

Supporting information

A truncated triangular prism constructed by using imidazole-terpyridine building blocks

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1. Supplemental Experimental Procedures

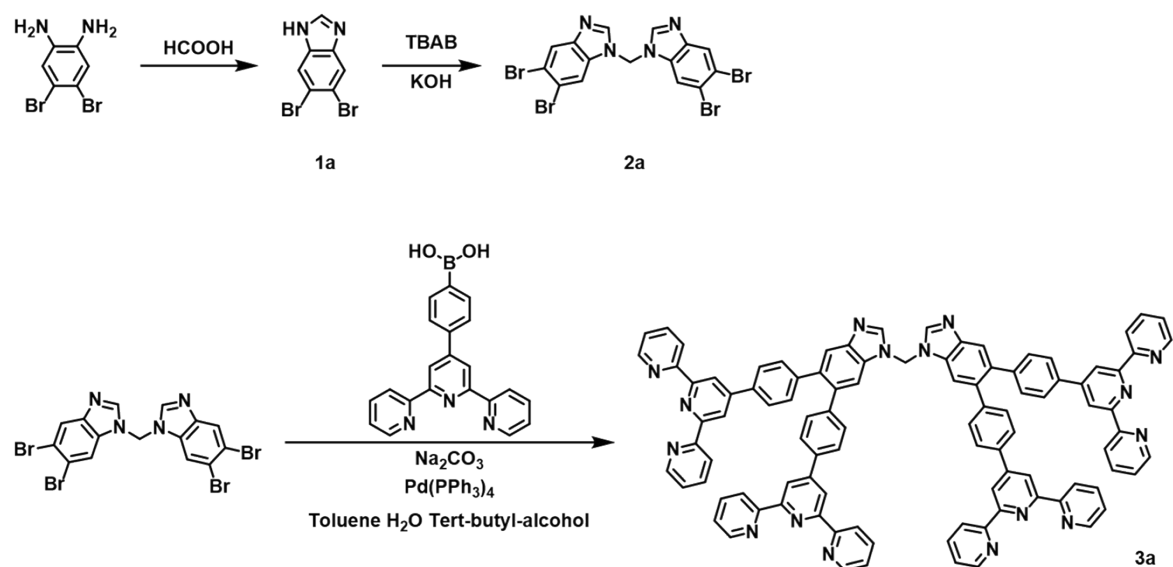
General Procedures. Reagents and solvents were purchased from Energy Chemical, Bidepharm, and used without purification. Thin-layer chromatography (TLC) was performed on flexible sheets (Greagent) precoated with Al_2O_3 (IB-F) and SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using neutral Al_2O_3 (200-300 mesh). ^1H , ^{13}C , 2D COSY, 2D ^1H - ^1H NOESY NMR, and 2D DOSY NMR spectra were recorded on a Bruker NMR 400, 500 MHz. Different NMR solvents were purchased from J&K Scientific and Sigma/Aldrich. ESI-MS and TWIM-MS were recorded with a Waters Synapt G Si tandem mass spectrometer, using solutions of 0.01 mg sample in 1 mL of $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:3, v/v) for ligands or 0.5 mg sample in 1 mL of MeCN/MeOH (3:1, v/v) for complexes and 0.5 mg sample in 1 mL of DMF/MeCN (3:1, v/v) for.

TWIM-MS. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 2 kV; sample cone voltage, 35 V; Source Offset, 42V; source temperature 150 °C; desolvation temperature, 250 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas flow, 0 mL/min; trap gas flow, 3 mL/min; helium cell gas flow, 120 mL/min; ion mobility (IM) cell gas flow, 30 mL/min; sample flow rate, 8 $\mu\text{L}/\text{min}$; IM traveling wave height, 25 V; and IM traveling wave velocity, 1200 m/s. Q was set in rf-only mode to transmit all ions produced by ESI into the triwave region for the acquisition of TWIM-MS data. Data were collected and analyzed by using Mass Lynx 4.2 and Drift Scope 2.9.¹

Molecular Modeling. Energy minimization of the macrocycles was conducted with the Materials Studio version 6.0 program, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. Geometry optimization used a universal forcefield with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters.

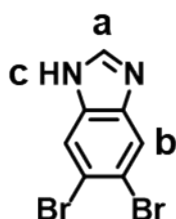
TEM. Transmission electron microscopy tests were performed on the JEOL JEM-2100F equipment. The sample solutions were drop-casted onto a lacey carbon-covered Cu grid (300 mesh, purchased from Beijing Zhongjingkeyi Technology Co., Ltd.) and the extra solution was absorbed by filter paper to avoid aggregation.

FL. Fluorescence properties were performed on Edinburgh-FS5 Fluorescence spectrometer at 298 K (10^{-6} M CHCl_3 or CH_3CN)



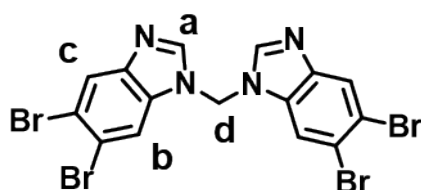
Scheme S1. Synthesis route of **L**.

2. Synthesis of compounds and supramolecules



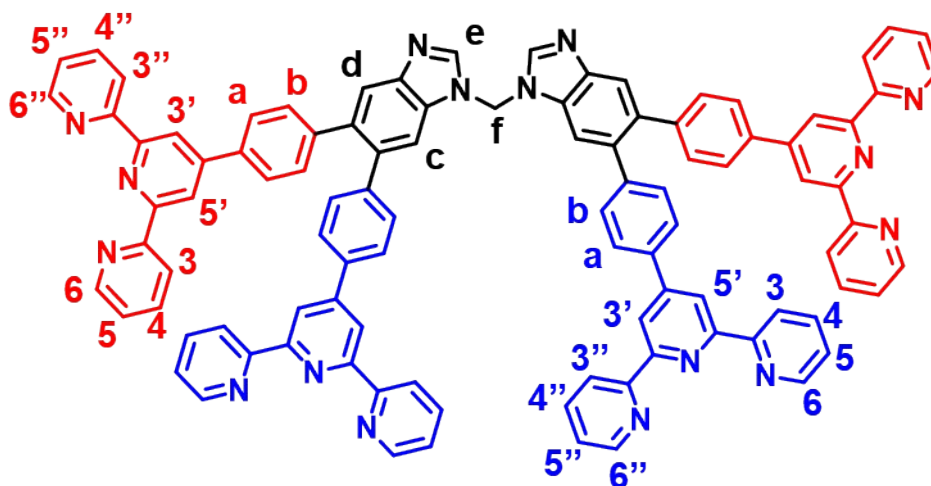
Synthesis of 5,6-dibromo-1H-benzo[d]imidazole (1a): In a 100 mL three-necked flask, 4,5-dibromo-o-phenylenediamine (3.3 g, 12.5 mmol) was added, 33 mL formic acid was added under the protection of N_2 , and refluxed at $110^\circ C$ for 4 h. After the reaction cool to room temperature, and then slowly add 4 mol/L of sodium hydroxide solution under stirring condition to adjust $pH = 7$. The filtration results **1a** in a yellow-white solid (3.0 g, 88 %).

1H NMR (500 MHz, $DMSO-d_6$, 298 K, ppm) δ 12.70 (s, 1H, H^a), 8.32 (s, 1H, H^b), 8.03 (s, 2H, H^c). ^{13}C NMR (101 MHz, $DMSO-d_6$, 298 K, ppm) δ 144.61 (s), 115.99 (s).



Synthesis of bis(5,6-dibromo-1*H*-benzo[*d*]imidazol-1-yl)methane (2a): **1a** (552 mg, 2 mmol), potassium hydroxide (224 mg, 4 mmol) and tetrabutylammonium bromide (19.3 mg, 0.06 mmol) were added to a 50 mL single-necked flask and stirred for 30 min at room temperature. Then 10 mL dibromide was added and stirred for 12 h at room temperature. Stop stirring and add dichloromethane, filter to get a white solid, and then wash with deionized water and methanol. Gain the result **2a**, which is pale solid (500 mg, 89 %).

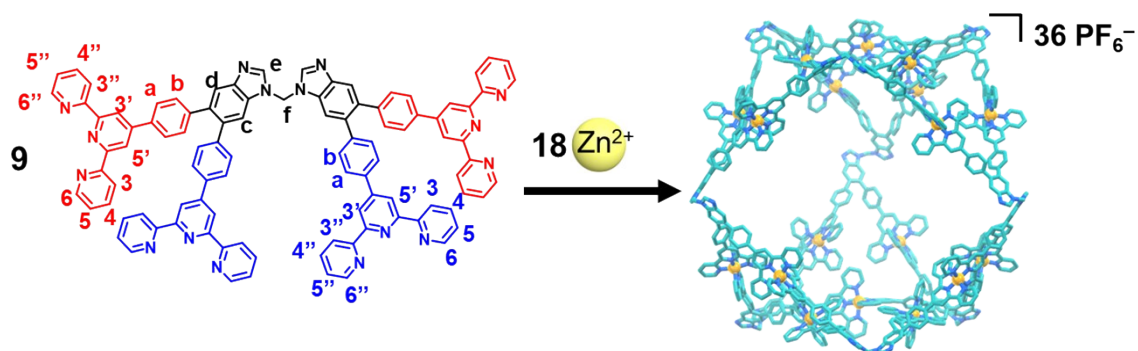
¹H NMR (400 MHz, CDCl₃/CD₃OD (10:1, v/v) 298 K, ppm) δ 8.24 (s, 2H, H^a), 7.94 (s, 2H, Ph-H^b), 7.80 (s, 2H, Ph-H^c), 6.48 (s, 2H, H^d). ¹³C NMR (101 MHz, DMSO-*d*₆ 298 K, ppm) δ 146.94 (s), 144.42 (s), 133.52 (s), 124.70 (s), 117.93 (d, *J* = 69.9 Hz), 115.98 (s), 81.20 – 76.56 (m), 53.10 (s). ESI-TOF (*m/z*): Calcd. for [C₁₅H₉Br₄N₄]⁺: 564.9046. Found:564.9046.



Synthesis of bis(5,6-bis(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-1*H*-benzo[*d*]imidazol-1-yl)methane (L): The mixture of **2a** (1.10 g, 0.99 mmol), 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (2.25 g, 6.36 mmol), Na₂CO₃ (0.90 g, 8.48 mmol), and Pd(PPh₃)₄ (0.25 g, 0.21 mmol) in the solution of toluene (80 mL), tert-butyl-alcohol (15 mL) and H₂O (30 mL) was refluxing for 96 h under N₂. After separating the toluene layer, the aqueous layer was extracted with CH₂Cl₂ (150 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The residue was column chromatographed eluting with a mixture of CH₂Cl₂ and MeOH (100:1, v/v) to give **L** (1.16 g, 58%), as a white powder.

^1H NMR (400 MHz, CDCl_3 298 K, ppm) δ 8.72 (s, 4H, tpy-H $^{3',5'}$), 8.68 – 8.64 (m, 4H, tpy-H $^{6,6''}$), 8.62 (t, $J = 4.0$ Hz, 8H, tpy-H $^{3',5'}$, tpy-H $^{3,3''}$), 8.57 (dd, $J = 4.5, 0.7$ Hz, 4H, tpy-H $^{6,6''}$), 8.51 (d, $J = 8.0$ Hz, 4H, tpy-H $^{3,3''}$), 8.28 (s, 2H, H e), 7.98 (s, 2H, H d), 7.79 (dddd, $J = 17.0, 15.5, 8.0, 2.0$ Hz, 16H, tpy-H $^{4,4''}$, H a , tpy-H $^{4,4''}$, H a), 7.70 (s, 2H, H c), 7.34 (d, $J = 8.5$ Hz, 4H, H b), 7.32 – 7.27 (m, 8H, tpy-H $^{5,5''}$, H b), 7.20 (ddd, $J = 7.5, 5.0, 1.0$ Hz, 4H, H $^{5,5''}$), 6.64 (s, 2H, H f).

^{13}C NMR (101 MHz, CDCl_3 298 K, ppm) δ 156.30 (s), 156.08 (s), 155.88 (s), 155.66 (s), 149.71 (s), 149.45 (s), 149.05 (d, $J = 13.0$ Hz), 143.68 (s), 142.23 (d, $J = 8.5$ Hz), 137.21 (s), 137.02 – 136.27 (m), 132.57 (s), 130.74 (d, $J = 9.5$ Hz), 127.14 (d, $J = 14.0$ Hz), 123.68 (d, $J = 13.5$ Hz), 122.84 (s), 121.28 (d, $J = 13.0$ Hz), 118.81 (d, $J = 6.0$ Hz), 111.19 (s). ESI-TOF (m/z): Calcd. for $[\text{C}_{99}\text{H}_{66}\text{N}_{16}]^+$: 1479.0974. Found: 1479.0974.

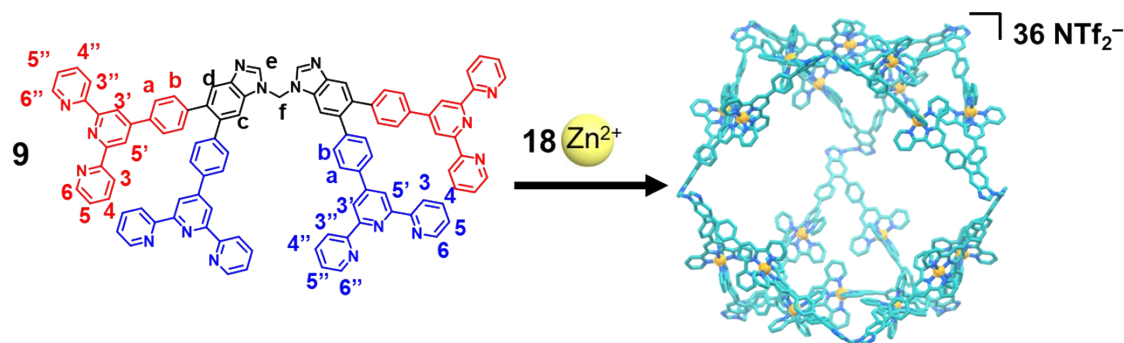


Complex G(PF $_6^-$): To a solution of L (10.4 mg, 7 μmol) in CHCl_3 and MeOH (1:1.5, 12 mL), a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.2 mg, 14 μmol) in MeOH (2 mL) was added. The mixture was stirred at 55°C for 8 h and then cooled to room temperature. Upon addition of excess NH_4PF_6 (87.31 mg), a precipitate was formed and washed with water and MeOH three times respectively, dried *in vacuo* to give complex G(PF $_6^-$) (14.9 mg, 97 %) as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$ 298 K, ppm) δ 9.79-9.28 (br, 36H, tpy-H $^{3',5'}$), 9.28-8.80 (m, 90H, tpy-H $^{3',5'}$, tpy-H $^{3,3''}$, H e), 8.78-8.41 (m, 54H, tpy-H $^{3,3''}$, H f), 8.40-8.13 (m, 126H, tpy-H $^{4,4''}$, tpy-H $^{6,6''}$, H d , H a), 8.10-7.69 (m, 162H, tpy-H $^{4,4''}$, tpy-H $^{6,6''}$, tpy-H $^{5,5''}$, H c , H a), 7.67-7.46 (br, 36H, H b), 7.45-6.77 (m, 54H, tpy-H $^{5,5''}$, H b).

ESI-MS(m/z): 2316.38 $[\text{M}-\text{Zn}(\text{PF}_6)_2-8\text{PF}_6]^{8+}$ (calcd m/z : 2316.91), 2042.73 $[\text{M}-\text{Zn}(\text{PF}_6)_2-9\text{PF}_6]^{9+}$ (calcd m/z : 2043.37), 1823.99 $[\text{M}-\text{Zn}(\text{PF}_6)_2-10\text{PF}_6]^{10+}$ (calcd m/z : 1824.54), 1645.08 $[\text{M}-\text{Zn}(\text{PF}_6)_2-11\text{PF}_6]^{11+}$ (calcd m/z : 1645.49), 1495.87 $[\text{M}-\text{Zn}(\text{PF}_6)_2-12\text{PF}_6]^{12+}$

(calcd m/z: 1496.29), 1369.68 [M-Zn(PF₆)₂-13PF₆]¹³⁺ (calcd m/z: 1370.04), 1261.58 [M-Zn(PF₆)₂-14PF₆]¹⁴⁺ (calcd m/z: 1261.83), 1167.74 [M-Zn(PF₆)₂-15PF₆]¹⁵⁺ (calcd m/z: 1168.04), 1085.68 [M-Zn(PF₆)₂-16PF₆]¹⁶⁺ (calcd m/z: 1085.98), 1013.33 [M-Zn(PF₆)₂-17PF₆]¹⁷⁺ (calcd m/z: 1013.57), 949.01 [M-Zn(PF₆)₂-18PF₆]¹⁸⁺ (calcd m/z: 949.21), 891.49 [M-Zn(PF₆)₂-19PF₆]⁸⁺ (calcd m/z: 891.62).



Complex G(NTf₂⁻).: To a solution of **L** (10.0 mg, 7 μmol) in CHCl₃ and MeOH (1:1.5, 12 mL), a solution of Zn(NO₃)₂·6H₂O (4.2 mg, 14 μmol) in MeOH (2 mL) was added. The mixture was stirred at 55°C for 8 h and then cooled to room temperature. Upon addition of excess LiNTf₂ (90.34 mg), a precipitate was formed and washed with water and MeOH three times respectively, dried *in vacuo* to give complex **G(NTf₂⁻)** (14.8 mg, 95 %) as a yellow solid.

¹H NMR (400 MHz, CD₃CN 298 K, ppm) δ 9.15-8.92 (br, 72H, tpy-H^{3',5'}, tpy-H^{3',5'}), 8.81 (m, 18H, H^e), 8.73-8.58 (m, 72H, tpy-H^{3,3''}, tpy-H^{3,3''}), 8.18-7.98 (m, 162H, tpy-H^{4,4''}, tpy-H^{4,4''}, H^d, H^a, H^a), 7.85-7.66 (m, 90H, tpy-H^{6,6''}, tpy-H^{6,6''}, H^c), 7.67-7.48 (br, 108H, tpy-H^{5,5''}, H^b, H^b), 7.39-7.23 (m, 36H, tpy-H^{5,5''}), 7.06-6.79 (m, 18H, H^f).

ESI-MS(m/z): 2449.05 [M-Zn(NTf₂)₂-9NTf₂]⁹⁺ (calcd m/z: 2448.87), 2176.23 [M-Zn(NTf₂)₂-10 NTf₂]¹⁰⁺ (calcd m/z: 2175.97), 1952.86 [M-Zn(NTf₂)₂-11 NTf₂]¹¹⁺ (calcd m/z: 1952.69), 1766.78 [M-Zn(NTf₂)₂-12 NTf₂]¹²⁺ (calcd m/z: 1766.62), 1609.42 [M-Zn(NTf₂)₂-13 NTf₂]¹³⁺ (calcd m/z: 1609.18), 1474.32 [M-Zn(NTf₂)₂-14NTf₂]¹⁴⁺ (calcd m/z: 1474.22), 1357.45 [M-Zn(NTf₂)₂-15NTf₂]¹⁵⁺ (calcd m/z: 1357.27), 1255.17 [M-Zn(NTf₂)₂-16 NTf₂]¹⁶⁺ (calcd m/z: 1254.93), 1164.69 [M-Zn(NTf₂)₂-17NTf₂]¹⁷⁺ (calcd m/z: 1164.63), 1084.32 [M-Zn(NTf₂)₂-18 NTf₂]¹⁸⁺ (calcd m/z: 1084.37).

3. NMR Spectra

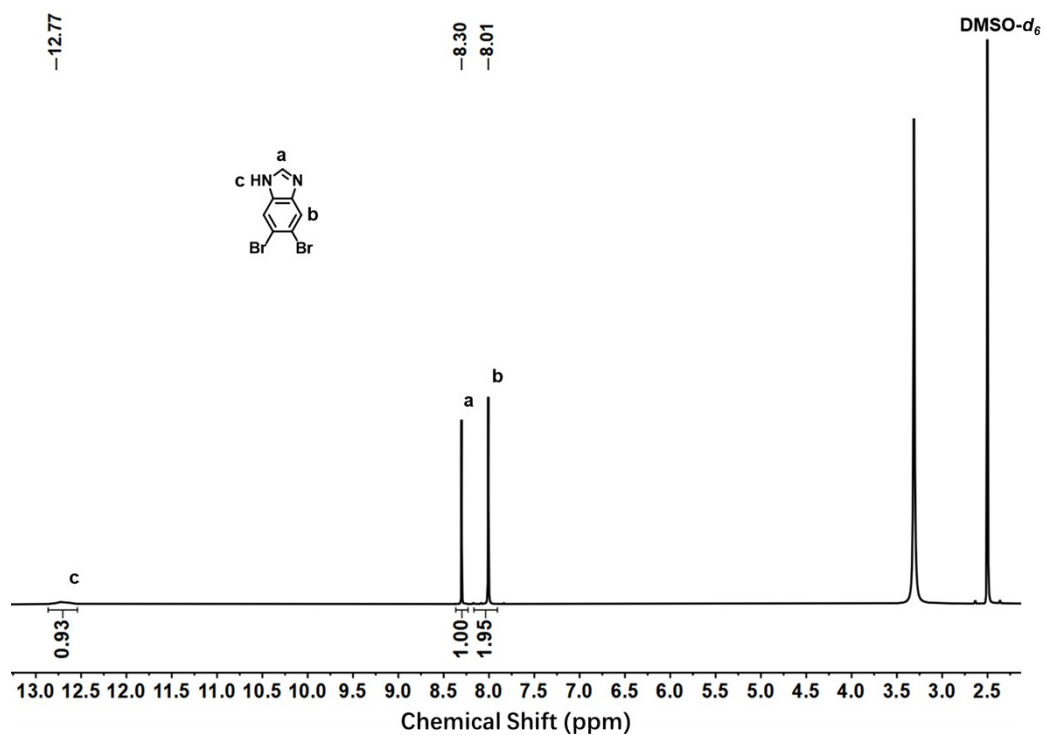


Figure S1. ^1H NMR (400 MHz, 298 K) spectrum of **1a** in $\text{DMSO-}d_6$

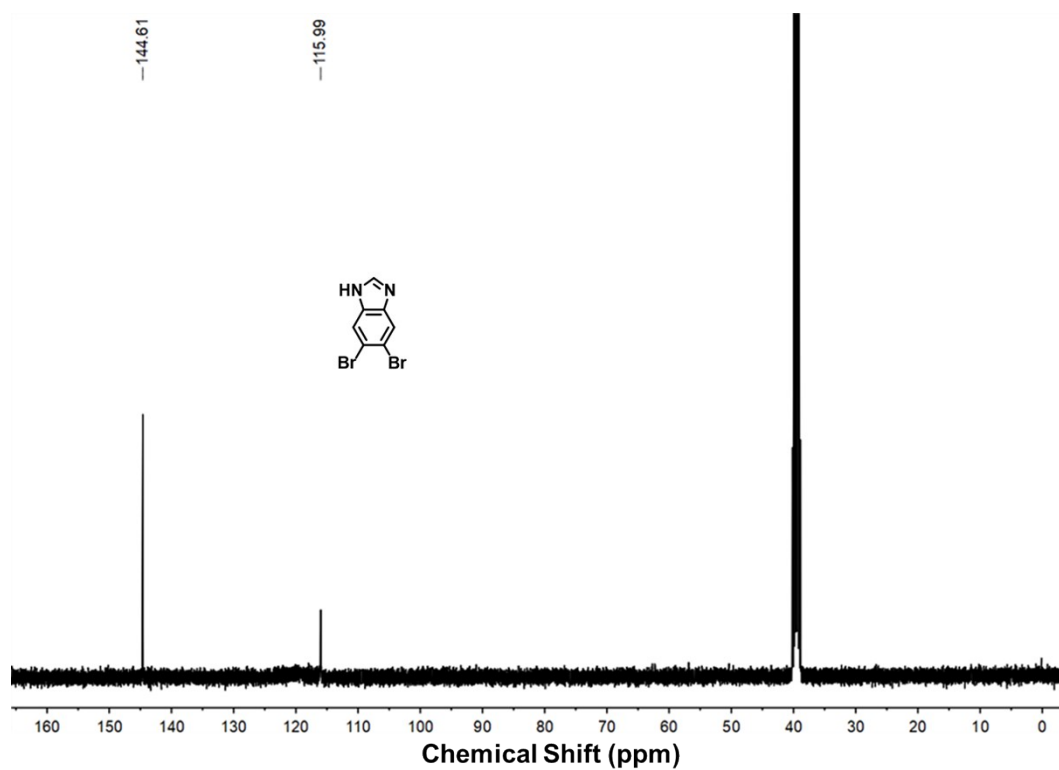


Figure S2. ^{13}C NMR (101 MHz, 298 K) spectrum of **1a** in $\text{DMSO-}d_6$

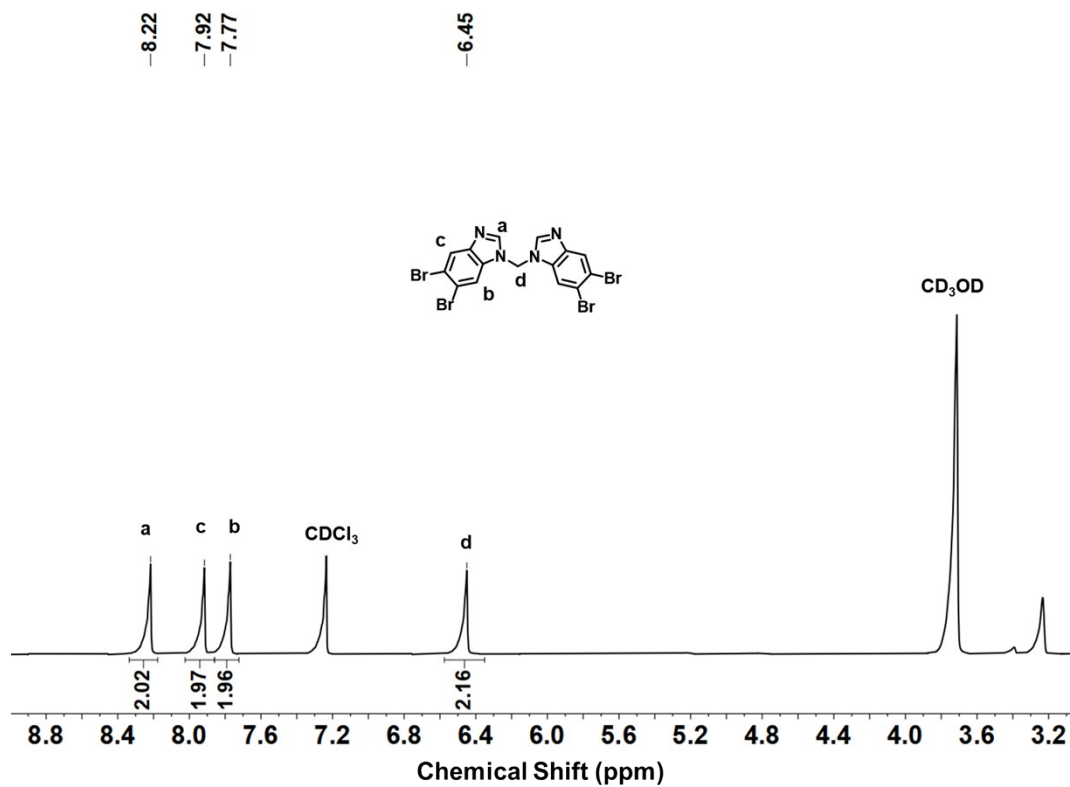


Figure S3. ¹H NMR (400 MHz, 298 K) spectrum of **2a** in CDCl₃/CD₃OD (10:1, v/v)

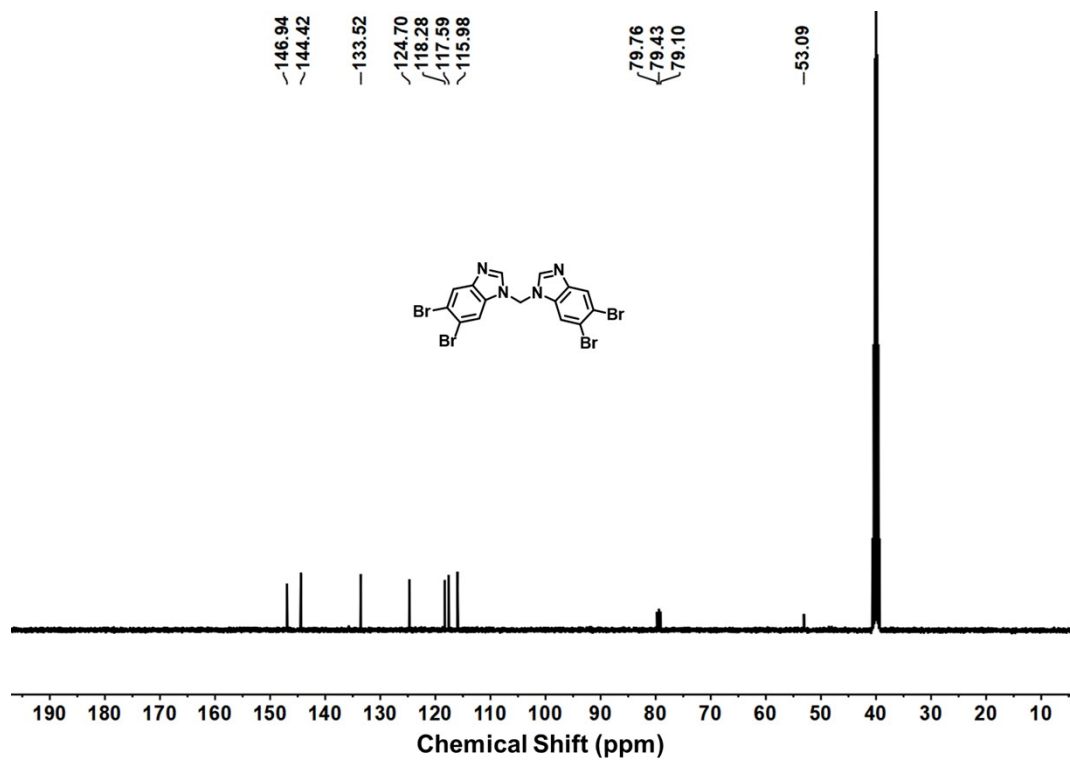


Figure S4. ¹³C NMR (101 MHz, 298 K) spectrum of **2a** in DMSO-*d*₆

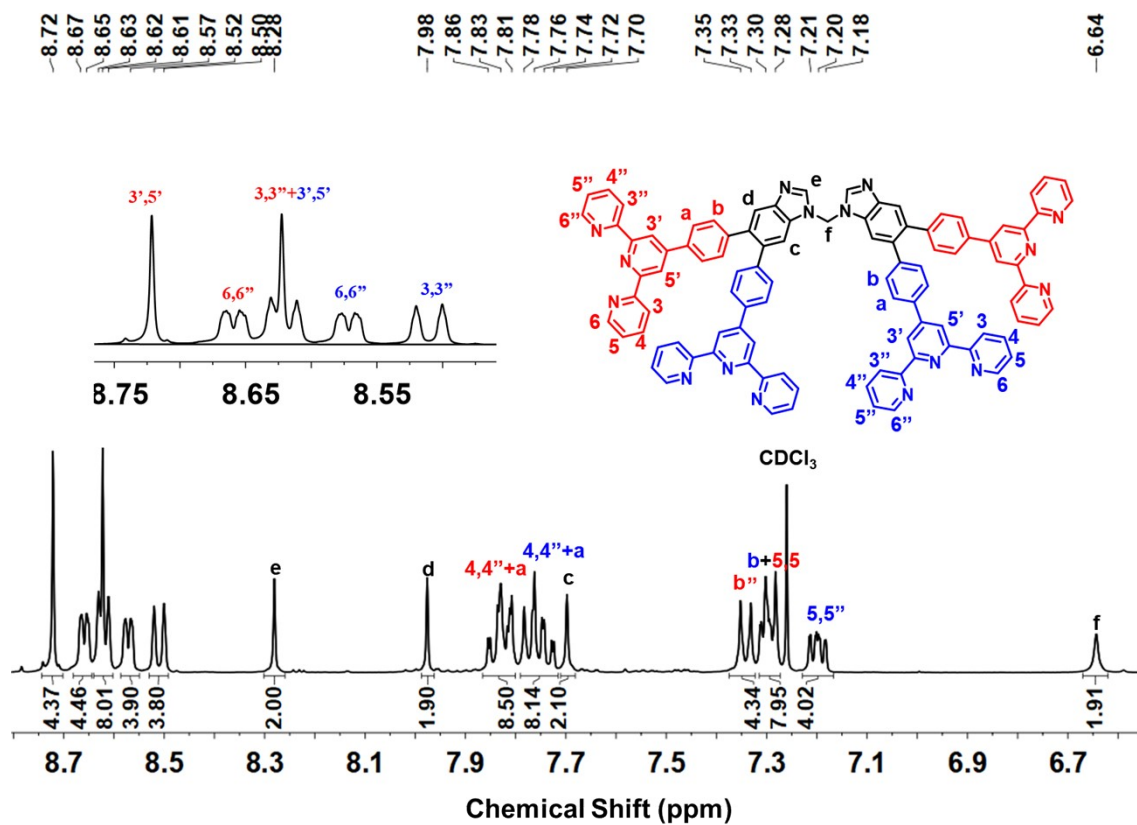


Figure S5. ^1H NMR (400 MHz, 298 K) spectrum of L in CDCl_3

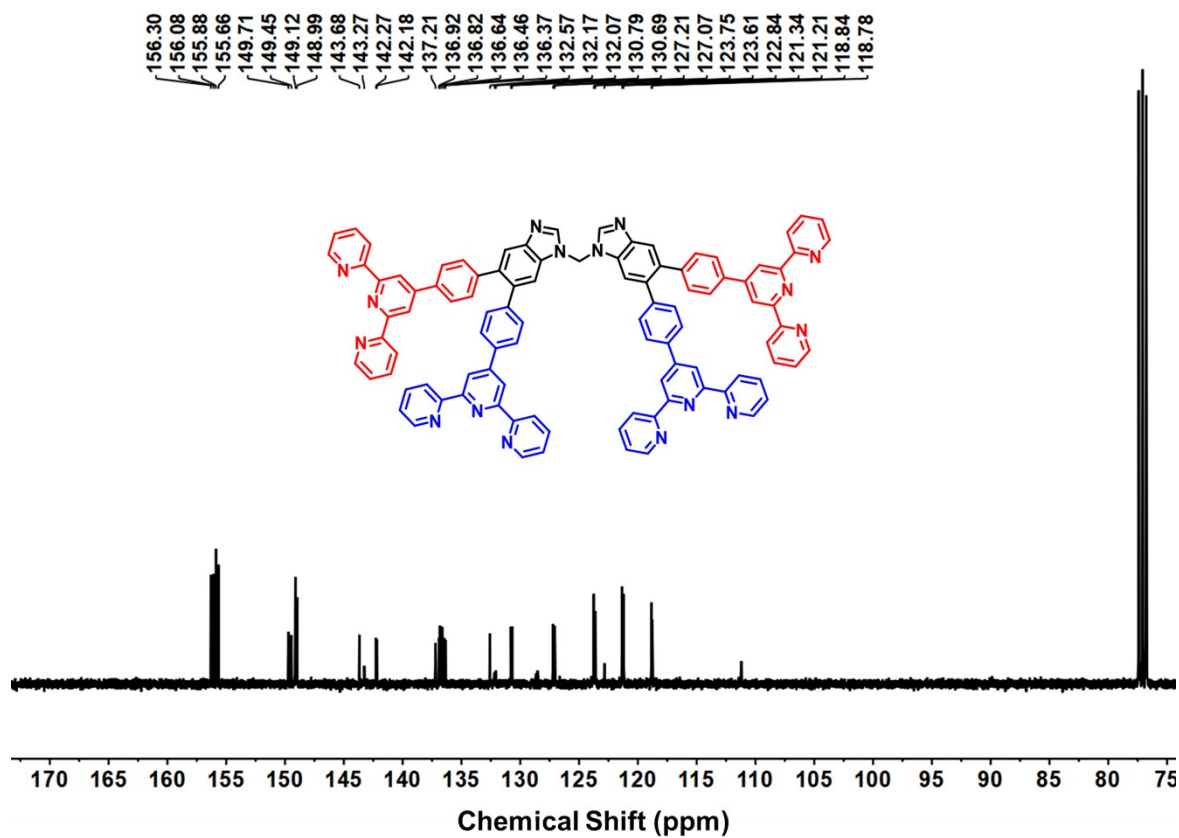


Figure S6. ^{13}C NMR (101 MHz, 298 K) spectrum of L in CDCl_3

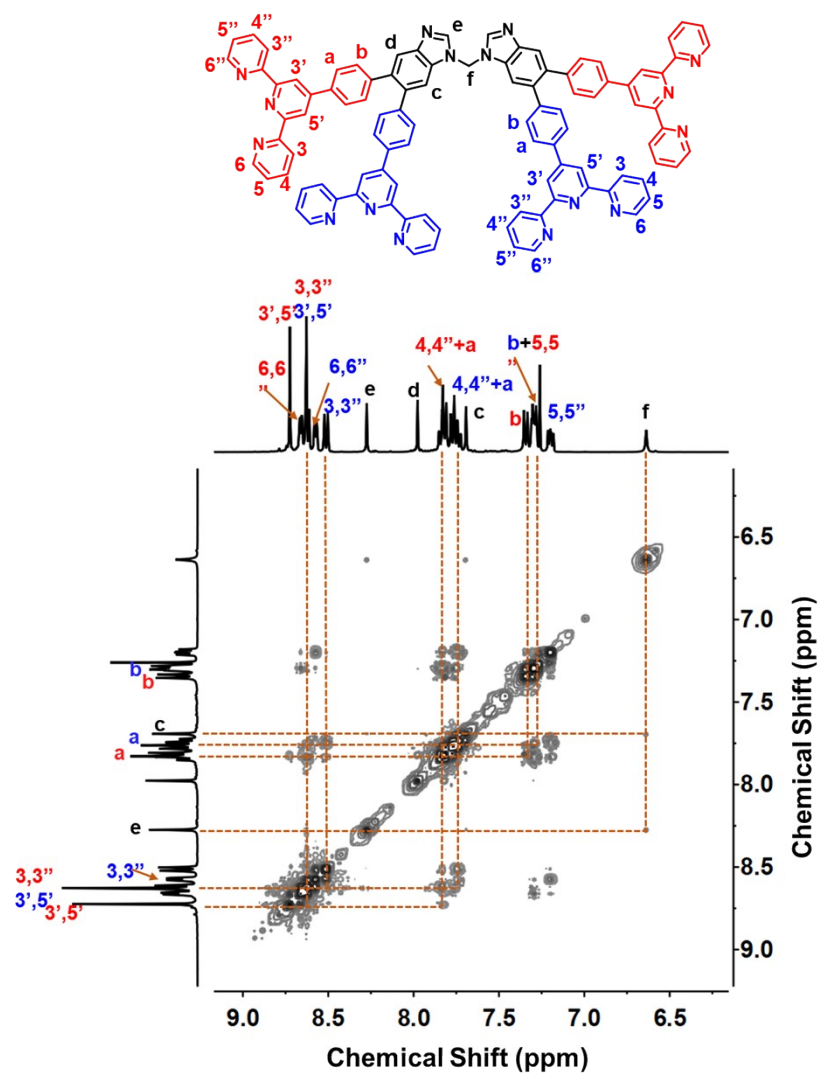


Figure S8. 2D ^1H - ^1H NOESY NMR (500 MHz, 298 K) spectrum of **L** in CDCl_3 (aromatic region)

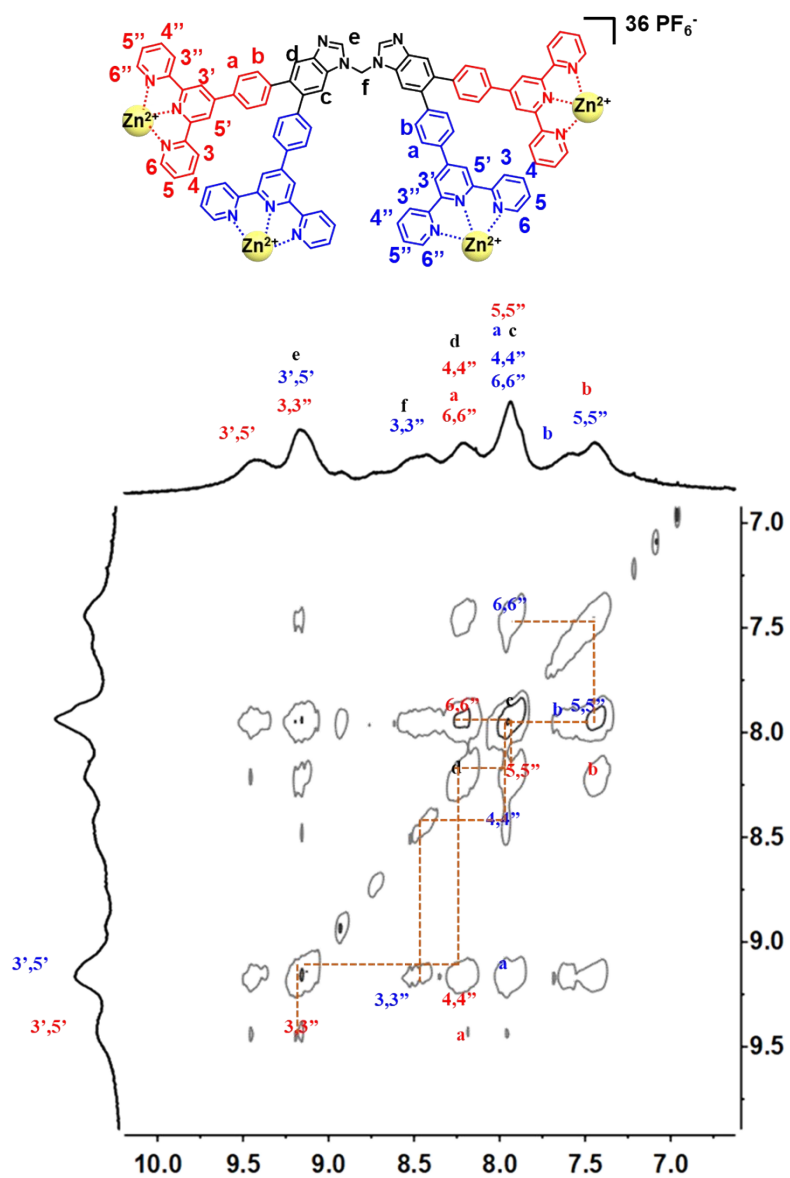


Figure S9. 2D ¹H-¹H NOESY NMR (500 MHz, 298 K) spectrum of **Supramolecular G(PF₆⁻)** in DMSO-*d*₆ (aromatic region)

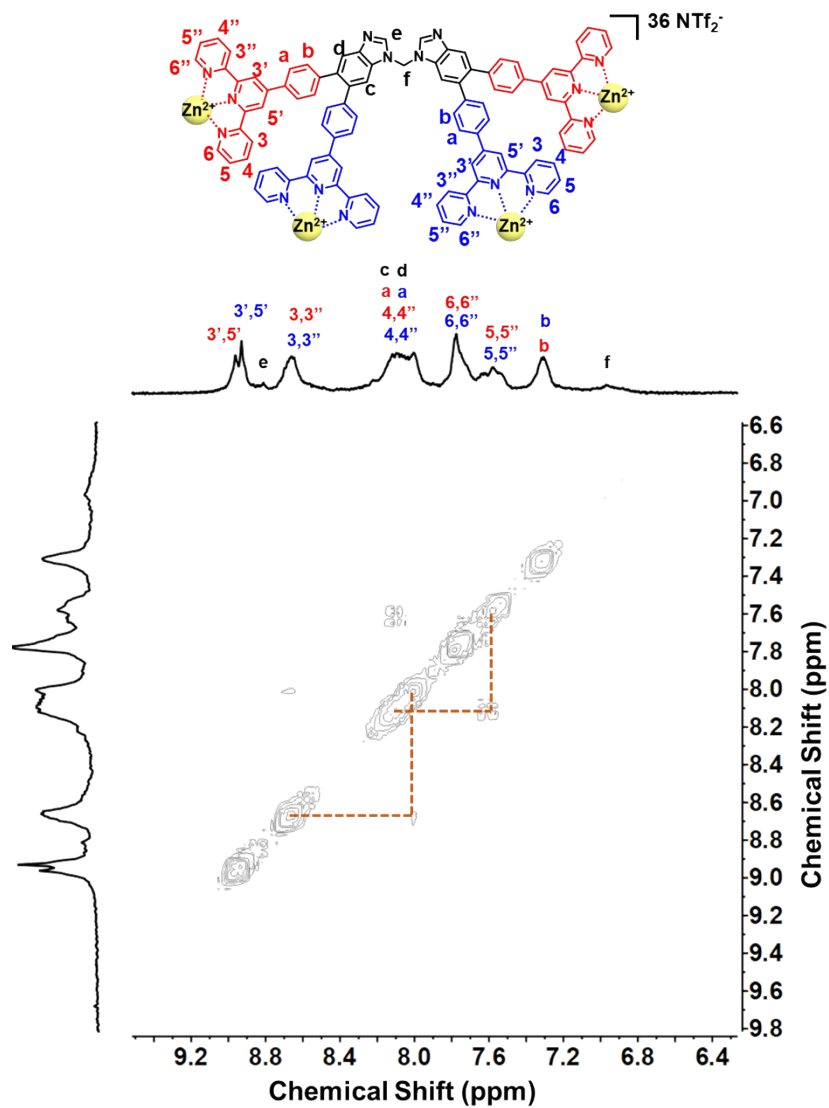


Figure S10. 2D ^1H - ^1H COSY NMR (500 MHz, 298 K) spectrum of **Supramolecular G(NTF₂⁻)** in CD₃CN (aromatic region)

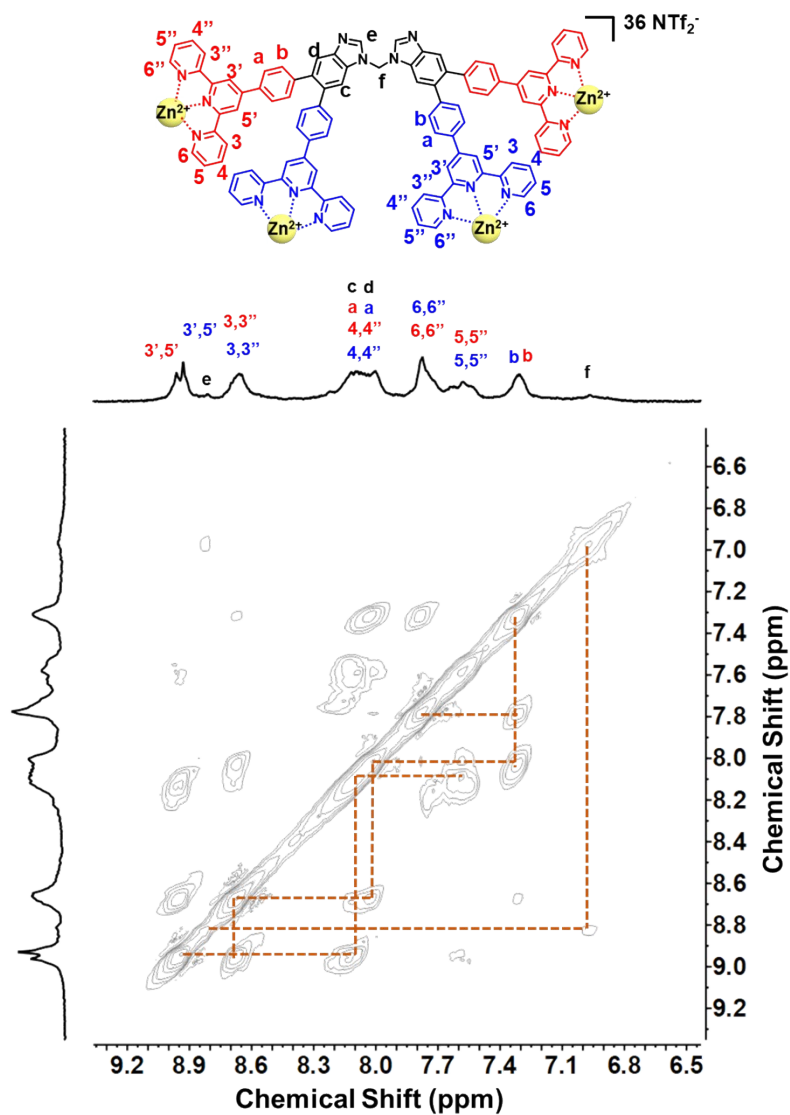


Figure S11. 2D ^1H - ^1H NOESY NMR (500 MHz, 298 K) spectrum of **Supramolecular G(NTf₂⁻)** in CD₃CN (aromatic region)

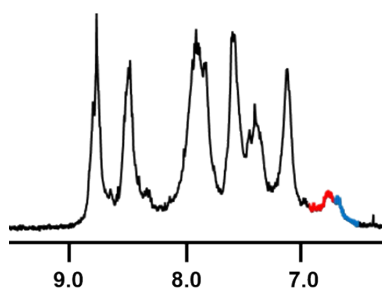


Figure S12. ^1H NMR spectra of supramolecular **G[NTf₂⁻]** at 333.15 K.

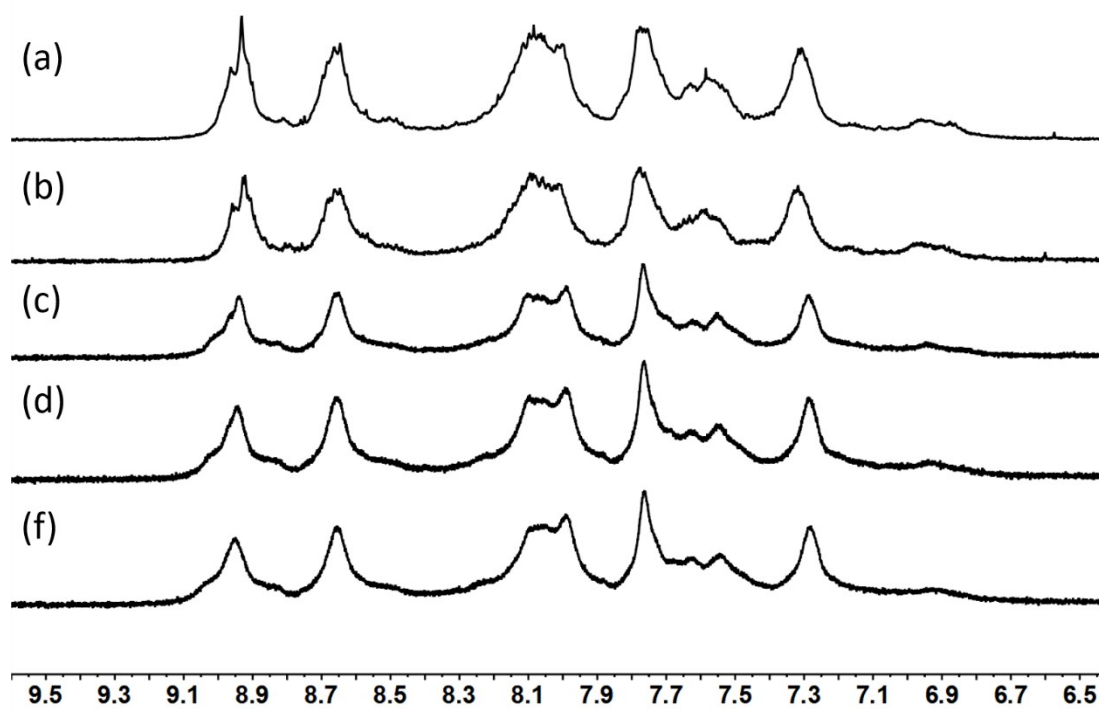


Figure S13. ^1H NMR spectra of supramolecular $\text{G}[\text{NTf}_2]$ at (a) 333.15 K (b) 313.15 K (c) 253.15 K (d) 243.15 K (f) 233.15 K.

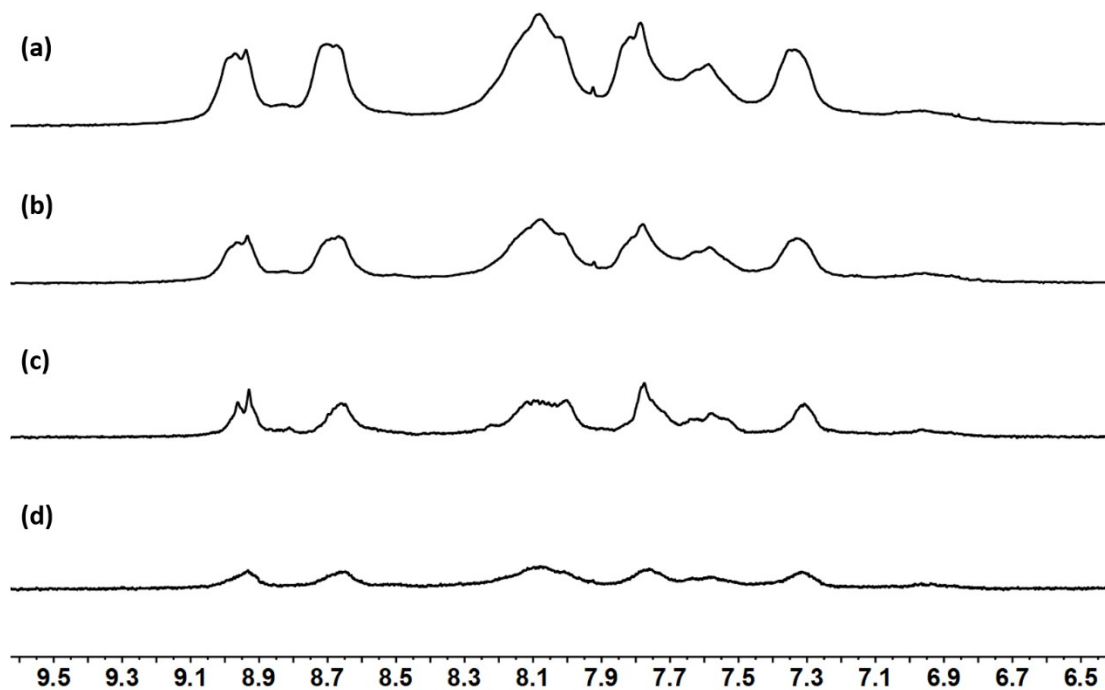


Figure S14. ^1H NMR data at different concentrations of (a) 1×10^{-3} mol/L ;(b) 5×10^{-4} mol/L (c) 1×10^{-4} mol/L (d) 1×10^{-5} mol/L.

Concentration dependent ^1H NMR of the supramolecular $\text{G}[\text{NTf}_2^-]$ experiments were performed. The chemical shifts were not changed, indicating that the aggregation was not due to solvent effects but simple intermolecular aggregation.

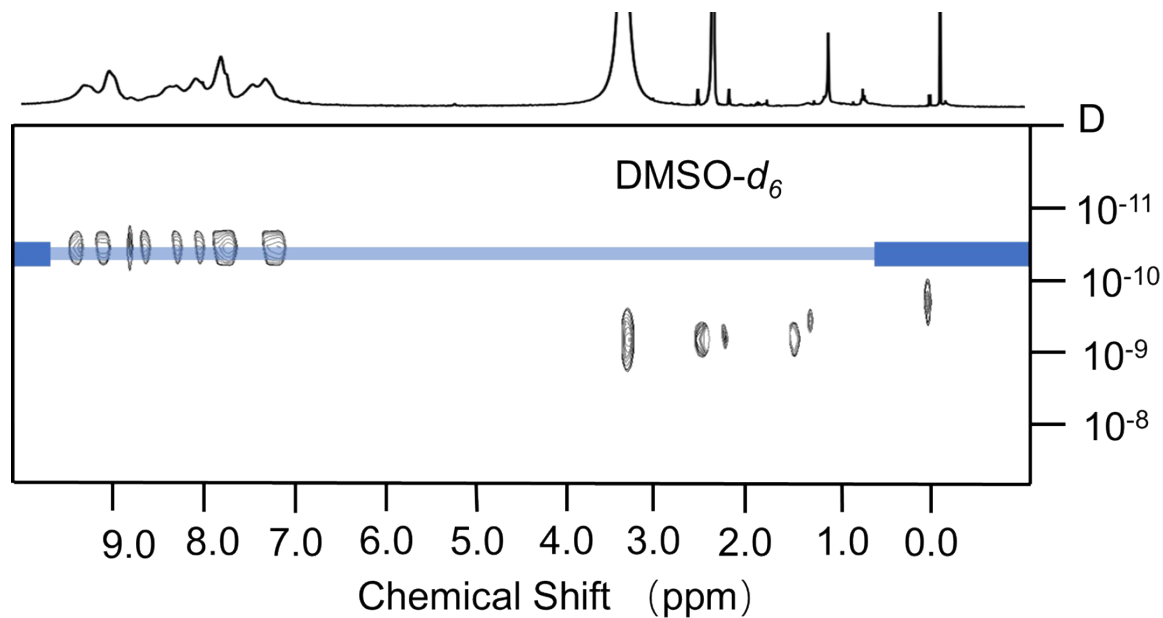


Figure S15. 2D ^1H - ^1H DOSY NMR spectrum of $\text{G}(\text{PF}_6^-)$ in $\text{DMSO-}d_6$

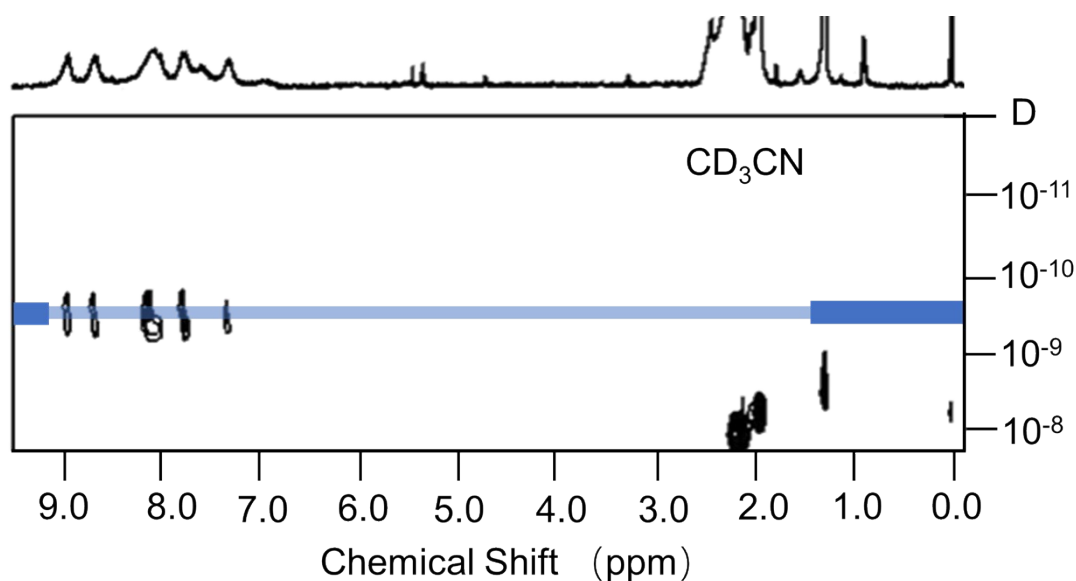


Figure S16. 2D ^1H - ^1H DOSY NMR spectrum of $\text{G}(\text{NTf}_2^-)$ in CD_3CN

The sphere hydrodynamic radius can be estimated as follow according to the Stokes Einstein Equation. Where D is the diffusion constant, k is the Boltzmann's constant, T is the temperature, μ is the viscosity of solvents, and R is the radius of the sphere-like particles:

$$D = \frac{kT}{6\pi\mu R}$$

$$D_{\text{Figure S12}} = 3.81 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \quad D_{\text{Figure S13}} = 2.69 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ N m K}^{-1}$$

$$T = 298 \text{ K}$$

$$\mu = 1.996 \times 10^{-3} \text{ N m}^{-2} \text{ s} (\text{CD}_3\text{CN})^2 \quad \mu = 3.67 \times 10^{-4} \text{ N m}^{-2} \text{ s} (\text{DMSO-}d_6)^3$$

$$r = \frac{kT}{6\pi\mu D} = 2.55 \times 10^{-9} \text{ m} = 2.55 \text{ nm}$$

$$r = \frac{kT}{6\pi\mu D} = 2.22 \times 10^{-9} \text{ m} = 2.22 \text{ nm}$$

The radius of the spherical G is 5.1 nm and 4.5 nm, which is consistent with the result of computer modeling.

4. ESI-MS Spectra

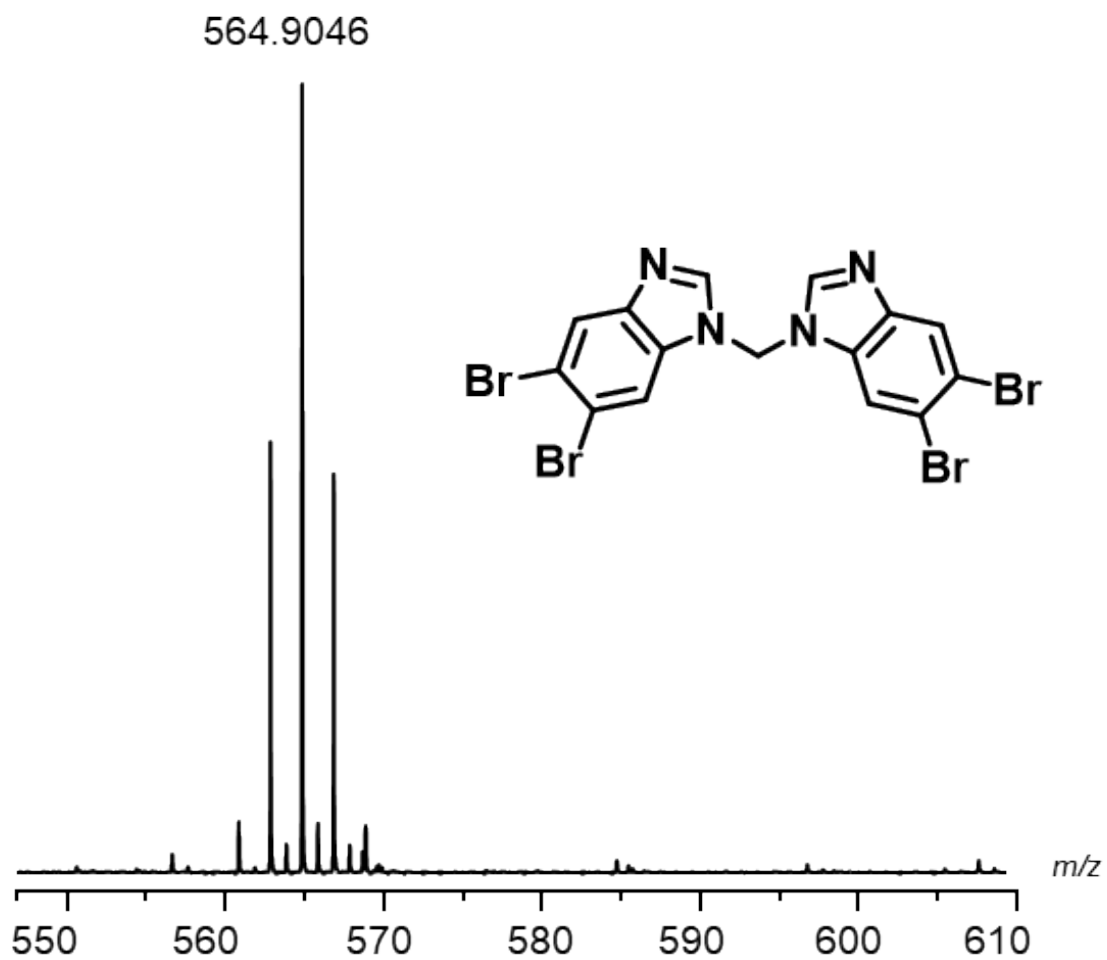


Figure S17. ESI-MS of 2a

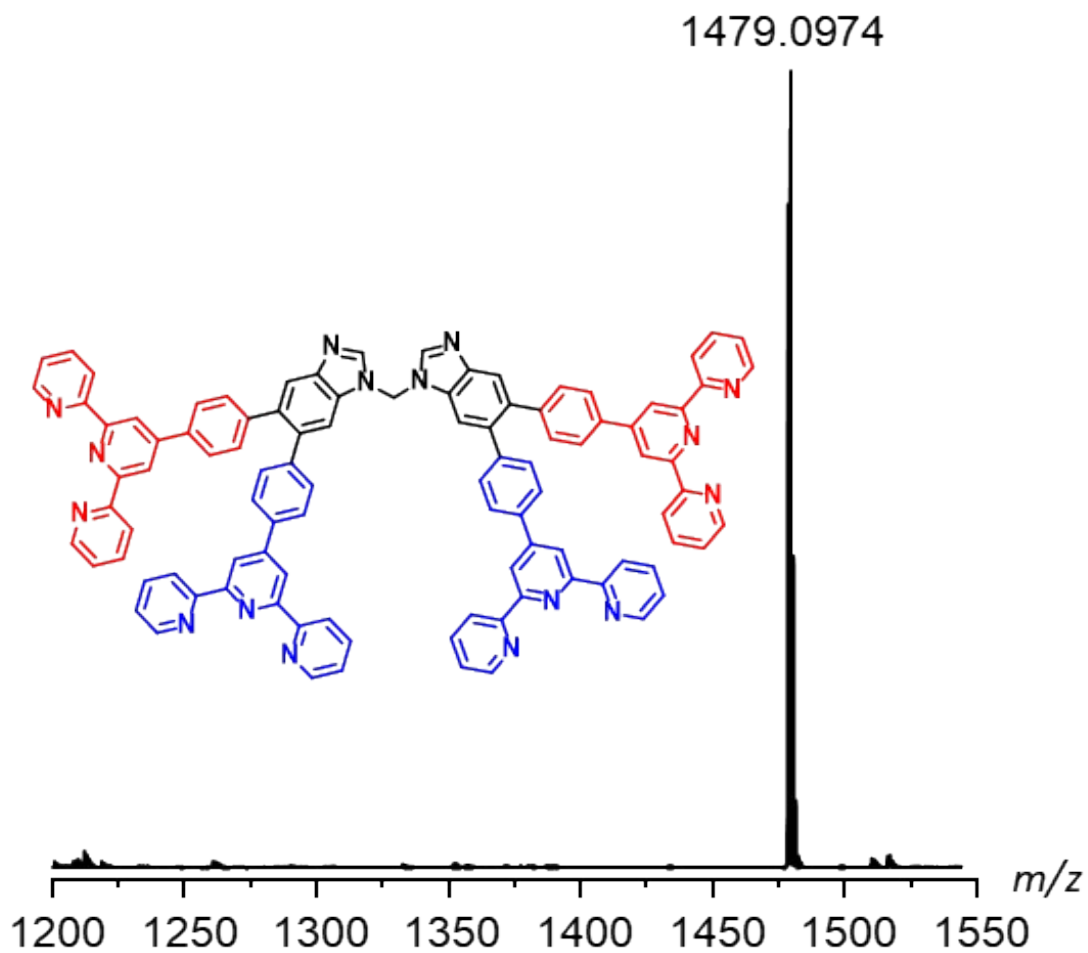


Figure S18. ESI-MS of L

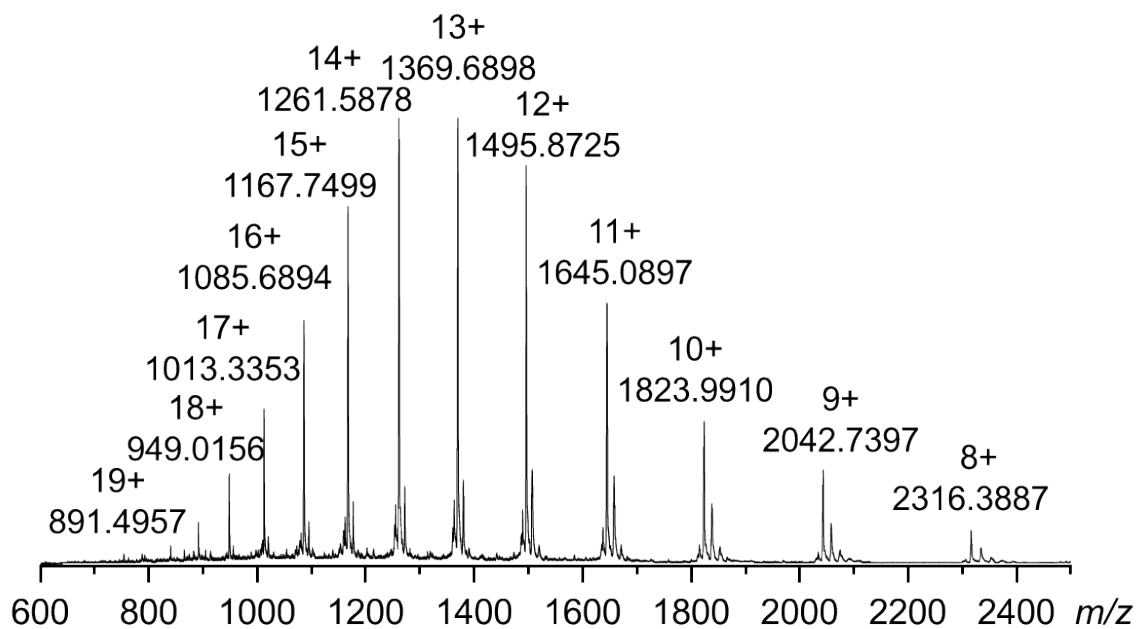


Figure S19. ESI-MS of truncated trigonometric column $G(PF_6^-)$

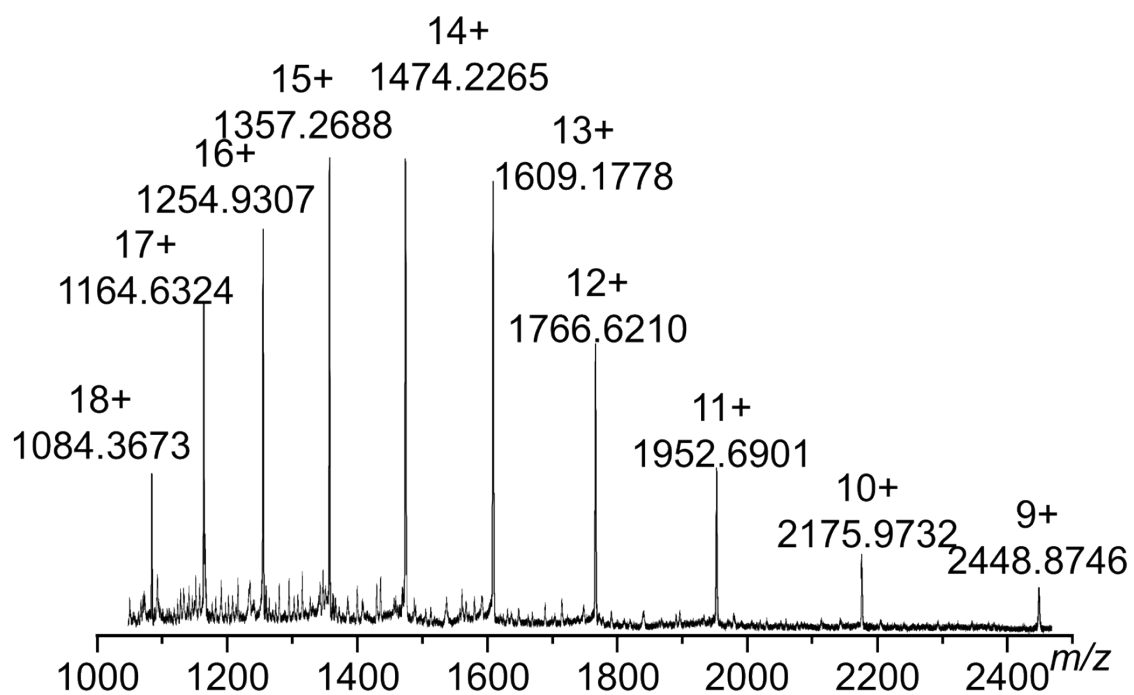


Figure S20. ESI-MS of truncated trigonometric column $G(NTf_2^-)$

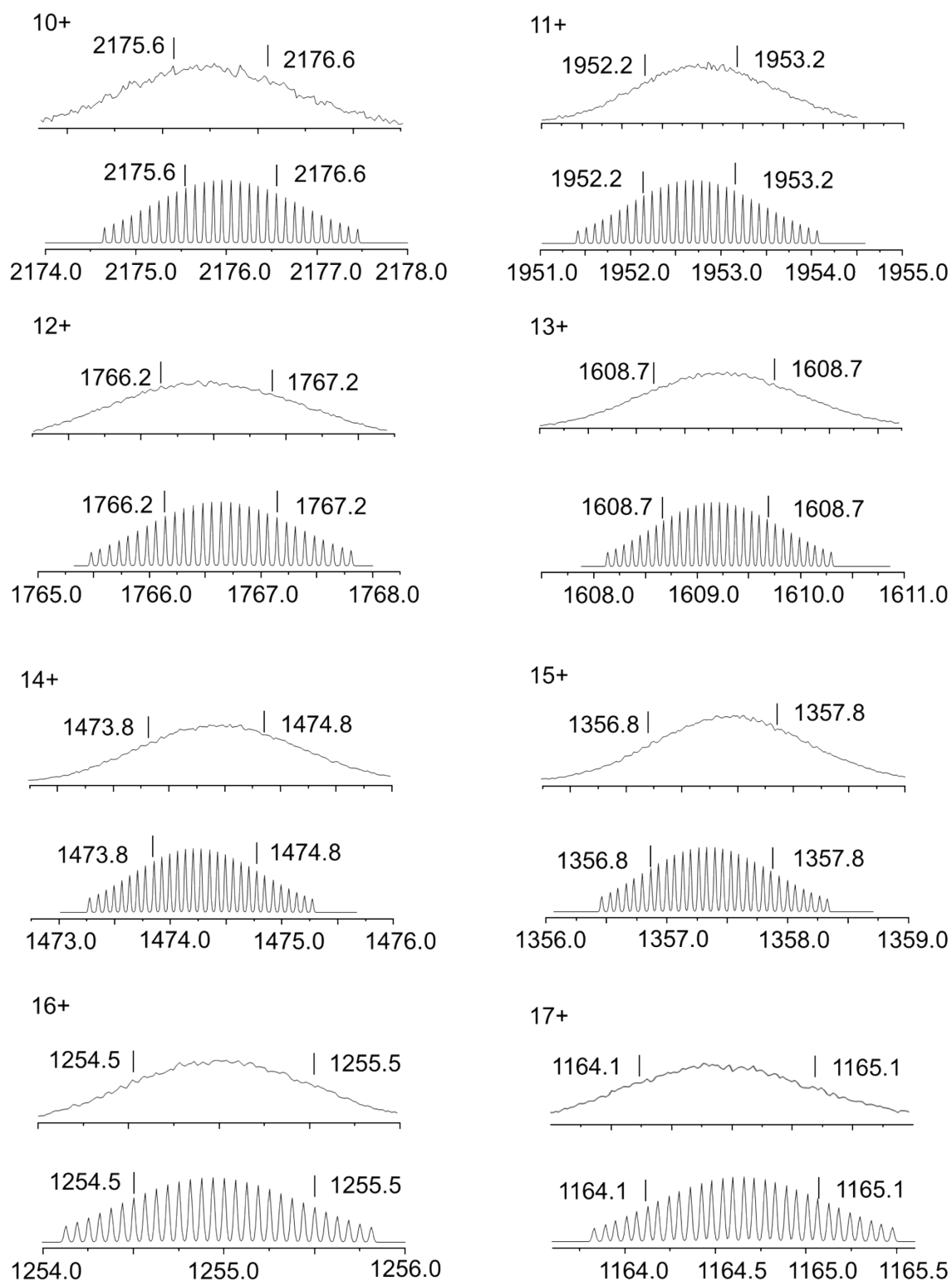


Figure S21. Simulated (top) and experimental (bottom) isotope patterns for different charge states observed from $G(\text{NTF}_2^-)$.

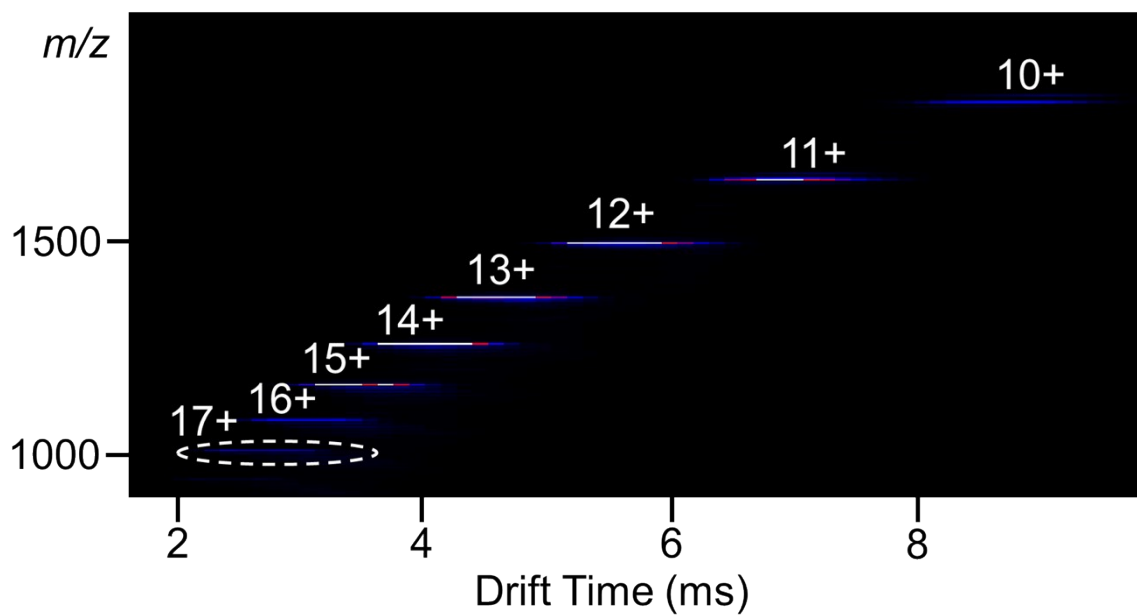


Figure S22. 2D ESI-IM-MS plot (m/z vs drift time) of $G(PF_6^-)$.

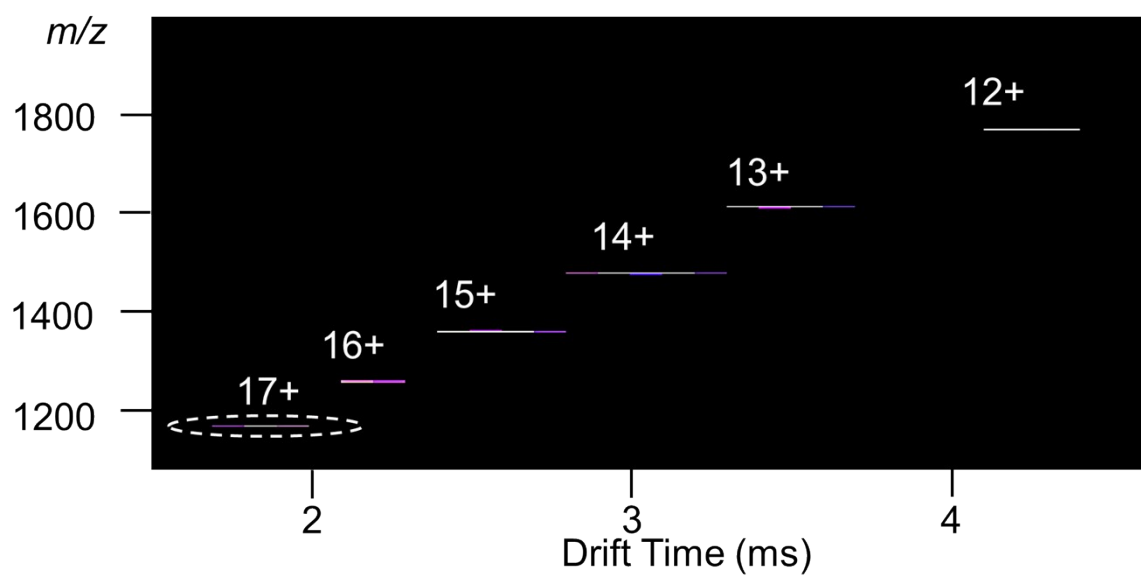


Figure S23. 2D ESI-IM-MS plot (m/z vs drift time) of $G(NTf_2^-)$.

5. Fluorescence emission measurement

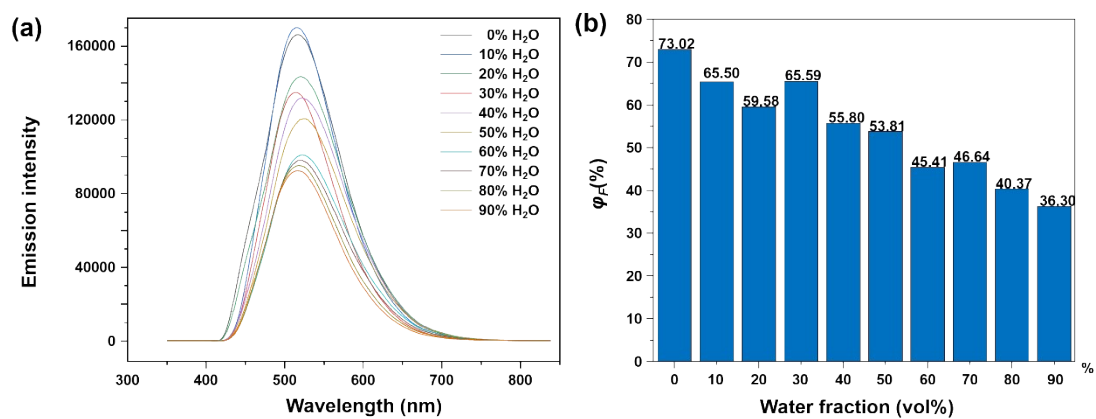


Figure S24. (a) Fluorescence spectra of G[PF₆⁻]. ($\lambda_{\text{ex}} = 320 \text{ nm}$, $c = 1.0 \mu\text{M}$). (b) Quantum yields of G[PF₆⁻].

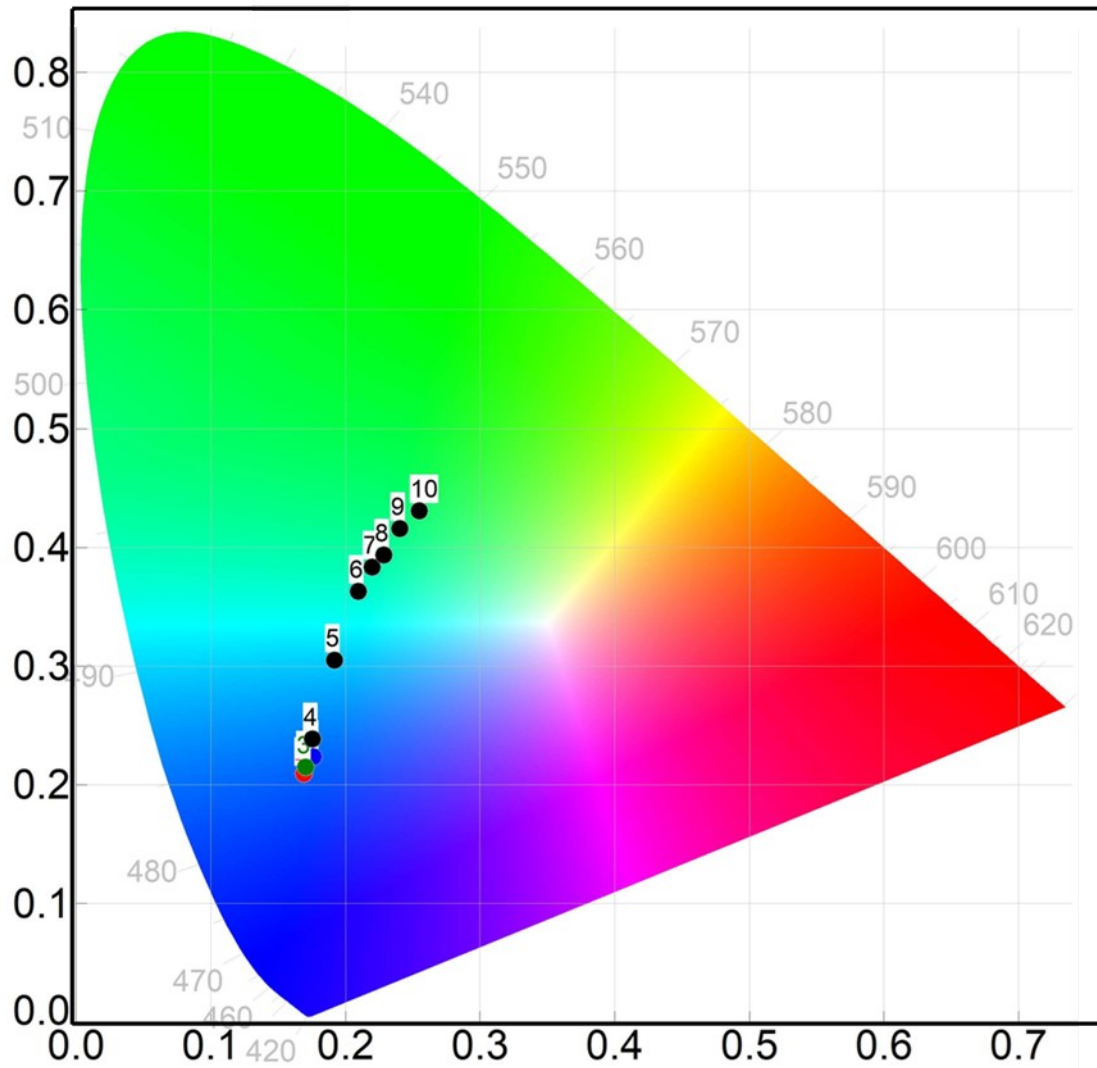


Figure S25. CIE 1931 chromaticity diagram of L

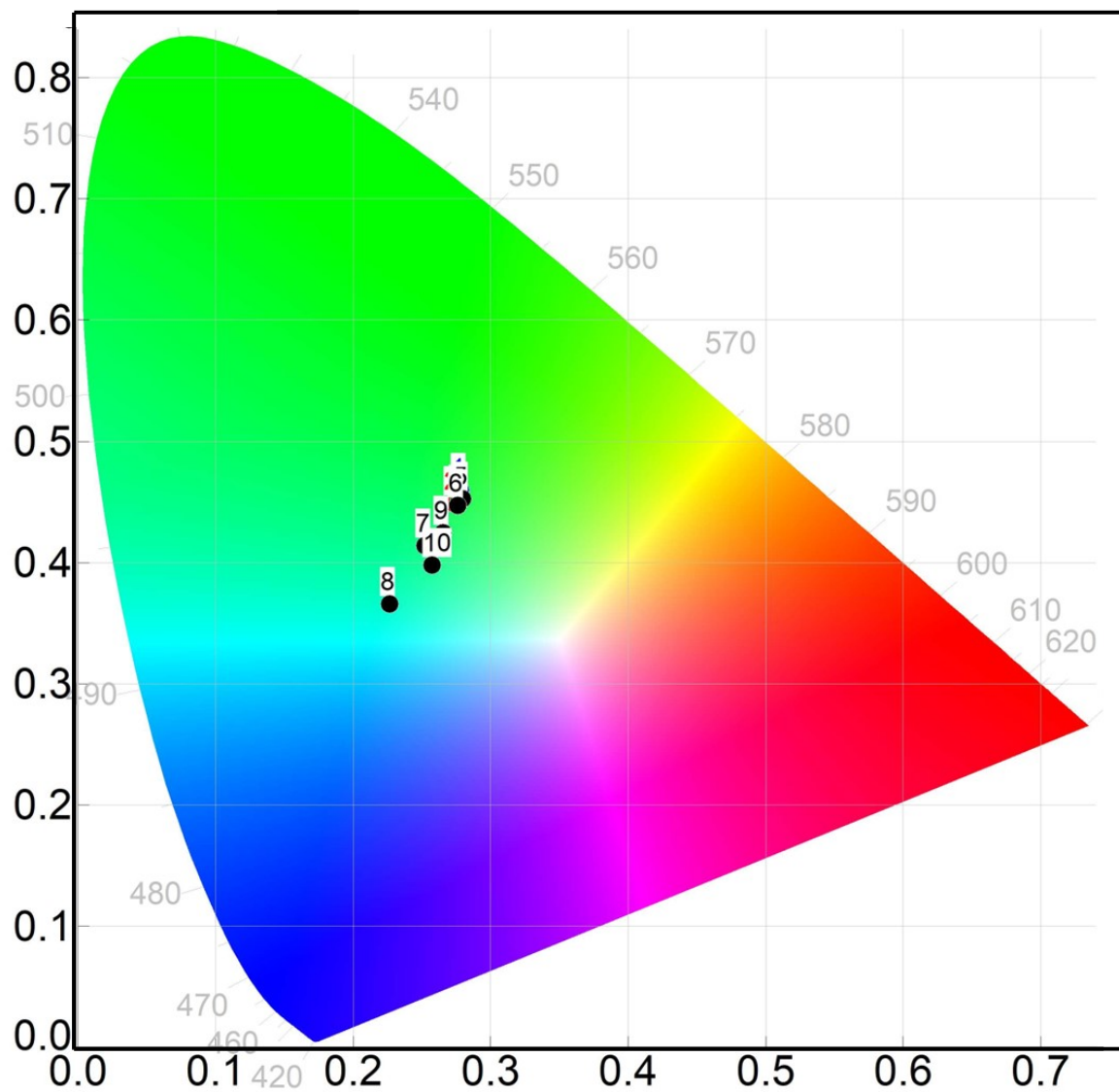


Figure S26. CIE 1931 chromaticity diagram of supramolecular G(NTf₂).

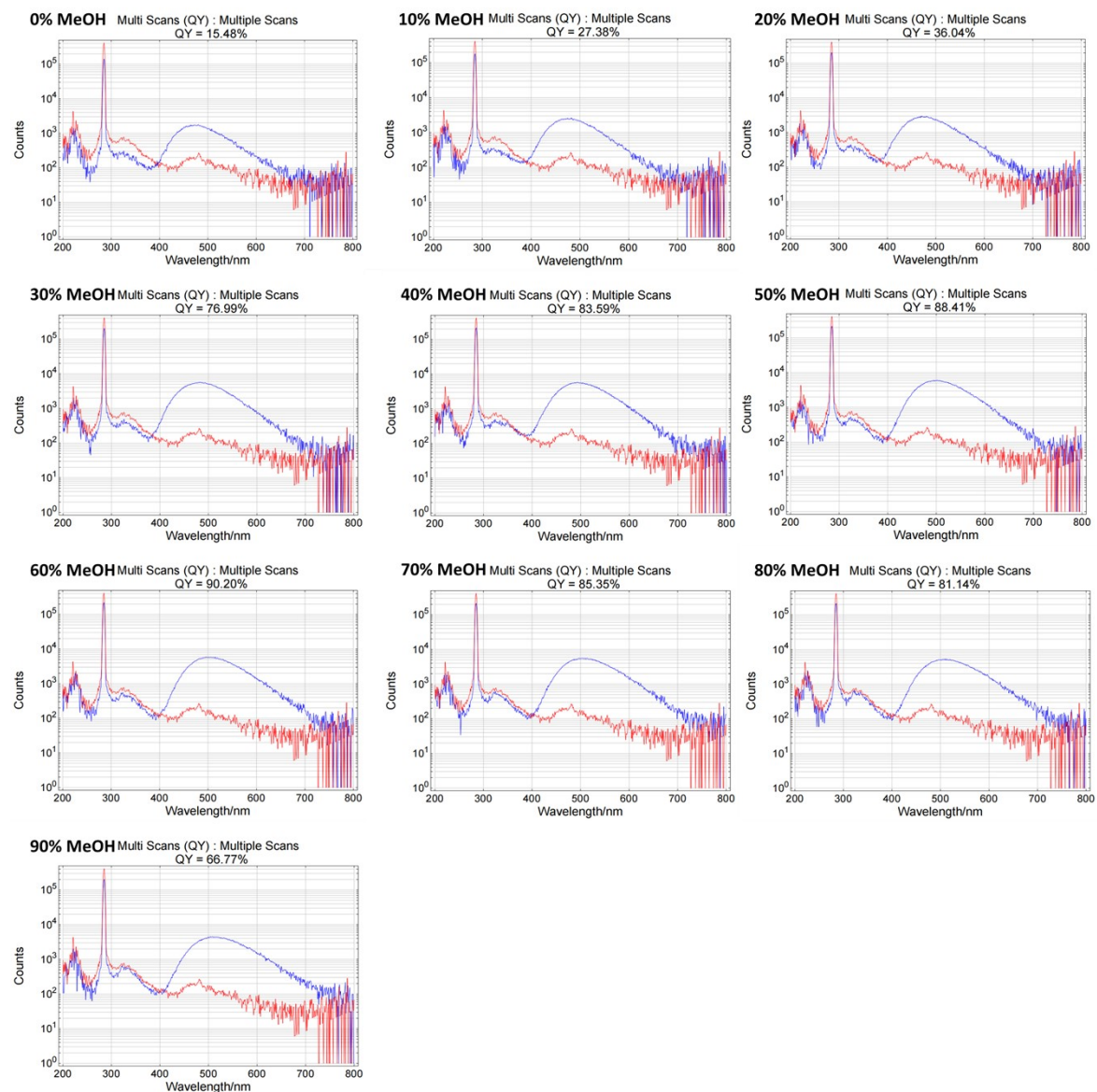


Figure S27. Fluorescence quantum yield of L (0%-90% MeOH).

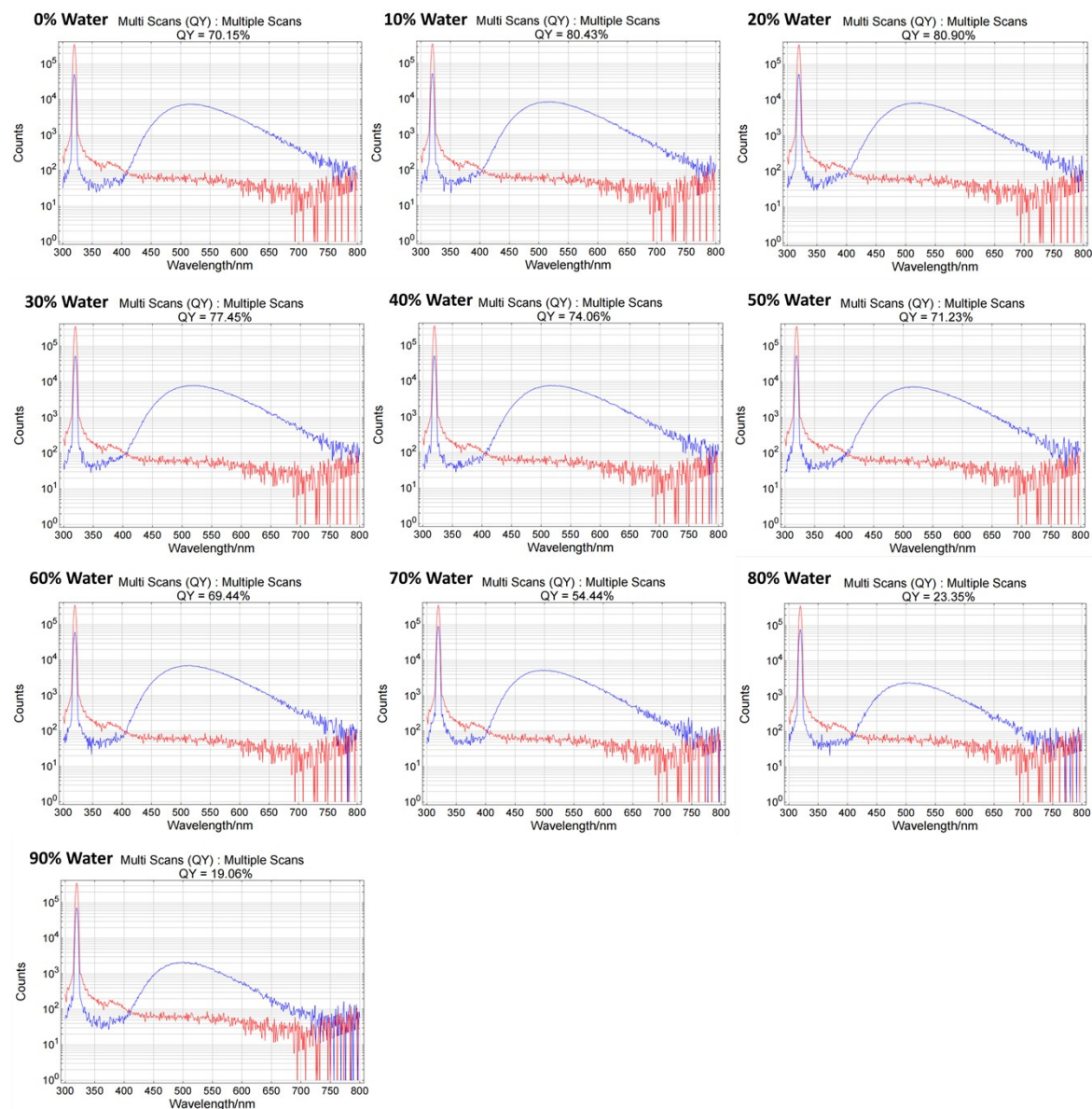


Figure S28. Fluorescence quantum yield of $G(\text{NTf}_2^-)$ (0%-90% H_2O).

6. References

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