Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

# Encapsulation of $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster in a metal organic framework of a pyridyl functionalized cyanuric acid based tris-Urea

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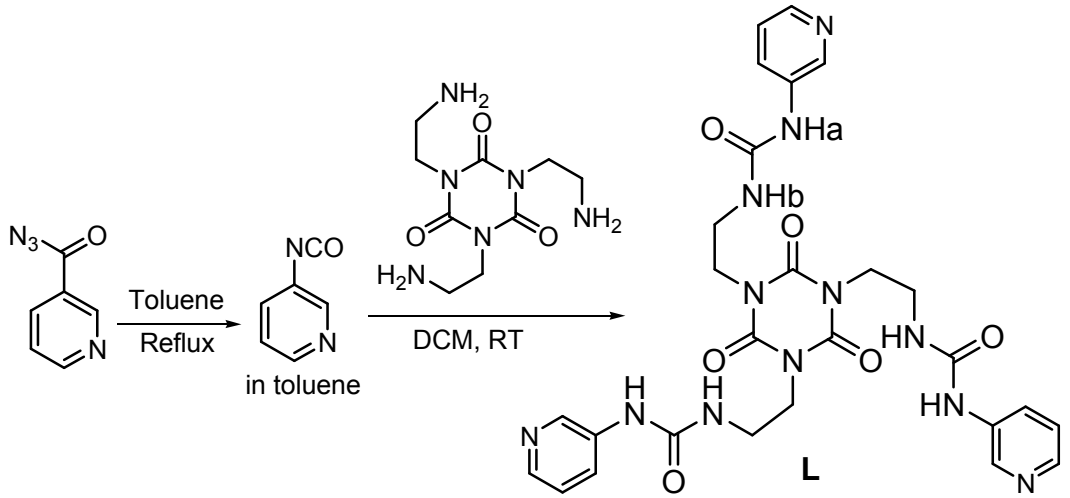
**Materials:** Cyanuric acid based precursor tripodal amine[1] and nicotinoyl azide[2] were synthesized following reported literature procedure. Dichloromethane (DCM) and toluene were freshly distilled before use. Zinc sulfate heptahydate, cadmium sulfate, magnesium sulfate, zinc acetate, zinc nitrate, zinc perchlorate, zinc chloride and sodium nitrate were purchased from Merck, India and were used as received. All solvents were procured from Merck.

**Methods:** FTIR was recorded on SHIMADZU FTIR-8400S infrared spectrophotometer with KBr pellets. $^1$H-NMR and $^{13}$C-NMR spectra were obtained on a 500/300 MHz and 125/75 MHz BrukerDPX-500 MHz NMR and BrukerAvance300 Spectrometer at 298 K. $^1$H-NMR titration experiments for **L** with $ZnSO_4$ was conducted on a Bruker300 MHz at 298 K respectively. Stock solution of host was prepared in DMSO-$d_6$. Stock solution of $ZnSO_4$,$7H_2O$ was prepared in DMSO-$d_6$. To evaluate the association constants and stoichiometry of binding in cases of $ZnSO_4$ with **L**, $^1$H-NMR titrations were performed at 298 K. Aliquots of anions were added from a standard stock solution of anion to the solution of **L**. The association constants, *K*, were calculated by fitting the change in the NHa chemical shift with a 1:1 association model with non-linear least square analysis. Job's plot revealed a best fit for 1:1 host to guest binding mode. The equation $\Delta\delta = \{([A]_0+[L]_0+1/K)\pm(([A]_0+[L]_0+1/K)^2 - 4[L]_0[A]_0)^{1/2}\}\Delta\delta_{max}/2[L]_0$ was used for calculating association constants.[3] The isothermal titration calorimetric experiments were performed on a MicroCal VP-ITC instrument. Titration was carried out at 298 K in anhydrous dimethyl sulfoxide (DMSO). A solution of 0.1212 mM of **L** in DMSO was taken in the measuring cell. This solution was then titrated with 30 injections of 10 µl of a 2.5 mM $ZnSO_4$,$7H_2O$ solution prepared in DMSO. An interval of 220 seconds was allowed between each injection, and the stirring speed was set at 329 rpm. The obtained data was processed using Origin 7.0 software supplied with the instrument and fitted to a one site binding model. Blank titration of $ZnSO_4$, $7H_2O$ into plain solvent were also performed and subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant.

**X-ray Crystallography**: The crystallographic details of complex **1-2** are given in Table S1. A crystal of suitable size was collected from the mother liquor, dipped in paratone oil, and was mounted on the tip of a glass fiber. Epoxy resin was used to cement the crystal on the top of the glass fiber. Intensity data of the crystal was collected using Mo Kα (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer, which was equipped with a CCD area detector at 150 K. SAINT[4] software was used to process the data integration and reduction. SADABS[5] was used to apply an empirical absorption correction to the collected reflections. Direct method was used to solve the structure using SHELXTL[6] and was refined on F2 by the full-matrix least-squares technique using the SHELXL-97[7] program

package. PLATON[8] and MERCURY 3.1[7] were used to generate graphics. The non-hydrogen atoms were refined anisotropically until convergence. Two water molecules namely O22 and O23 are disordered over two positions and treated by FVAR command. In case of complex **1**, the packing generates cavities that are filled with disordered molecules from the solvent of crystallization (methanol and water). No reasonable disorder model could be obtained for these solvent molecules despite many attempts. Therefore, the R1 and wR2 values are found to be slightly higher for complex **1**, although the data collection is carried out at 150 K. They were therefore accounted for by the SQUEEZE/PLATON program. The program calculated a total solvent-accessible volume per unit cell of 2180 $Å^3$, or 22.2% of the total unit cell volume, corresponding to 831 e-/cell. Although we have collected the data several times at 150 K in case of complex **2**, we could not improve the R1(0.0769) and wR2 (0.2351) values further. CCDC: **1024314** (Complex **1**), CCDC: **1024315** (Complex **2**).




**Scheme 1S.** Synthetic route for **L**

**Receptor L:** Precursor tripodal amine was synthesized in high yield following our reported literature procedure.[1] Nicotinoyl aizde[2] (0.51 g) was dissolved in 30 ml anhydrous toluene and refluxed for 2h under argon atmosphere. Then it was cooled to room temperature and an anhydrous dichloromethane (DCM) suspension of triamine (278 mg, 0.31 equiv.) was added to it at once. Immediately a white color precipitate appeared and the solution was further allowed to stir at *rt* for another 2h. The solution was then filtered and the ppt washed with DCM and diethylether. Crude product was finally purified by flash column chromatography on silica gel in DCM/MeOH to afford analytically pure **L** (410 mg, 60%) as white powder. ESI-MS (+Ve): *m/z* calcd. for $C_{27}H_{31}N_{12}O_6$ $[M + H]^+$, 619.6118, found 619.3458. $^1$H-NMR (500 MHz, DMSO-$d_6$): δ (ppm) = 8.73 (s, 3H, Urea-N$H_a$), 8.50 (d, 3H, $J$ = 2.5 Hz, Ar-C*H*), 8.09 (d, 3H, $J$ = 4.5 Hz, Ar-C*H*), 7.82 (d, 3H, $J$ = 8.5 Hz, Ar-C*H*), 7.23-7.21 (m, 3H, Ar-C*H*), 6.37 (t, 3H, $J$ = 7 Hz, Urea-N$H_b$), 3.86 (t, 6H, $J$ = 6 Hz, -C$H_2$), 3.32-3.27 (m, 6H, -C$H_2$). $^{13}$C-NMR (125 MHz, DMSO-$d_6$): δ (ppm) = 155.36 (-*C*O), 149.09 (Ar-*C*), 142.15 (Ar-*C*), 139.73 (Ar-*C*), 136.98 (Ar-*C*), 124.65 (Ar-*C*), 123.35 (Ar-*C*), 42.30 (-*C*H$_2$), 37.05 (-*C*H$_2$).

**Complex 1**: Crystal of complex **1** is obtained by the slow evaporation of a mixture of **L** (15 mg) and $ZnSO_4$,$7H_2O$ (~2equiv.) in MeOH/$H_2O$ (1:1, v/v) solvent mixture within a week. Yield: 75%. $^1$H-NMR (300 MHz, DMSO-$d_6$): δ (ppm) = 8.96 (s, 3H, Urea-N$H_a$), 8.61 (s, 3H, Ar-C*H*), 8.03 (d, 3H, *J* = 4.2 Hz, Ar-C*H*), 7.94 (d, 3H, *J* = 8.4 Hz, Ar-C*H*), 7.79 (s, 3H, Urea-N$H_b$), 7.23-7.19 (m, 3H, Ar-C*H*), 3.85 (s, 6H, -C$H_2$), 3.22 (d, 6H, *J* = 3.9 Hz, -C$H_2$). $^{13}$C-NMR (75 MHz, DMSO-$d_6$): δ (ppm) = 155.62 (-*C*O), 149.26 (Ar-*C*), 141.18 (Ar-*C*), 139.32 (Ar-*C*), 138.36 (Ar-*C*), 124.97 (Ar-*C*), 123.81 (Ar-*C*), 42.06 (-*C*$H_2$), 36.33 (-*C*$H_2$).

**Complex 2**: Crystals of complex **2** are obtained by the slow evaporation of a MeOH/$H_2O$ or DMF/$H_2O$ solution of **L** and $MgSO_4$ after one month. Yield: 30%. $^1$H-NMR (300 MHz, DMSO-$d_6$): δ (ppm) = 8.53 (br, 3H, Urea-N$H_a$), 8.55 (s, 3H, Ar-C*H*), 8.04 (s, 3H, Ar-C*H*), 7.81 (d, 3H, *J* = 7.5 Hz, Ar-C*H*), 7.79 (s, 3H, Urea-N$H_b$), 7.17 (m, 3H, Ar-C*H*), 3.85 (s, 6H, -C$H_2$), 3.24 (s, 6H, -C$H_2$).

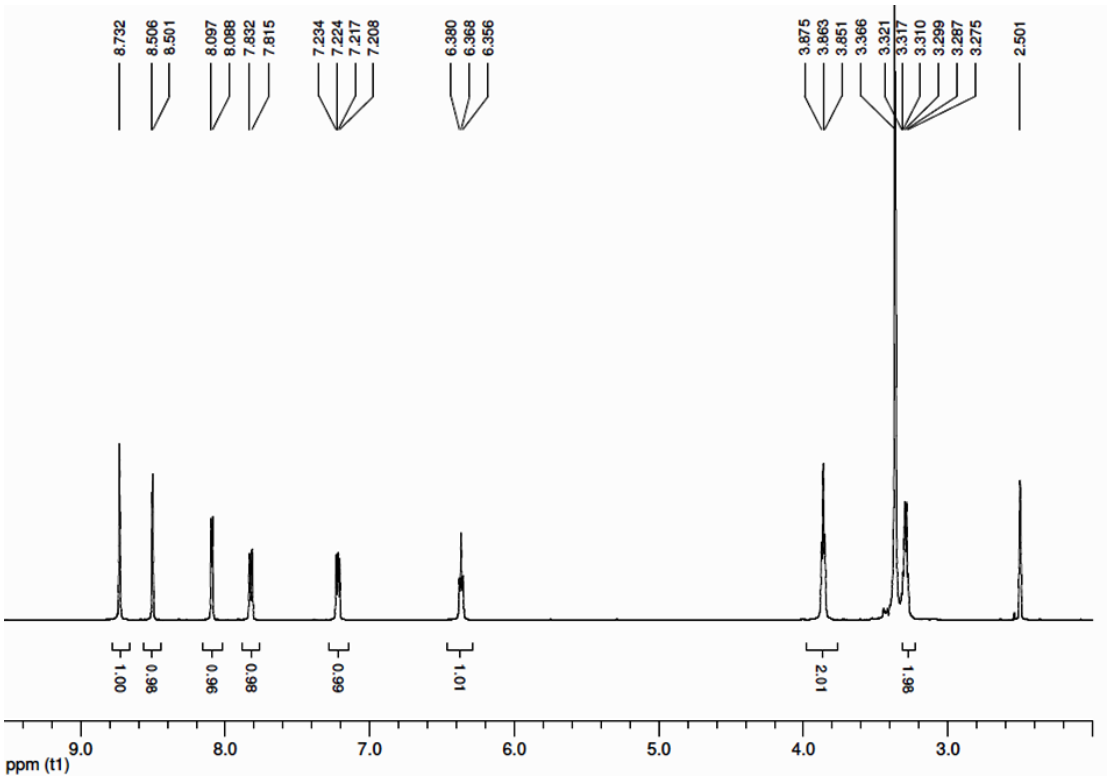



**Figure 1S.** [1]H-NMR (500 MHz) spectrum of **L** in DMSO-$d_6$

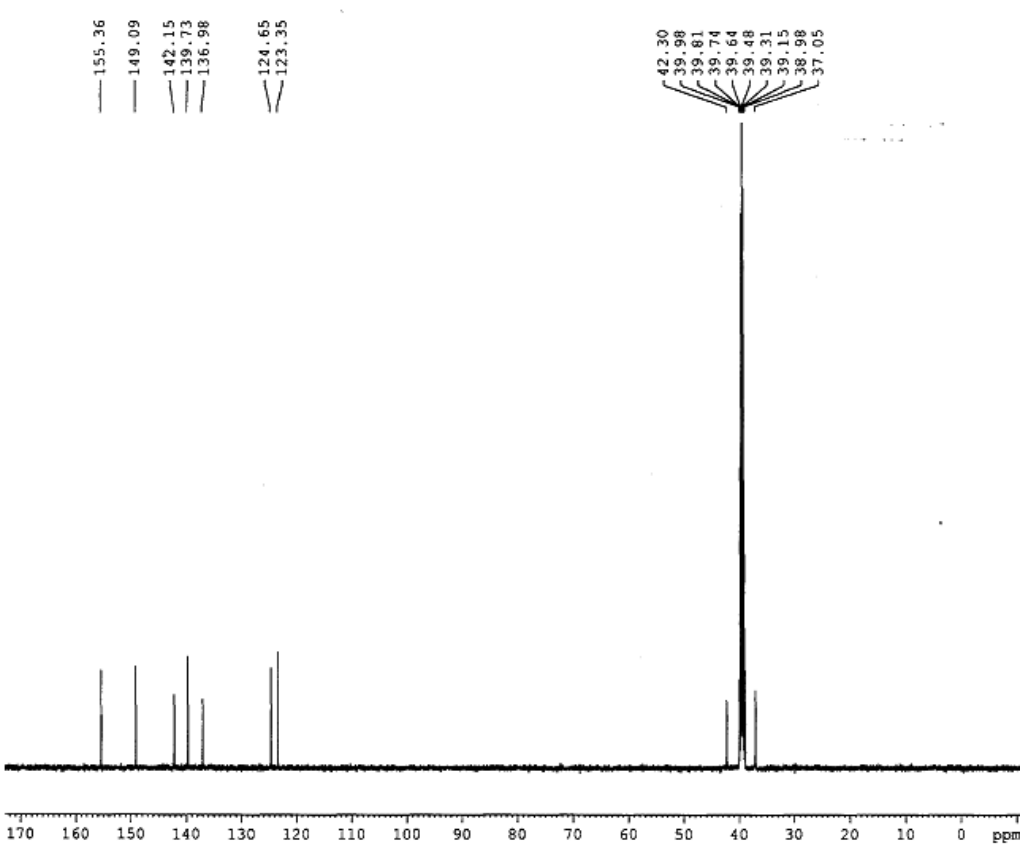



**Figure 2S**. [13]C-NMR (125 MHz) spectrum of **L** in DMSO-$d_6$

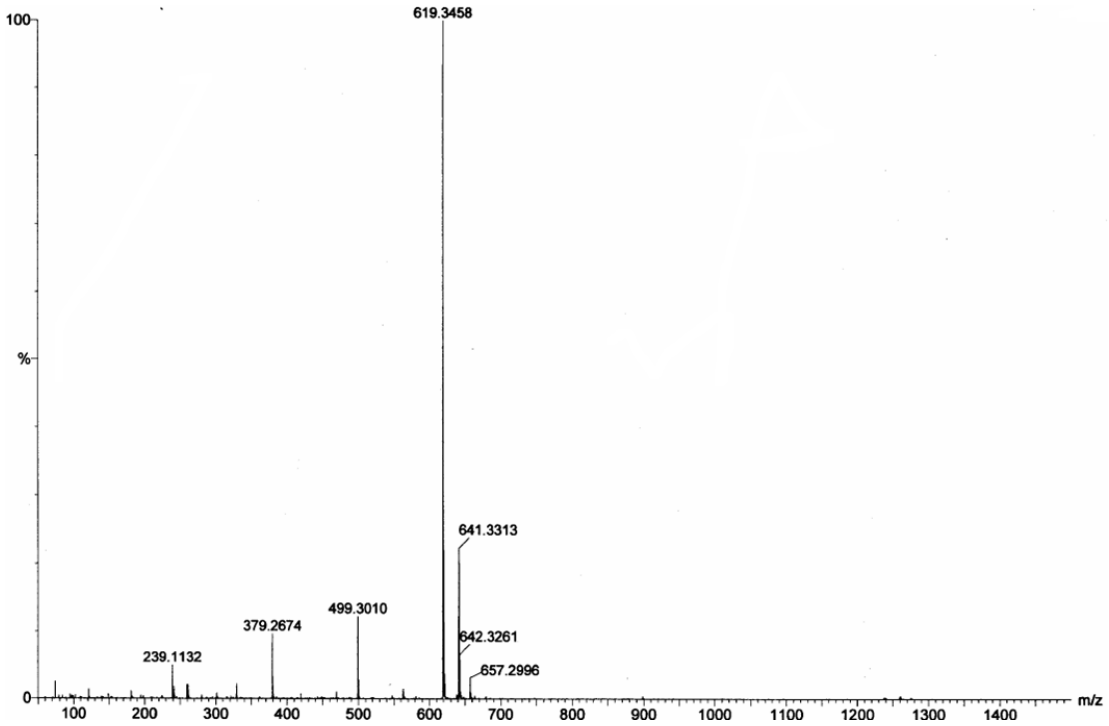



**Figure 3S**. ESI-MS of spectrum of **L**

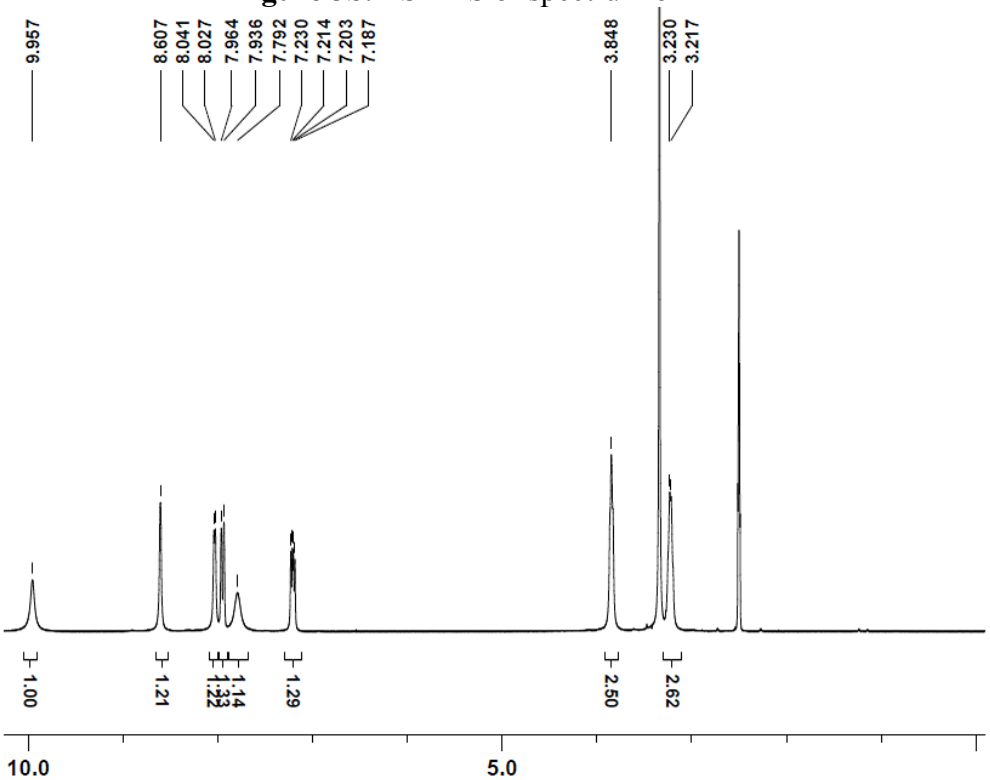



**Figure 4S**. $^{1}$H-NMR spectrum (300MHz) of complex **1**

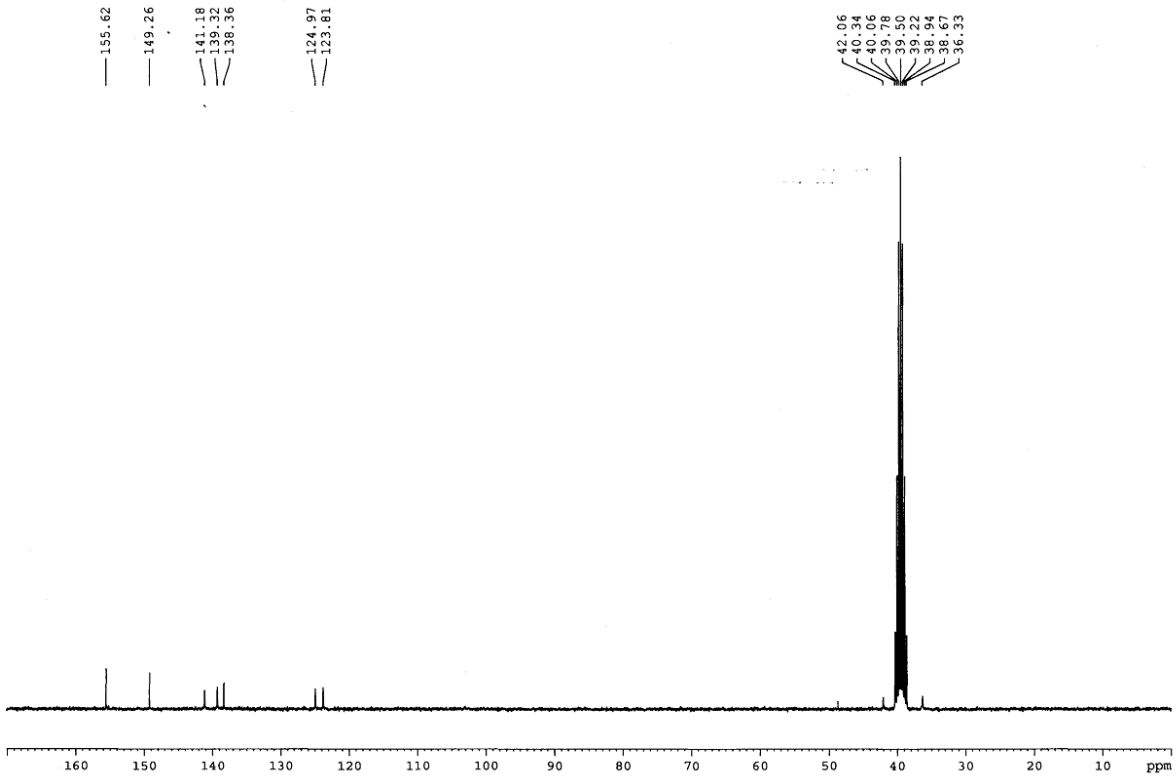



**Figure 5S**. $^{13}$C-NMR (75 MHz) spectrum of complex **1**

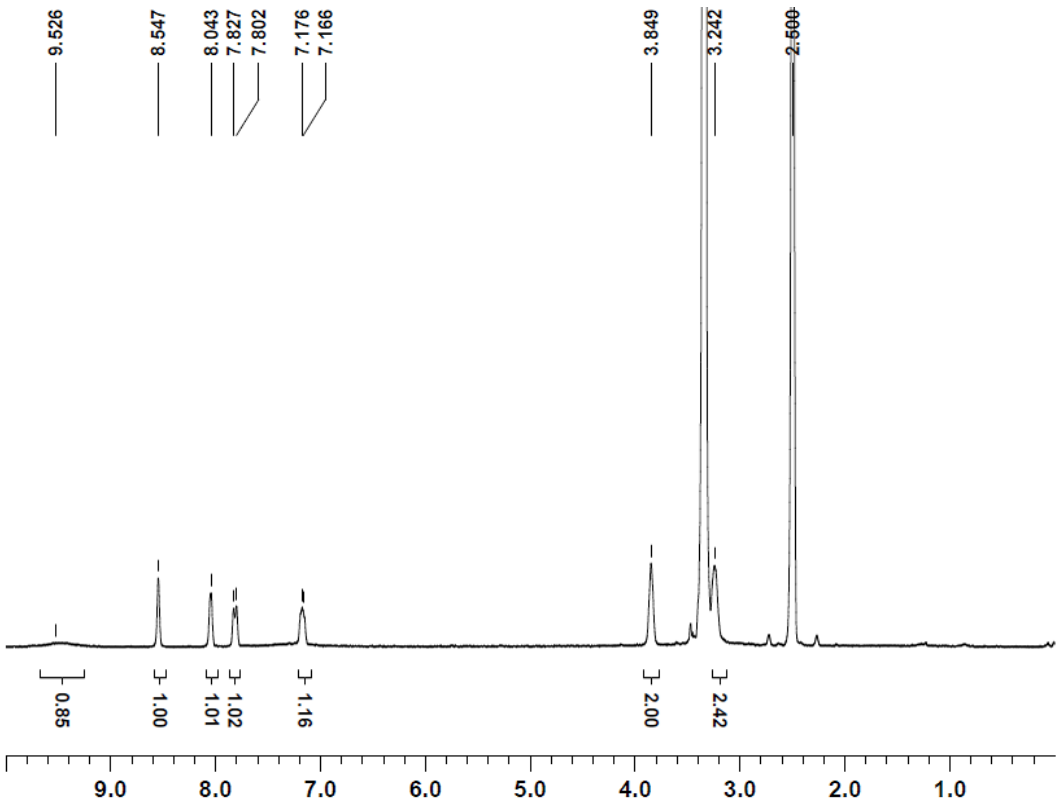



**Figure 6S**. $^{1}$H-NMR (300 MHz) spectrum of complex **2**

**Table 1S**. Crystallographic table for complex **1-2**

| Compound reference | Complex **1** | Complex **2** |
|---|---|---|
| Chemical formula | $C_{216}H_{240}N_{96}O_{140}S_8Zn_8$ | $C_{54}H_{60}MgN_{24}O_{28}S$ |
| Formula Mass | 7200.48 | 1549.63 |
| Crystal system | Trigonal | Triclinic |
| *a*/Å | 26.799(3) | 12.4885(8) |
| *b*/Å | 26.799(3) | 12.5016(9) |
| *c*/Å | 15.7884(18) | 12.9772(9) |
| *α*/° | 90.00 | 66.933(2) |
| *β*/° | 90.00 | 69.943(2) |
| *γ*/° | 120.00 | 68.825(2) |
| Unit cell volume/Å$^3$ | 9819.5(19) | 1689.6(2) |
| Temperature/K | 150(2) | 150(2) |
| Space group | *P***Error!** | *P***Error!** |
| No. of formula units per unit cell, *Z* | 1 | 1 |
| Radiation type | MoKα | MoKα |
| Absorption coefficient, *μ*/mm$^{-1}$ | 0.613 | 0.162 |
| No. of reflections measured | 101126 | 16382 |
| No. of independent reflections | 10157 | 5952 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0712 | 0.0769 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.2638 | 0.2351 |
| Final $R_1$ values (all data) | 0.0859 | 0.1000 |
| Final $wR(F^2)$ values (all data) | 0.2759 | 0.2593 |
| Goodness of fit on $F^2$ | 1.170 | 1.654 |

**Table 2S**. Hydrogen bonding table for complex **1**

| D-H···X | H···X (Å) | D···X (Å) | D-H···X (°) |
|---|---|---|---|
| N1-H1···O4$^{b}$ | 2.09 | 2.93 | 167 |
| N2-H2···O2$^{b}$ | 2.01 | 2.85 | 166 |
| N4-H4···O6$^{a}$ | 2.21 | 3.02 | 157 |
| N5-H5···O5$^{a}$ | 2.04 | 2.87 | 164 |
| N9-H9A···O3$^{a}$ | 2.01 | 2.83 | 158 |
| N10-H10A···O4$^{a}$ | 2.20 | 2.96 | 147 |
| N12-H12···O1$^{c}$ | 2.07 | 2.87 | 153 |
| N13-H13···O4$^{c}$ | 2.22 | 2.99 | 151 |
| *a*: *x, y, z*; *b*: *x, y, z*; *b*: *1-x+y, 1-x, z*; *c*: *x-y, x, -z* | | | |

**Table 3S**. Hydrogen bonding parameters for complex **2**

| D-H···X | H···X (Å) | D···X (Å) | D-H···X (°) |
|---|---|---|---|
| N4-H4···O7$^{a}$ | 2.30 | 2.99 (8) | 138 |
| N4-H4···O8$^{b}$ | 2.01 | 2.86 (7) | 169 |
| N5-H5···O9$^{a}$ | 2.22 | 3.04 (7) | 162 |
| N5-H5···O10$^{a}$ | 2.25 | 2.99 (8) | 144 |
| N7-H7···O7$^{a}$ | 2.31 | 3.03 (7) | 140 |
| N7-H7···O10$^{a}$ | 1.95 | 2.81 (8) | 171 |
| N8-H8···O8$^{a}$ | 2.24 | 3.07 (8) | 162 |
| N8-H8···O9$^{b}$ | 2.17 | 2.94 (7) | 149 |
| N10-H10···O7$^{a}$ | 2.27 | 3.01 (7) | 144 |
| N10-H10···O9$^{b}$ | 2.03 | 2.85 (8) | 160 |
| N11-H11···O8$^{b}$ | 2.24 | 3.02 (7) | 151 |
| N11-H11···O10$^{b}$ | 2.28 | 3.09 (8) | 157 |
| *a*: *x, y, z*; b: *1-x, 1-y, 1-z* | | | |

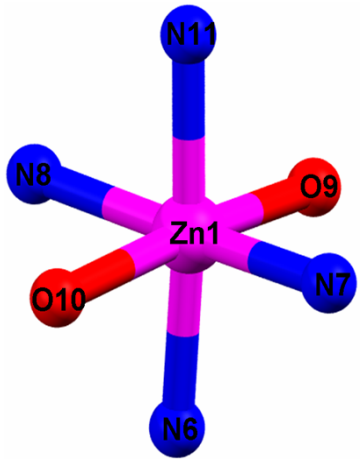



**Figure 7S**. Coordination environment of $Zn^{2+}$ in **1**

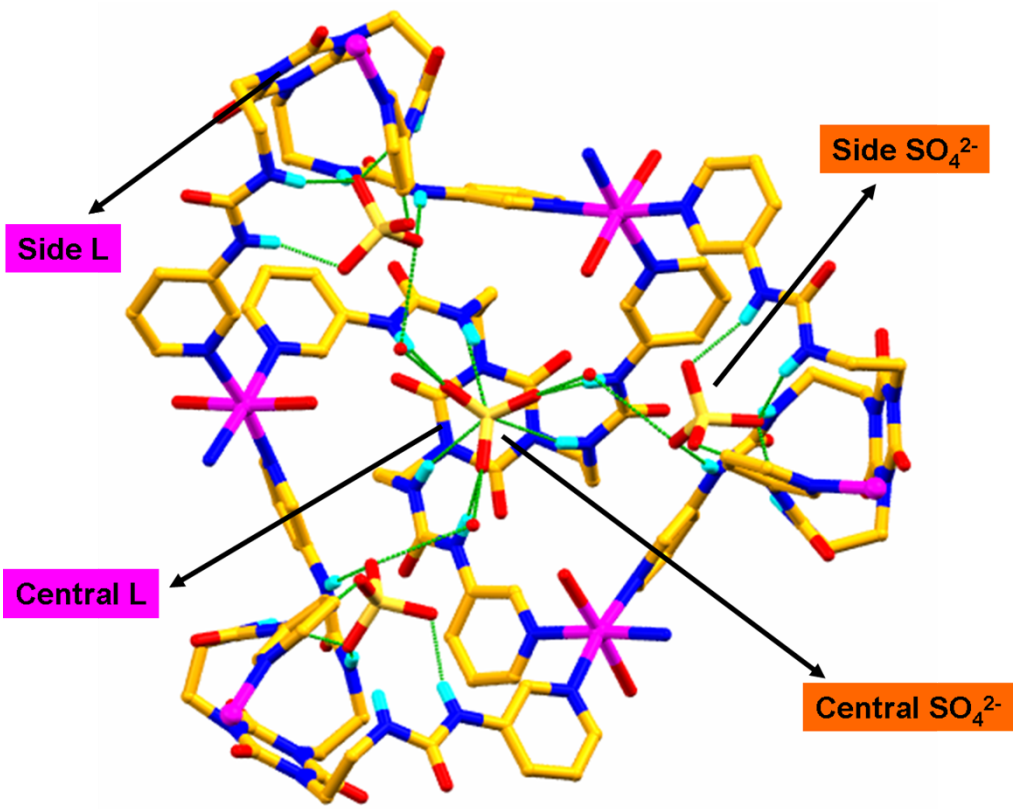



**Figure 8S**: Top view of hydrogen bonding pattern of four $SO_4^{2-}$ with the –NH group of **L**

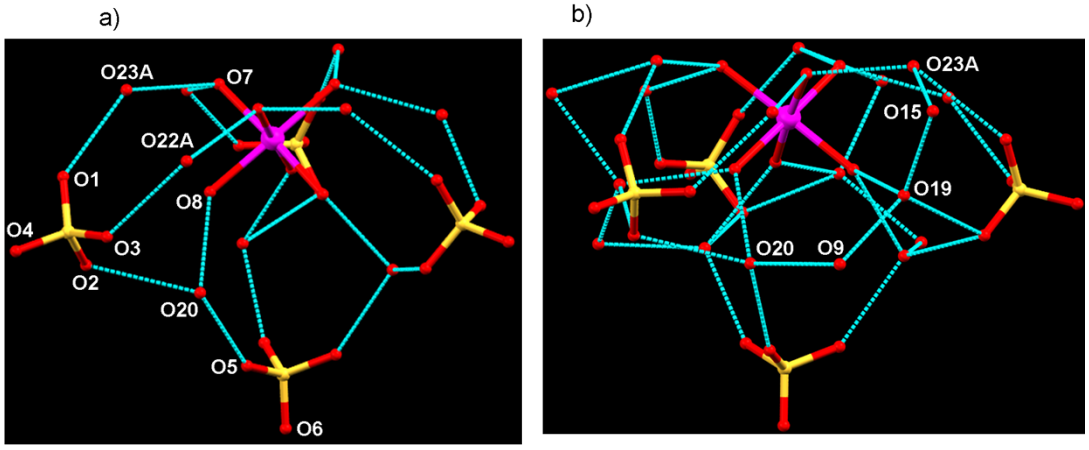



**Figure 9S**. a) View of $Zn(H_2O)_6$ capped $[(SO_4)(H_2O)_{12}]^{8-}$ cluster and b) its interaction with receptor functionality (**O15**) and coordinated water (**O9**)

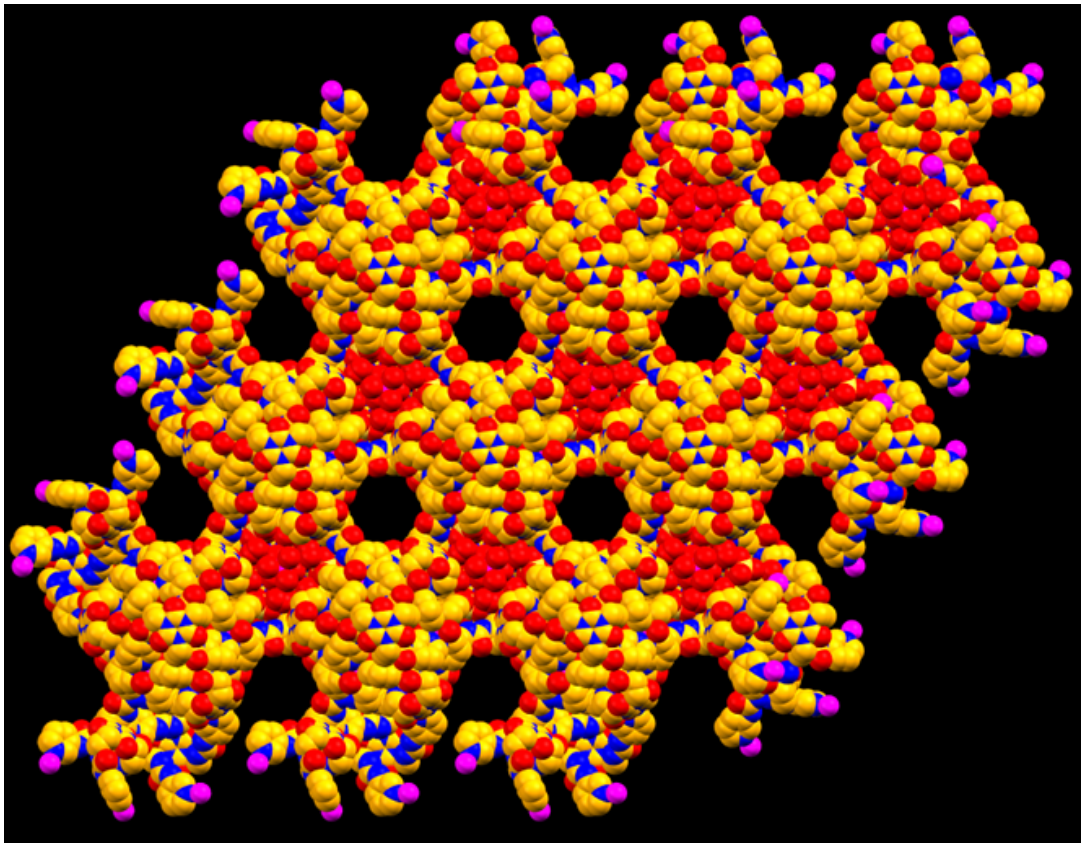


**Figure 10S**. Packing diagram of complex **1** as viewed along *c* axis showing presence of porous channel occupied by disordered solvent molecules (which are removed by squeeze).

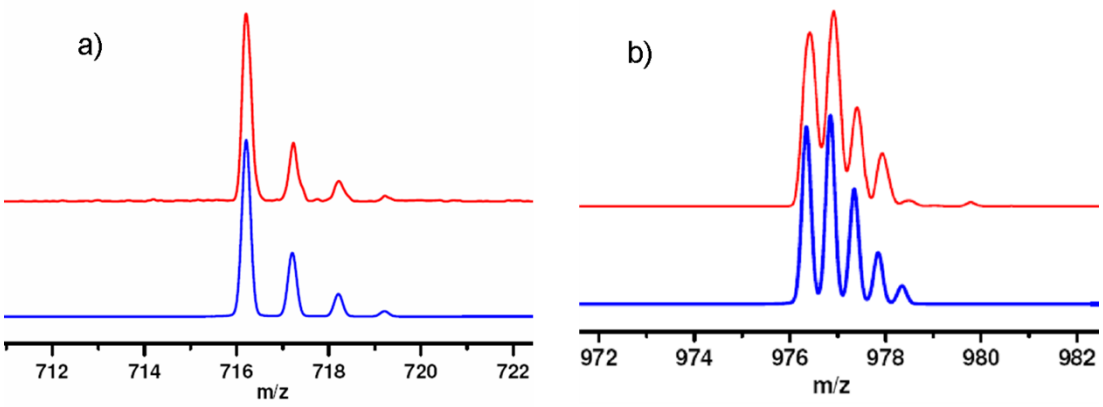



**Figure 11S**. ESI-MS (negative) spectra of complex **1** (red: experimental and blue: calculated) showing similar isotopic distribution pattern.

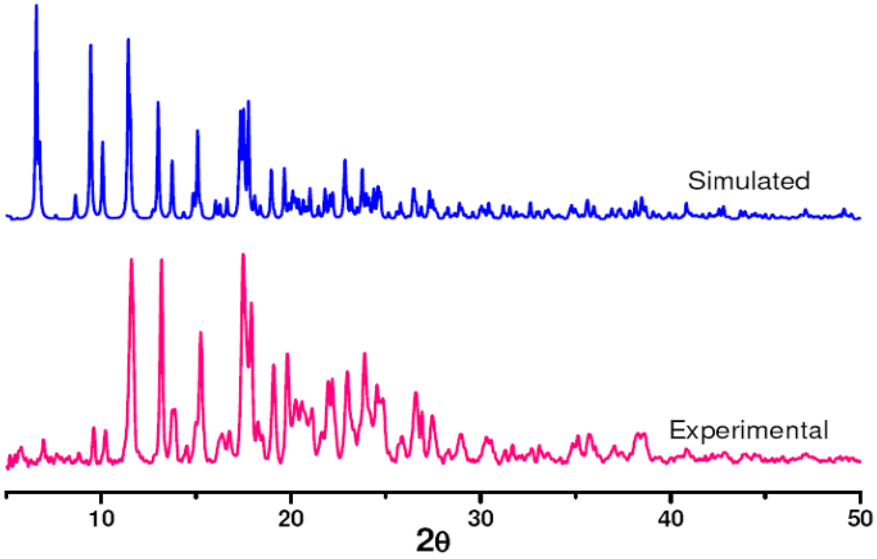



**Figure 12S**. PXRD pattern for complex **1** (simulated and experimental)

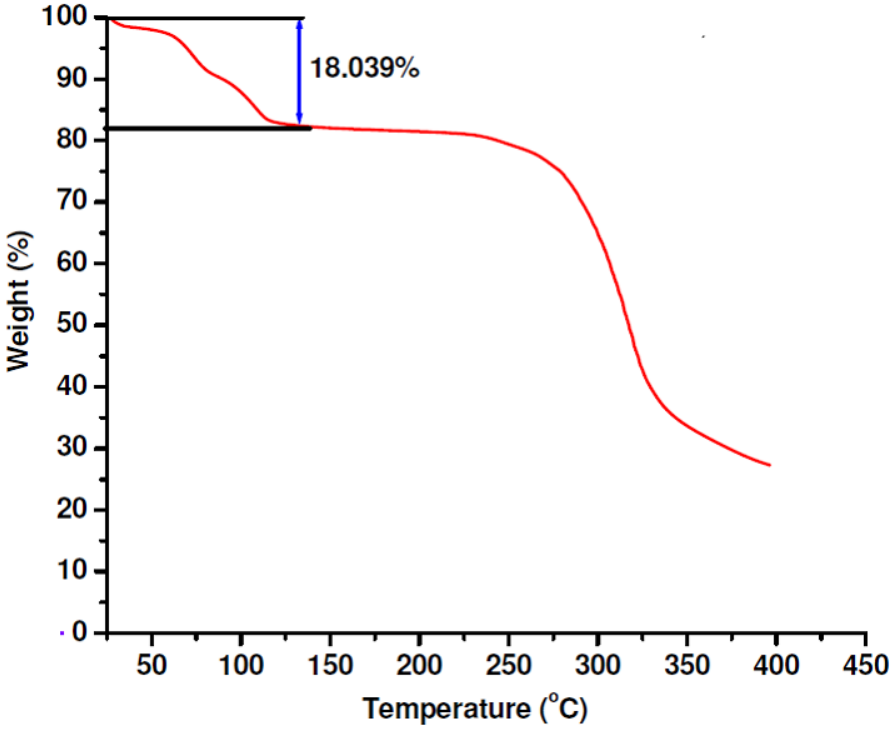



**Figure 13S**. TGA plot of complex **1**. Weight loss of ~18.039% is observed around 130°C for complex **1**. Molecular weight of complex **1**, calculated from CIF and squeezed solvent amount is estimated as ~8126. Amount (weight) of total lattice solvent (including squeezed solvent) is calculated as ~1478. Thus the calculated value is 18.18% which closely matches with the experimental value (18.039%).

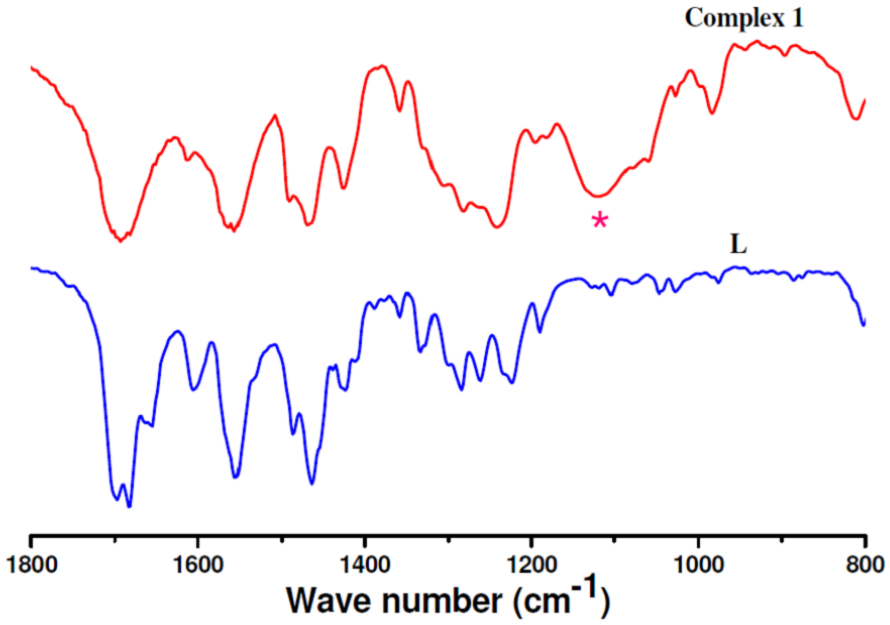



**Figure 14S**: Comparative IR spectra of **L** and complex **1**, showing presence of peak at 1120 $cm^{-1}$

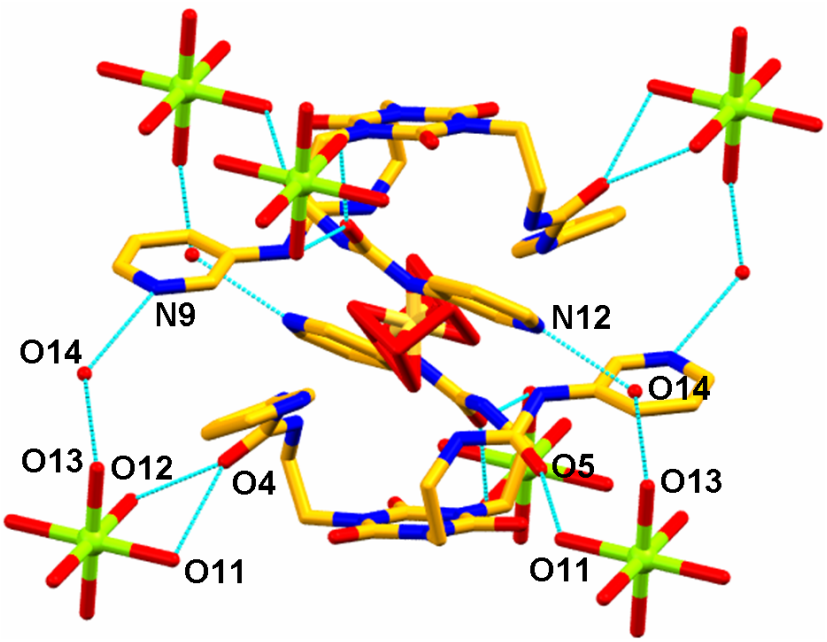



**Figure 15S**. Hydrogen bonding pattern of $[Mg(H_2O)_6]^{2+}$ cluster with the $[\mathbf{L}_2(SO_4)]^{2-}$ capsule in complex **2**

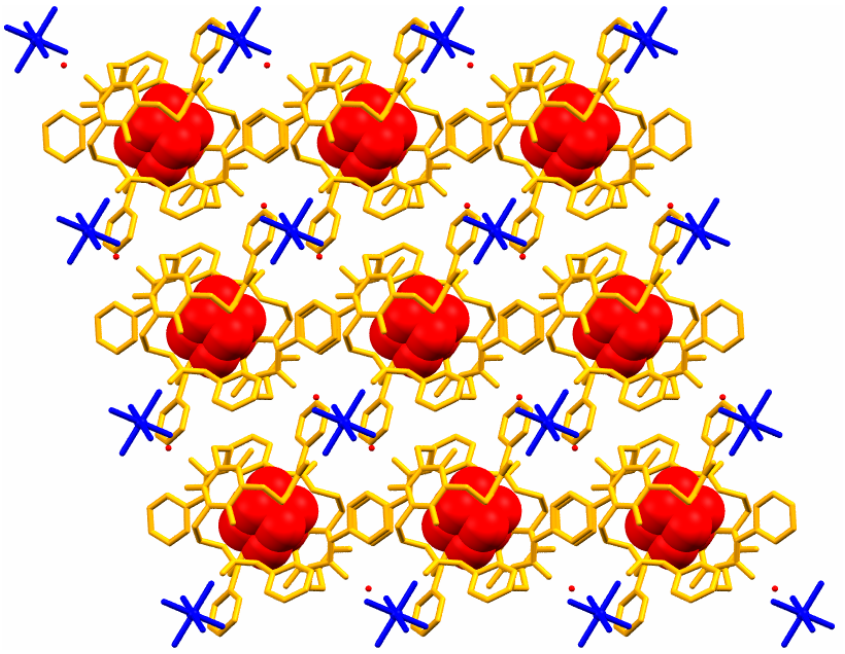


**Figure 16S**. Packing pattern of complex **2** as viewed along *c* axis

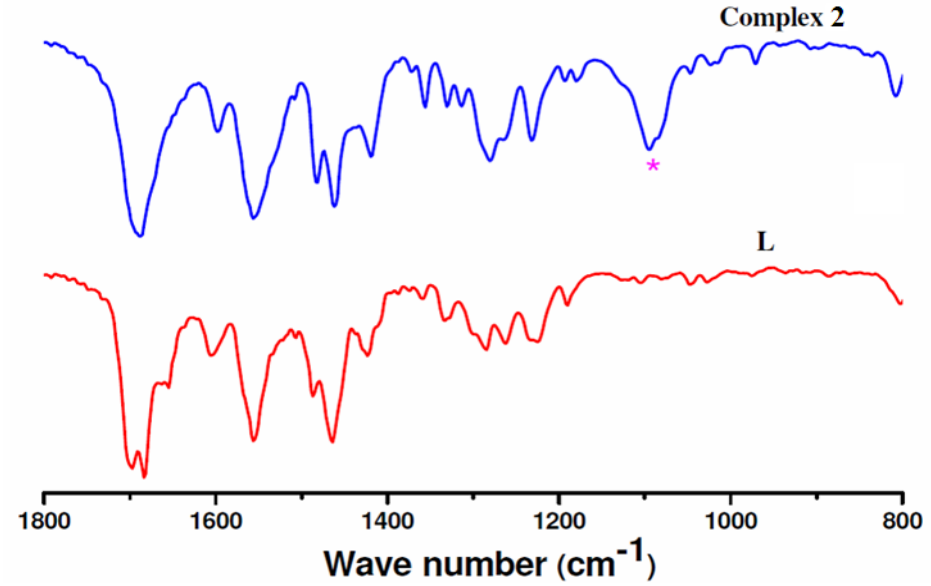



**Figure 17S**. Comparative IR spectra of **L** and complex **2**, showing presence of peak at 1095 $cm^{-1}$ (*) corresponding to the stretching frequency of $SO_4^{2-}$.

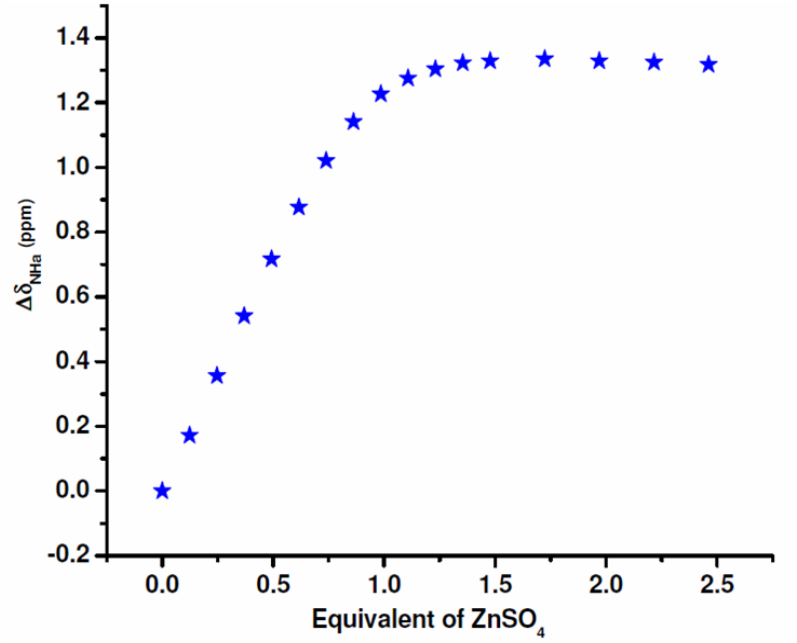



**Figure 18S**. Plot of chemical shift change (NHa) of **L** *vs* equivalent of $ZnSO_4$ in DMSO-$d_6$

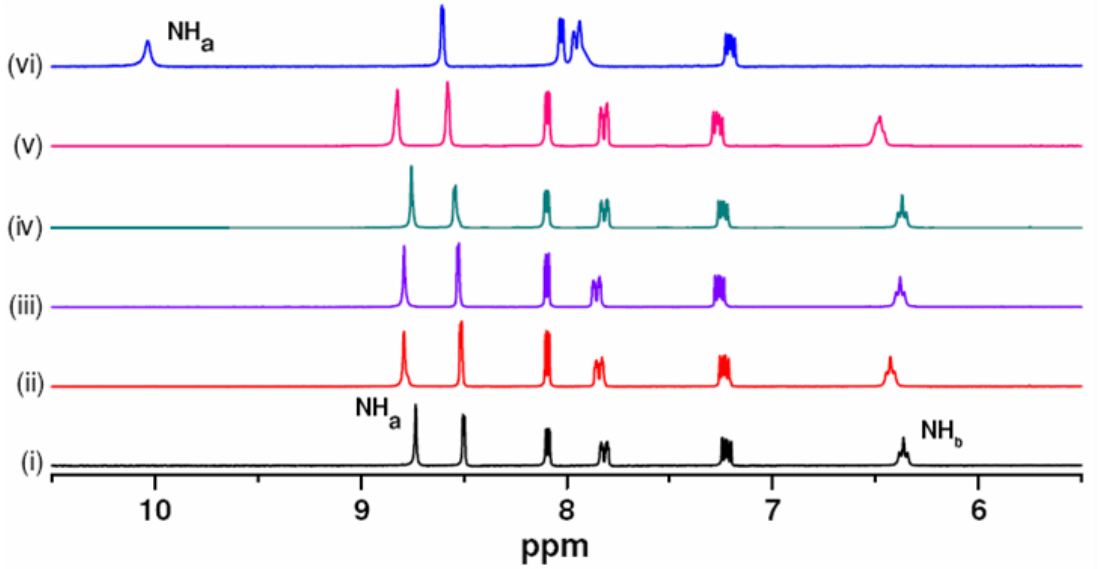



**Figure 19S**. Qualitative $^1$H-NMR spectra of **L** with ~1 equivalent of different Zn-salt in DMSO-$d_6$: i) **L**, ii) $ZnCl_2$, iii) $Zn(NO_3)_2$, iv) $Zn(ClO_4)_2$, v) $Zn(AcO)_2$ and vi) $ZnSO_4$.

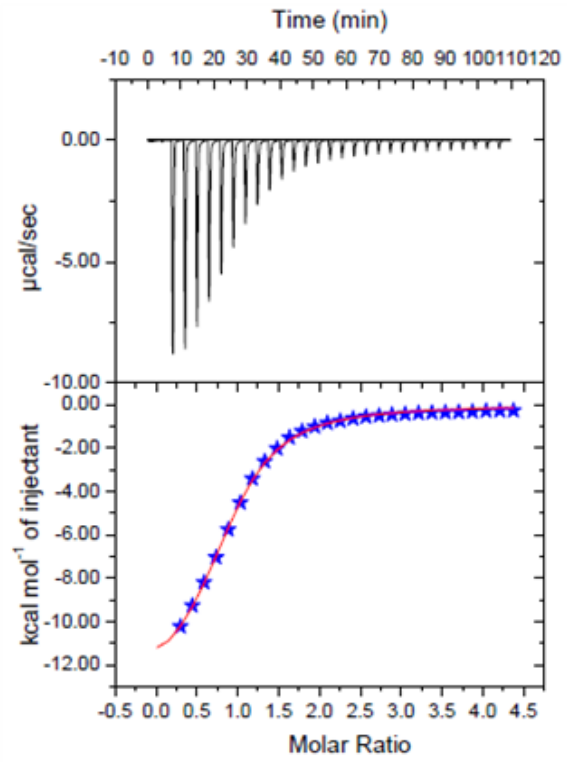



**Figure 20S**. ITC profile for the titration **L** (0.1212 mM) with $ZnSO_4$ (2.5 mM) in DMSO at 298K. The upper panel shows the heat pulses experimentally observed in each titration. The lower panel reports the respective time integrals translating as the heat evolved for each aliquot and its coherence to the 1:1 binding model. $\chi^2$/DoF = 7499, *n* = 0.87±0.01, K = 5.28E4±2.28E3 $M^{-1}$, ΔH = -1.323E4±218.1 cal/mol, TΔS = -6765 cal/mol, ΔG = -6465 cal/mol.

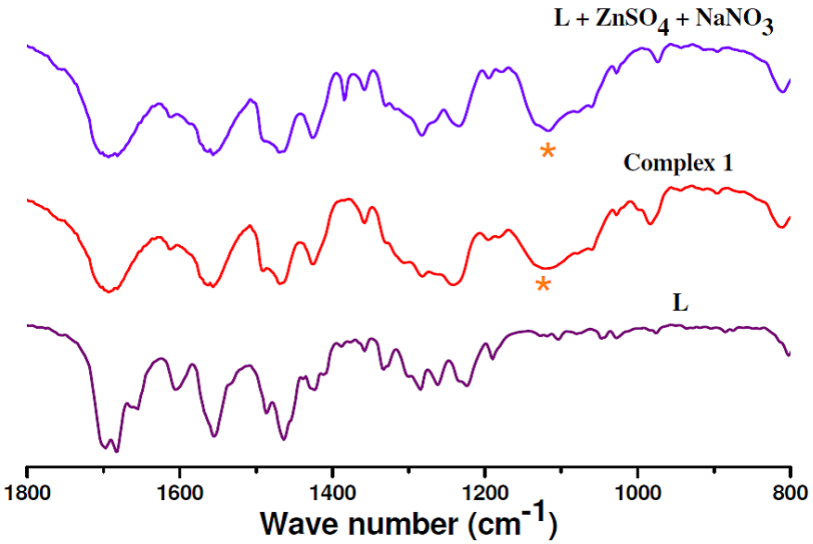



**Figure 21S**. Comparative IR spectra of **L**, complex **1** and crystals isolated from a mixture of **L**, $ZnSO_4$ and $NaNO_3$, suggesting formation of complex 1 in presence of excess $NO_3^-$ (10 equivalent).

**References**

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