Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information for

2D Supramolecular Organic Framework with Tunable Luminescence via Cucurbit[n]urils-Based Hydrogen Bonds, Outer-Surface Interactions and Host-Guest Interactions

Shuai-Peng Jin,†[1] Huai-Li Wu,†[1] Le-Ping Zhang,[1]Guan-Yu Yang,[1] and Bo Yang*[1]

[1]College of Chemistry, Zhengzhou University, Zhengzhou 450001, China. E-mail: yangbohy@zzu.edu.cn

Experimental Methods

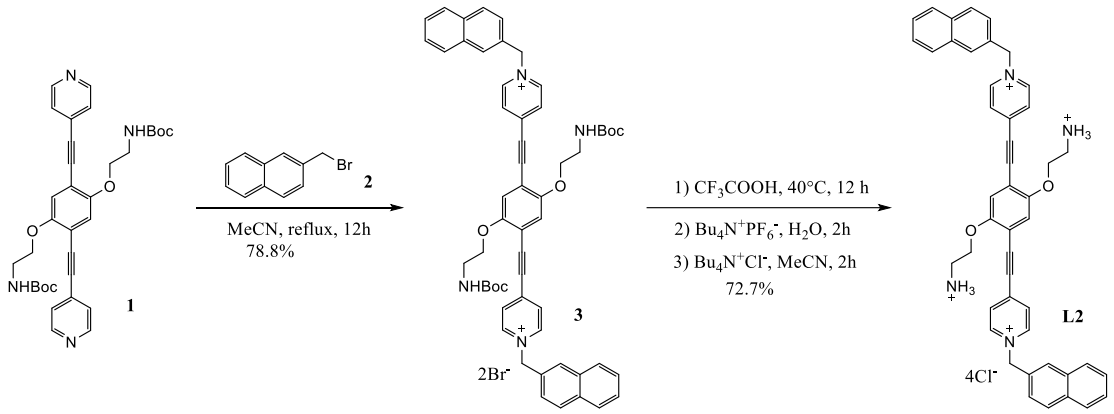
Materials and methods. All reagents were purchased from supplier and used without further purification. Column chromatography was performed on silica gel (200-300 mesh), and thin-layer chromatography (TLC) was performed on precoated silica gel plates (0.2 ± 0.03 mm thick). ^{1}H, ^{13}C NMR, 2D NOESY and COSY spectra were recorded on 400 MHz spectrometers. 2D DOSY spectra were measured on 600 MHz spectrometer. The experiments were performed in the indicated solvents at room temperature (298 K). UV-Vis absorption spectra were performed on an UV-2600i (1 cm quartz cell was used). Fluorescence spectra were recorded on a RF-6000 (Excitation slit = 10 nm, Emission slit = 10 nm). Solid state fluorescence spectra were recorded on a RF-6000 (Excitation slit = 5 nm, Emission slit = 5 nm for **L2**@TMeCB[6] and Excitation slit = 5 nm, Emission slit = 10 nm for **L2**, **L2**@CB[8] and **L2**@TMeCB[6]&CB[8]). Dynamic light scattering (DLS) measurement was conducted on a Malvern Zetasizer Nano ZS90 using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90°. Confocal luminescence imaging was carried out on a Leica SP8 confocal microscope. Fluorescence lifetime were obtained with an Edinburgh Instrument FLS 980 fluorospectrometer. Quantum yield were obtained with an Edinburgh Instrument FLS 1000 fluorospectrometer. Atomic Force Microscopy (AFM) measurement was performed at Bruker Dimension-Icon with ScanAsyst mode under ambient condition and on a Cypher S microscope (Oxford Instruments, Asylum Research). Compound **1** was prepared according to reported method.[1]

The X-ray crystallographic analysis was obtained on a Bruker D8 VENTURE diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Data were corrected for absorption effects using the Multi-Scan method (SADABS). Data collection and reduction was performed using the APEX 3 software. The structure was solved and refined using the Bruker SHELXTL Software Package. The crystal structures were solved by direct methods and refined on F2 by full-matrix least- squares techniques using all unique data.

CCDC 2224140-2224141 contains the crystallographic data of complex **L1**@TMeCB[6] and **L2**@TMeCB[6]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

General methods for structural simulation. Structure modelling of **L2**⊂2TMeCB[6], **L2**⊂2CB[8] and **L2**⊂TMeCB[6]&CB[8] was performed using the Accelrys Materials Studio 7.0 program suite.[2] The lattice was in P1 space group, and the parameters are a = 19.318, b = 35.598 Å, c = 22.000 Å, a = 19.318, b = 25.616 Å, c = 32.613 Å, $\alpha = \beta$ = 90°, γ = 78.178° and a = 20.318, b = 25.616 Å, c = 22.143 Å, respectively, $\alpha = \beta$ = 90°, γ = 78.178°.

Synthesis Procedures



Compound 3. A mixture of compound **1** (0.3 g, 0.50 mmol) and 2-bromomethylnaphthalene (**2**) (0.25 g, 1.1 mmol) in acetonitrile (20 mL) was stirred at 120 °C for 12 h. After cooling to room temperature, the precipitate was filtrated and washed with acetonitrile (20 mL) and dried under vacuum to afford **3** (0.41 g, 78.8%) as a orange-yellow solid. M.p. > 220 °C (decomp). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (d, J = 6.6 Hz, 4H), 8.27 (d, 4H), 8.12 (s, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.99 – 7.92 (m, 4H), 7.64 (dd, J = 8.5, 1.8 Hz, 2H), 7.62 – 7.56 (m, 4H), 7.44 (s, 2H), 7.01 (t, J = 5.8 Hz, 2H), 6.04 (s, 4H), 4.07 (t, J = 5.6 Hz, 4H), 3.37 (t, J = 5.8 Hz, 4H), 1.25 (s, 18H).^{13}C NMR (101 MHz, DMSO) δ 156.15, 154.43, 145.41, 139.42, 133.45, 133.19, 132.11, 130.16, 129.57, 128.94, 128.53, 128.22, 127.63, 127.41, 126.26, 118.08, 113.60, 99.33, 92.02, 78.23, 68.88, 63.76, 28.62. HRMS (ESI): Calc for $C_{56}H_{55}N_4O_6$: 879.4116 [M-H$^+$-2Br$^-$] $^+$. Found 879.4110.

Compound L2. A mixture of compound **3** (0.21 g, 0.2 mmol) in CF_3COOH (5 mL) was stirred at 40 °C for 12 h. The reaction system was decompressed to remove CF_3COOH solvents. The residue was dissolved in water of the least amount. To the solution was added dropwise an saturated solution of hexafluorophosphate in water (2 mL). After stirring for 2 h at room temperature, the precipitate formed was filtrated off and wash with water(10 mL) and dried under vacuum. Then the precipitate was dissolved in acetonitrile (15 mL). To the solution was added dropwise an saturated solution of tetrabutylammonium chloride in acetonitrile (2 mL) and the mixture stirred for 2 h at room temperature. The precipitate formed was filtrated, washed with acetonitrile(20 mL) and dried under vacuum to afford **L2** (0.12 g, 72.7%) as a reddish brown solid. M.p. > 185 °C (decomp). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.95 (d, J = 6.5 Hz, 4H), 8.14 (d, J = 6.5 Hz, 4H), 8.01 (m, 8H), 7.65 (m, 4H), 7.54 (dd, J = 8.5, 1.9 Hz, 2H), 7.43 (s, 2H), 5.97 (s, 4H), 4.41 (t, J = 4.9 Hz, 4H), 3.51 (t, J = 4.9 Hz, 4H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 153.18, 144.10, 140.08, 133.21, 132.86, 130.05, 129.82, 129.54, 129.05, 128.11, 127.79, 127.55, 127.23, 125.54, 118.58, 113.78, 98.34, 91.17, 65.89, 64.49, 38.72. HRMS (ESI): Calc for $C_{46}H_{42}N_4O_2F_{24}P_4$: 1117.2228 [M-$PF_6$]$^+$. Found 1117.2240.

Preparation of solid state L2⊂TMeCB[6]: To a solution of **L2** (8.2 mg, 0.010 mmol) in H_2O (1mL), TMeCB[6](10.2 mg, 0.010 mmol) was added. The mixure was heated until complete dissolution. Slowly evaporation of the solvent at 40 °C in vacuum for 12 h. Acetone (2 ml) was added to the soild. After stewing for 2 h at room temperature, the precipitate was filtrated off and wash with acetone(2 mL) and air dry to get **L2**⊂TMeCB[6]**.**

Preparation of solid state L2⊂2TMeCB[6]: To a solution of **L2** (8.2 mg, 0.010 mmol) in H_2O (1mL), TMeCB[6](20.4 mg, 0.020 mmol) was added. The mixure was heated until complete dissolution. Slowly evaporation of the solvent at 40 °C in vacuum for 12 h. Acetone (2 ml) was added to the soild. After stewing for 2 h at room temperature, the precipitate was filtrated off and wash with acetone(2 mL) and air dry to get **L2**⊂2TMeCB[6]**.**

Preparation of solid state L2⊂CB[8]: To a solution of **L2** (8.2 mg, 0.010 mmol) in H_2O (1mL), CB[8](13.3 mg, 0.010 mmol) was added. The mixure was heated until complete dissolution. Slowly evaporation of the solvent at 40 °C in vacuum for 12 h. Acetone (2 ml) was added to the soild. After stewing for 2 h at room temperature, the precipitate was filtrated off and wash with acetone(2 mL) and air dry to get **L2**⊂ CB[8]**.**

Preparation of solid state L2⊂TMeCB[6]&CB[8]: To a solution of **L2** (8.2 mg, 0.010 mmol) in H2O (1mL), CB[8](13.3 mg, 0.010 mmol) and TMeCB[6](10.2 mg, 0.010 mmol) was added. The mixure was heated until complete dissolution. Slowly evaporation of the solvent at 40 °C in vacuum for 12 h. Acetone (2 ml) was added to the soild. After stewing for 2 h at room temperature, the precipitate was filtrated off and wash with acetone(2 mL) and air dry to get **L2**⊂TMeCB[6]&CB[8]**.**

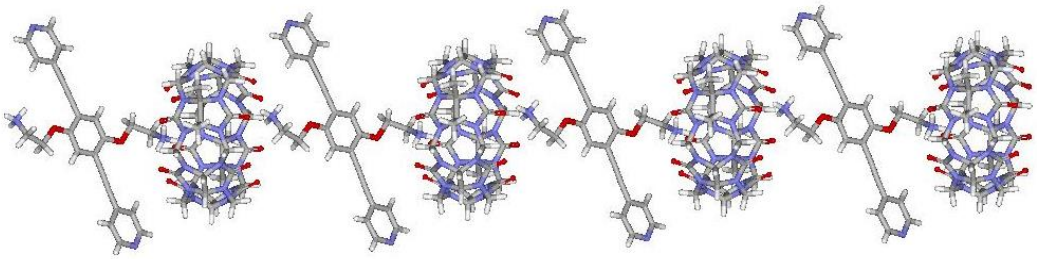


Fig.Fig. S1 1D supramolecular chain construct by **L1** and TMeCB[6] through hydrogen bonds.

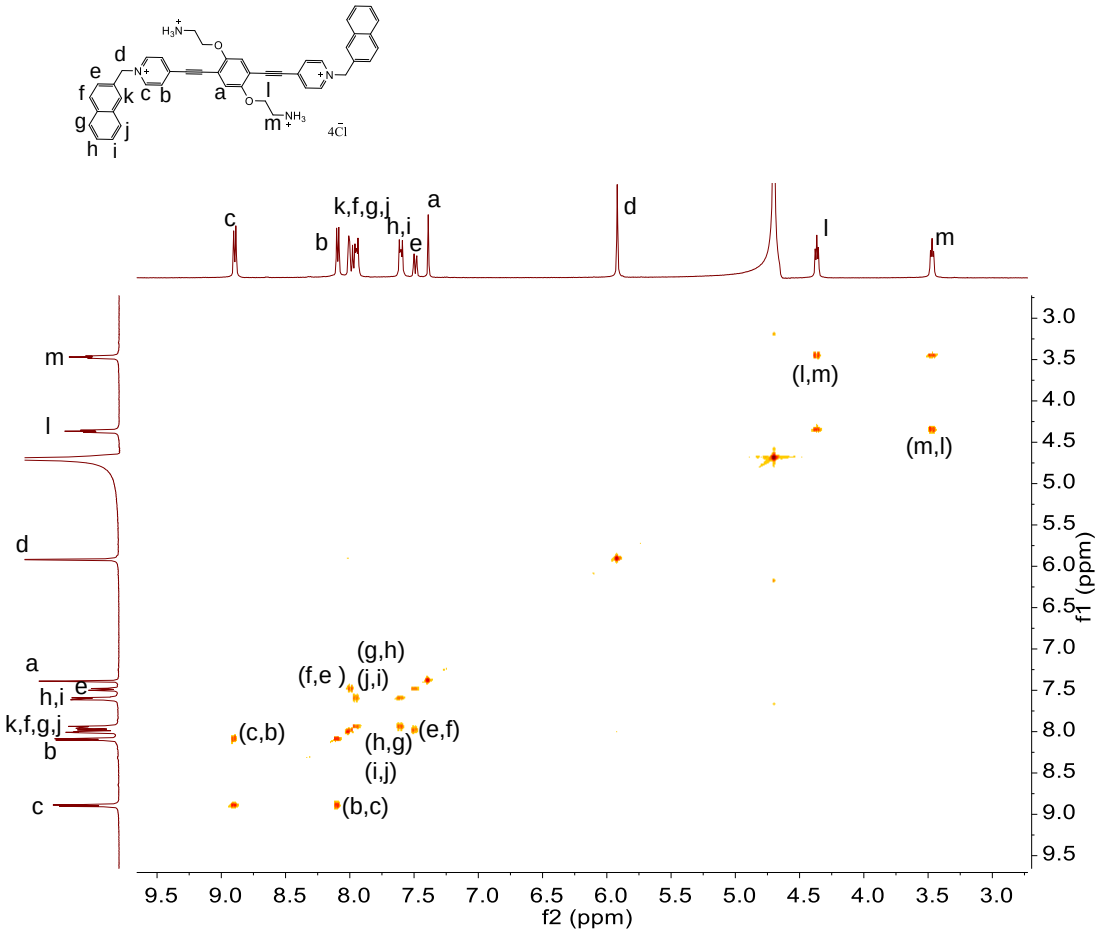


Fig. S2 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**.

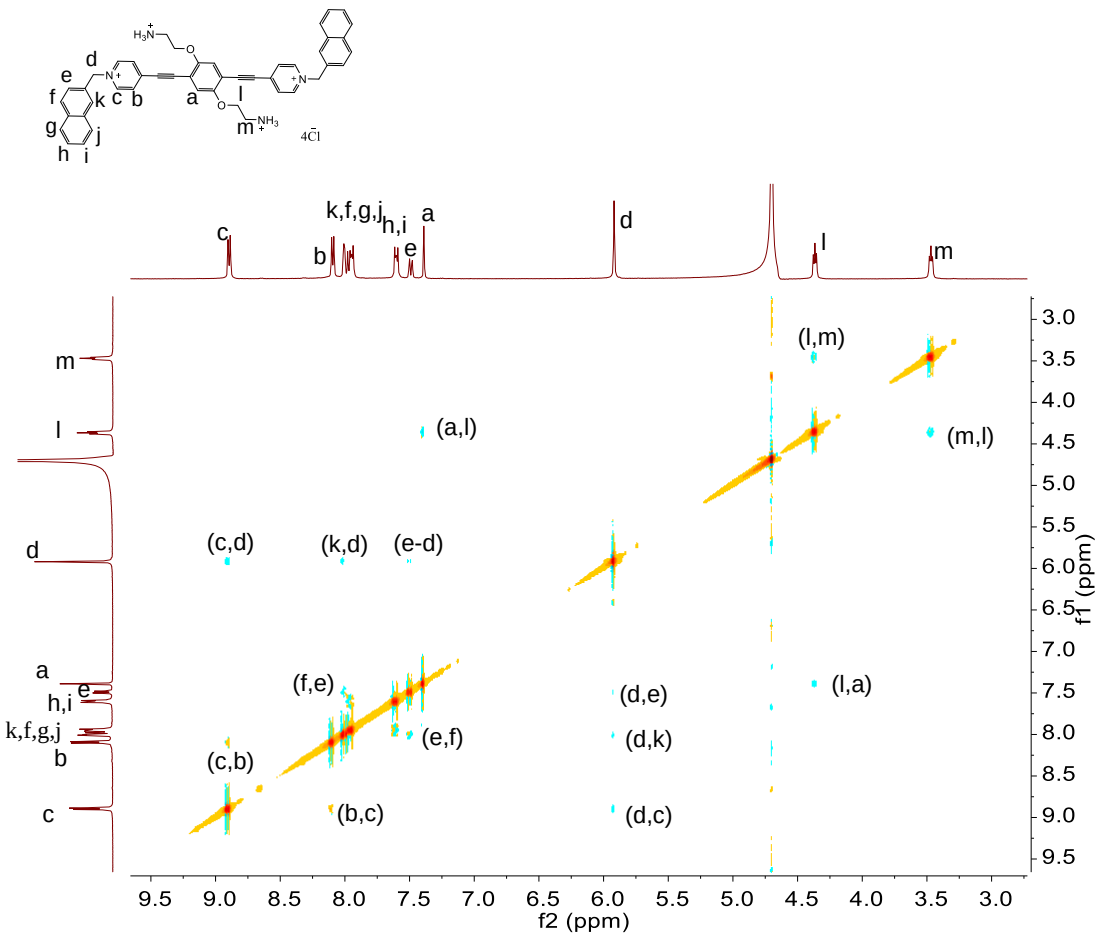


Fig. S3 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**.

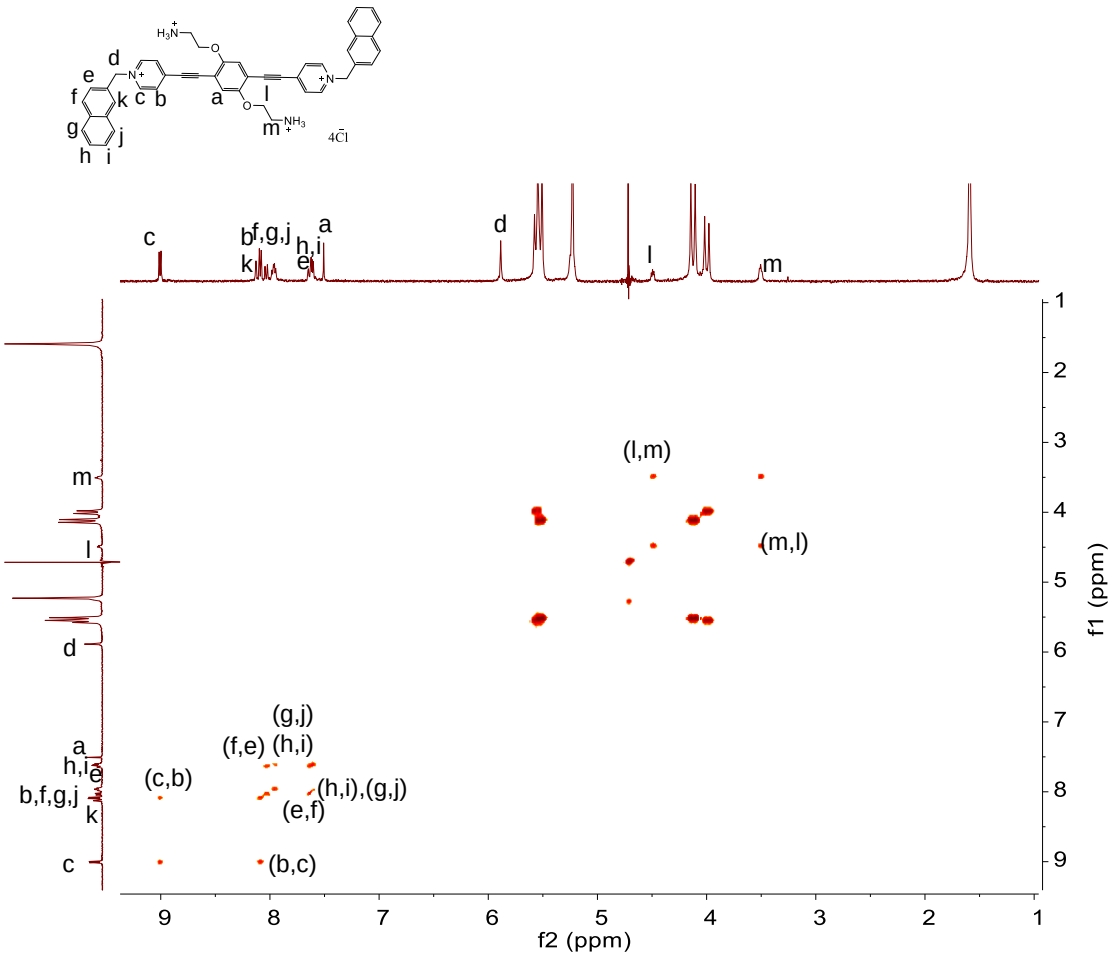


Fig. S4 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**⊂2TMeCB[6].

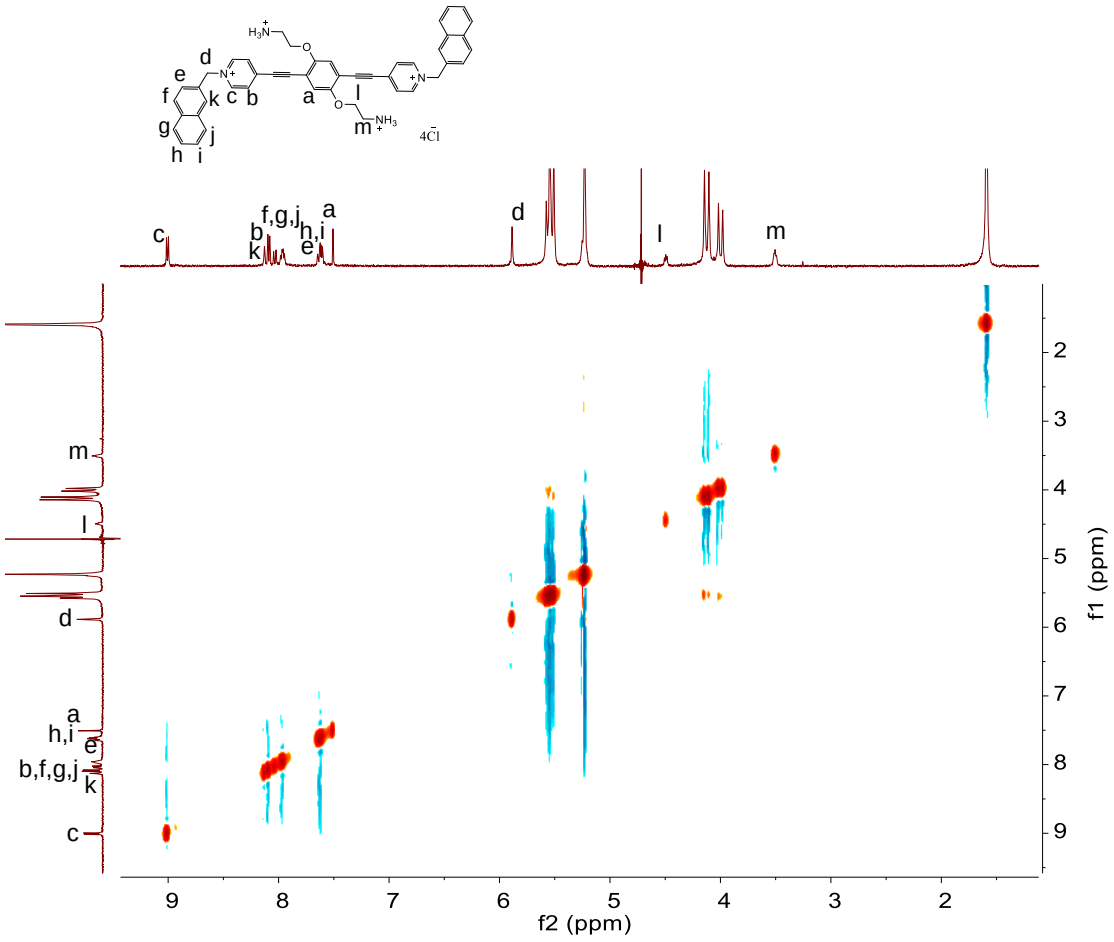


Fig. S5 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**⊂2TMeCB[6].

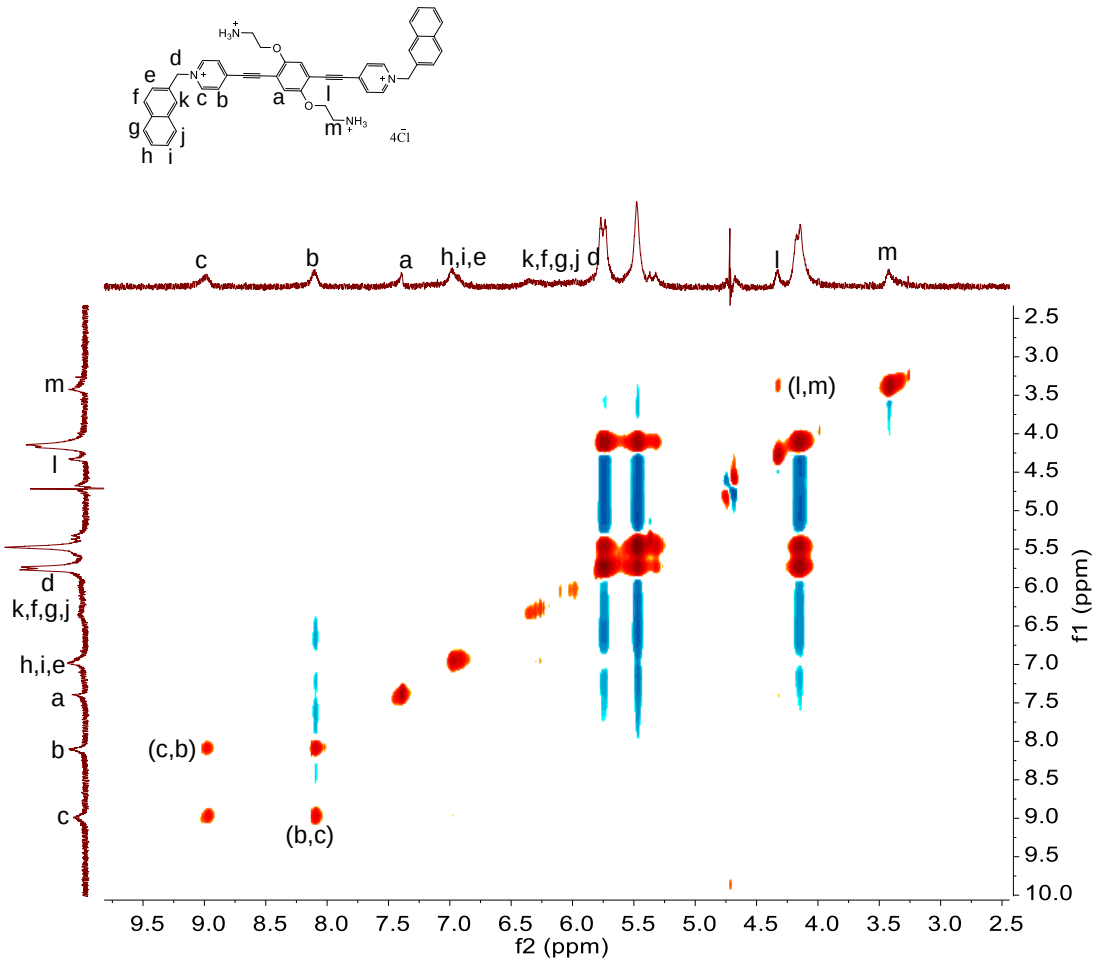


Fig. S6 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**⊂2CB[8].

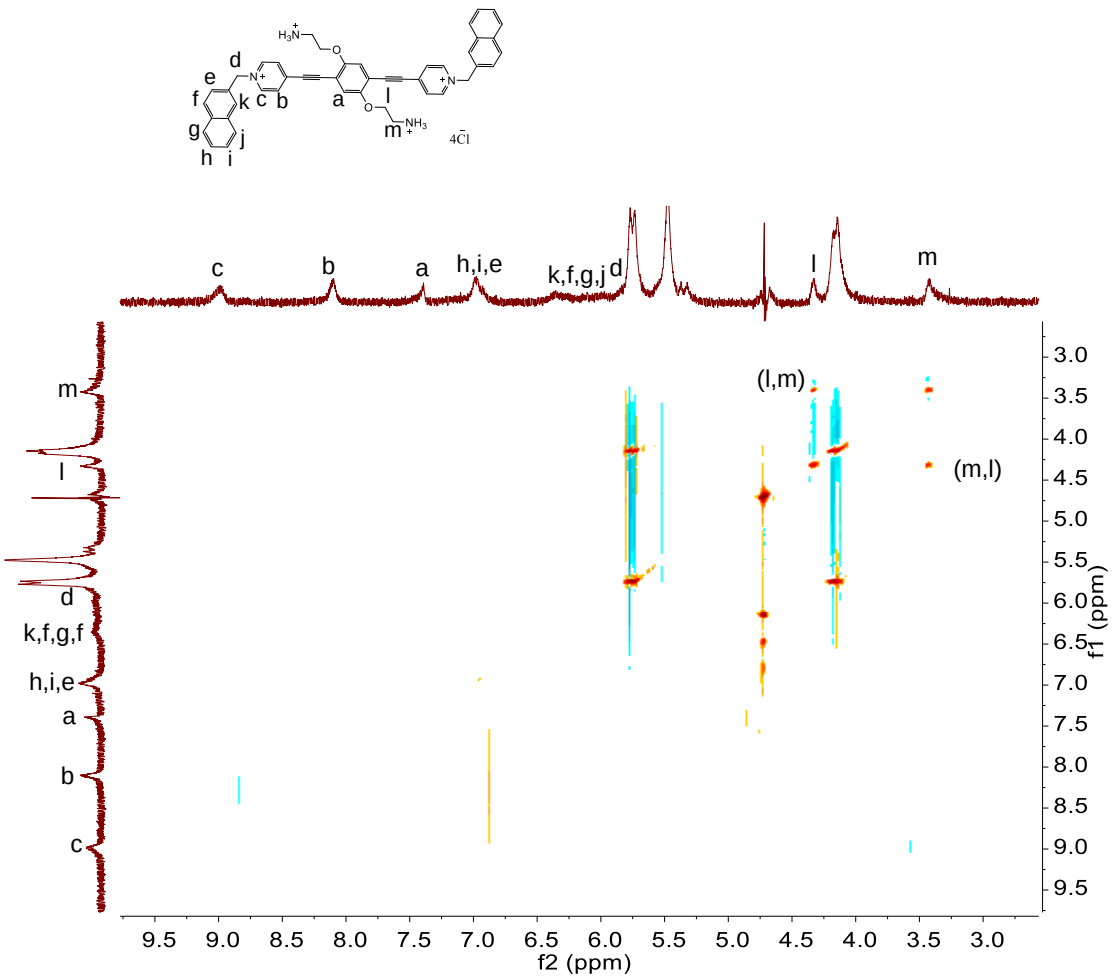


Fig. S7 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of **L2**⊂CB[8].

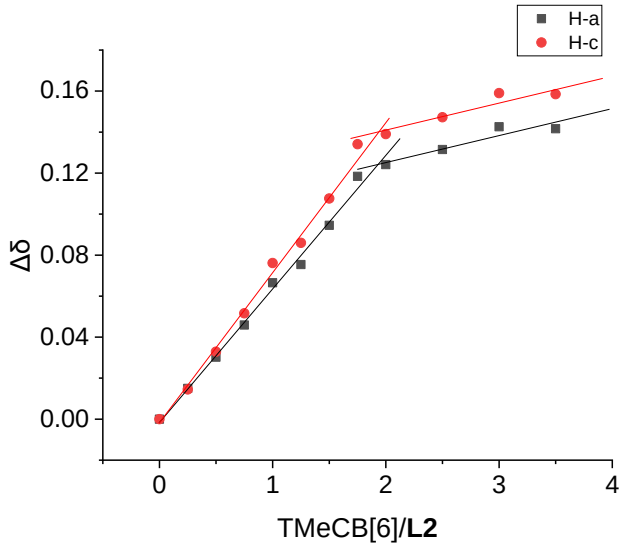


Fig. S8 The resonances change for H-a and H-c of the **L2** on comparing with the ^{1}H NMR spectra of free **L2**, upon the addition of more and more TMeCB[6] (0-3.5 eq).

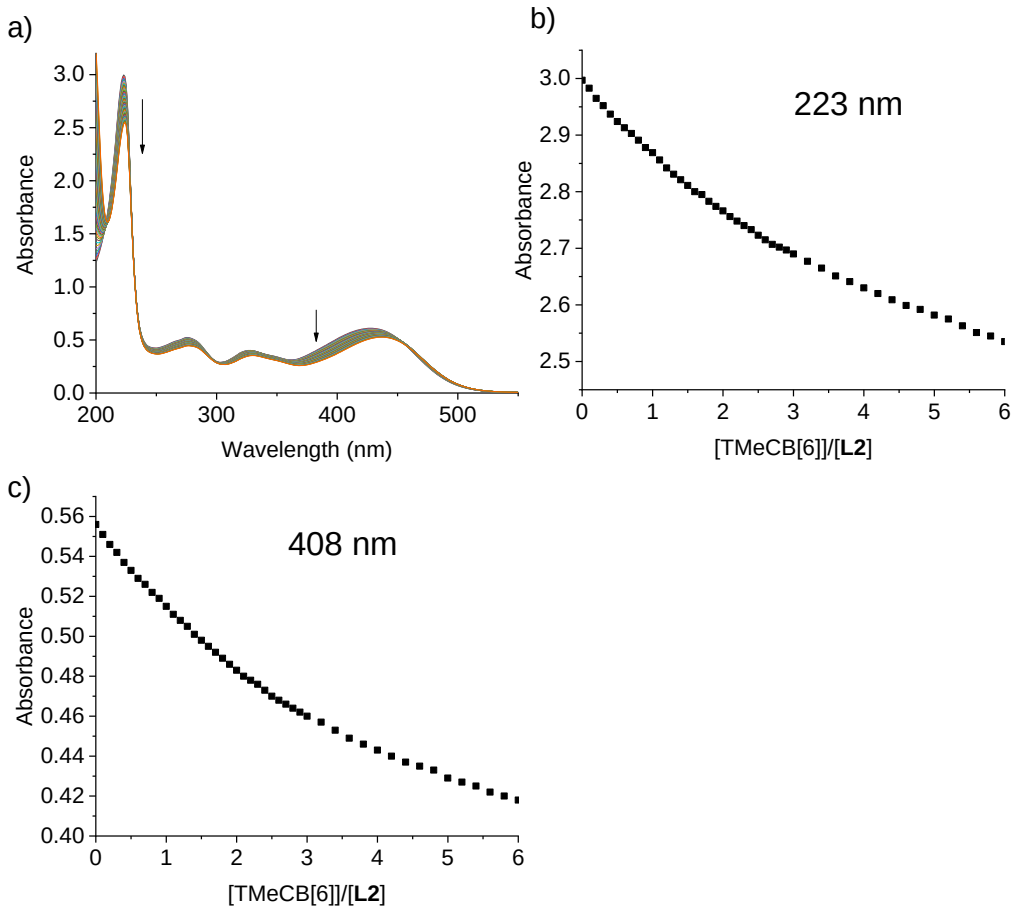


Fig. S9 a) UV-vis spectroscopy of **L2** (20 μM) with the addition of TMeCB[6] (0-6.0 equiv.) in water at 25 °C, b,c) the plot of the absorbance change at 223 nm and 408 nm.

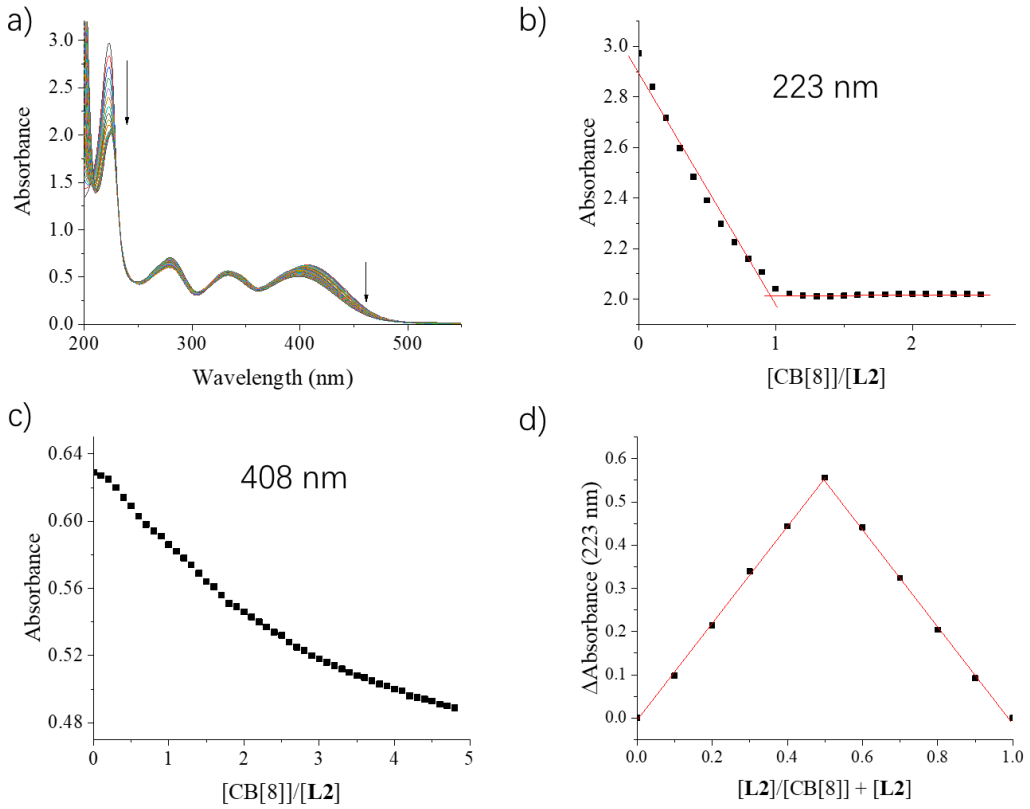


Fig. S10 a) UV-vis spectroscopy of **L2** (20 μM) with the addition of CB[8] (0-5.0 equiv.) in water at 25 °C, b, c) the plot of the absorbance change at 223 nm and 408 nm. d) Job's plot indicated a stoichiometry of 1:1 of **L2** and CB[8]. [**L2**] + [CB[8]] = 0.02 mM, T = 298 K.

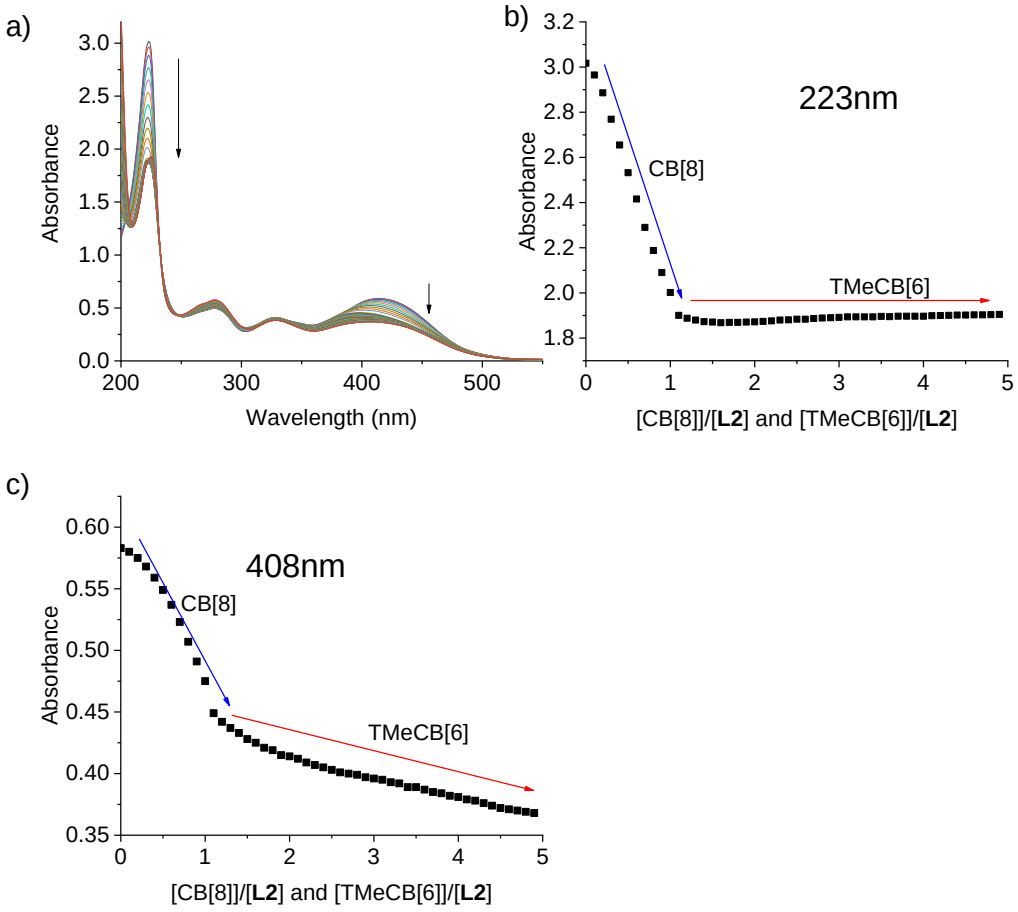


Fig. S11 a) UV-vis spectroscopy of **L2** (20 μM) with the addition of CB[8] (0-1.0 equiv.) and TMeCB[6] (0-4.0 equiv.) in water at 25 °C, b, c) the plot of the absorbance change at 223 nm and 408 nm.

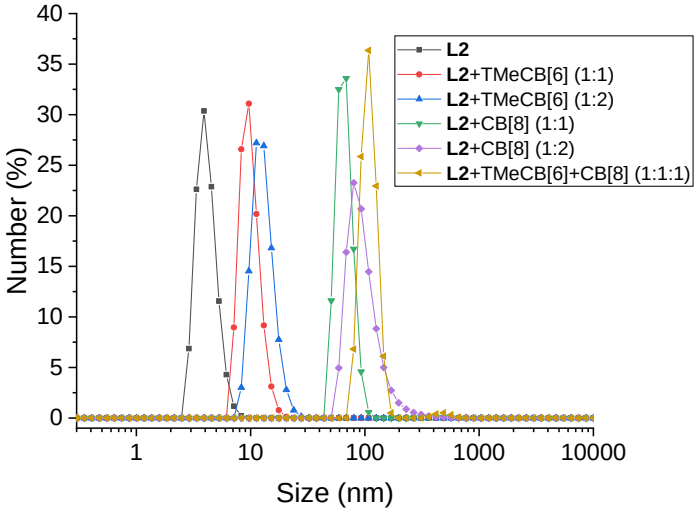


Fig. S12 Dynamic light scattering (DLS) experiments for the solution of **L2**, **L2**-TMeCB[6] (1:1), **L2**-TMeCB[6] (1:2), **L2**-CB[8] (1:1), **L2**-CB[8] (1:2) and **L2**-TMeCB[6]-CB[8] (1:1:1) ([**L2**] = 0.02 mM)

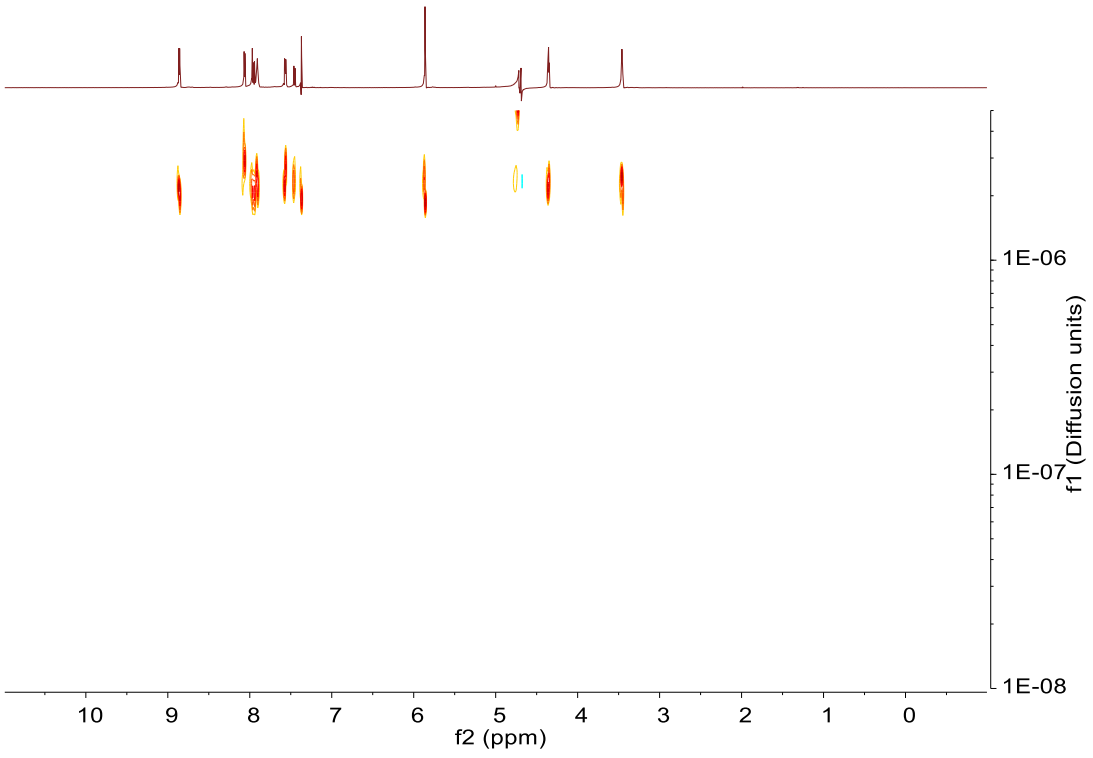


Fig. S13 2D diffusion-ordered NMR spectroscopy (DOSY) of **L2** (600 MHz, D_2O, 298 K).

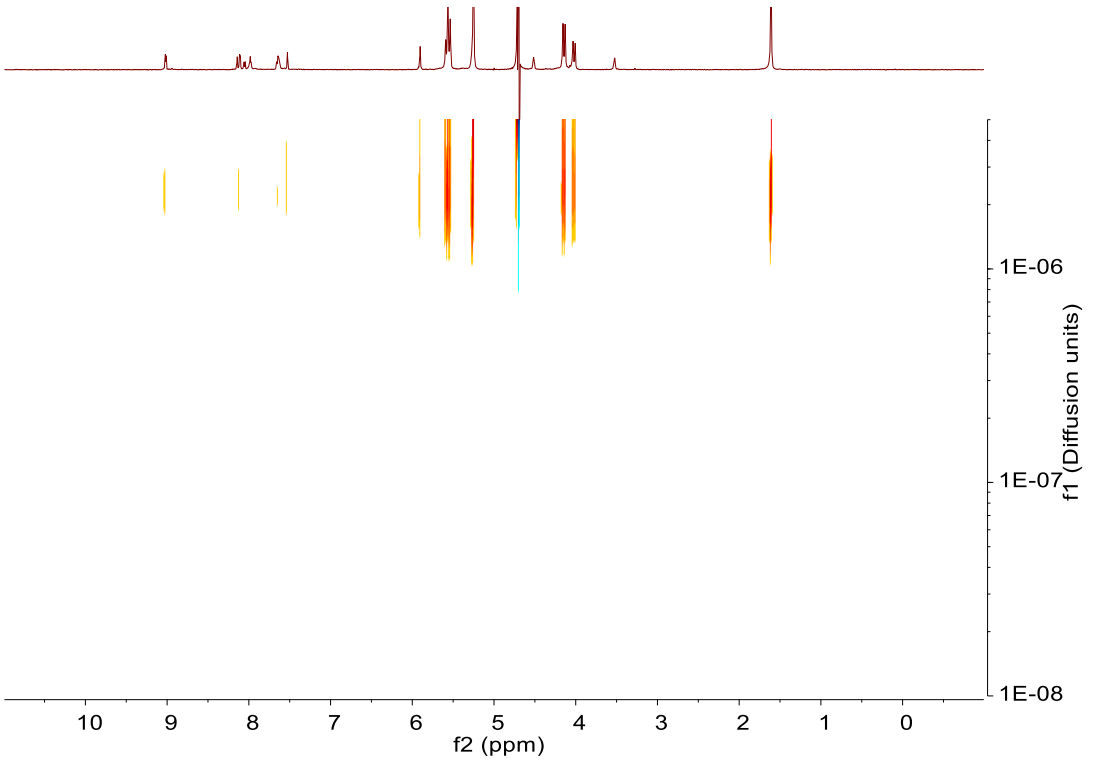


Fig. S14 2D diffusion-ordered NMR spectroscopy (DOSY) of **L2**@TMeCB[6](1:2) (600 MHz, D_2O, 298 K).

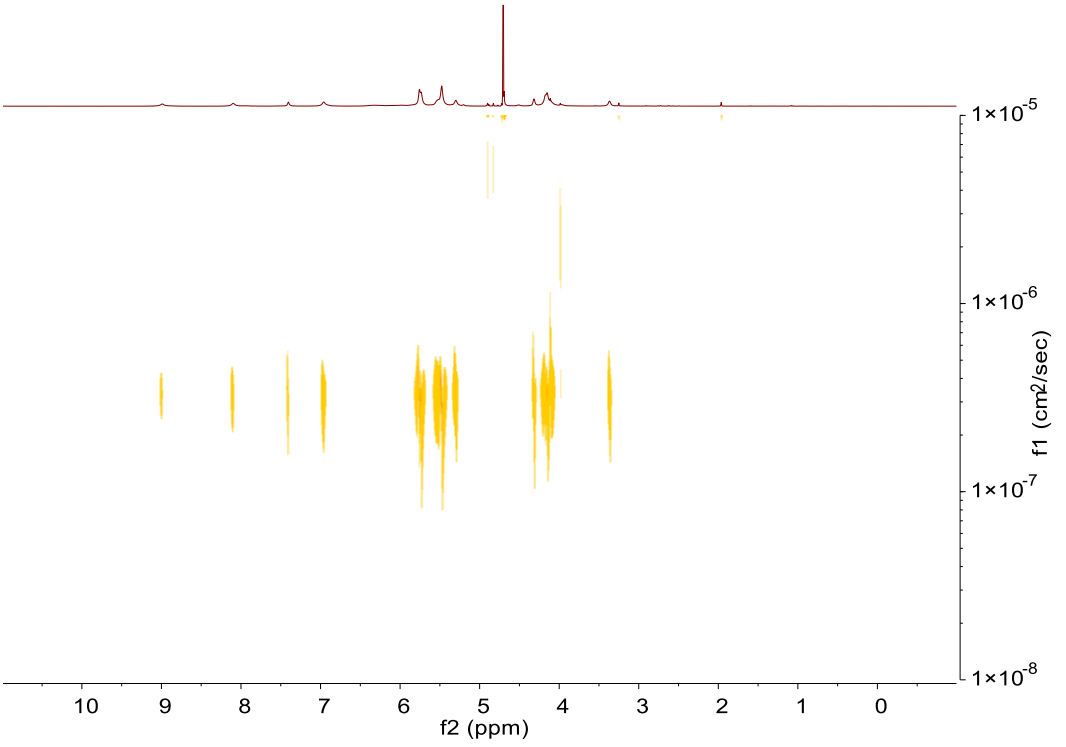


Fig. S15 2D diffusion-ordered NMR spectroscopy (DOSY) of **L2**@CB[8](1:2) (600 MHz, D_2O, 298 K).

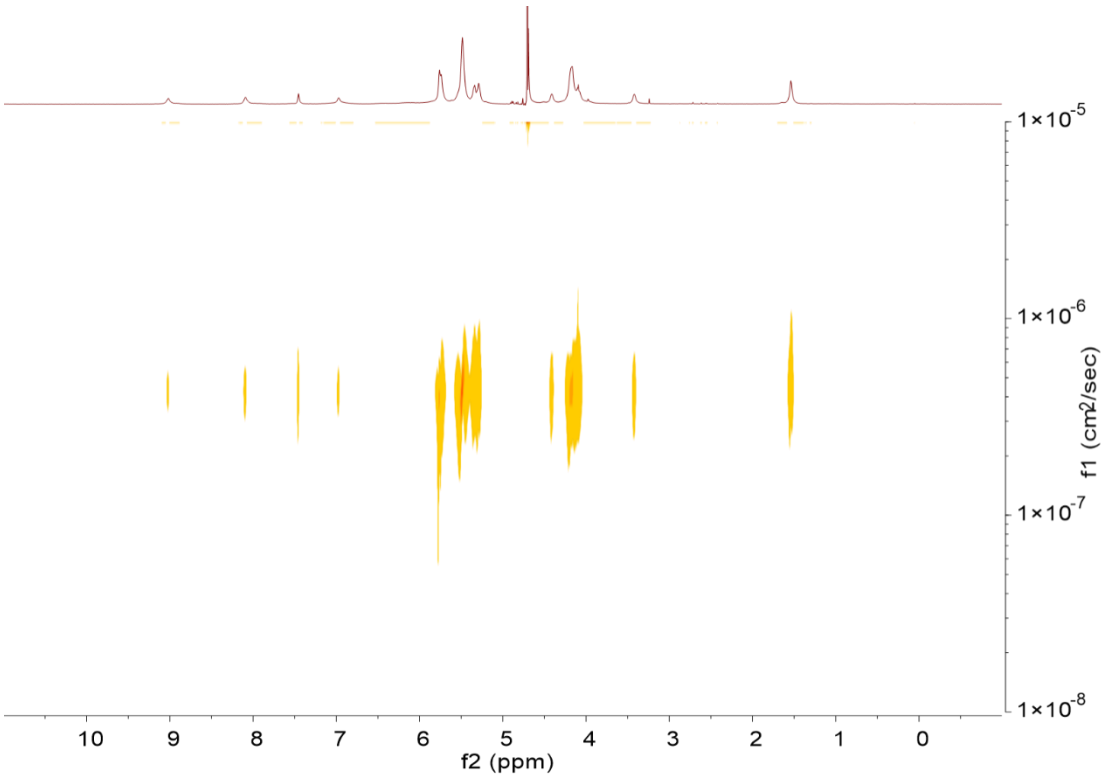


Fig. S16 2D diffusion-ordered NMR spectroscopy (DOSY) of **L2**@CB[8]&TMeCB[6](1:1:1) (600 MHz, D_2O, 298 K).

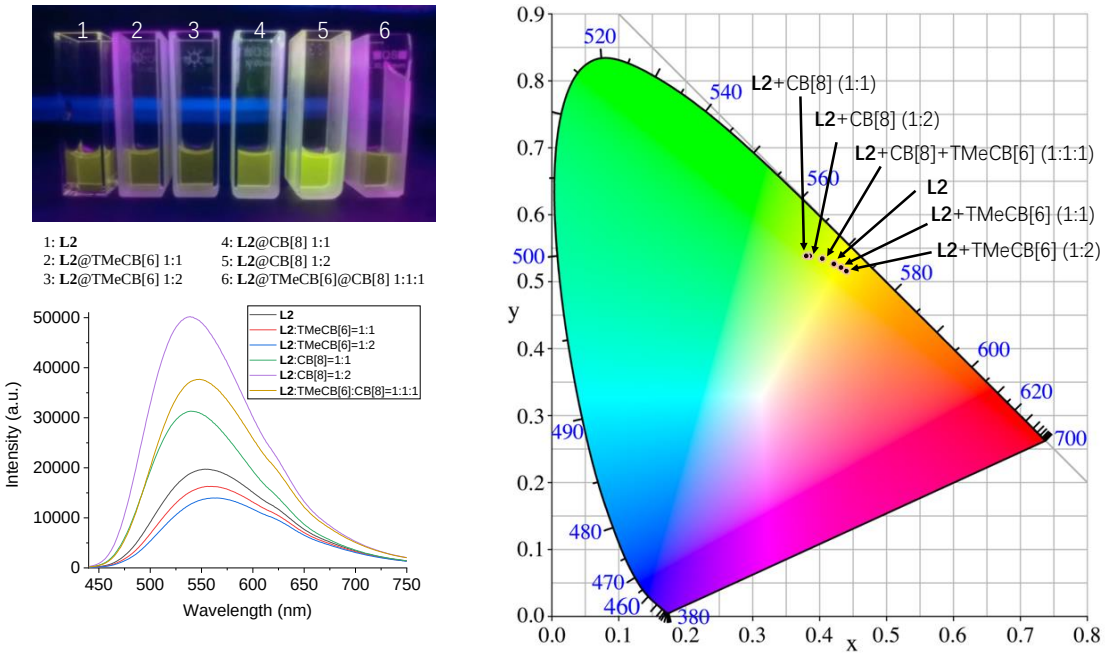


Fig. S17 (a) The solution of **L2**, **L2**⊂TMeCB[6], **L2**⊂(TMeCB[6])$_2$, **L2**⊂CB[8], **L2**⊂(CB[8])$_2$ and **L2**⊂TMeCB[6]&CB[8], under natural light and UV(365 nm) ([**L2**] = 20 μM). (b) Emission spectra ([**L2**] = 20 μM, λ_{ex} = 365 nm, H_2O, 298 K) of **L2**, **L2**⊂TMeCB[6], **L2**⊂(TMeCB[6])$_2$, **L2**⊂CB[8], **L2**⊂(CB[8])$_2$ and **L2**⊂TMeCB[6]&CB[8]. (c) Chromaticity coordinate (CIE) of **L2**, **L2**⊂TMeCB[6], **L2**⊂(TMeCB[6])$_2$, **L2**⊂CB[8], **L2**⊂(CB[8])$_2$ and **L2**⊂TMeCB[6]&CB[8] in different concentration, corresponding to b).

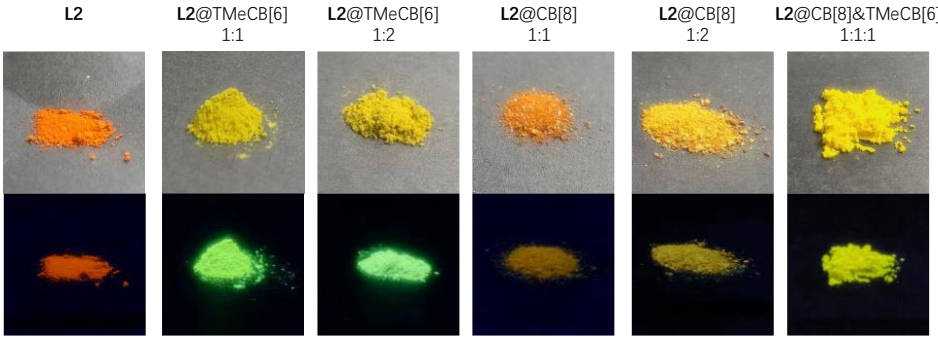


Fig. S18 The solid of **L2**, **L2**⊂TMeCB[6], **L2**⊂(TMeCB[6])$_2$, **L2**⊂CB[8], **L2**⊂(CB[8])$_2$ and **L2**⊂TMeCB[6]&CB[8], under natural light and UV(365 nm).

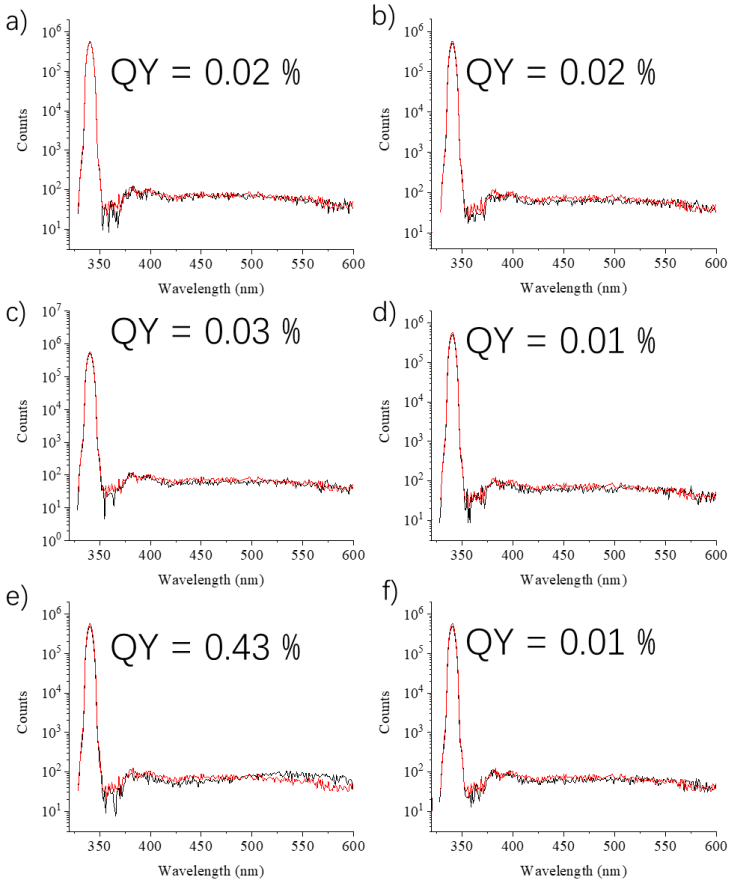


Fig. S19 Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2** (λ_{ex} = 340 nm) in aqueous solution. b) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-TMeCB[6](1:1) (λ_{ex} = 340 nm) in aqueous solution. c) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-TMeCB[6](1:2) (λ_{ex} = 340 nm) in aqueous solution. d) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-CB[8](1:1) (λ_{ex} = 340nm) in aqueous solution. e) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-CB[8](1:2) (λ_{ex} = 340 nm) in aqueous solution. f) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-TMeCB[6]-CB[8](1:1:1) (λ_{ex} = 340 nm) in aqueous solution.

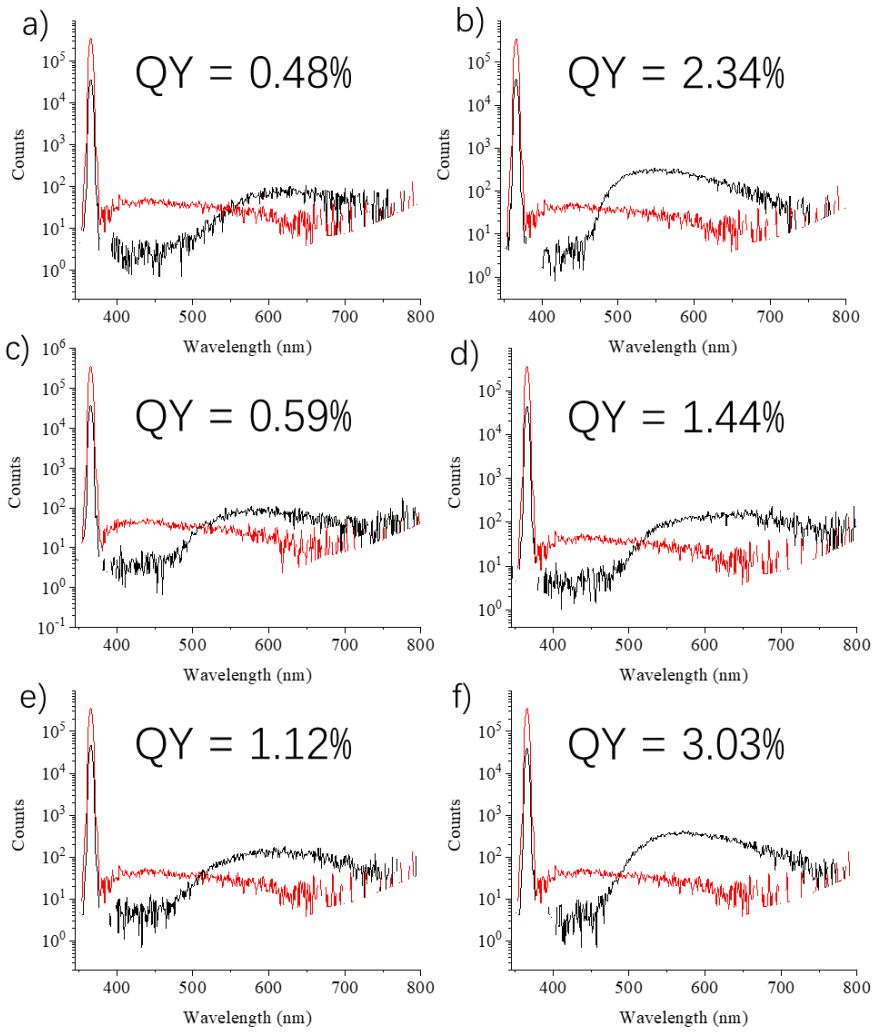


Fig. S20 a) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2** (λ_{ex} = 365 nm) in solid state. b) Absolute fluorescence quantum yield ($\Phi_{f(abs)}$) of **L2**-TMeCB[6](1:1) (λ_{ex} = 365 nm) in solid state. c) Absolute fluorescence quantum yield (Φf(abs)) of **L2**-TMeCB[6](1:2) (λ_{ex} = 365 nm) in solid state. d) Absolute fluorescence quantum yield (Φf(abs)) of **L2**-CB[8](1:1) (λ_{ex} = 365 nm) in solid state. e) Absolute fluorescence quantum yield (Φf(abs)) of **L2**-CB[8](1:2) (λ_{ex} = 365 nm) in solid state. f) Absolute fluorescence quantum yield (Φf(abs)) of **L2**-TMeCB[6]-CB[8](1:1:1) (λ_{ex} = 365 nm) in solid state.

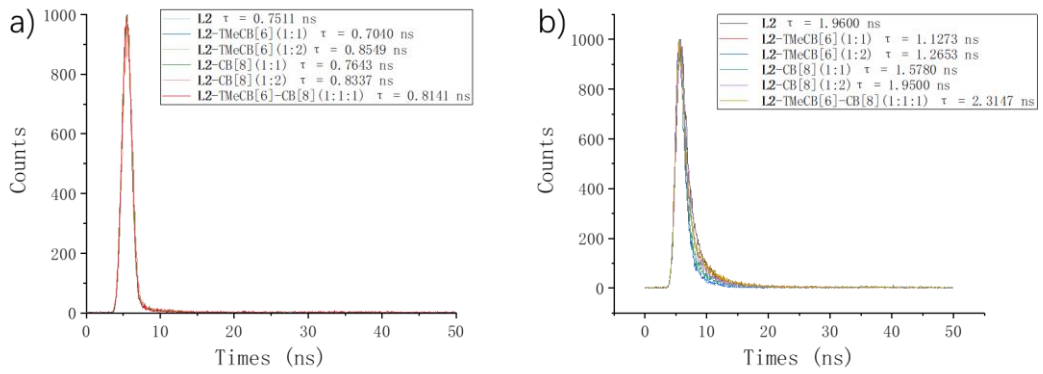


Fig. S21 Time-dependent fluorescence intensity of the solution of **L2**, **L2**-TMeCB[6](1:1), **L2**-TMeCB[6](1:2), **L2**-CB[8](1:1), **L2**-CB[8](1:2) and **L2**-TMeCB[6]-CB[8](1:1:1) in water (a) and the solid state (b).

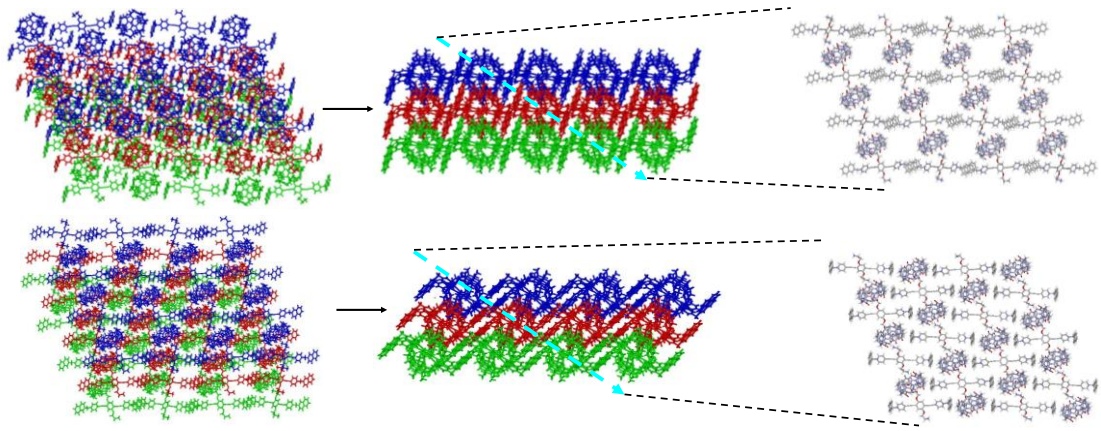


Fig. S22 The staggered layered packing structure through outer-surface interaction.

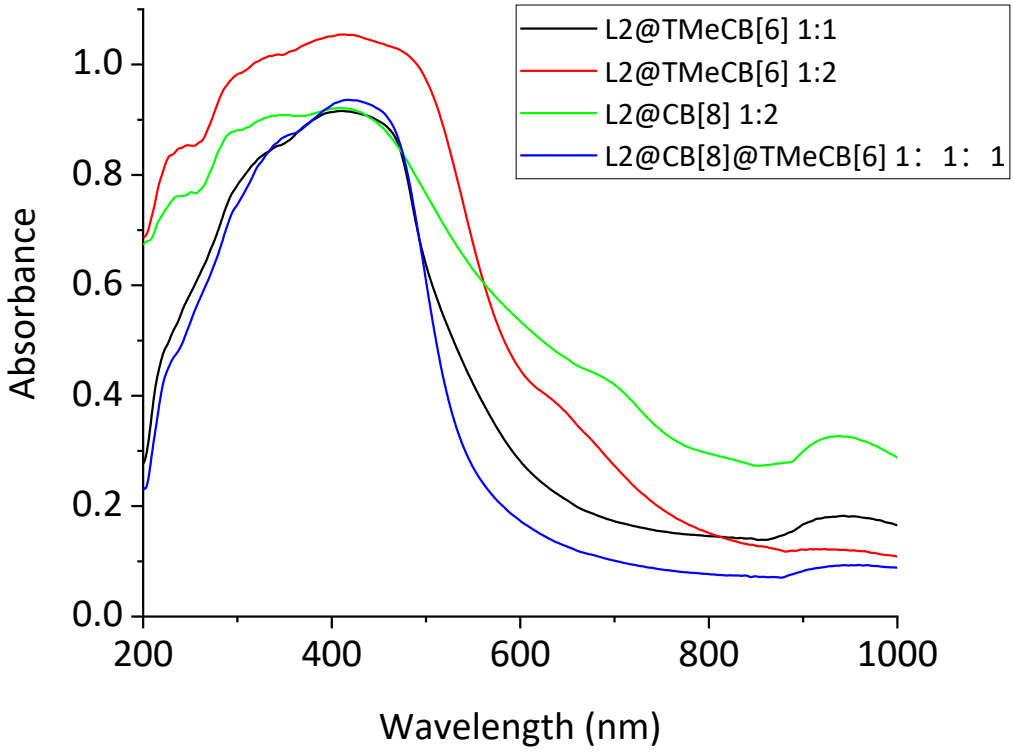


Fig. S23 The UV-vis spectroscopy of solid state **L2**⊂TMeCB[6], **L2**⊂2TMeCB[6], **L2**⊂2CB[8] and **L2**⊂TMeCB[6]&CB[8] at 25 °C.

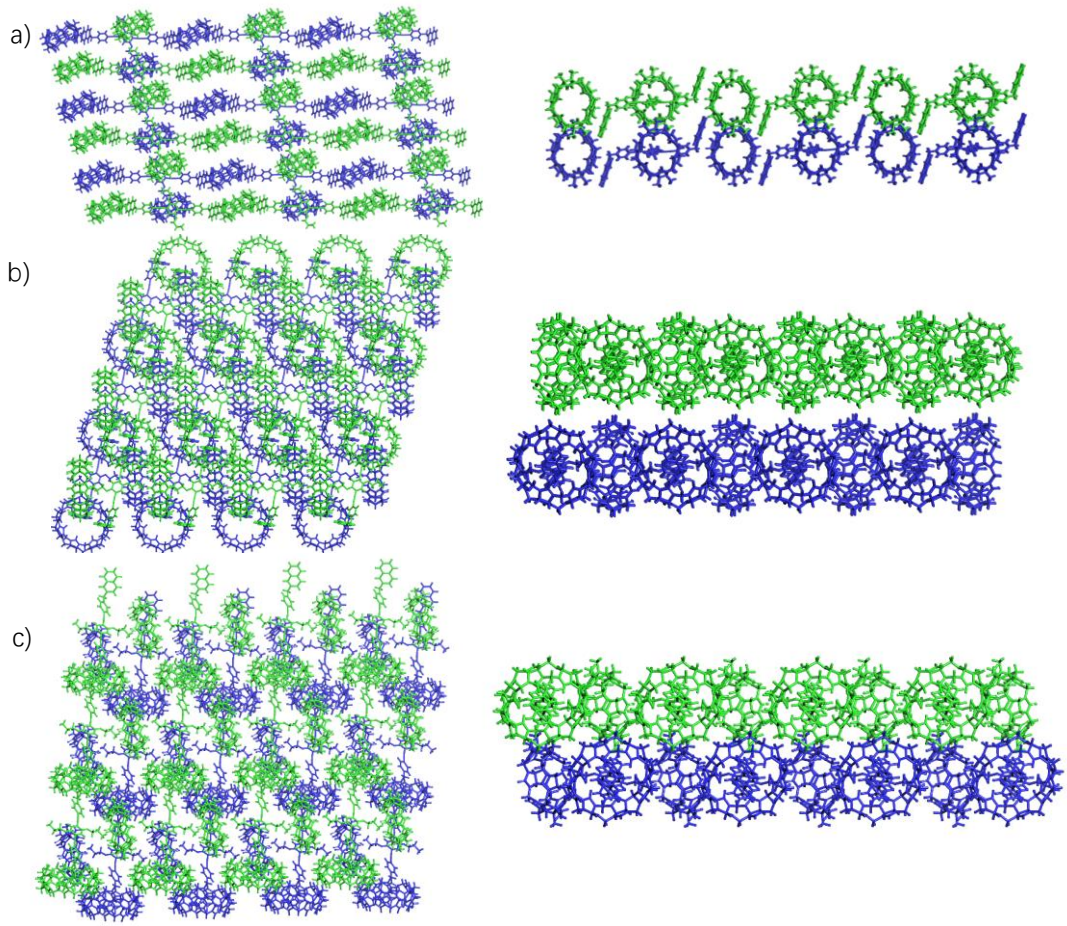


Fig. S24 The staggered layered packing structure of **L2**⊂2TMeCB[6]**, L2**⊂2CB[8] and **L2**⊂TMeCB[6]&CB[8].

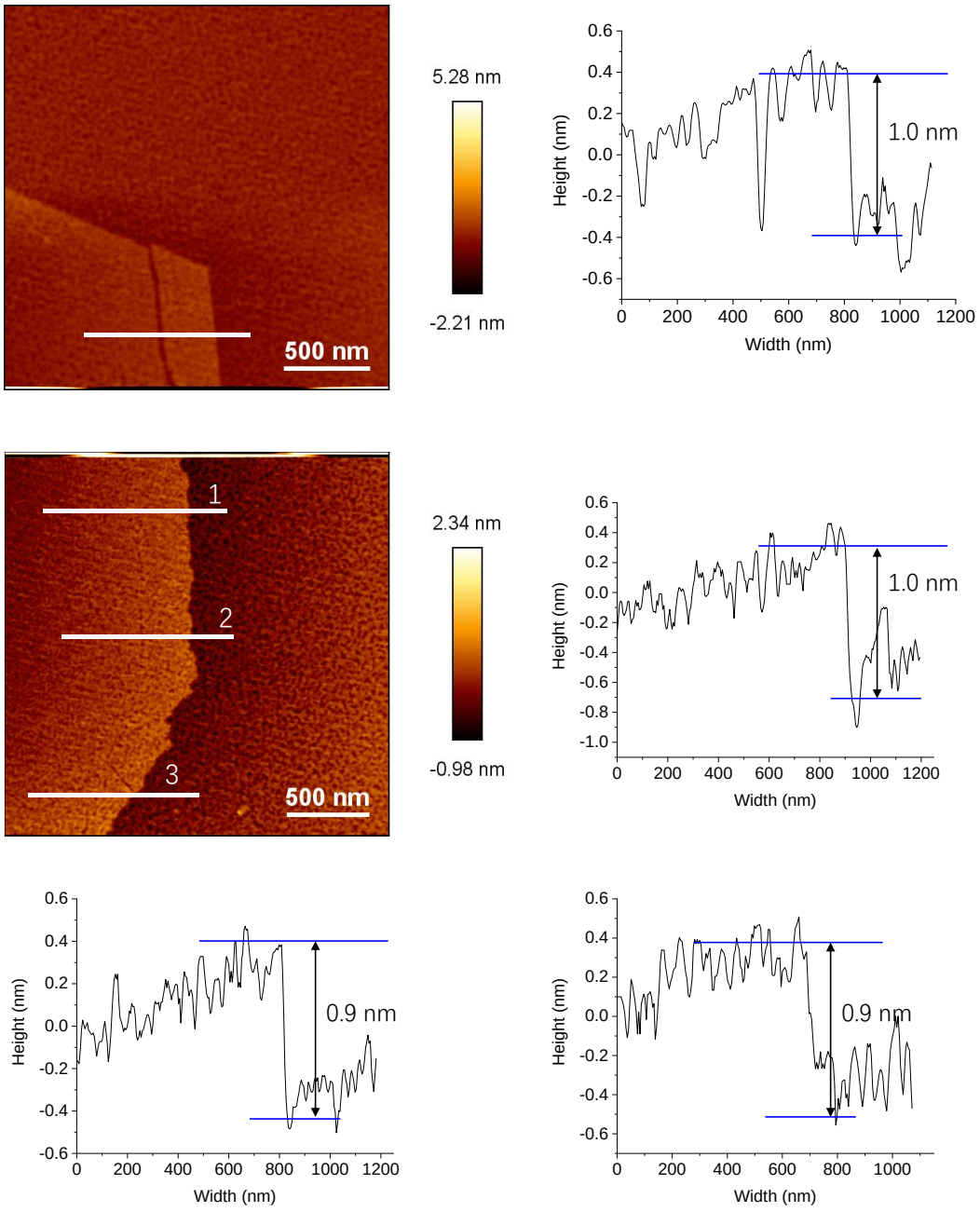


Fig. S25 Tapping-mode AFM image of **L2**⊂TMeCB[6] and section analysis of the aggregates on silicon wafers from dried solution of **L2** (1 μM), TMeCB[6] (1:1).

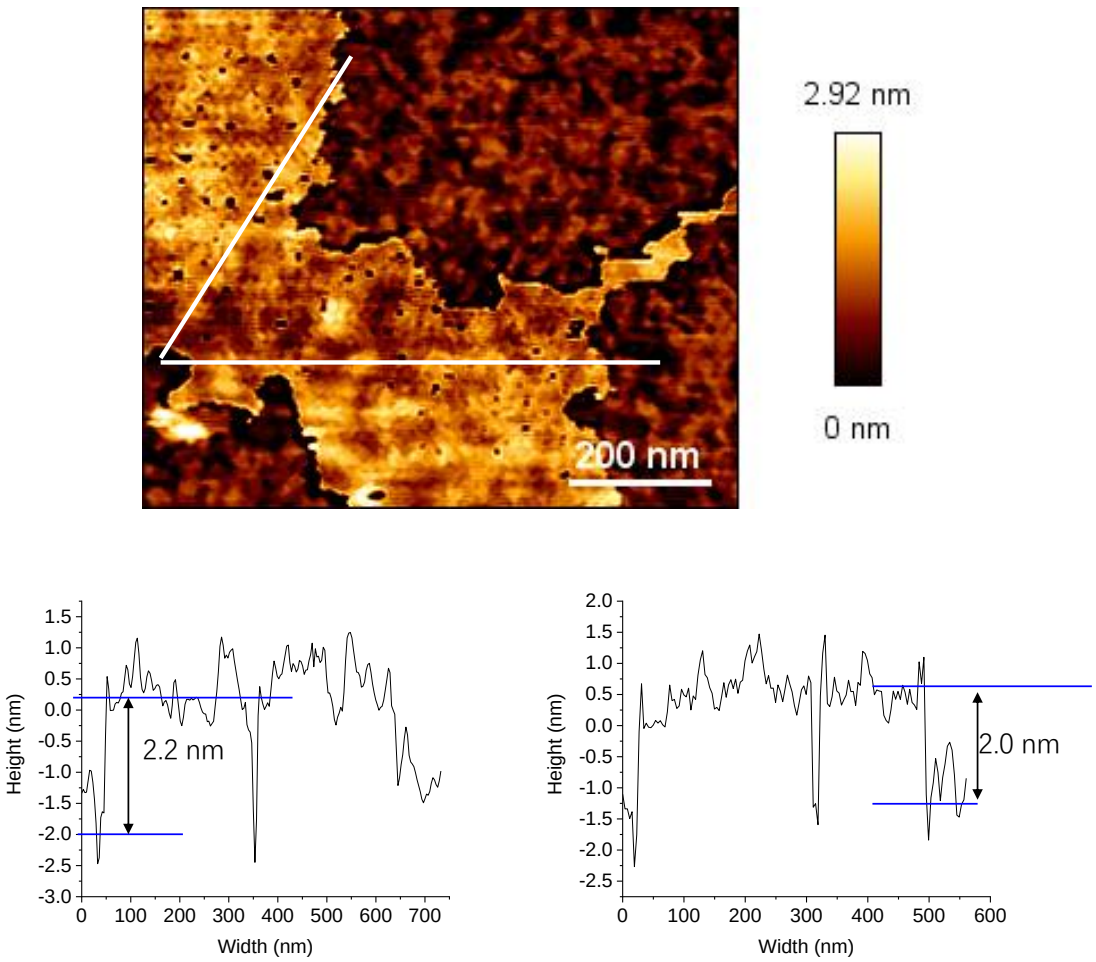


Fig. S26 Tapping-mode AFM image of **L2**⊂TMeCB[6]&CB[8] and section analysis of the aggregates on silicon wafers from dried solution of **L2** (1 μM), TMeCB[6] and CB[8] (1:1:1).

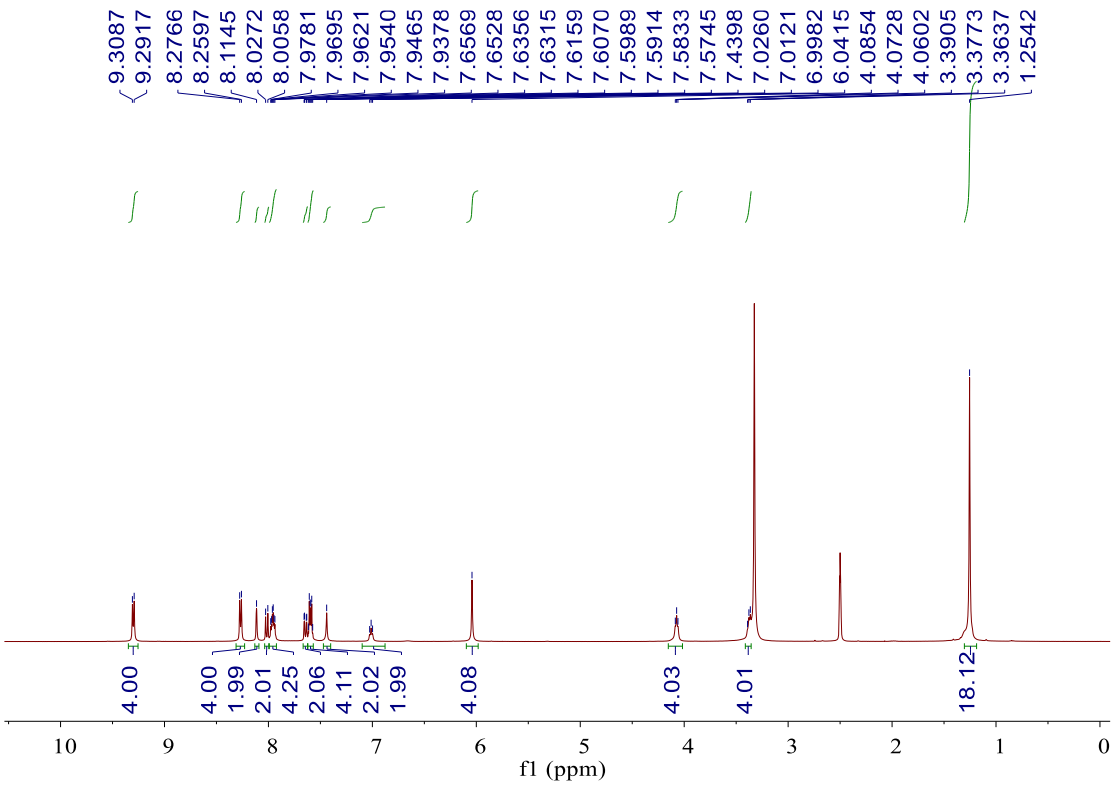


Fig. S27 ^{1}H NMR spectrum (400 MHz) of compound **3** in DMSO-d_6.

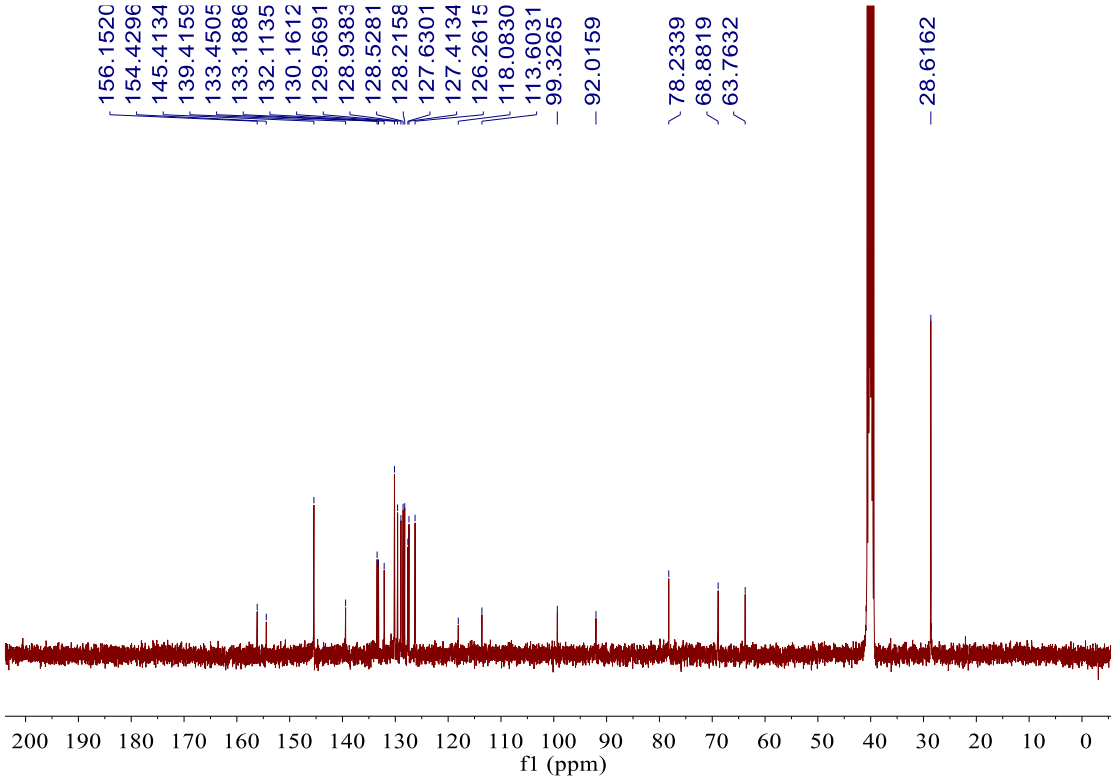


Fig. S28 ^{13}C NMR spectrum (100 MHz) of compound **3** in DMSO-d_6.

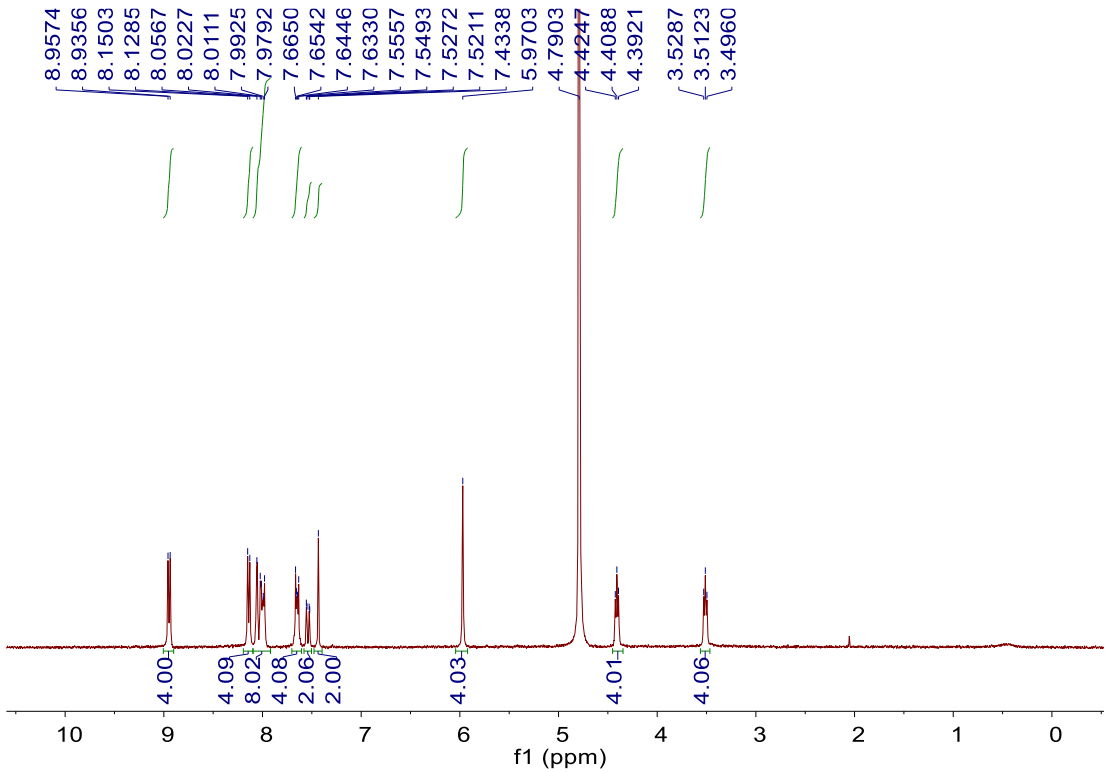


Fig. S29. ^{1}H NMR spectrum (400 MHz) of compound **L2** in D_2O.

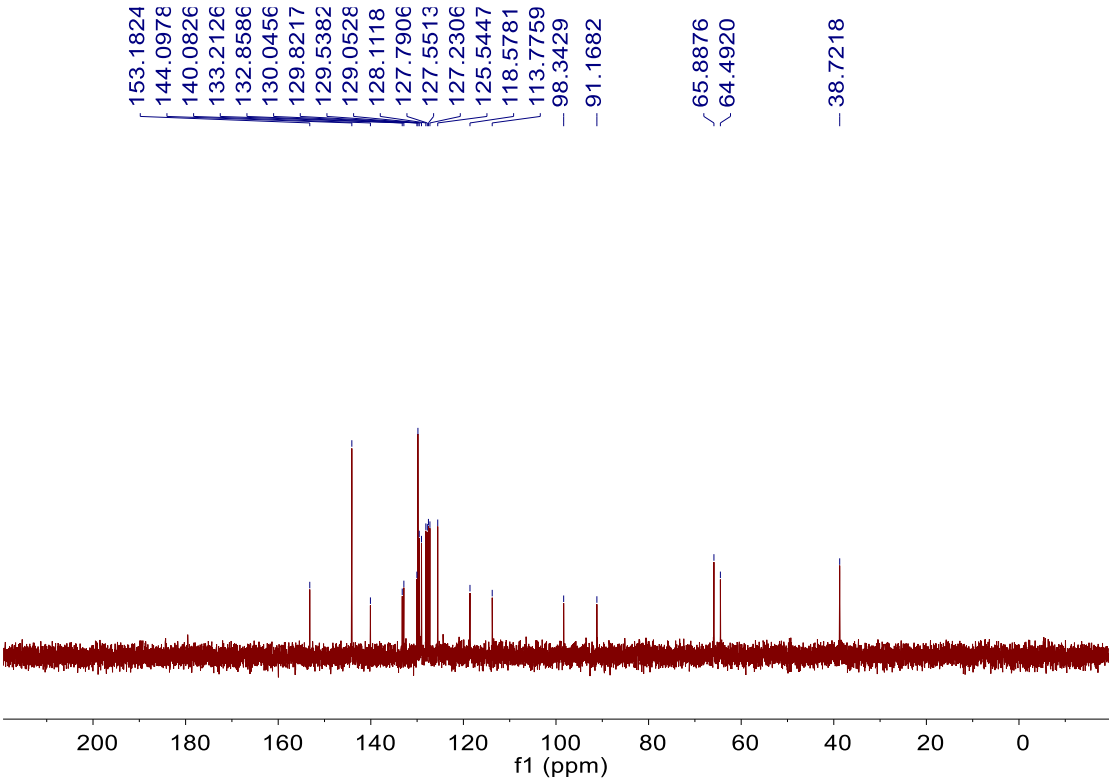


Fig. S30. ^{13}C NMR spectrum (100 MHz) of compound **L2** in D_2O.

References

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(2) Accelrys, Material Studio Release Notes, Release 7.0, Accelrys Software, San Diego 2013.