# Electronic Supplementary Information (ESI)

# Sulfate ion encapsulation in caged supramolecular structures assembled by second-sphere coordination

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## S1. Experimental

### S1.1 General:

$^1$H NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal (DMSO-$d_6$ 2.50 ppm for $^1$H). IR spectra were carried out using a Nicolet AVATAR 360 FT-IR spectrometer as KBr disks. Elemental analyses were done on a VarioEL from Elementaranalysensysteme GmbH. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer with methanol/water being the solvent. Melting points were detected on an X-4 Digital Vision MP Instrument.

### S1.2 Synthesis of L:

To a solution of 3-isocyanatopyridine (0.43 g, 3.6 mmol) in toluene (5 mL) was added tris(2-aminoethyl)amine (0.15 g, 1.0 mmol). A mass of precipitate appeared immediately. The reaction mixture was stirred at 60 °C for 1 h, and cooled to room temperature before filtration. The crude solid was purified by recrystallization from $C_2H_5OH/H_2O$ (1:4) as colorless crystals. Yield: 0.48 g (92%). M.p. 175 °C. Anal. Found: C 57.10, H 5.74, N 27.51; Calcd for $C_{24}H_{30}N_{10}O_3$ (506.57): C 56.91, H 5.97, N

27.65%. ESI-MS: $m/z$ 507 ([L+H$^+$]$^+$). $^1$H NMR (DMSO-$d_6$), $\delta$ = 2.63 (t, $J$ = 6.4 Hz, 6H, N-C$H_2$-), 3.22 (dd, $J$ = 12.0, 6.4 Hz, 6H, urea-C$H_2$-), 6.33 (t, $J$ = 5.6 Hz, 3H, N*H*), 7.24 (dd, $J$ = 8.4, 4.4 Hz, 3H, Py-*H*5), 7.88 (dd, $J$ = 6.4, 1.6 Hz, 3H, Py-*H*4), 8.11 (dd, $J$ = 4.4, 1.6 Hz, 3H, Py-*H*6), 8.53 (d, $J$ = 2.4 Hz, 3H, Py-*H*2), 8.77 ppm (s, 3H, N*H*). $^{13}$C NMR (DMSO-$d_6$), $\delta$ 37.63 (N-*C*$H_2$-), 53.78 (urea-*C*$H_2$-), 123.37 (Py-*C*5), 124.51 (Py-*C*4), 137.09 (Py-*C*3), 139.61 (Py-*C*2), 142.07 (Py-*C*6), 155.20 ppm (*C*=O). FT-IR (cm$^{-1}$): 3329, 3267, 2829, 1646, 1567, 1472, 1253, 811, 708.

### S1.3 IR and $^1$H NMR spectra of compounds 1 and 2:

***[Mn(H$_2$O)$_6$] [SO$_4$⊂L$_2$] (1)*:** FT-IR (KBr, cm$^{-1}$): 3295, 2819, 1668, 1552, 1484, 1292, 1093, 1066, 1048, 802, 707, 606.

***[Zn(H$_2$O)$_6$] [SO$_4$⊂L$_2$] (2)*:** $^1$H NMR (DMSO-$d_6$): $\delta$ = 2.54 (t, $J$ = 1.6 Hz, 6H, N-CH$_2$-), 3.16 (dd, $J$ = 4.8, 1.6 Hz, 6H, urea-CH$_2$-), 7.31 (s, 3H, NH), 7.12 (dd, $J$ = 8.0, 4.4 Hz, 3H, Py-H5), 7.91 (dd, $J$ = 8.4, 1.6 Hz, 3H, Py-H4), 8.03 (d, $J$ = 4.4 Hz, 3H, Py-H6), 8.71 (d, $J$ = 1.6 Hz, 3H, Py-H2), 9.49 ppm (s, 3H, NH). FT-IR (KBr, cm$^{-1}$): 3295, 2819, 1668, 1553, 1483, 1291, 1093, 1066, 1048, 802, 708, 606.

## S2. Results and Discussion

### S2.1 X-ray crystal structure of L:

The tris(3-pyridylurea) compound L crystallizes with 0.3 equivalent of water, $C_{24}H_{30}N_{10}O_3 \cdot 0.3H_2O$ (Fig. S1a). There are two intramolecular N−H···O hydrogen bonds between the urea NH and C=O groups of two ligand arms, and an intramolecular π-π stacking interaction between two pyridyl rings (Fig. S1b). The extended structure of L shows a 1D chain formed by eight bifurcated intermolecular urea···urea hydrogen bonds around each L molecule. The parameters for the π-π stacking interaction are: dihedral angle 8.97°, centroid-centroid distance 3.637 Å. The intra- and intermolecular hydrogen bond parameters are given in Table S1.

**Table S1**. Hydrogen bonding parameters (Å, °) in **L**.

| N−H···O | H···O | N···O | ∠N−H···O |
|---|---|---|---|
| Intra- | | | |
| N5−H5B···O1 | 2.14 | 2.927(2) | 151 |
| N6−H6A···O1 | 2.05 | 2.858(2) | 157 |
| Inter- | | | |
| N8−H8C···O2$^{a}$ | 2.09 | 2.901(2) | 158 |
| N9−H9B···O2$^{a}$ | 2.16 | 2.923(2) | 148 |
| N2−H2B···O3$^{b}$ | 2.06 | 2.898(2) | 164 |
| N3−H3B···O3$^{b}$ | 2.40 | 3.164(2) | 148 |

Symmetrical codes: $^{a}$ -x+0.5, -y+1.5, -z; $^{b}$ -x, -y+1, -z

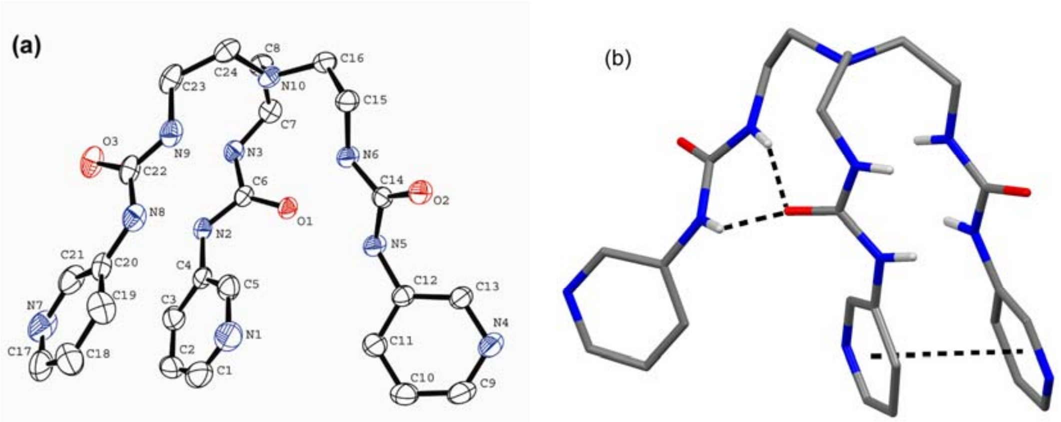

**Fig. S1** The crystal structure of the ligand L. (a) Molecular structure with atomic labeling; (b) The intramolecular hydrogen bonds and π-π stacking interaction.

## S2.2 Hydrogen bond data and ESI-MS spectrum of complex 2:

**Table S2**. Hydrogen bonding parameters (Å, °) for $SO_4^{2-}$ binding in **2**

| N−H···O | H···O | N···O | ∠N−H···O |
|---|---|---|---|
| N2−H2A···O8 | 2.23 | 3.035(3) | 155 |
| N2'−H2A···O9 | 2.18 | 2.974(3) | 154 |
| N3−H3A···O7 | 2.29 | 3.144(4) | 173 |
| N3'−H3A···O9 | 2.38 | 3.138(4) | 147 |
| N5−H5A···O9 | 2.34 | 2.971(4) | 130 |
| N5'−H5A···O10 | 1.96 | 2.818(4) | 178 |
| N6−H6A···O7 | 2.11 | 2.948(4) | 166 |
| N8−H8A···O10 | 2.17 | 2.939(4) | 149 |
| N8'−H8A···O8 | 2.09 | 2.911(3) | 159 |
| N9−H9A···O7 | 2.25 | 3.106(4) | 175 |
| N9'−H9A···O9 | 2.42 | 3.163(4) | 146 |
| N5'−H5A···O8 | 2.72 | 3.246(3) | 120 |
| N6'−H6A···O10 | 2.73 | 3.419(4) | 138 |
| N5−H5A···O7 | 2.59 | 3.303(4) | 141 |
| N9'−H9A···O8 | 2.62 | 3.328(3) | 141 |
| N6'−H6A···O8 | 2.67 | 3.311(4) | 132 |

Symmetry code: -x, 1-y, 1-z

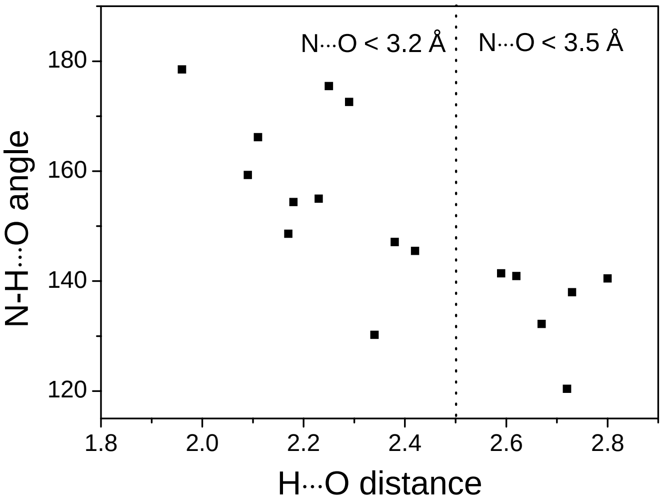

**Fig. S2** The scatterplot of N−H···O angle versus H···O distance of the hydrogen bonds (including the weaker contacts) in compound **2**.

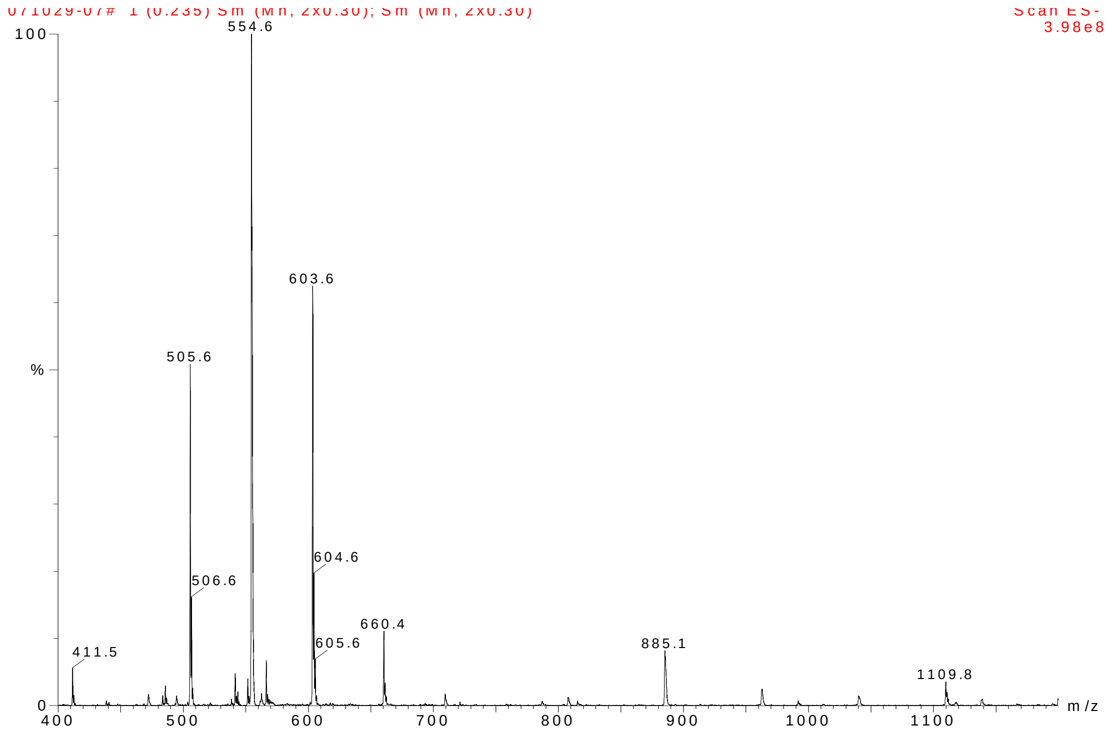

**Fig. S3** Negative-ion mode ESI-MS spectrum of $[Zn(H_2O)_6]$ $[SO_4\subset L_2]$ (**2**).