

Supporting Information

The recognition of 1,5-naphthalenedisulfonate by a protonated azamacrocyclic ligand

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Experimental section

General remarks. All chemicals are commercially available and used without further purification. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the $4000\text{-}400\text{ cm}^{-1}$ region in the form of KBr pellets using a Bruker EQUINOX 55 spectrometer. Fluorescent spectra were recorded using a Shimadzu RF-5301PC spectrofluorophotometer.

Synthesis of the receptors. Protonated receptors $\text{H}_8\text{L}^1\text{Cl}_8$ and $\text{H}_6\text{L}^2\text{Cl}_6$ were synthesized according to the literature methods (Refs. 8 and 9 in the manuscript). ^1H NMR for $\text{H}_8\text{L}^1\text{Cl}_8$ (300 MHz, D_2O): $\delta = 3.02$ (8H, s), 3.12 (8H, t, $J = 6.6$ Hz), 3.33 (8H, t, $J = 6.3$ Hz), 5.07 (8H, s), 7.65 (8H, m), 8.16 (8H, m). ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 129.4, 127.9, 123.8, 123.5, 43.7, 43.2, 43.0, 42.6$. MS (ESI): m/z 349.4 ($[\text{H}_2\text{L}^1]^{2+}$); 697.4 ($[\text{HL}^1]^+$).

^1H NMR for $\text{H}_6\text{L}^2\text{Cl}_6$ (300 MHz, D_2O): $\delta = 2.56\text{-}2.81$ (16H, m, CH_2 , polyamine), 4.57 (8H, s, ArCH_2), 7.39 (8H, m, ArH), 7.62 (8H, m, ArH). ^{13}C NMR (75 MHz,

CDCl_3 , TMS): = 129.3, 127.8, 123.7, 123.0, 43.3, 42.2. MS (ESI): m/z 306.3 ($[\text{H}_2\text{L}^2]^{2+}$); 611.3 ($[\text{HL}^2]^+$).

Synthesis of the complexes.

$[(\text{H}_8\text{L}^1)(1,5\text{-NDS})][1,5\text{-NDS}]_2[\text{HPO}_4](\text{H}_2\text{O})_{16}$ (**1·16H₂O**). A solution (5 mL) of $\text{H}_8\text{L}^1\text{Cl}_8$ (15.0 mg) in Britton-Robinson buffer (pH 1.81) was diffused with a methanol solution (5 mL) of 1,5-naphthalenedisulfonic acid tetrahydrate (10.0 mg) in a tube. One week later, bright yellow crystals formed at the water/methanol interface. Yield: 5.2 mg, 28.9%. The water molecules in the crystals were partly lost upon exposure to the atmosphere. Anal. Calcd (%) for $\text{C}_{74}\text{H}_{111}\text{N}_8\text{O}_{36}\text{PS}_6$ (**1·14H₂O**): C, 46.48; H, 5.85; N, 5.86. Found (%): C, 46.93; H, 5.70; N, 5.55. IR (KBr, cm^{-1}): 3445m, 3013m, 2789m, 1624m, 1500m, 1450m, 1239s, 1158s, 1032s, 796m, 767m, 612s, 568m, 528m.

$[\text{H}_6\text{L}^2][1,5\text{-NDS}]_3(\text{H}_2\text{O})_6$ (**2·6H₂O**). A solution (5 mL) of $\text{H}_6\text{L}^2\text{Cl}_6$ (15.0 mg) in Britton-Robinson buffer (pH 1.81) was diffused with a methanol solution (5 mL) of 1,5-naphthalenedisulfonic acid tetrahydrate (10.0 mg) in a tube. One week later, bright yellow acicular crystals formed at the water/methanol interface. Yield: 3.1 mg, 21.1%. Anal. Calcd (%) for $\text{C}_{70}\text{H}_{82}\text{N}_6\text{O}_{24}\text{S}_6$ (**2·6H₂O**): C, 53.08; H, 5.22; N, 5.31. Found (%): C, 53.02; H, 5.28; N, 5.34. IR (KBr, cm^{-1}): 3462m, 3010m, 2800m, 2718m, 2467m, 1612m, 1496m, 1452m, 1218s, 1175s, 1029s, 794m, 764m, 608s, 571m, 525m.

X-ray crystallography. Single-crystal X-ray diffraction data for the complexes **1**·16H₂O and **2**·6H₂O were collected at 150(2) K on an Agilent Technologies Gemini A Ultra system, with Cu-K α radiation ($\lambda = 1.54178$ Å). The empirical absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.¹ The structures were solved by direct methods, which yielded the positions of all nonhydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (except those of water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The water molecules in **1**·16H₂O were refined isotropically, and hydrogen atoms of water molecules were not added due to lots of disordered water molecules. The hydrogen atoms of the water molecules in **2**·6H₂O were located in the difference Fourier maps and refined isotropically. All calculations were performed using the SHELXTL system of computer programs.² Selected hydrogen bonds distances and angles for **1**·16H₂O and **2**·6H₂O are provided in Table S1.

Fluorescent experiments. Stock solutions of [H₈L¹]⁸⁺ (conc. 0.001 M) and sodium salts of different anions (conc. 0.005 M) were prepared in aqueous solution (Britton-Robinson buffer, pH 1.81). 50 μ L solution of [H₈L¹]⁸⁺ and 500 μ L solution of the substrate (or without substrate) were added into a 10 mL volumetric flask, and then extra Britton-Robinson buffer was added to adjust the concentration of [H₈L¹]⁸⁺ to 5 μ M, and then the fluorescent experiments were performed.

Fluorescent titration experiments. Fluorescent titration experiments of $[\text{H}_8\text{L}^1]^{8+}$ and $[\text{H}_6\text{L}^2]^{6+}$ with 1,5-NDS were performed in aqueous solution (Britton-Robinson buffer, pH 1.81) at room temperature. The association constant (K_a) of $[\text{H}_8\text{L}^1]^{8+}$ with 1,5-NDS was calculated from the changes of the fluorescent intensities of $[\text{H}_8\text{L}^1]^{8+}$ at $\lambda_{\text{em}} 425$ nm using a nonlinear curve-fitting and the following equation:³

$$I = I_0 - \{(I_0 - I_{\text{min}})/(2[\text{H}_0])\} \{([\text{H}_0] + [\text{G}_0] + 1/K_a) - \{([\text{H}_0] + [\text{G}_0] + 1/K_a)^2 - 4[\text{H}_0][\text{G}_0]\}^{1/2}\};$$

Where I is the intensity of $[\text{H}_8\text{L}^1]^{8+}$ at 425 nm in the presence of 1,5-NDS, I_0 is the initial intensity of $[\text{H}_8\text{L}^1]^{8+}$ at 425 nm without 1,5-NDS, I_{min} is the intensity of $[\text{H}_8\text{L}^1]^{8+}$ at 425 nm in the presence of excess amount of 1,5-NDS, $[\text{H}_0]$ is the concentration of $[\text{H}_8\text{L}^1]^{8+}$, $[\text{G}_0]$ is the concentration of 1,5-NDS, $K_a = [\text{complex}]/\{[\text{H}_0] \times [\text{G}_0]\}$;

The nonlinear curve-fitting tools of Origin[®] (v.7.5) package were used for calculating the value of K_a .

Job plots measurement: Stock solutions of $[\text{H}_8\text{L}^1]^{8+}$ (0.004 M) and the sodium salt of 1,5-NDS (0.004 M) were prepared in DMSO- d_6 /D₂O (1:1 v/v, pD 1.81, adjusted by DCl). Ten NMR tubes were filled with the mixing solutions of $[\text{H}_8\text{L}^1]^{8+}$ and 1,5-NDS in a total volume of 500 μL , with the following volume ratios: 50:450, 100:400, 150:350, 200:300, 250:250, 300:200, 350:150, 400:100, 450:50 and 500:0, respectively. The changes in the chemical shifts of H_f for each solution were measured,

and the plot of $\Delta\delta \times X$ versus X ($X = [\text{H}_8\text{L}^1]/\{[\text{H}_8\text{L}^1] + [1,5\text{-NDS}]\}$) was performed.

The maximum of the curve indicates the stoichiometry of the new entity formed.

¹H NMR titration experiments. ¹H NMR titration experiments of $[\text{H}_8\text{L}^1]^{8+}$ with 1,5-NDS were performed in DMSO-*d*₆/D₂O (1:1 v/v, pD 1.81, adjusted by DCl) at room temperature. To ten stock solutions of $[\text{H}_8\text{L}^1]^{8+}$ (50 μL, 0.02 M), 0, 10, 20, 30, 40, 50, 100, 150, 200, 250 μL of stock solutions containing 1,5-NDS (0.02 M) were added, respectively, and then additional solvent was added to adjust the concentration of $[\text{H}_8\text{L}^1]^{8+}$ to 0.002 M for each case. The association constant (K_a) of $[\text{H}_8\text{L}^1]^{8+}$ with 1,5-NDS was calculated by monitoring the chemical shifts of the proton H_f in $[\text{H}_8\text{L}^1]^{8+}$ using a nonlinear curve-fitting and the following equation:⁷

$$\Delta\delta = \{\Delta\delta_0(1 + K_a[\text{H}_0] + K_a[\text{G}_0]) - \{\Delta\delta_0^2(1 + K_a[\text{H}_0] + K_a[\text{G}_0])^2 - 4K_a^2[\text{H}_0][\text{G}_0] \Delta\delta_0^{21/2}\}/(2K_a[\text{H}_0])\}$$

Where $\Delta\delta$ is the change of the chemical shift of the proton H_f in $[\text{H}_8\text{L}^1]^{8+}$ in the presence of 1,5-NDS, $\Delta\delta_0$ is the maximum change of the chemical shift of the proton H_f in $[\text{H}_8\text{L}^1]^{8+}$ in the presence of 5 equiv of 1,5-NDS, $[\text{H}_0]$ is the concentration of $[\text{H}_8\text{L}^1]^{8+}$, $[\text{G}_0]$ is the concentration of 1,5-NDS, $K_a = [\text{complex}]/\{[\text{H}_0] \times [\text{G}_0]\}$;

The nonlinear curve-fitting tools of Origin[®] (v.7.5) package were used for calculating the value of K_a .

References

1. *CrysAlis RED, Version 1.171.31.7*, Oxford Diffraction Ltd, 2006.

2. G.M. Sheldrick, *SHELXTL-97, Program for solution and refinement of crystal structures*, University of Göttingen, Germany, 1997.
3. Y. Shiraishi, S. Sumiya and T. Hirai, *Chem. Commun.*, 2011, **47**, 4953.

Table S1 Hydrogen-bonding distances (Å) and angles (°) in **1** and **2**^a

Interaction	D...H	H...A	D...A	∠D-H...A
1·16H₂O				
N1-H1C...O2	0.92	1.93	2.840(4)	171.8
N1-H1D...O16	0.92	1.92	2.791(4)	156.6
N2-H2C...O9W#2	0.92	1.88	2.783(4)	165.2
N2-H2D...O1	0.92	2.07	2.859(4)	143.4
N2-H2D...O16	0.92	2.29	2.880(4)	121.1
N3-H3C...O1	0.92	2.11	2.885(4)	140.7
N3-H3C...O17	0.92	2.2	2.793(4)	121.7
N3-H3D...O7W	0.92	1.75	2.662(4)	171.5
N4-H4C...O14#1	0.92	1.84	2.735(4)	163.4
N4-H4D...O11#1	0.92	1.87	2.758(4)	160.3
N5-H5D...O8	0.92	1.86	2.777(5)	172.3
N6-H6C...O7#2	0.92	1.97	2.746(5)	141
N6-H6C...O5W#2	0.92	2.45	2.993(6)	117.8
N6-H6D...O19	0.92	1.79	2.700(6)	168.4
N7-H7C...O22#2	0.92	1.75	2.668(5)	173.1
N7-H7D...O21	0.92	1.84	2.748(5)	169.1
N8-H8C...O21	0.92	1.9	2.739(5)	150.7
N8-H8D...O6	0.92	1.82	2.721(5)	165.6
2·6H₂O				
O1W-H1F...O6#3	0.85	2.39	2.876(5)	116.3

O1W-H1E...O5#1	0.86	2.26	3.034(7)	150.3
O2W-H2E...O3W#3	0.85	1.93	2.719(8)	153.4
O2W-H2F...O1W	0.85	2.24	2.672(9)	111.3
O3W-H3E...O2	0.89	2.03	2.912(5)	171.9
O3W-H3F...O5#1	0.8	2.2	2.898(5)	145.6
O3W-H3F...O1W	0.8	2.4	2.992(7)	131.1
N1-H1C...O3#3	0.92	1.92	2.763(4)	151.7
N1-H1D...O1	0.92	1.77	2.679(4)	170.9
N2-H2C...O8#2	0.92	1.84	2.755(3)	179.1
N2-H2D...O9	0.92	1.88	2.773(3)	162.3
N3-H3C...O4	0.92	1.9	2.791(4)	163.5
N3-H3D...O6#3	0.92	2.13	3.003(4)	157.7

^a Symmetry transformations used to generate equivalent atoms: #1 x, y, z; #2 - x, - y, - z; #3 x, - y - 1/2, z - 1/2.

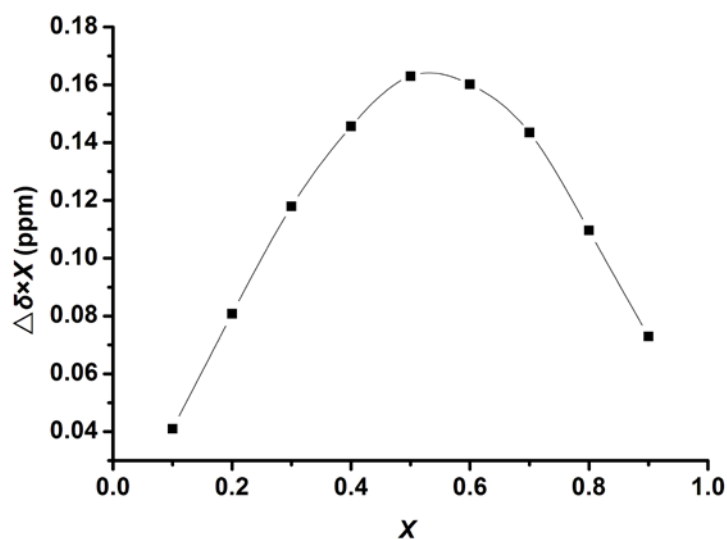


Fig. S1 Job's plot of the complexation between $[\text{H}_8\text{L}^1]^{8+}$ and 1,5-NDS in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (1:1 v/v, pD 1.81, adjusted by DCI). Total concentration of $[\text{H}_8\text{L}^1]^{8+}$ and 1,5-NDS was kept constant at 4 mM. $X = [\text{H}_8\text{L}^1]/\{[\text{H}_8\text{L}^1] + [1,5\text{-NDS}]\}$.

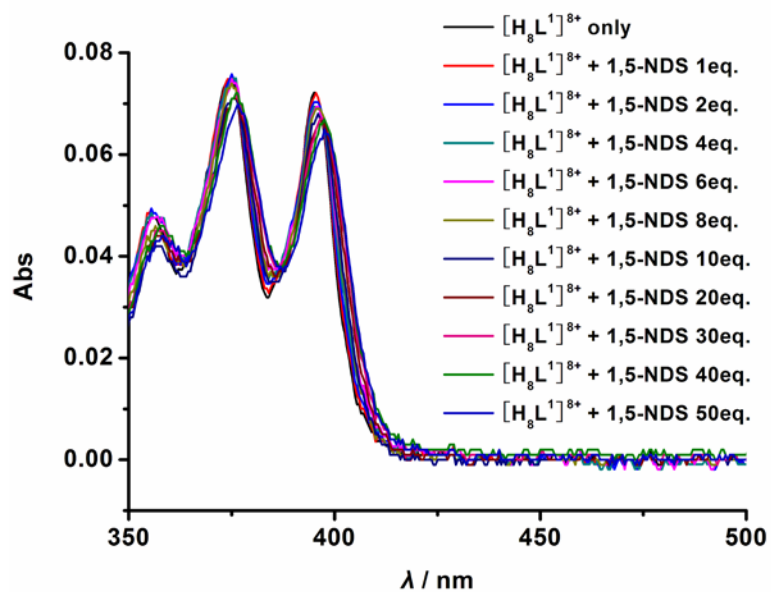


Fig. S2 UV-vis titration of $[H_8L^1]^{8+}$ (5 μ M) upon additions of 1,5-NDS at pH 1.81 (Britton-Robinson buffer).

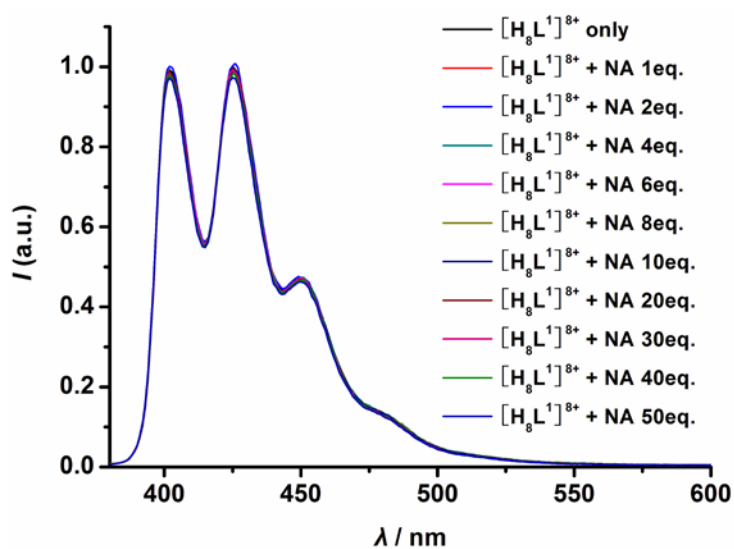


Fig. S3 Fluorescent titration of $[H_8L^1]^{8+}$ (5 μ M) upon additions of NA at pH 1.81 (Britton-Robinson buffer) (excitation at 368 nm). The buffer was prepared by using methanol/water 1:1 as solvent.

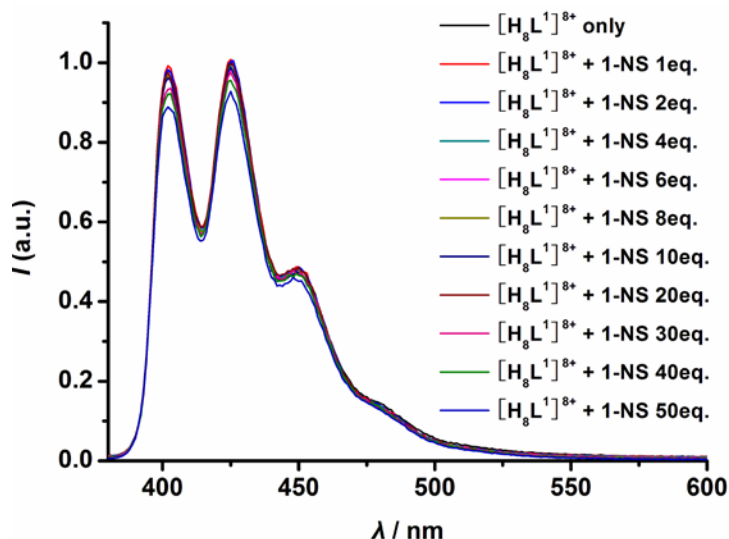


Fig. S4 Fluorescent titration of $[H_8L^1]^{8+}$ (5 μ M) upon additions of 1-NS at pH 1.81 (Britton-Robinson buffer) (excitation at 368 nm)

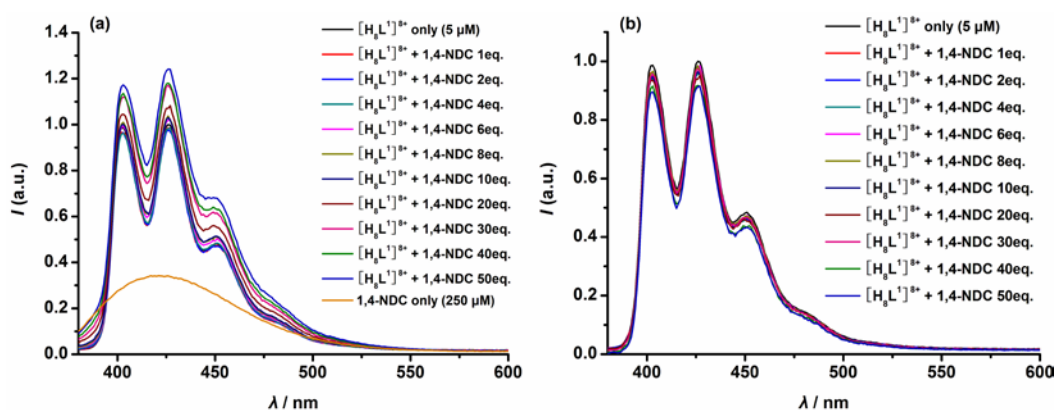


Fig. S5 Fluorescent titration of $[H_8L^1]^{8+}$ (5 μ M) upon additions of 1,4-NDC at pH 1.81 (Britton-Robinson buffer) (excitation at 368 nm). (a) Original spectra; (b) corrected spectra after deducting the emission intensity of 1,4-NDC (As 1,4-NDC displays a broad fluorescent emission around 425 nm (Fig S5a), thus the fluorescent intensities of $[H_8L^1]^{8+}$ increase upon additions of 1,4-NDC (Fig S5a). However, after deducting the emission intensity of 1,4-NDC, the fluorescent intensities of $[H_8L^1]^{8+}$ slightly decrease upon additions of 1,4-NDC).

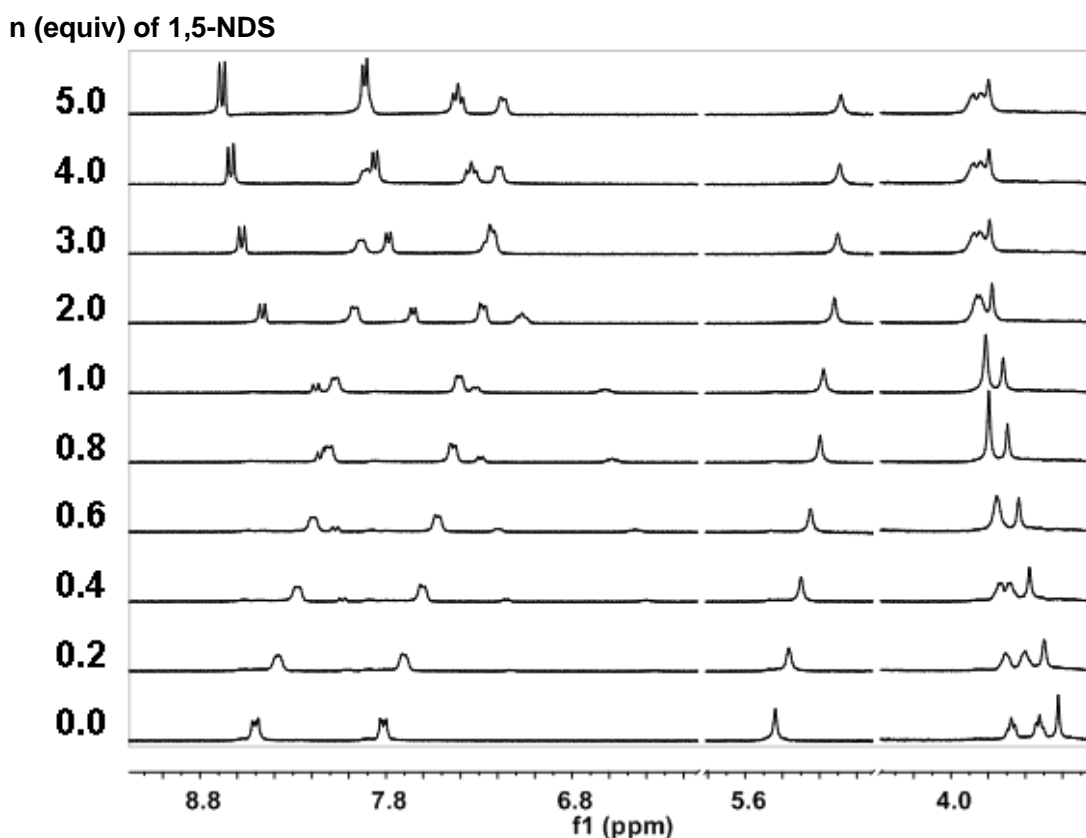


Fig. S6 ^1H NMR titration of $[\text{H}_8\text{L}^1]^{8+}$ (2 mM) with increasing the concentrations of 1,5-NDS in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (1:1 v/v, pD 1.81, adjusted by DCl).

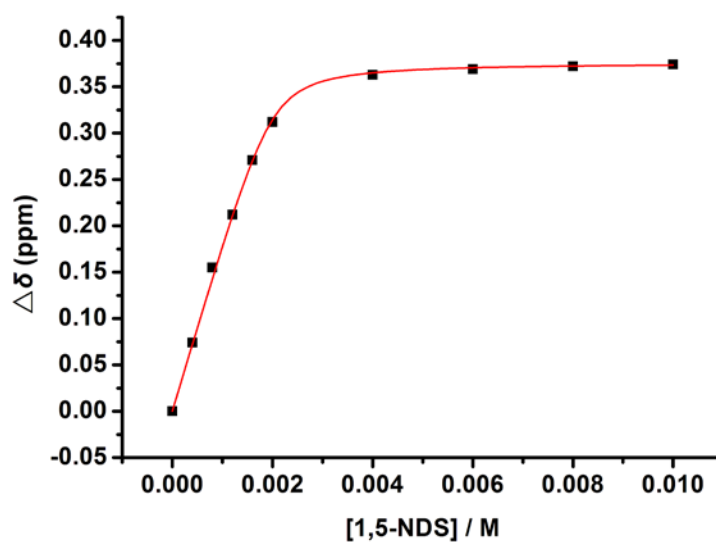


Fig. S7 Curve-fitting for chemical shifts of H_f in $[\text{H}_8\text{L}^1]^{8+}$ (2 mM) upon increasing the concentrations of 1,5-NDS in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (1:1 v/v, pD 1.81, adjusted by DCl).

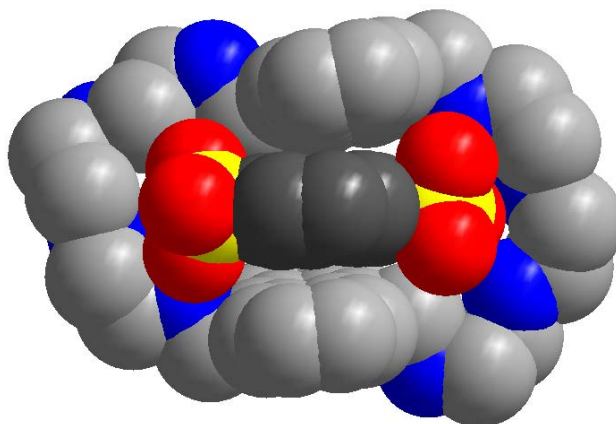


Fig. S8 The space filling model of $[(H_8L^1)(1,5-NDS)]^{6+}$ cation in **1**.

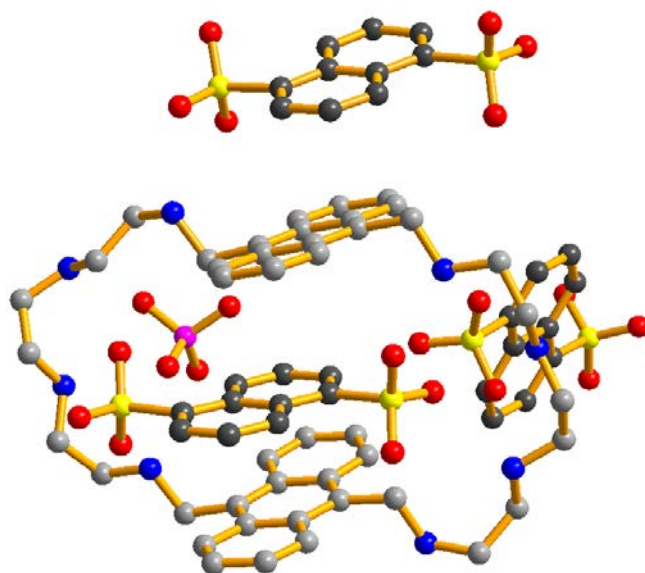


Fig. S9 The X-ray crystal structure of complex **1** (water molecules are omitted for clarity).

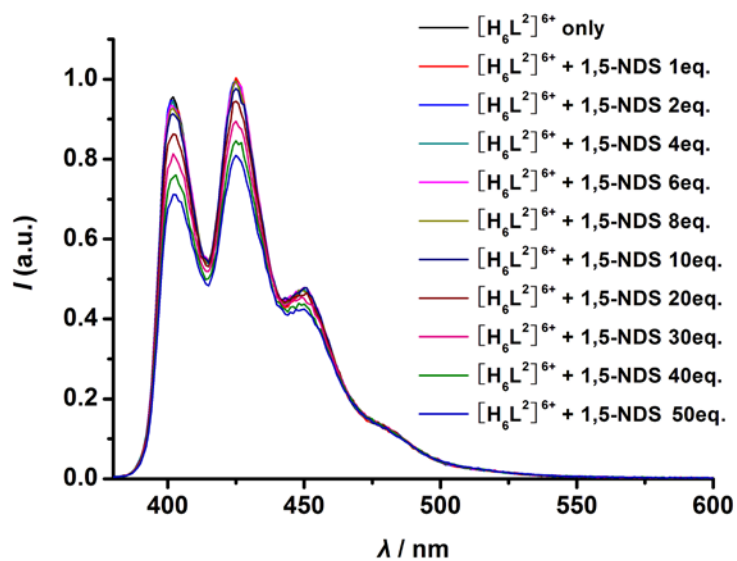
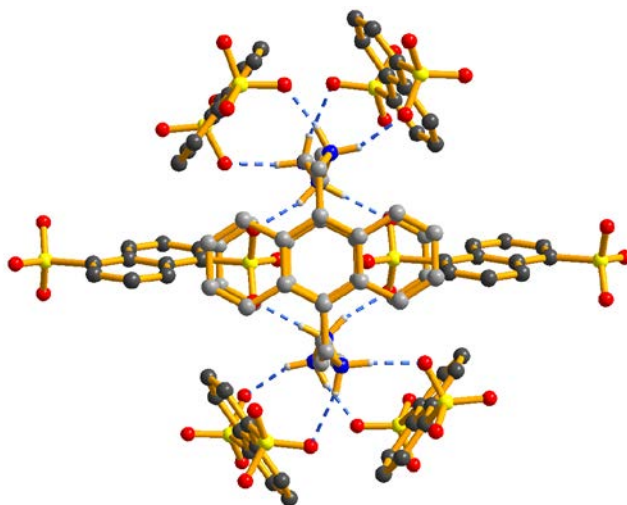
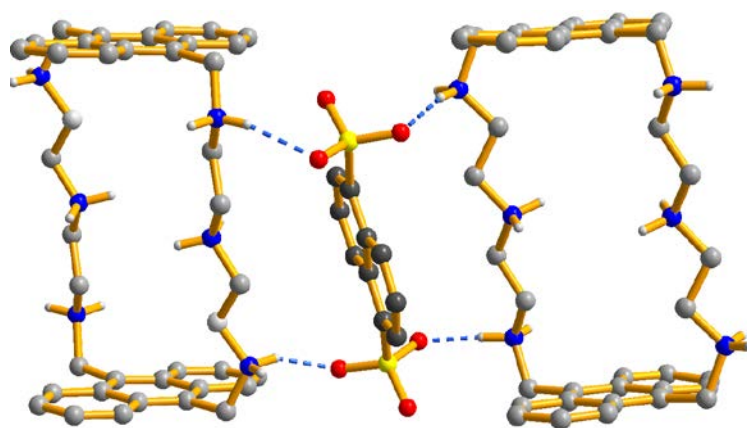


Fig. S10 Fluorescent titration of $[H_6L^2]^{6+}$ ($5 \mu\text{M}$) upon additions of 1,5-NDS at pH 1.81 (Britton-Robinson buffer) (excitation at 368 nm).

(a)



(b)



(c)

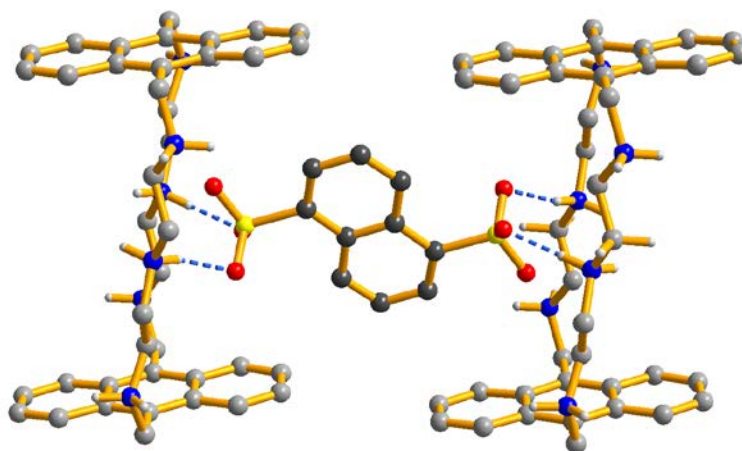


Fig. S11 Hydrogen-bonding interactions between $[H_6L^2]^{6+}$ and 1,5-NDS in **2**.