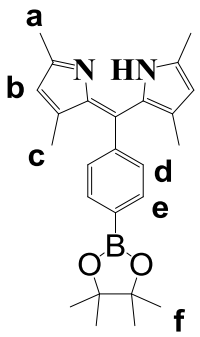
Self-assembly of emissive metallocycles with tetraphenylethylene, BODIPY and terpyridine in one system

Table of contents

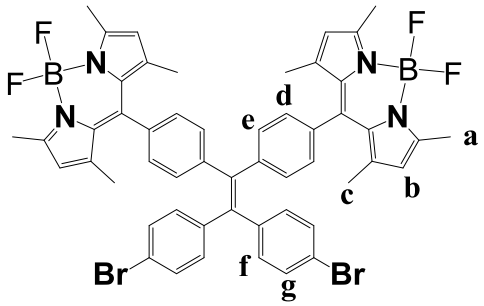
1. Experimental section

General procedures. All reagents were purchased from Sigma-Aldrich, Alfa Aesar, Matrix Scientific, and were used without further purification. Column chromatography was conducted by using SiO_2 (VWR, 40–60 μm, 60 Å) or Aluminum oxide, neutral (ACROS Organics 50-200 μm, 60 Å). NMR spectra were recorded on Varian 400 MHz and 500MHz spectrometers in $CDCl_3$, CD_3CN, and DMSO-d_6 with TMS as reference. ESI-TOF-MS and TWIM-MS data were recorded on a Waters Synapt G2 mass spectrometer. UV-Vis and fluorescence spectra were recorded on HORIBA FLOROMAX-4C-L. The quantum yield experiments are conducted with an integrating sphere.

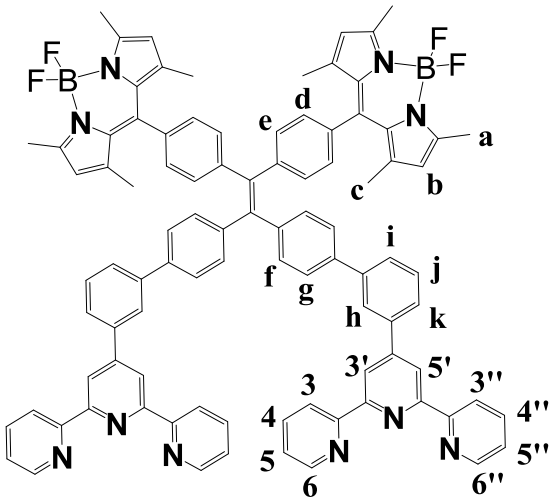
2. Preparation of ligand and supramolecular architecture.



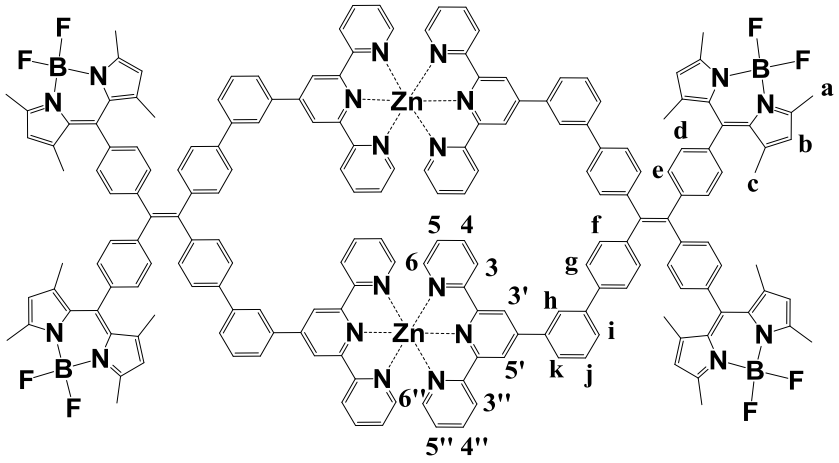
Compound 1: One drop of trifluoroacetic acid (TFA) was added into a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (251 mg, 1.15 mmol) and 3-ethyl-2,4-dimethyl-1H-pyrrole (0.30 g, 2.5 mmol) in 100 mL of dichloromethane. The mixture was stirred overnight at room temperature under nitrogen. After confirming the disappearance of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde by TLC, p-chloranil (285 mg, 1.16 mmol) in dichloromethane was added to the reaction mixture. The mixture was further stirred for 1.5 h, and the reaction was quenched with water. The organic layer was separated, and the water layer was further extracted with chloroform. The combined organic layer was evaporated and partially purified by column chromatography on alumina with hexane/ethyl acetate (7/3, v/v) as the eluent to give the target product as a reddish powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 14.4 Hz, 2H, Ph-*H*^{e}), 7.33 (d, *J* = 7.4 Hz, 2H, Ph-*H*^{d}), 6.15 (s, 2H, dipyrromethane-*H*^{b}), 2.49 (s, 6H, alkyl-*H*^{a}), 1.39 (s, 6H, alkyl-*H*^{c}), 1.24 (s, 12H, alkyl-*H*^{c}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.44, 139.23, 135.35, 130.95, 120.81, 119.60, 84.50, 82.94, 75.28, 29.80, 24.61, 14.73, 14.34. ESI-TOF (*m/z*): Calcd. for $[C_{25}H_{32}BN_2O_2]^+$: 403.25, Found for $[M+H]^+$: 403.19.



Compound 4: To a Schlenk flask containing compound **1** (491 mg, 1.22 mmol), compound **3** (400 mg, 0.508 mmol), $Pd(PPh_3)_2Cl_2$ (28mg, 0.04 mmol) and K_2CO_3 (552 mg, 4 mmol) were added. After removing air and back-filling with nitrogen, 21 mL of toluene, 21 mL of water and 7 mL of *t*-butanol were added. After stirring at 80 °C for 48 h, the mixture was cooled to 25 °C. The aqueous layer was extracted with CH_2Cl_2, and then the combined organic phase was washed with brine and dried with Na_2SO_4. The solvents were then removed under reduced pressure. The crude product was confirmed by ESI-MS and used in the following step without purification. To a flask containing solution of intermediate products in 20 mL CH_2Cl_2, 7.6 mL Et_3N and 8.5 mL $BF_3{\cdot}Et_2O$ were added. After stirring at room temperature for overnight, the reaction was quenched by slowly adding water. The aqueous layer was extracted with CH_2Cl_2, and then the solvents were then removed under reduced pressure. The residue was purified by silica gel chromatography with CH_2Cl_2 as eluent to afford compound **4** as orange solid (75 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4H, Ph-H^d), 7.15 (d, J = 7.8 Hz, 4H, Ph-H^g), 7.12 (d, J = 8.0 Hz, 4H, Ph-H^f), 6.97 (d, 4H, Ph-H^e), 6.00 (s, 4H, dipyrromethane-H^b), 2.55 (s, 12H, alkyl-H^a), 1.39 (s, 12H, alkyl-H^c). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.31, 143.83, 142.67, 141.12, 141.03, 140.57, 140.17, 133.48, 132.75, 131.59, 131.09, 130.74, 128.26, 127.79, 121.21, 14.39.



L: To a Schlenk flask containing compound **4** (110 mg, 0.112 mmol), compound **5** (99 mg, 0.28 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 6.7 μmol) and K_2CO_3 (93 mg, 0.67 mmol) were added. After the air was removed and the flask was flushed with nitrogen, 15 mL of toluene, 15 mL of water and 5 mL of t-butanol were added. After stirring at 85 °C for overnight, the mixture was cooled to 25 °C. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phase was washed with brine and dried with Na_2SO_4. The solvents were then removed under reduced pressure. The residue was purified by Al_2O_3 chromatography with chloroform to afford compound **L** as orange solid (62 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 2H, tpy-$H^{3',5'}$), 8.74 (d, J = 1.5 Hz, 2H, tpy-$H^{3, 3''}$), 8.73 (d, J = 2.1 Hz, 2H, tpy-$H^{6, 6''}$), 8.04 (s, 1H, Ph-H^{h}), 7.91 (dd, J = 7.9, 1.9 Hz, 4H, tpy-$H^{4, 4''}$, Ph-H^{k}), 7.64 (s, 1H, Ph-H^{i}), 7.61 (s, 1H, Ph-H^{j}), 7.49 (d, J = 8.3 Hz, 2H, Ph-H^{g}), 7.40 – 7.36 (m, 2H, tpy-$H^{5, 5''}$), 7.31 (d, J = 1.9 Hz, 2H, Ph-H^{f}), 7.30 (d, J = 2.8 Hz, 2H, Ph-H^{d}), 7.16 (d, J = 8.2 Hz, 2H, Ph-H^{e}), 5.90 (s, 2H, dipyrromethane-H^{b}), 2.51 (s, 6H, alkyl-H^{a}), 1.49 (s, 6H, alkyl-H^{c}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.26, 156.12, 155.44, 150.40, 149.29, 144.88, 142.88, 142.27, 141.51, 139.89, 139.69, 139.30, 138.29, 137.01, 136.71, 133.47, 132.11, 131.41, 129.55, 127.98, 127.71, 126.99, 126.69, 126.56, 126.18, 124.03, 123.85, 121.47, 119.08, 14.78, 14.67. ESI-TOF (*m/z*): Calcd. For $[C_{94}H_{73}B_2F_4N_{10}]^+$: 1439.61, Found for $[M+H]^+$: 1439.66.



D: To a solution of ligand **L** (8.3 mg, 5.8 μmol) in $CHCl_3$ (1.5 mL), a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.89 mg, 6.3 μmol) in MeOH (3 mL) was added. The mixture was stirred at 50 ºC for 3 h. After cooling to room temperature, 210 mg of NH_4PF_6 was added and orangish precipitate was observed. The precipitate was washed by water, and the orangish powder (9.6 mg, 90%) as final product was obtained. ^{1}H NMR (400 MHz, CD_3CN) δ 9.02 (s, 4H, tpy-$H^{3',5'}$), 8.69 (d, J = 8.1 Hz, 4H, tpy-$H^{3,3''}$), 8.31 (s, 2H, Ph-H^{h}), 8.18 (d, J = 6.7 Hz, 2H, Ph-H^{k}), 8.07 (t, J = 7.8 Hz, 4H, tpy-$H^{4,4''}$), 7.85 (d, 4H, Ph-H^{i} and Ph-H^{j}), 7.77 (d, J = 5.1 Hz 4H, tpy-$H^{6,6''}$), 7.70 (d, J = 8.0 Hz, 4H, Ph-H^{g}), 7.40 (d, J = 7.8 Hz, 8H, Ph-H^{f} and Ph-H^{d}), 7.31 (t, J = 5.8 Hz, 4H, tpy-$H^{5,5''}$), 7.26 (d, J = 7.9 Hz, 4H, Ph-H^{e}), 6.15 (s, 4H, dipyrromethane-H^{b}), 2.51 (s, 12H, alkyl-H^{a}), 1.52 (s, 12H, alkyl-H^{c}). ^{13}C DEPT-45 NMR (126 MHz, DMSO-d_6) δ 148.18, 132.12 , 131.85 , 128.23 , 128.06 , 127.20 , 124.09 , 122.05, 56.50. ESI-TOF (*m/z*): Calcd. For $[C_{188}H_{144}B_4F_8N_{20}Zn_2]^{4+}$: 752.25, Found for $[M-4PF_6]^{4+}$: 752.21. Calcd. For $[C_{188}H_{144}B_4F_{14}N_{20}PZn_2]^{3+}$: 1051.30, Found for $[M-3PF_6]^{3+}$: 1051.33.

3. Isotope distributions for D.

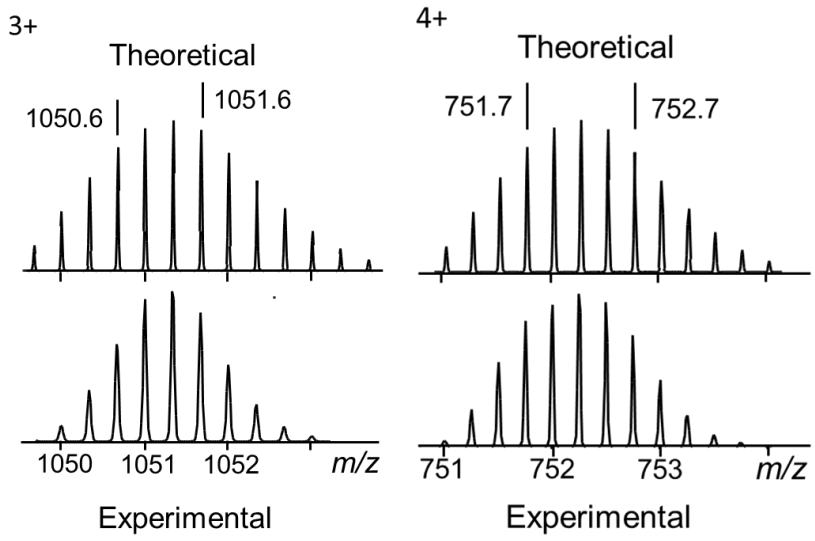


Figure S1. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from **D** (PF_6^- as counterion).

4. Molecular modeling.

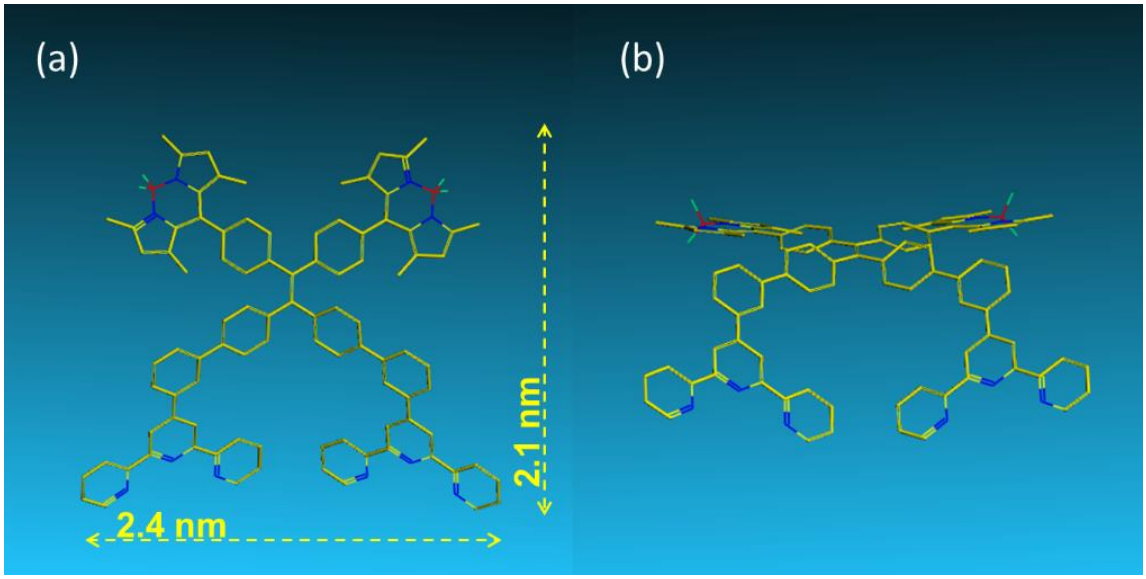


Figure S2. The modeling structures of **L**. (a) top-view, (b) side-view.

5. ^{1}H NMR, ^{13}C NMR, 2D COSY NMR spectra.

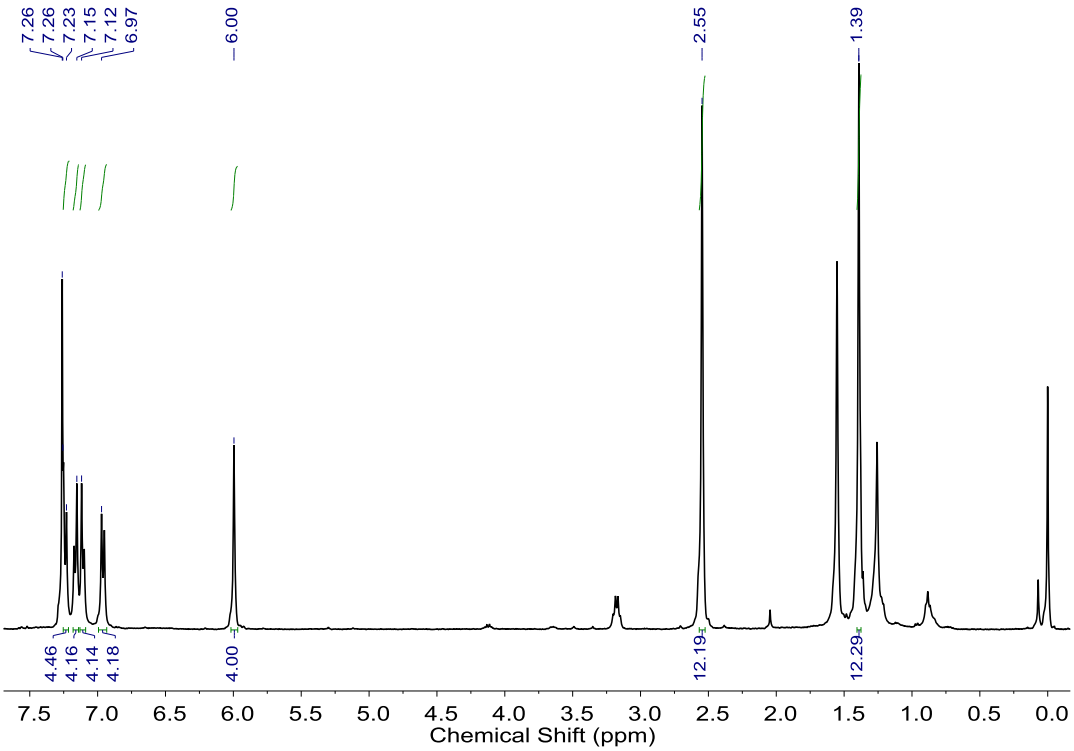


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectrum of compound **4.**

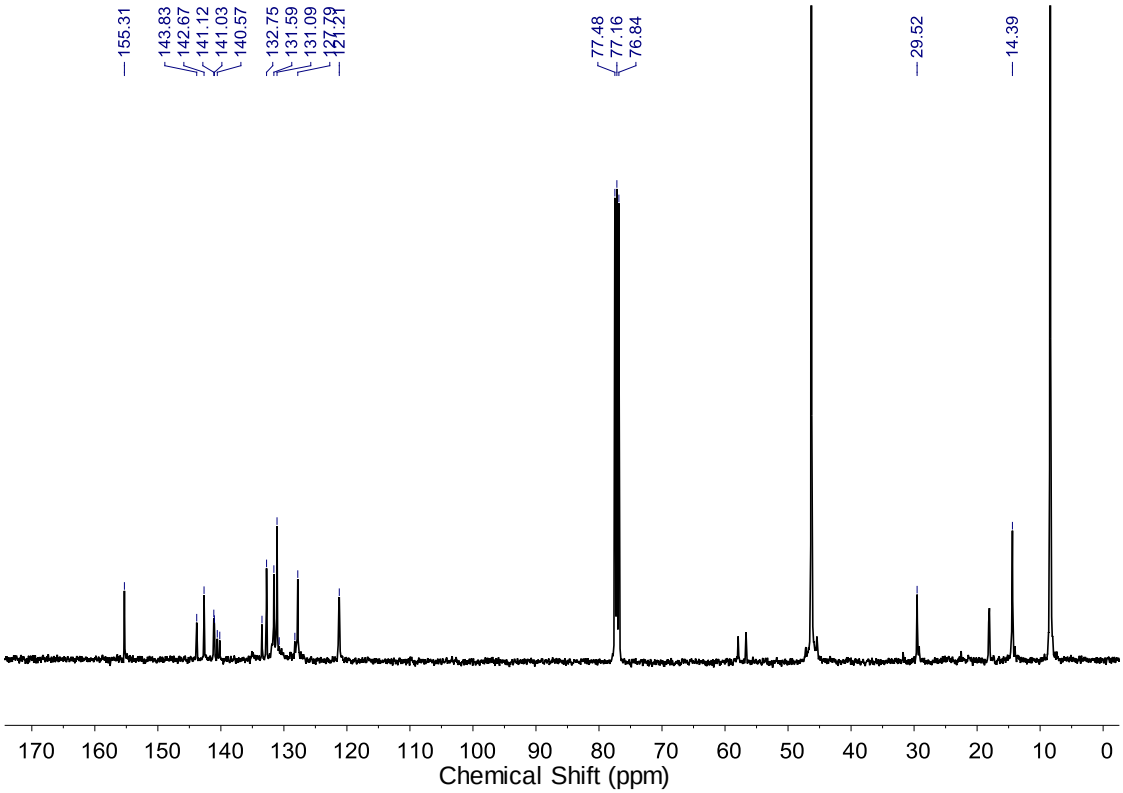


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) spectrum of compound **4**.

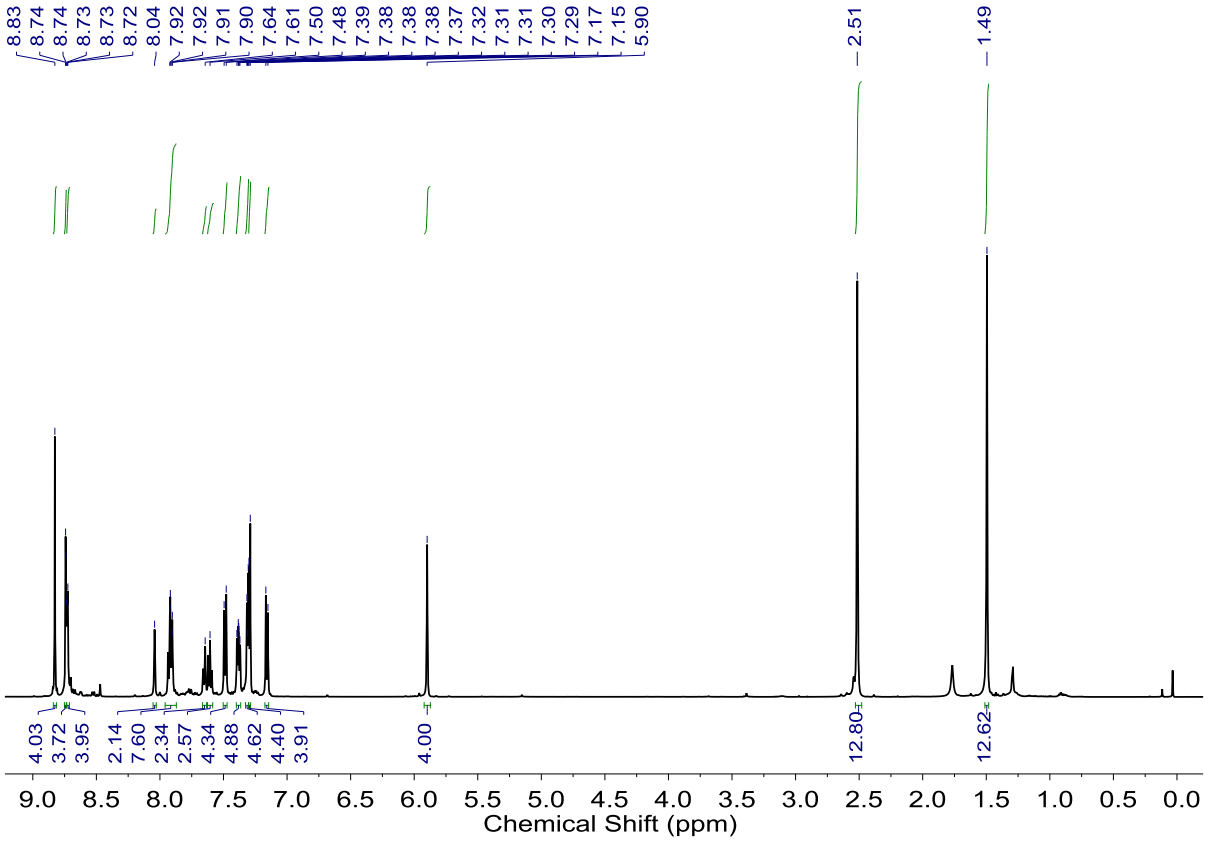


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of ligand **L.**

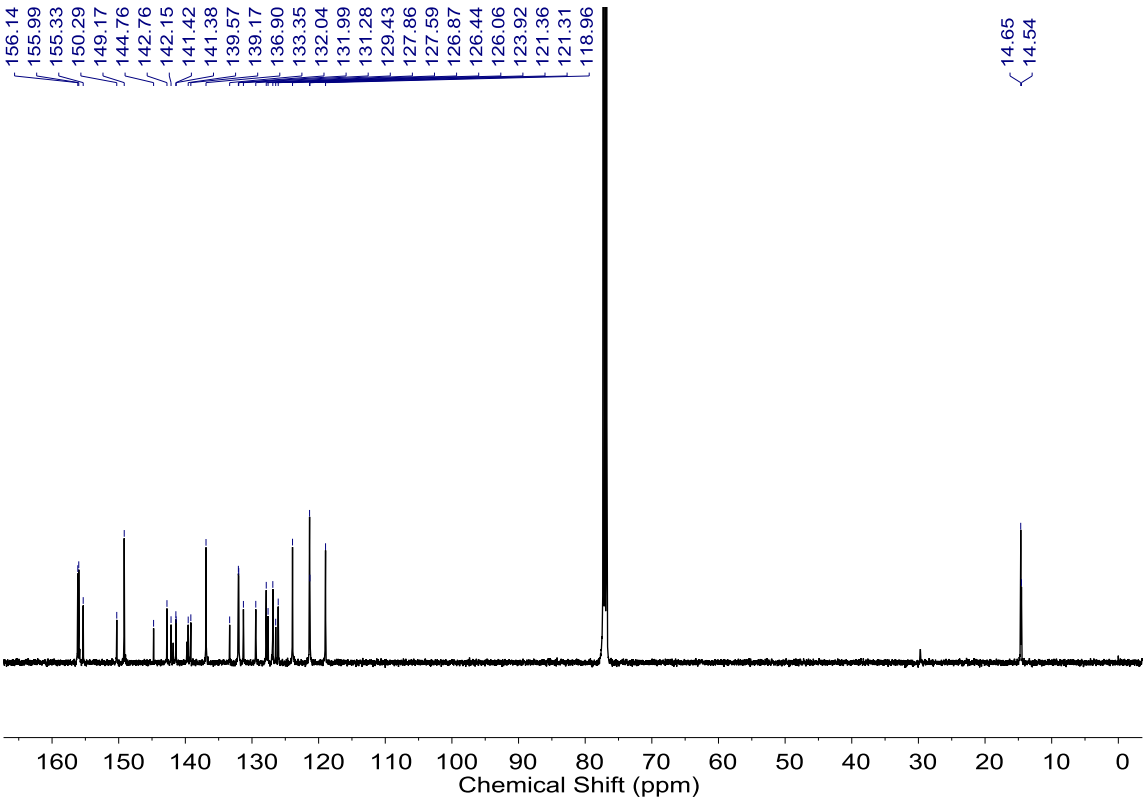


Figure S6. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) spectrum of ligand **L.**

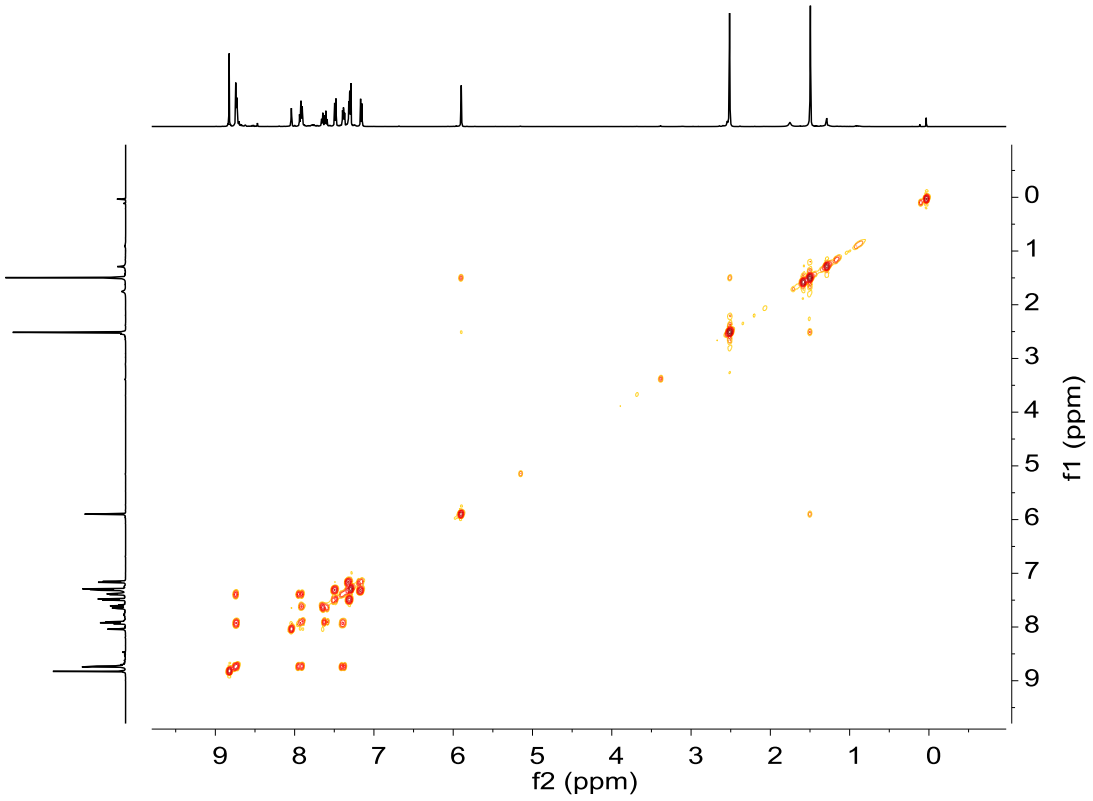


Figure S7. 2D COSY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of ligand **L**.

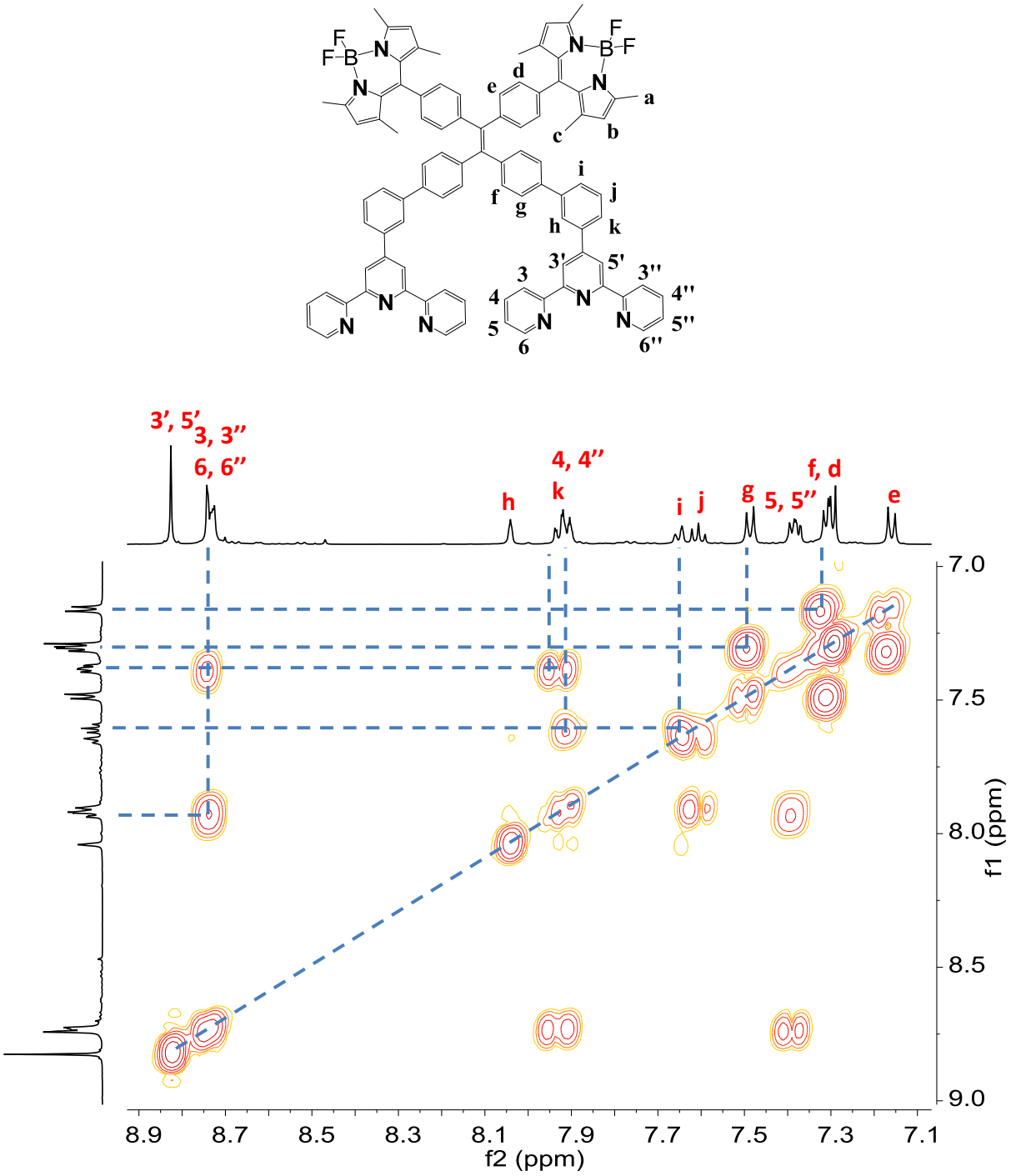


Figure S8. 2D COSY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of ligand **L** (aromatic region).

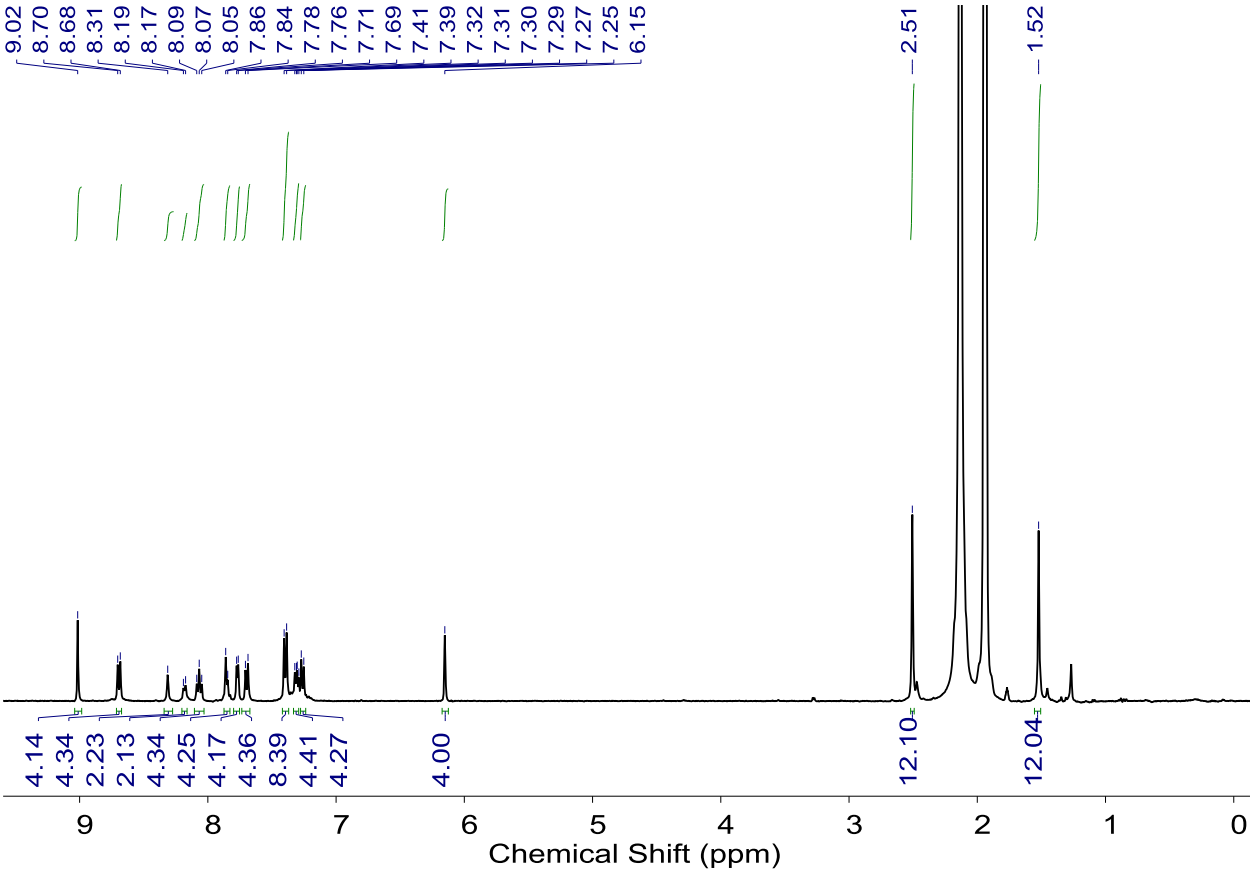


Figure S9. ^{1}H NMR (400 MHz, CD_3CN, 300 K) spectrum of **D**.

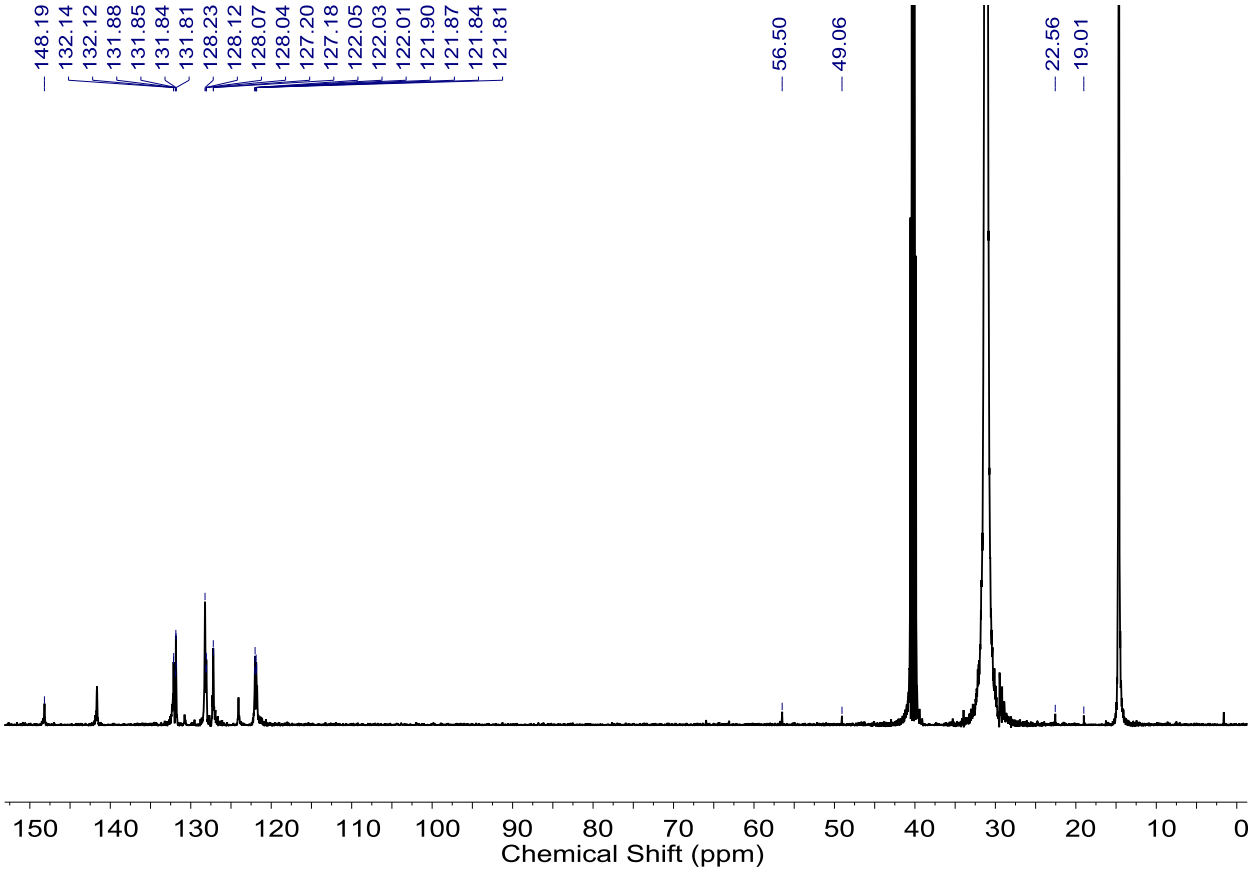


Figure S10. ^{13}C DEPT-45 NMR (125 MHz, DMSO, 300 K) spectrum of **D**.

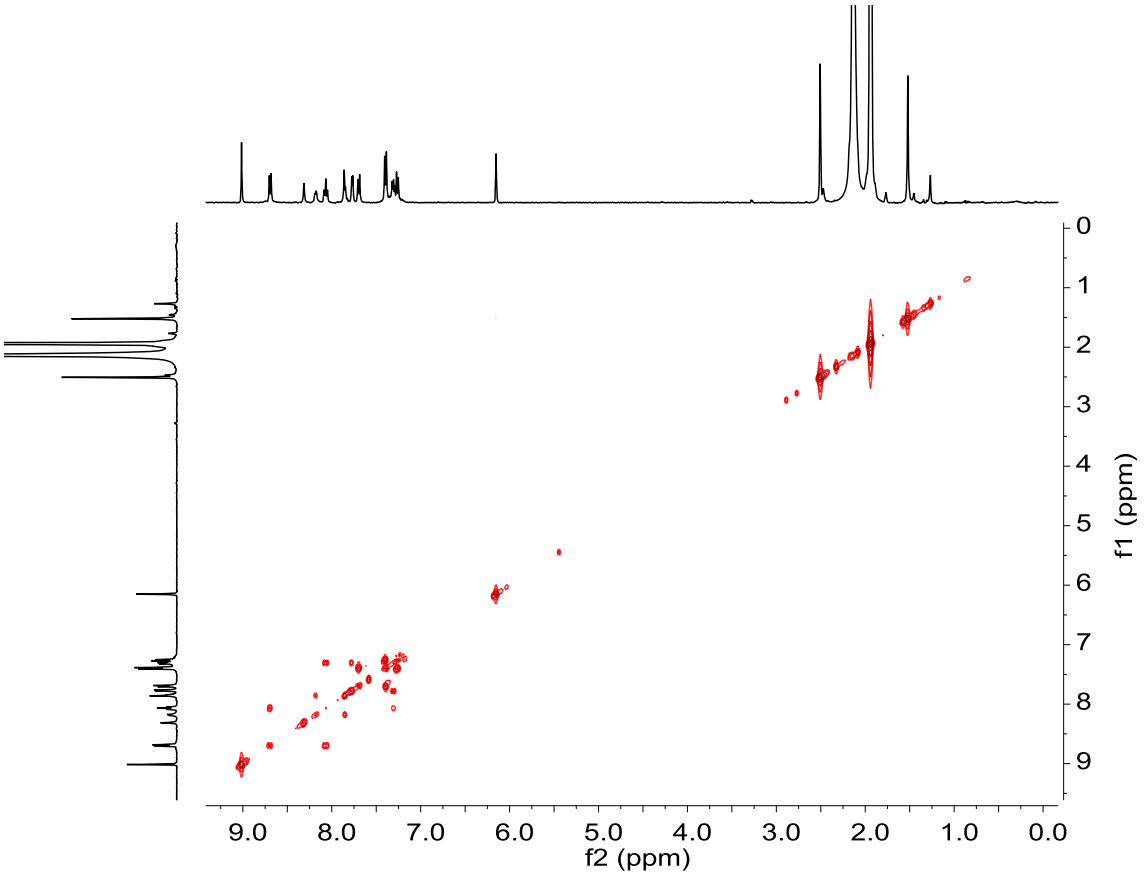


Figure S11. 2D COSY NMR (400 MHz, CD_3CN, 300 K) spectrum of **D**.

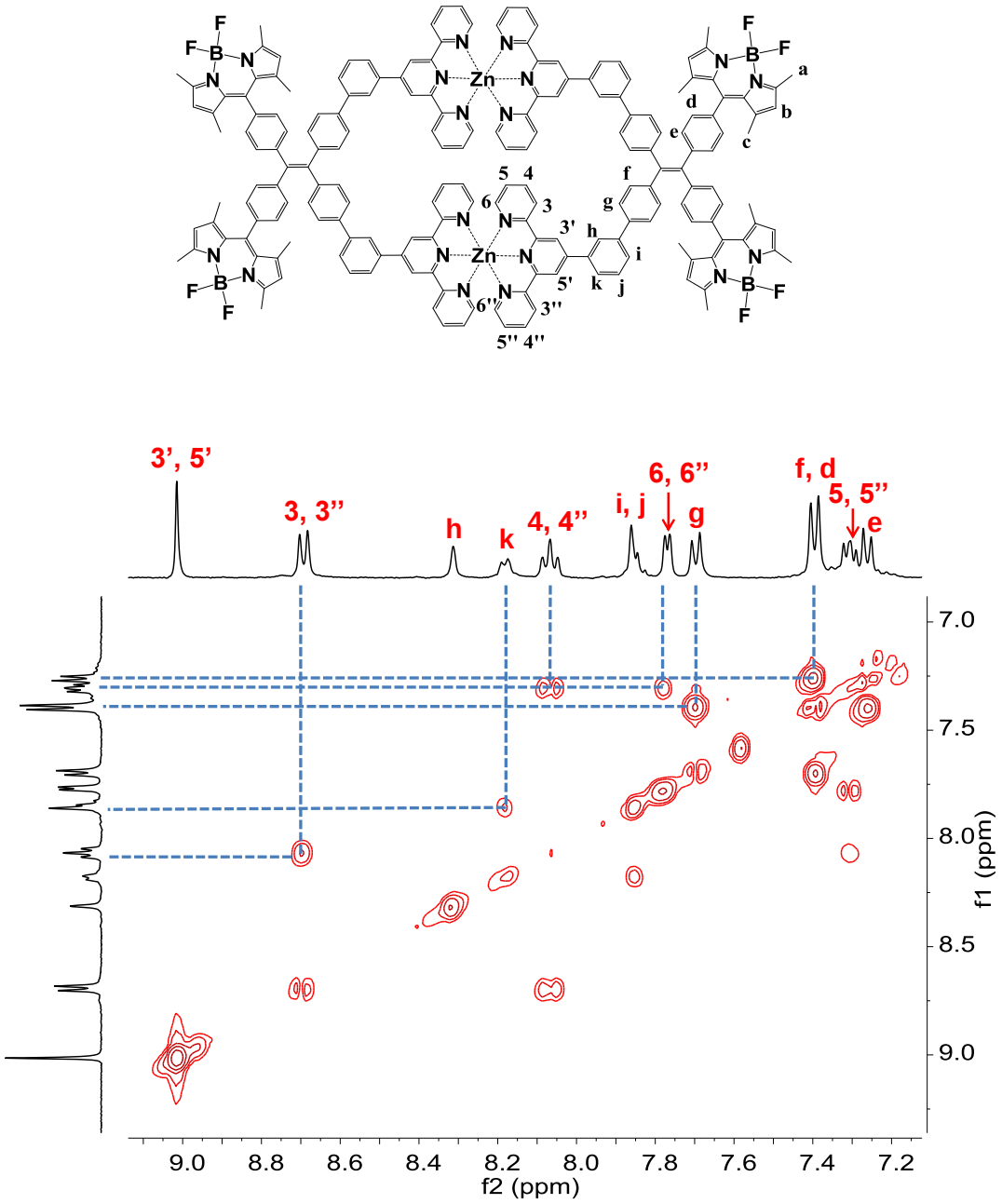


Figure S12. 2D COSY NMR (400 MHz, CD_3CN, 300 K) spectrum of **D** (aromatic region).

6. Absorption spectra of ligands and supramolecular architecture.

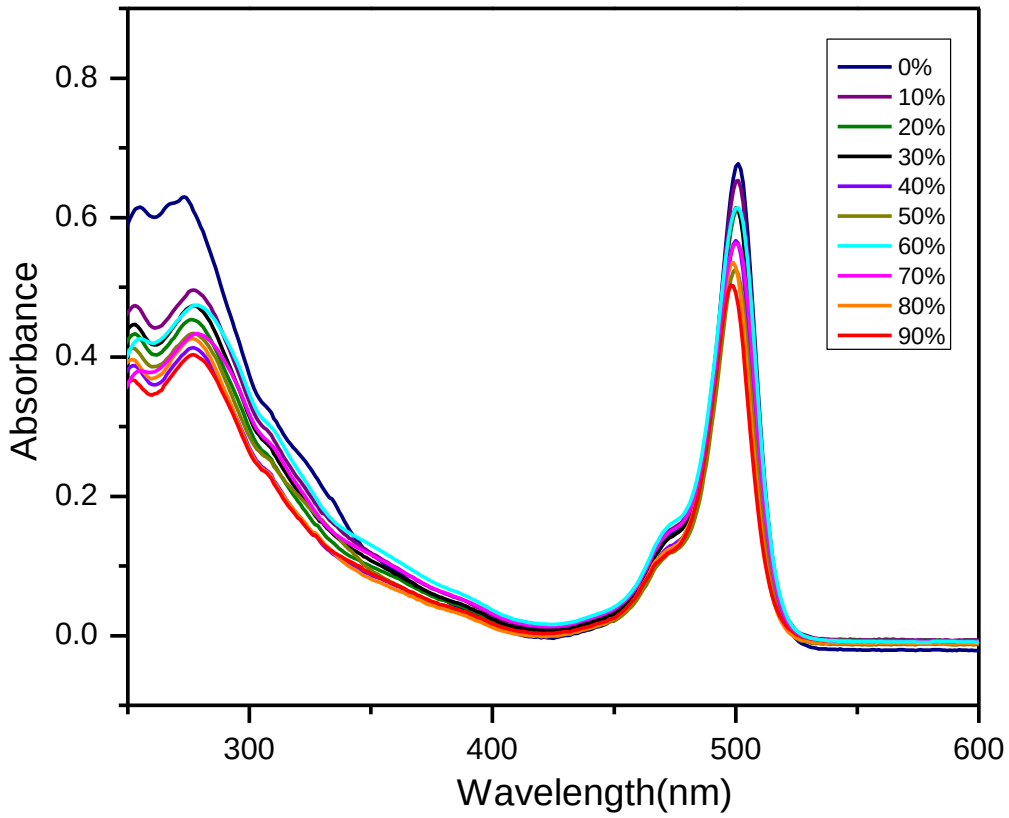


Figure S13. Absorption spectra of **L** in $CHCl_3$/methanol mixtures with different methanol fractions (c = 5.0 μM).

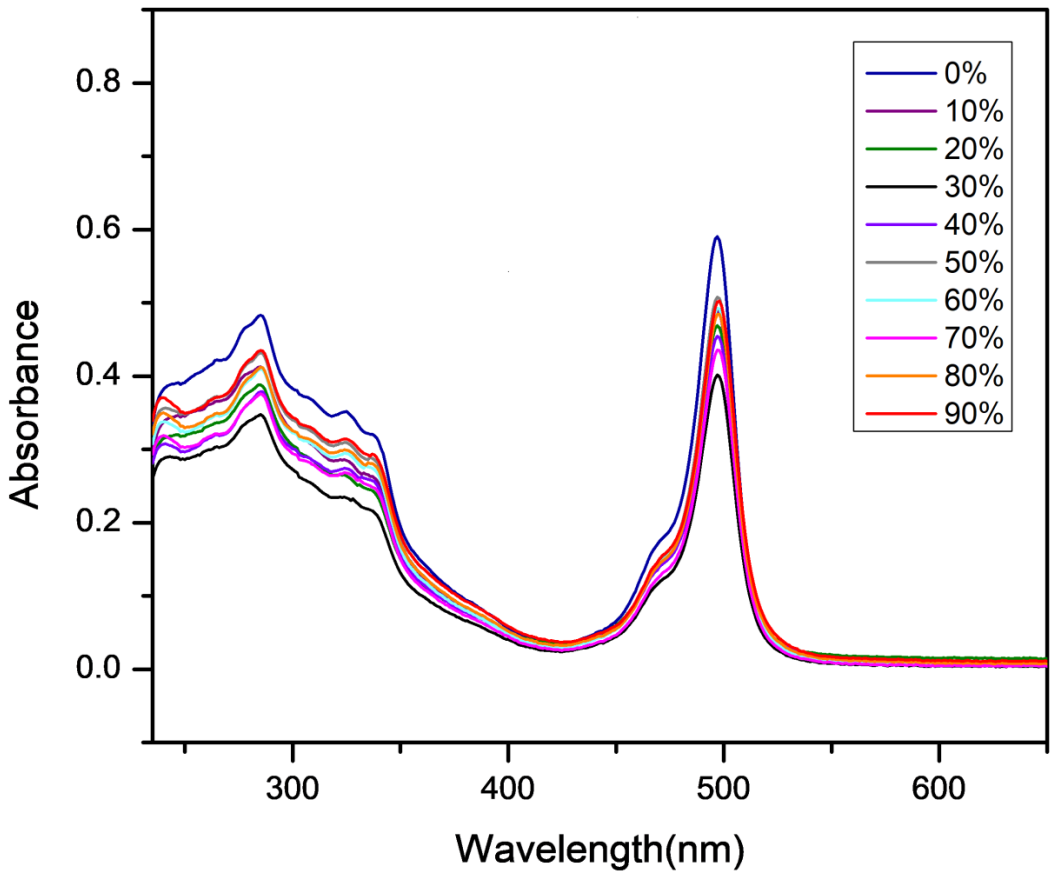


Figure S14. Absorption spectra of **D** in CH_3CN/methanol mixtures with different methanol contents (c = 7.67 μM).

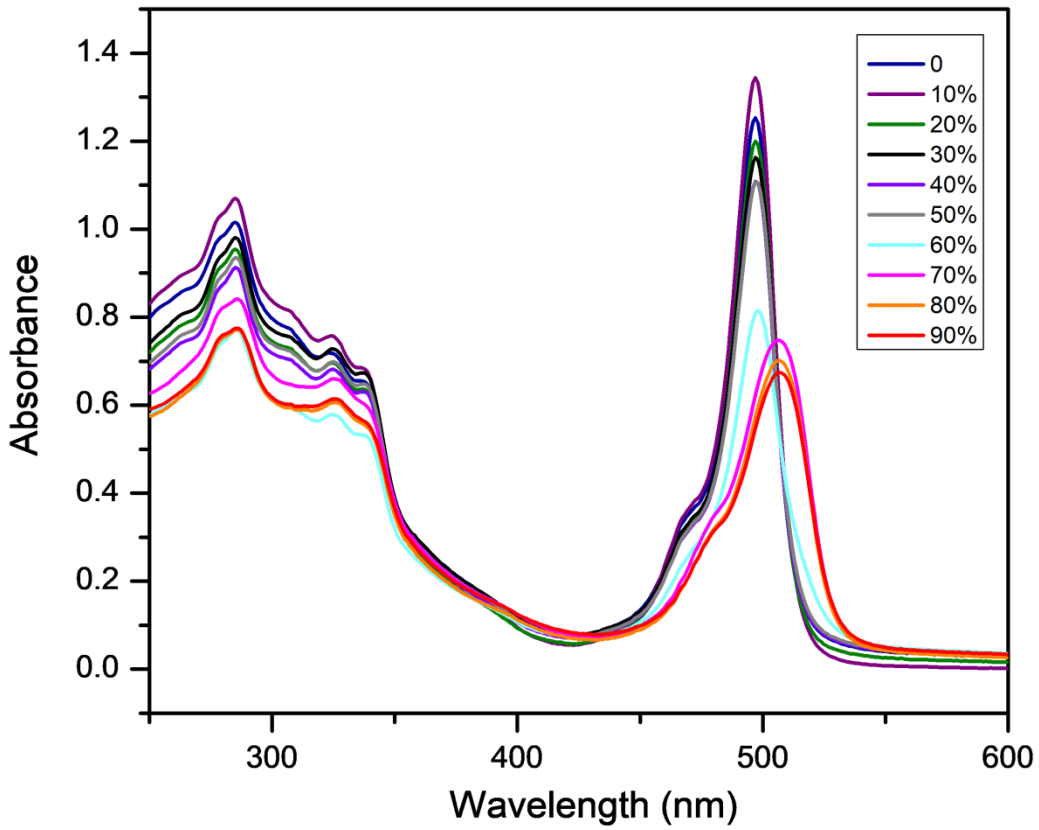


Figure S15. Absorption spectra of **D** in CH_3CN/water mixtures with different water contents (*c* = 9.59 μM).

7. Fluorescence spectrum of L.

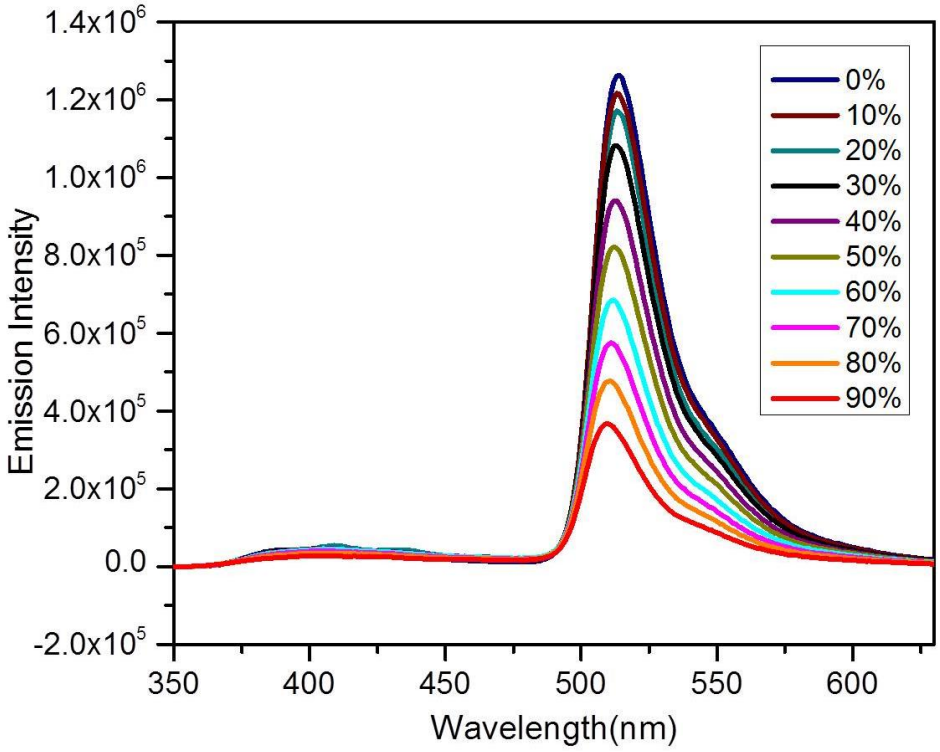


Figure S16. Fluorescence spectra of **L** in $CHCl_3$/methanol with various methanol fractions. (λ_{ex} = 325 nm, c = 5.0 μM).

8. DLS data of the aggregates of D in CH_3CN/methanol and CH_3CN/water mixtures.

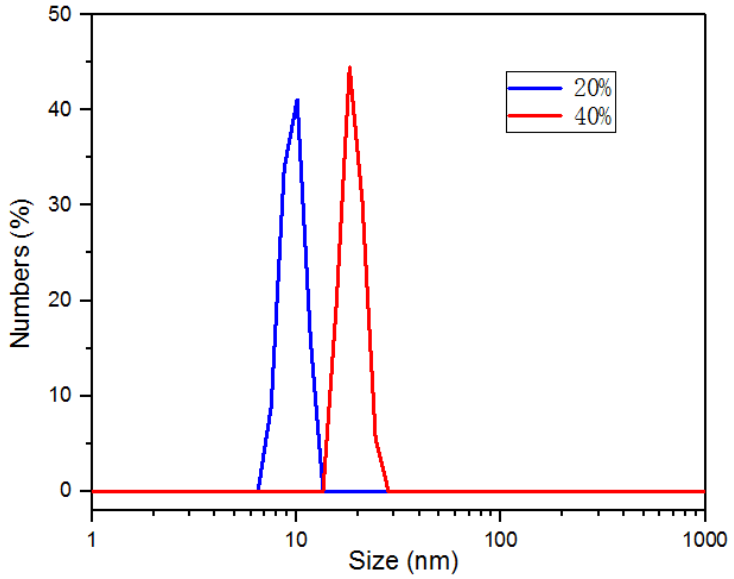


Figure S17. Size distribution of **D** in acetonitrile/methanol. The percentages in the graphs are methanol contents.

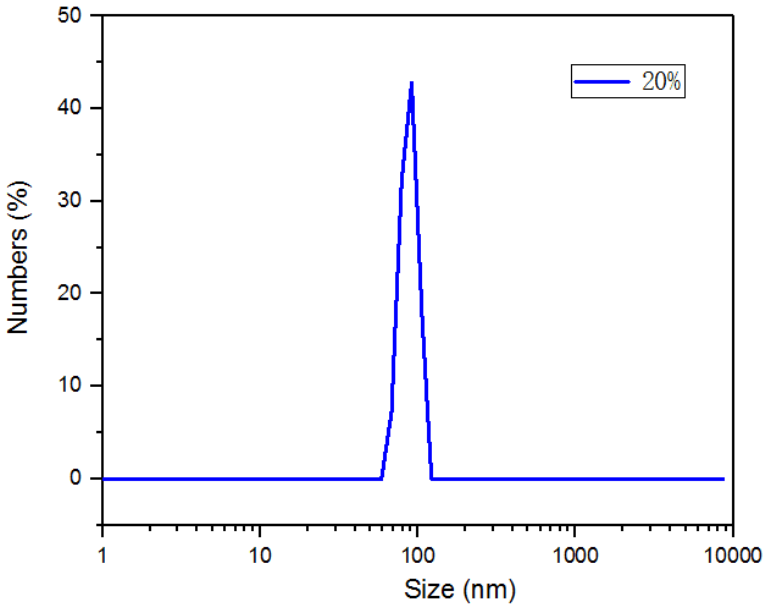


Figure S18. Size distribution of **D** in acetonitrile/water. The percentages in the graphs are water contents.

9. TEM images of D in acetonitrile/water mixtures.

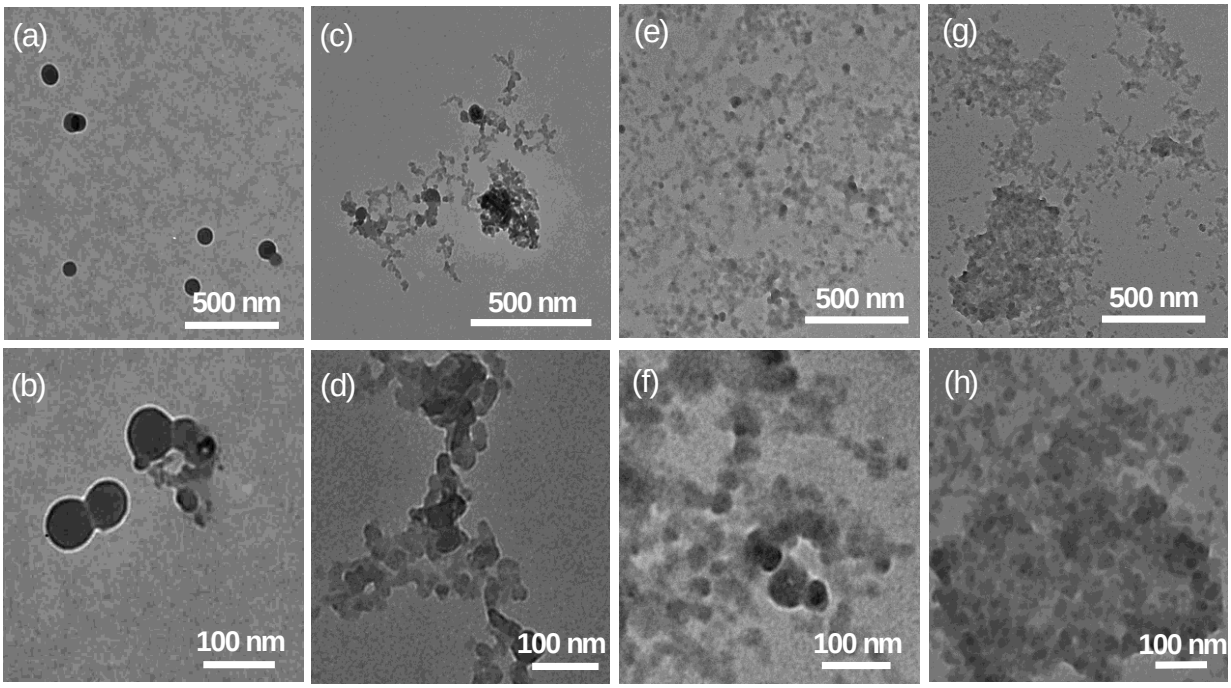


Figure S19. TEM images of the aggregates of **D** formed in acetonitrile/water mixtures containing (c, d) 20%, (e, f) 40%, (g, h) 60%, and (i, j) 80% water.