Supporting information

A BODIPY-Carbazole hybrid as fluorescent probe: design, synthesis, discrimination of surfactants and determination of the CMC values

Table of Contents

1. Fluorescence Spectra

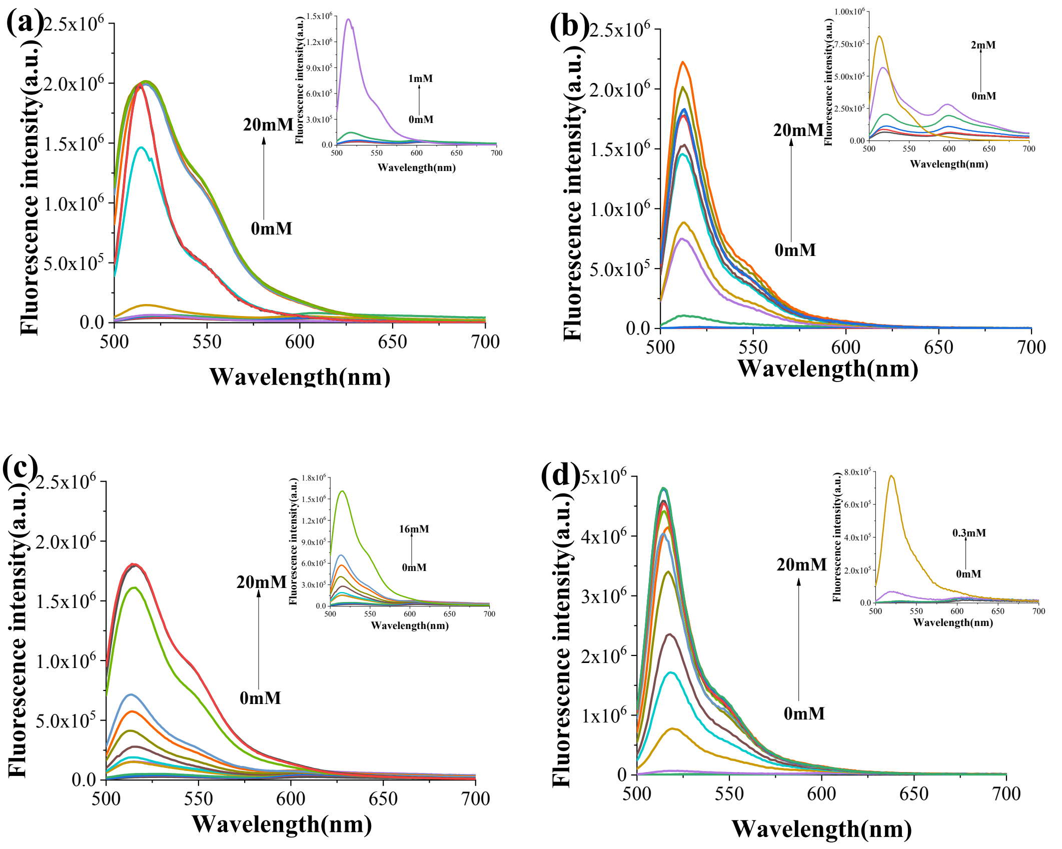
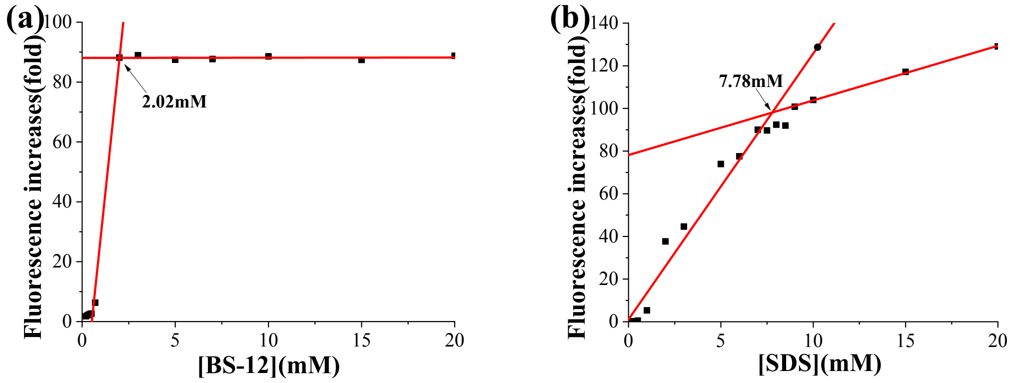


Figure S1. The fluorescence spectra of 10 μM BDP-Zn^{2+} in different concentrations of surfactants (a) BS-12 (b) SDS (c) DTAB (d) Triton X-100.



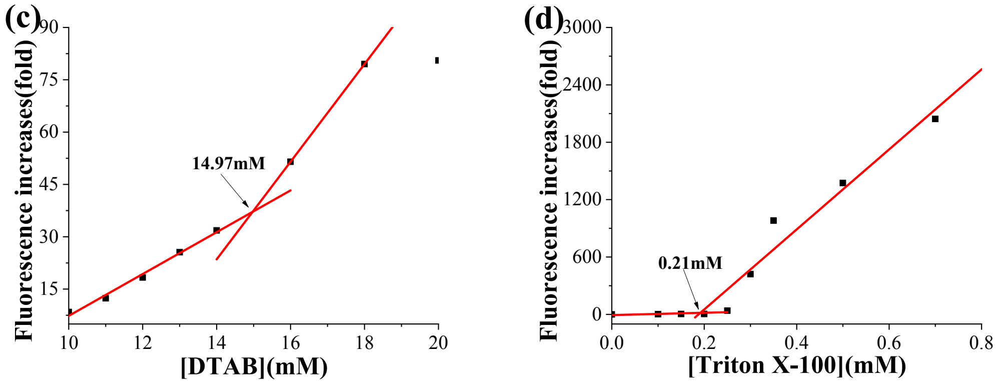


Figure S2. The fluorescence intensity increases as a signal to determine the CMC of surfactants (a)BS-12 (b) SDS (c) DTAB (d) Triton X-100.

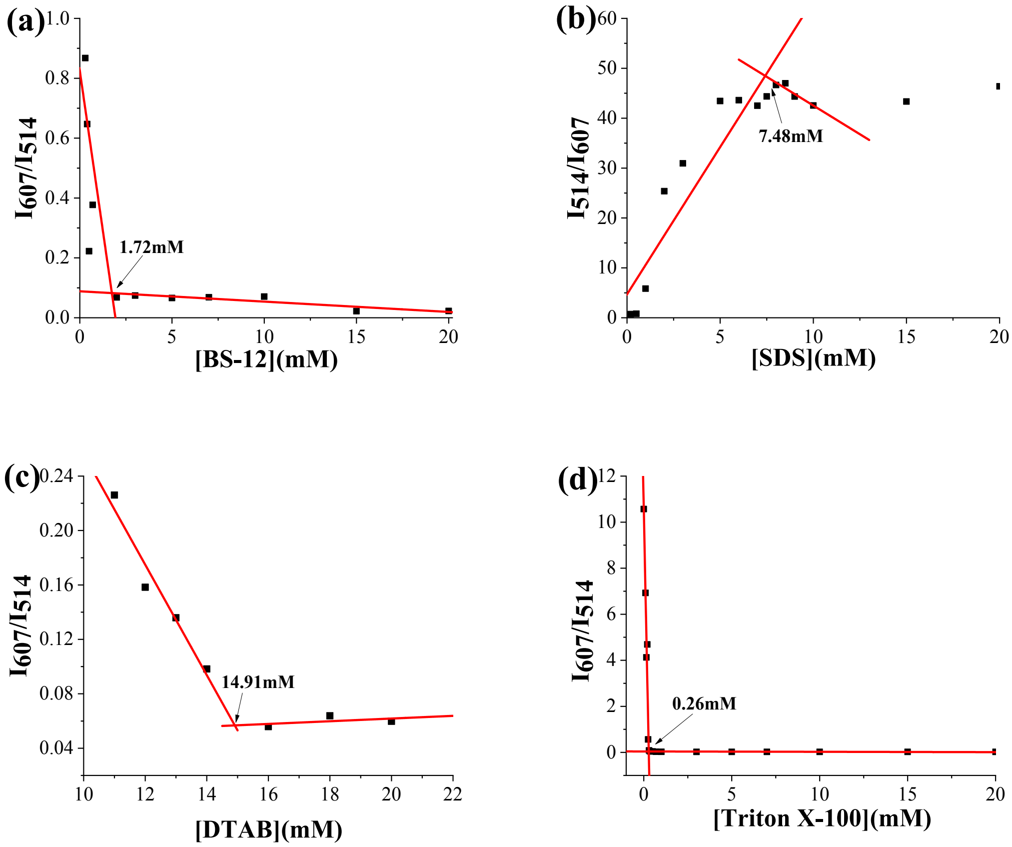


Figure S3. The ratio of I_{607}/I_{514} as a signal to determine the CMC of surfactants (a) BS-12 (b) SDS (I_{514}/I_{607} used) (c) DTAB (d) Triton X-100.

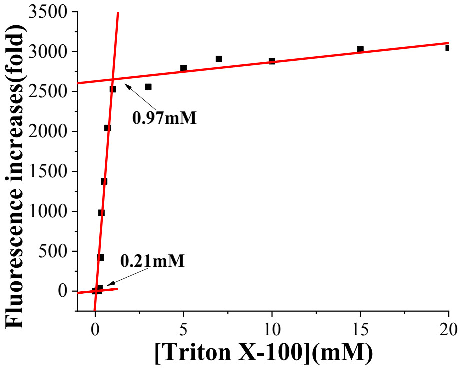


Figure S4. The results of fluorescence titration for Triton X-100.

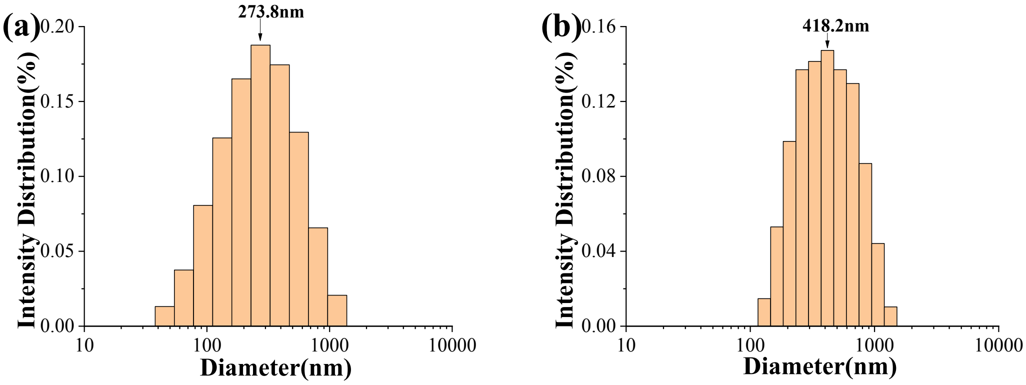


Figure S5. DLS analysis of the particle-size distribution of the self-assembled BDP-Zn^{2+} (10 μM) in different concentration of Triton X-100 (a) 0.25mM (b) 1mM.

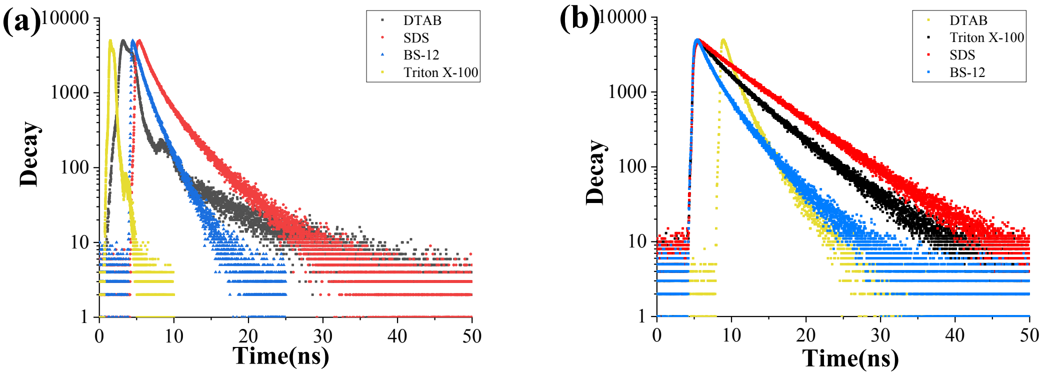
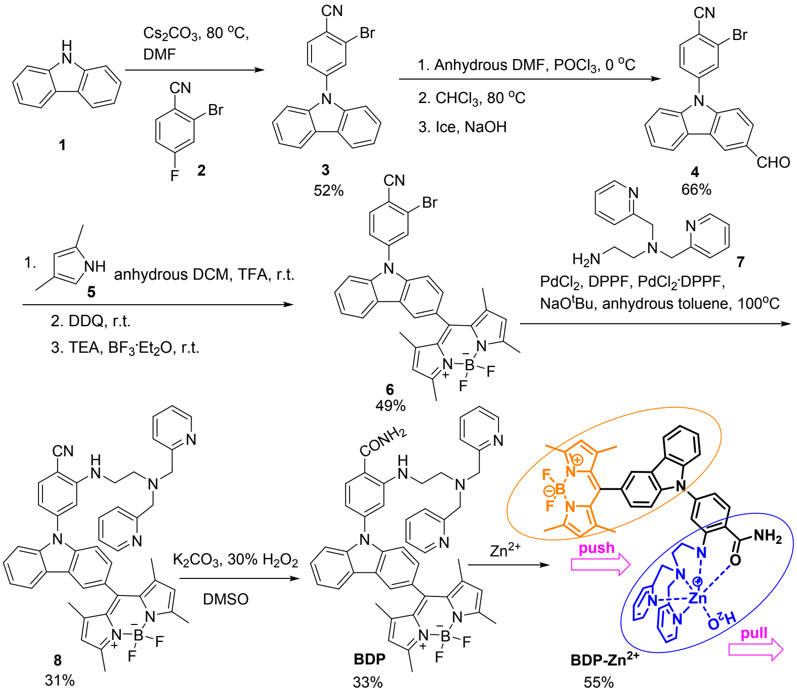


Figure S6. Lifetime decay of BDP-Zn^{2+} at below (a) or above (b) CMC concentration. Concentration of BDP-Zn^{2+} was 10 μM.

2. Experimental Section

General. All reagents were purchased and used without further purification. Universial buffer solution (HEPES) was prepared and adjusted to pH 7.4 using saturated NaOH solution. Toluene and acetonitrile were distilled from calcium hydride. Vilsmeier-Haack reaction and Buchwald-Hartwig cross coupling reaction were performed in flame-dried glassware under argon. The reactions were monitored by TLC (analytical thin-layer chromatography) on silica gel F254 glass plates and observed under UV light (254 and 365 nm) or by staining with ninhydrin. Flash column chromatography was performed on silica gel (200-300 mesh) and Al_2O_3 (200-300 mesh). ^{1}H NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer at 20 °C, and the chemical shifts (in ppm) were related to solvent peaks. ^{13}C NMR spectra were recorded with the 100 MHz NM spectrometer and calibrated with $CDCl_3$, which is 77.23 ppm. High resolution electrospray ionization mass spectra (HRMS-ESI) were recorded with AB SCIEX Triple TOF 5600 mass spectrometer. UV-vis absorption was recorded with UV-2450 spectrophotometer and emission spectra were recorded with FS5 Fluorescence Spectrometer, in a quartz cell with 1 cm path length. Fluorescence lifetime was recorded with FLS-980.

Synthesis.



2-bromo-4-(9H-carbazol-9-yl) benzonitrile (3):

Carbazole (1.0 g, 5.99 mmol), 2-bromo-4-fluorobenzonitrile (1.5450 g, 7.73 mmol), Cs_2CO_3 (4.88 g, 14.98 mmol) and DMF (24 ml) were added to 100 ml flask. The reaction mixture was stirred at 80 °C for about 2 days. After cooling to the room temperature, removing solvent under vacuum, the brown solid was obtained. The solid was dissolved in CH_2Cl_2 (150 ml), and the mixture was washed with saturated NaCl solution, and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (Hex/EtOAc=40:1) to get **3** (1.07 g, 52%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.14 (d, J = 7.8 Hz, 2H), 7.97 (d, J = 1.4 Hz, 2H), 7.88 (d, J = 8.3 Hz, 1H),7.69 (dd, J = 8.3, 2.0 Hz,1H), 7.44-7.49 (m, 4H), 7.34-7.38 (m, 2H).

2-bromo-4-(3-formyl-9H-carbazol-9-yl) benzonitrile (4):

$POCl_3$ (4 ml) was slowly added into a dried flask with DMF (4 ml) at 0°C, the mixture was further stirred for 30 min at 0°C, then removing the ice bath, continuing to stir about 1h at room temperature. Then **3** (586 mg, 1.69 mmol) in 2 ml $CHCl_3$ was added dropwise to the resulting mixture. Lastly, the mixture was stirred at 80 °C for 20 h until the TLC showed that the reaction had been almost completed. Then the mixture was poured into ice-water and was neutralized with saturated NaOH solution. The solution was extracted with CH_2Cl_2, was washed with saturated NaCl and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (Hex/EtOAc=10:1) to give light yellow solid **4** (417.3 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 10.13 (s, 1H), 8.66 (d, J = 1.44 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 7.99 (dd, J = 8.48 , 1.6 Hz, 1H), 7.96 (d, J = 2.04 Hz, 1H), 7.93 (d, J = 8.32 Hz, 1H), 7.69 (dd, J = 8.32, 2.04 Hz, 1H), 7.51 (m, 2H), 7.45 (d, J = 2.56 Hz, 1H), 7.41 (d, J = 7.56Hz, 1H).

2-bromo-4-(3-(5,5-difuoro-1,3,7,9-tetramethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f] [1,3,2] diazaborinin-10-yl)-9H-carbazol-9-yl) benzonitrile (6):

A Schlenk flask was charged with aromatic aldehyde **4** (285 mg, 0.76 mmol), anhydrous CH_2Cl_2 (70 ml), 2,4-dimethyl pyrrole (0.2 ml, 1.90 mmol) and trifluoroacetic acid (38 μl, 0.502 mmol), the mixtures were stirred at room temperature overnight. The whole reaction was detected by TLC, until the initial material compound **4** disappeared. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (172.6 mg, 0.76 mmol) in CH_2Cl_2 (35 ml) was added to the reaction, and the reaction was stirred for 30 min. Next, triethylamine was dropwise added into the reaction mixture, and the reaction was further stirred for 10 min. In the end, $BF_3{\cdot}Et_2O$ (3.7 ml) was added and stirred at room temperature about 2.5 h. The mixture was washed by water, aqueous HCl and saturated $NaHCO_3$ respectively, and extracted with CH_2Cl_2 repeatedly for three times, finally dried with $MgSO_4$. The crude product was purified by column chromatograph (Hex/EtOAc=5:1) on silica gel to get **6** (224.1 mg, 49%) as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.105 (d, J = 0.72 Hz, 1H), 8.04 (dd, J = 9.16, 0.78 Hz, 2H), 7.93 (d, J = 5.4 Hz, 1H), 7.75 (dd, J = 5.52, 1.32 Hz, 1H), 7.58 (d, J = 5.24 Hz, 1H), 7.52 (d, J = 3.2 Hz, 2H), 7.35-7.40 (m, 2H), 5.99 (s, 2H), 2.58 (s, 6H), 1.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 155.53, 143.11, 142.37, 141.95, 140.12, 139.66, 135.63, 132.03, 130.74, 128.00, 127.31, 126.79, 126.36, 125.53, 124.76, 123.74, 121.89, 121.27, 120.99, 116.69, 114.22, 110.18, 109.87, 29.69, 14.76, 14.61.

HRMS(ESI-TOF): m/z Calcd for $C_{32}H_{32}BBrF_2N_4$ $[M+H]^+$ 593.1245, found:593.1323.

2-((2-(bis(pyridine-2-ylmethyl)amino) ethyl) amino)-4-(3-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c: 2',1'-f][1,3,2]diazaborinin-10-yl)-9H-carbazol-9-yl) benzonitrile (8):

The red solid **6** (224.1 mg, 0.373 mmol), compound **7** (99.5 mg, 0.41 mmol), palladium chloride (6.6 mg, 0.0373 mmol), 1,1'-bis(diphenylphosphino) ferrocene (DPPF, 20.7 mg, 0.0373 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (60.9 mg, 0.0746 mmol), sodium *tert*-butoxide (89.5 mg, 0.933 mmol) and toluene (40 ml) were added into a Schlenk flask under argon. The mixtures were stirred at 100 °C until the starting material had disappeared by TLC analysis and the whole process sustained for 20 h. When the reaction system was cooled to room temperature, the solvent toluene was removed under vacuum, and the crude product was further purified by column chromatograph (DCM/MeOH=75:1) to get orange red solid **8** (86.6 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.55 (dd, J = 4.08, 0.68 Hz, 2H), 8.09 (d, J =7.76 Hz, 1H), 8.02 (d, J = 1.28 Hz, 1H), 7.72 (d, J = 1.76 Hz, 2H), 7.69 (d, J = 1.74 Hz, 3H), 7.66 (d, J = 9.56 Hz, 1H), 7.64 (d, J = 8.36 Hz, 2H), 7.61 (d, J = 7.88 Hz, 1H), 7.55 (d, J = 8.44 Hz, 1H), 7.47 (m, 1H), 7.35 (d, J = 3.28 Hz, 1H), 7.33 (d, J = 2.96 Hz, 1H), 7.29 (d, J = 6.8 Hz, 1H), 7.27 (d, J = 7.2 Hz, 2H), 7.15 (m, 1H), 6.90 (dd, 8.2, 1.76Hz, 1H), 6.77 (d, 1.68 Hz, 1H), 6.15 (s, 2H), 3.92 (s, 4H), 3.25 (t, 5.52 Hz, 2H), 2.93 (t, 5.92 Hz, 2H), 2.57 (s, 6H), 1.33 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 158.78, 155.32, 151.79, 149.14, 143.19, 142.80, 142.48, 140.56, 136.83, 134.51, 132.11, 126.97, 126.83, 125.89, 124.23,123.35, 123.30, 122.27, 121.14, 120.95, 120.59, 120.14, 117.66, 114.15, 110.62, 110.37, 108.58, 94.67, 60.28, 51.56, 40.43, 14.74, 14.58.

HRMS(ESI-TOF): m/z Calcd for $C_{46}H_{41}BF_2N_8[M+H]^+$ 755.3515, found: 755.3598.

2-((2-(bis(pyridine-2-ylmethyl) amino) ethyl) amino)-4-(3-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2’,1’-f][1,3,2]diazaborinin-10-yl)-9H-carbazol-9-yl) benzamide (BDP):

Compound **8** (86.6 mg, 0.115 mmol) was dissolved in DMSO (4 ml), followed by the addition of anhydrous potassium carbonate (269 mg, 1.88 mmol), 30% of hydrogen peroxide (0.45 ml) respectively. The reaction mixture was stirred at room temperature, and the reaction was monitored by TLC until the material was disappeared. Then, the mixture was extracted by DCM, and washed by saturated NaCl solution. The whole process was repeated twice, and the solution was dried with $MgSO_4$. Finally, the crude product was purified by column chromatograph (DCM/MeOH=20:1), the orange-red solid **BDP** (29.6 mg, 33%) was obtained.

^{1}H NMR (400 MHz, CDCl3), δ (ppm): 8.50 (d, J = 3.36 Hz, 2H), 8.10 (d, J = 5.2 Hz, 1H), 8.02 (s, 1H), 7.71 (d, J = 1.73 Hz, 2H), 7.60(d, J = 1.16 Hz, 1H), 7.58 (d, J = 1.36 Hz, 2H), 7.52 (d, J = 4.96 Hz, 1H), 7.45 (d, J = 3.72 Hz, 2H), 7.33 (m, 2H), 7.07 (t, J = 5.56Hz, 2H), 6.79 (d, J = 6.96 Hz, 2H), 5.97 (s, 3H), 4.90 (s, 4H), 3.29 (t, J = 5.72 Hz, 2H), 2.90 (t, J = 5.72 Hz, 2H), 2.57 (s, 6H), 1.34 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 171.19, 158.94, 155.25, 151.21, 148.78, 143.24, 142.72, 141.86, 140.83, 140.40, 136.69, 132.16, 130.05, 126.69, 125.74, 124.04, 123.30, 123.19, 122.13, 121.10, 120.62, 120.48, 120.03, 112.42, 110.74, 110.49, 109.45, 60.46, 52.53, 40.49, 31.90, 30.37, 29.67, 29.33, 22.95, 22.66, 14.73, 14.57, 14.07.

HRMS(ESI-TOF): m/z Calcd for $C_{46}H_{43}BF_2N_8O[M+H]^+$ 773.3721, found: 773.3743.

BDP-Zn^{2+}:

The compound BDP (17.00 mg, 0.022 mmol) was dissolved in 2 ml ethanol, and an ethanol (1 ml) solution containing the compound $Zn(ClO_4)_2{\cdot}6H_2O$ (9.89 mg, 0.026 mmol) was added to the reaction system. Then the solution was stirred at room temperature for about 2 h until the starting material disappeared. When the reaction was completed, petroleum ether was added to the system. The solid was filtered and dried under vacuum, and the final product [**BDP-Zn^{2+}-H]$^+$[ClO$_4^-$**] was obtained (11.33 mg, 55%).

MS(ESI-TOF): m/z Calcd for [BDP-Zn^{2+}-H]$^+$ 853.2929, found: 853.2887.

3. ^{1}H NMR, ^{13}C NMR and HRMS Spectrum of New Compounds

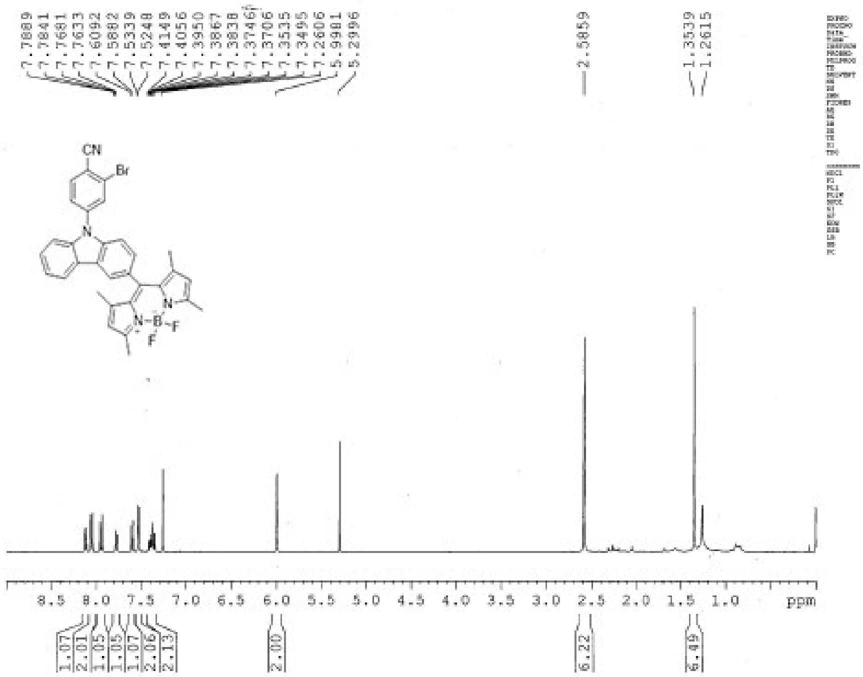


Figure S7. ^{1}H NMR spectra of compound **6**.

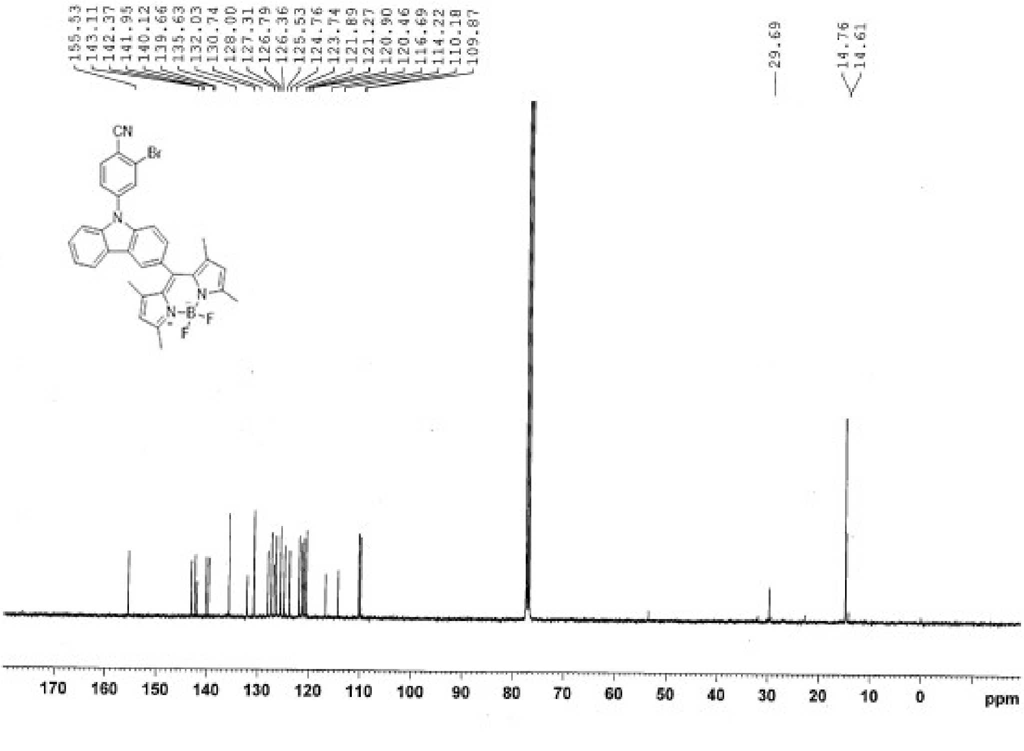


Figure S8. ^{13}C NMR spectra of compound **6**.

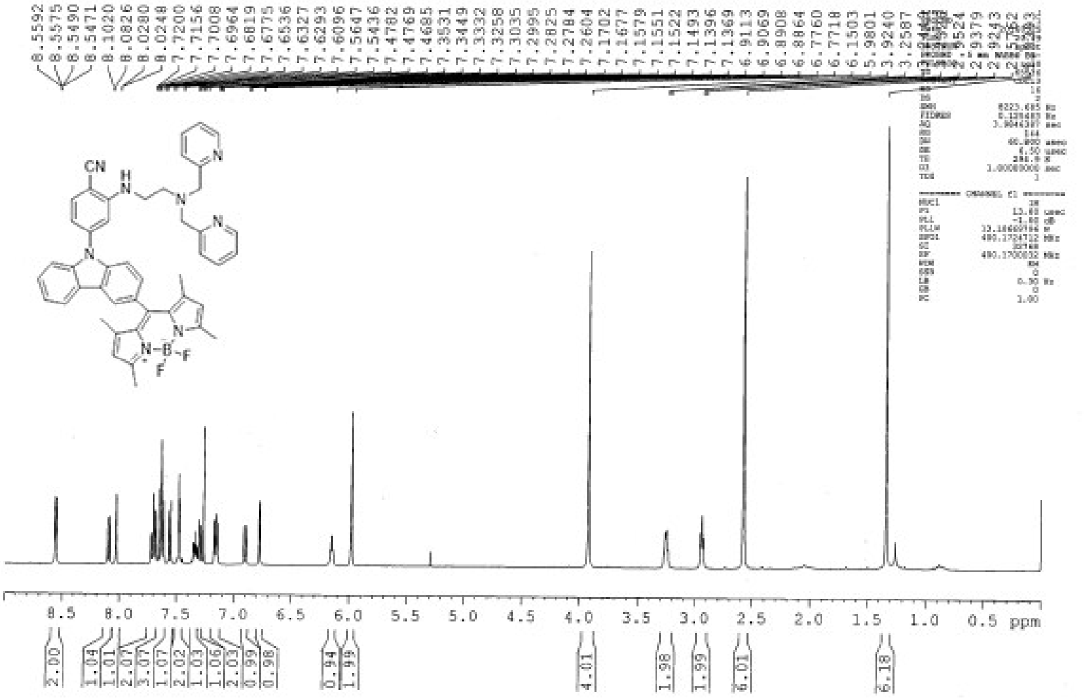


Figure S9. ^{1}H NMR spectra of compound **8**.

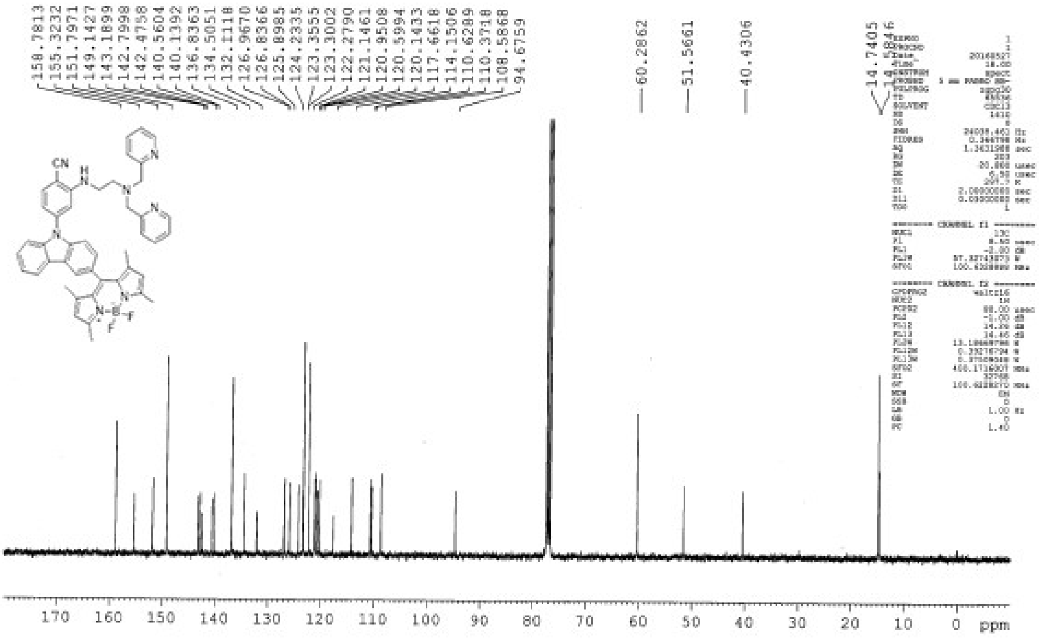


Figure S10. ^{13}C NMR spectra of compound **8**.

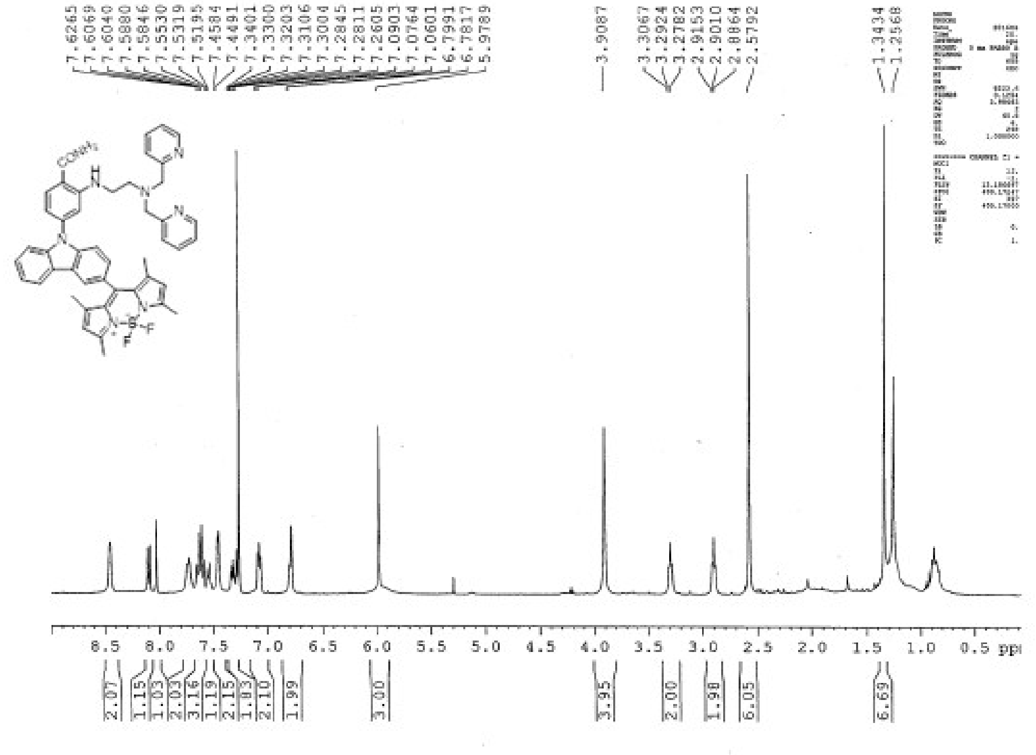


Figure S11. ^{1}H NMR spectra of **BDP.**

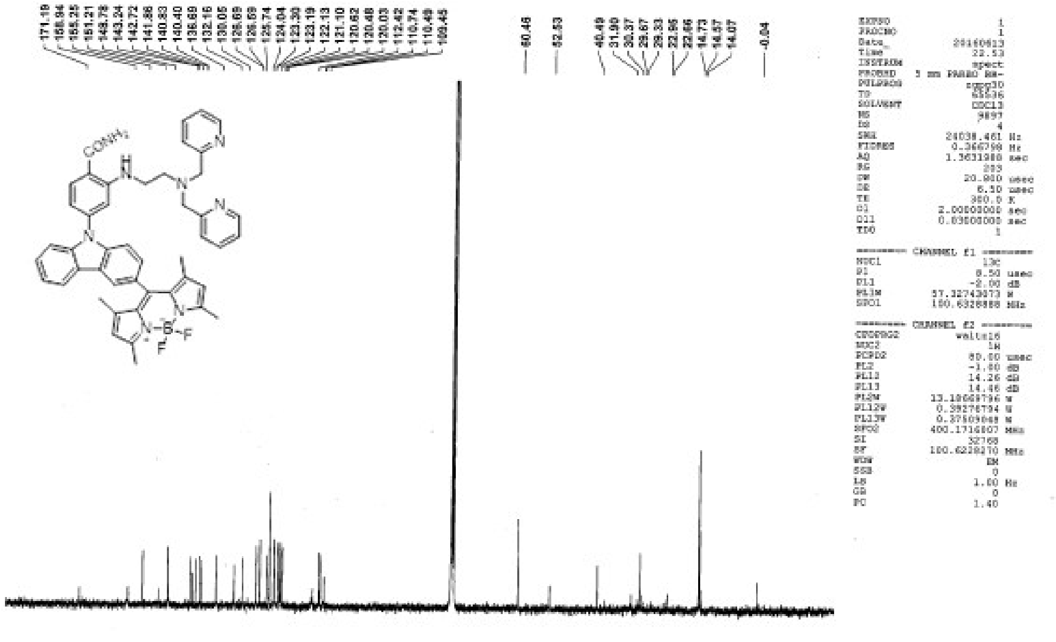


Figure S12. ^{13}C NMR spectra of **BDP.**

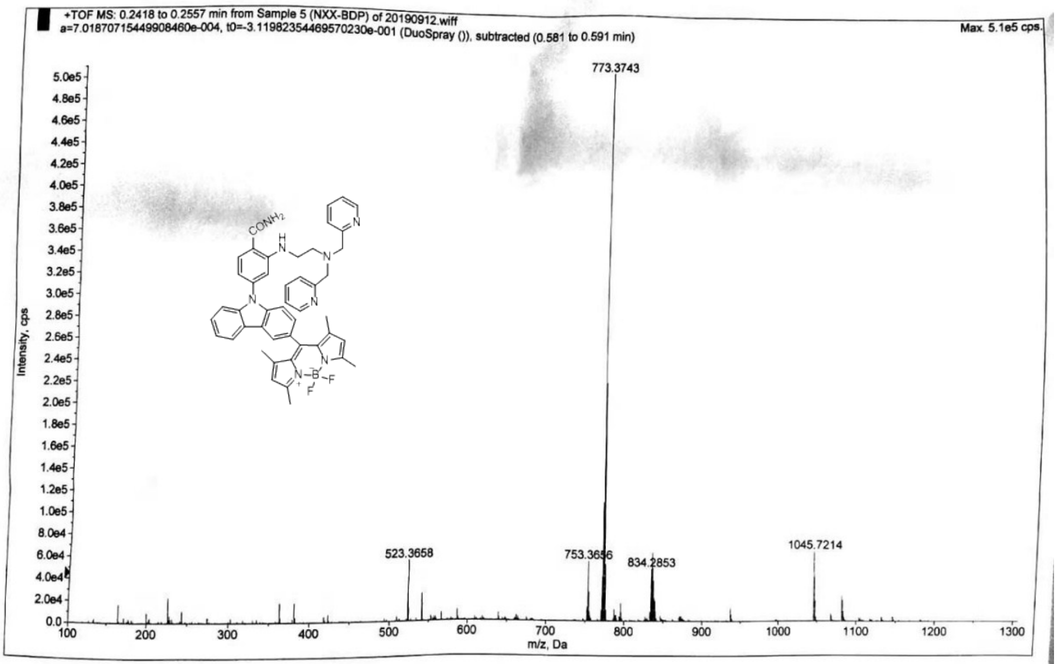


Figure S13. MS spectra of **BDP.**

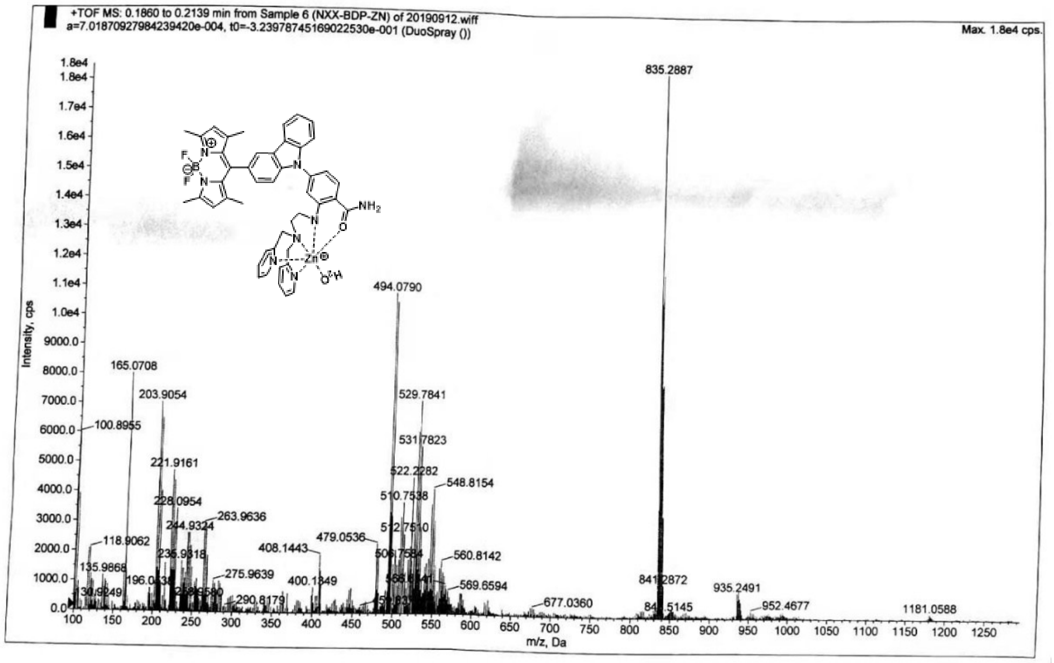


Figure S14. MS spectra of **BDP-Zn^{2+}**