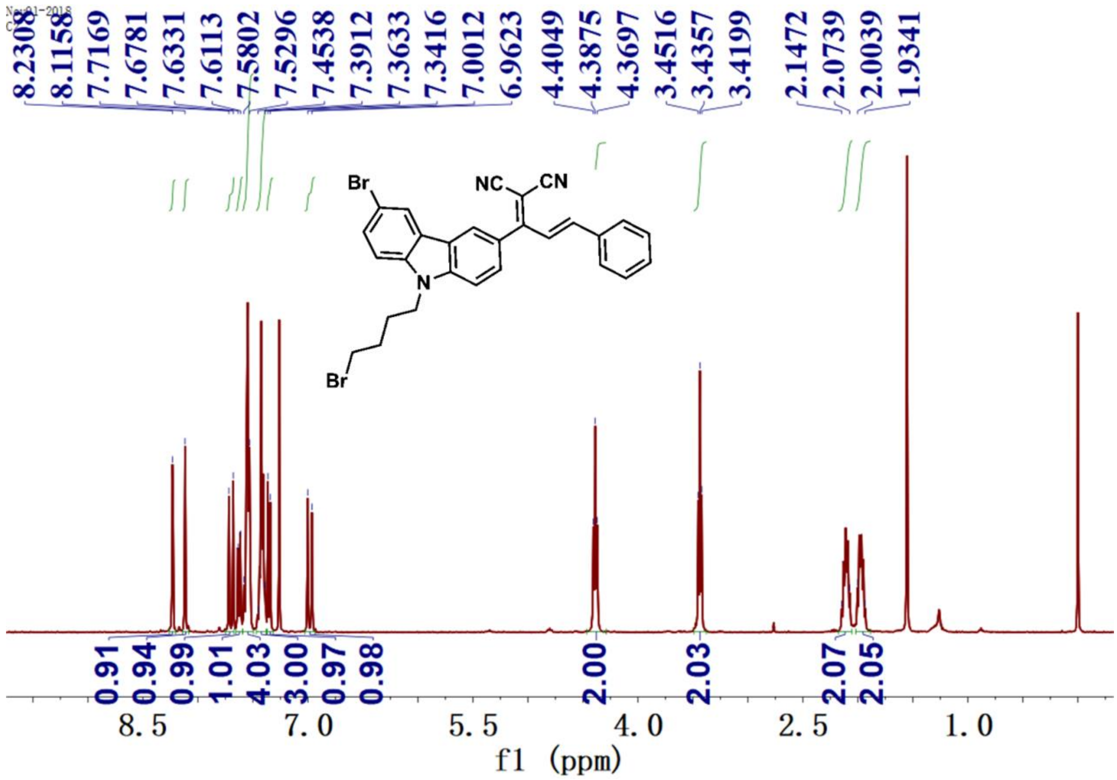
^{1}H NMR data of compound **Br-CZ-N**



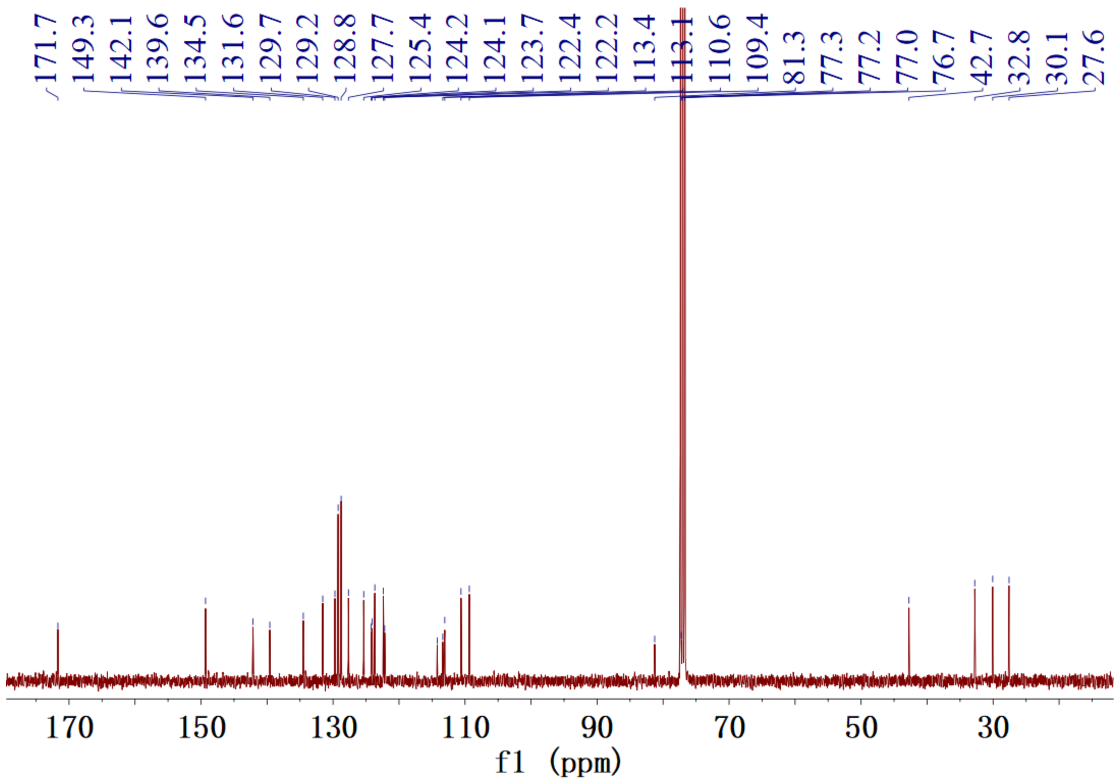
^{13}C NMR data of compound **Br-CZ-N**



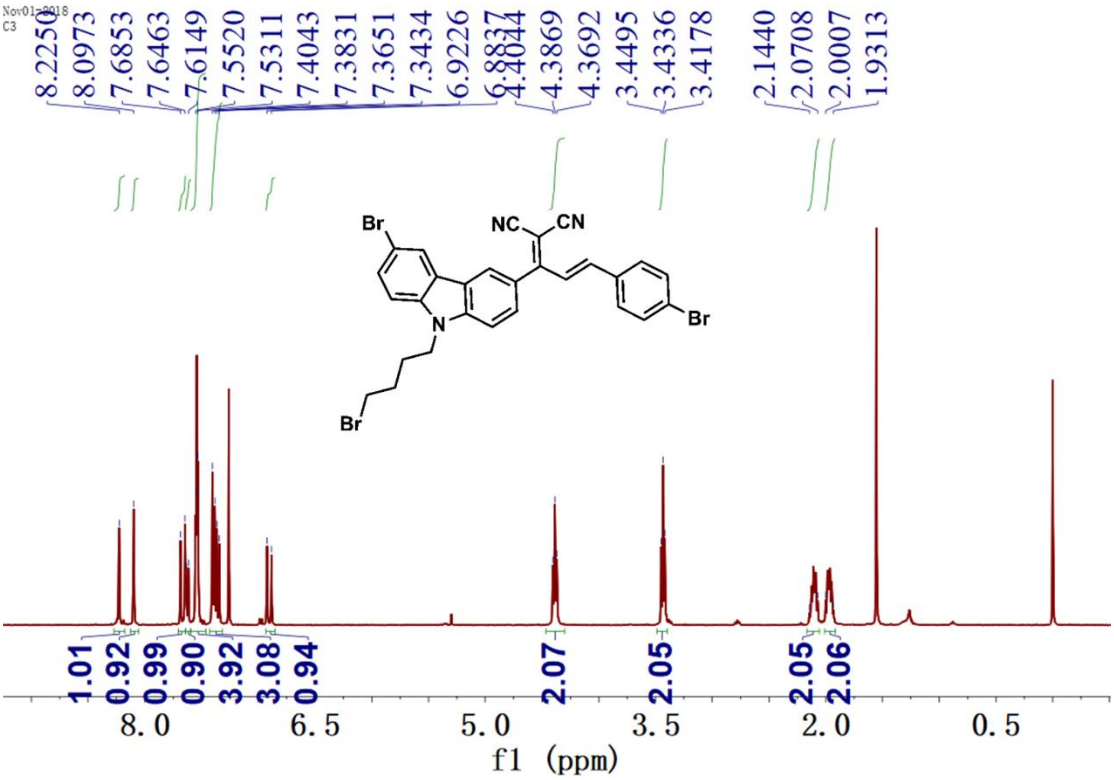
[1]H NMR data of compound **Br-CZ-H**



[13]C NMR data of compound **Br-CZ-H**



[1]H NMR data of compound **Br-CZ-Br**



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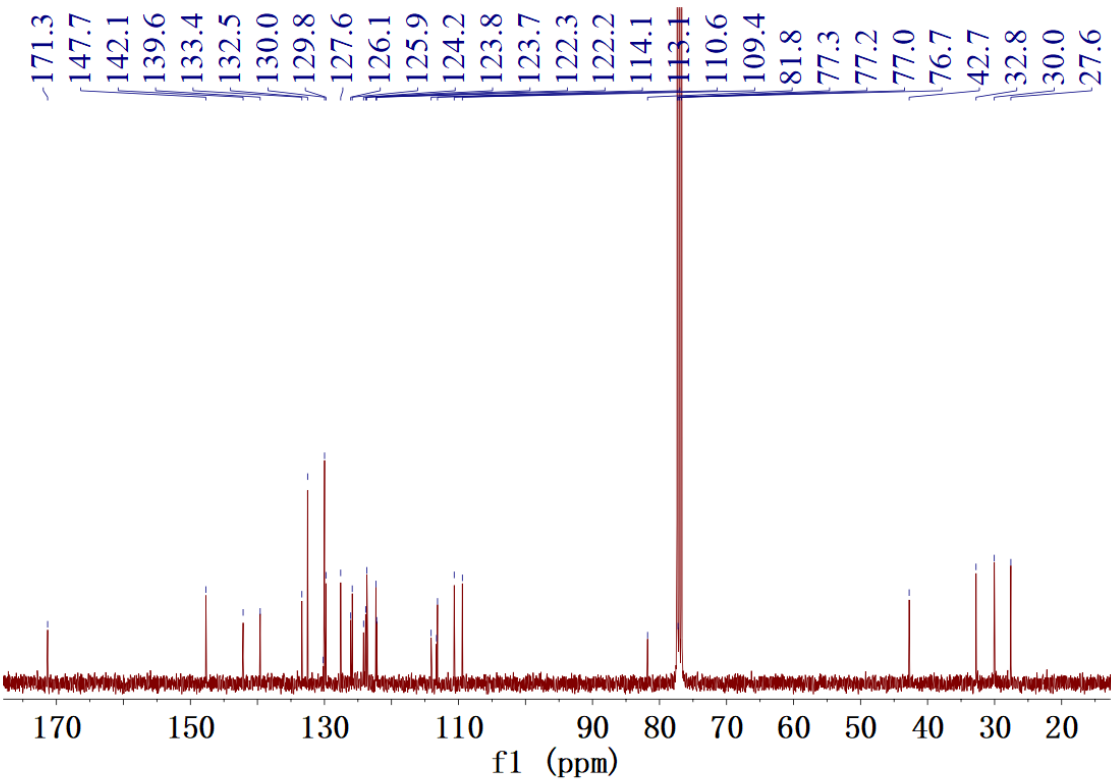
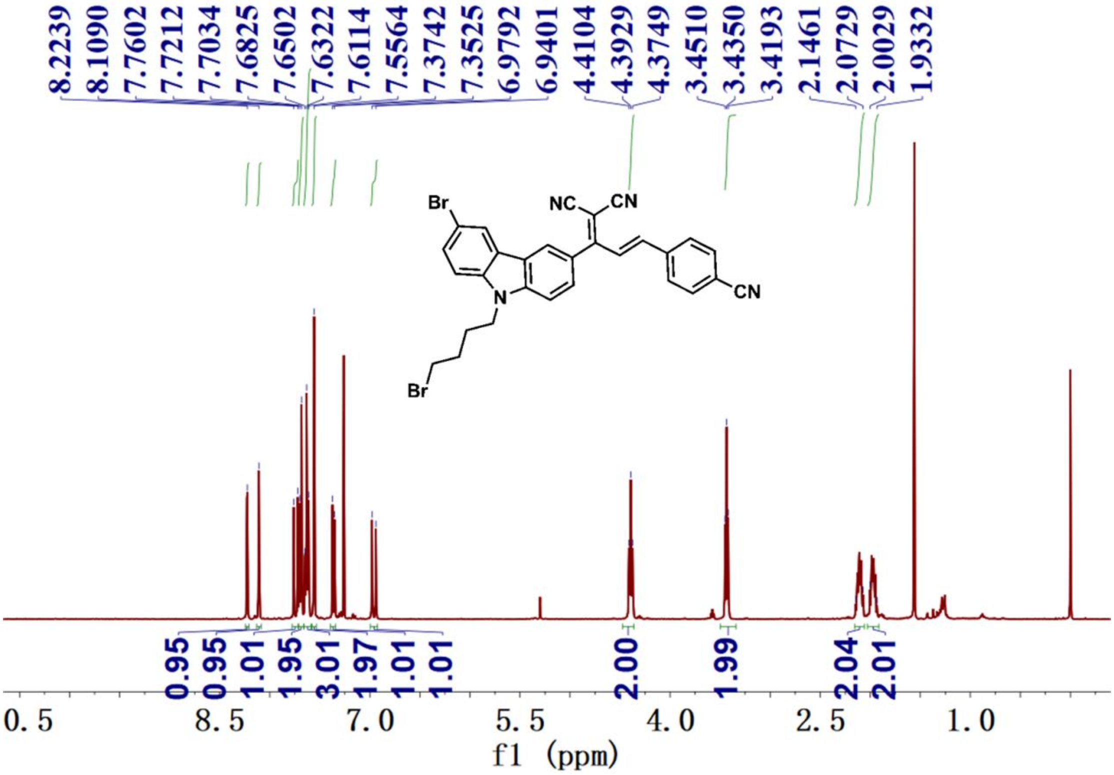


^{1}H NMR data of compound **Br-CZ-CN**



^{13}C NMR data of compound **Br-CZ-CN**