

# Efficient and Selective Separation of Aqueous Sulfate through Recognition and Precipitation

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## Electronic Supporting Information

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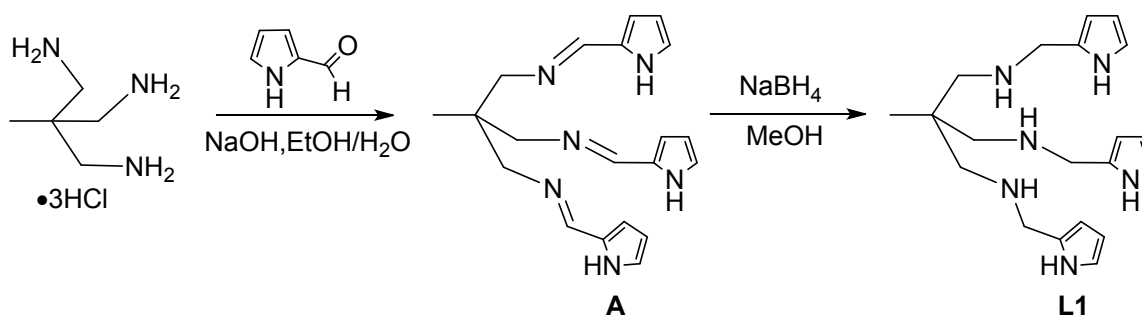
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## Materials and Methods

### General Information

Commercially available chemicals were purchased from Aldrich or Acros, and used as received. Organic compounds 1,1,1-Tris(aminomethyl)ethane trihydrochloride<sup>1</sup> and pyrrole-2-carboxaldehyde,<sup>2</sup> were prepared according to published procedure. Solution <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectra were collected on a Bruker Avance 300 spectrometer. Infrared spectra were recorded on a Bio-Rad FTS-185 instrument using KBr discs. The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II diffractometer with graphite monochromated Mo K<sub>α</sub> radiation ( $\lambda = 0.71073\text{\AA}$ ). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against  $F^2$  with SHELXL-97.<sup>3</sup> Tables of neutral atom scattering factors,  $f'$  and  $f''$ , and absorption coefficients are from a standard source.<sup>4</sup> All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Crystallographic data collection and refinement parameters of complexes [H<sub>2</sub>L1][SO<sub>4</sub>], [HL2]<sub>2</sub>[SO<sub>4</sub>], and [HL2][AcO] were listed in Table S1. The crystal structure of [HL2]<sub>2</sub>[SO<sub>4</sub>] contains heavily disordered water molecules in the void spaces. These disordered solvent molecules were not further identified or refined. Instead, a new set of  $F^2$  (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON program.<sup>5</sup> Elemental analyses and MS spectrometry were performed on a Heraeus CHN-OS Rapid Elemental Analyzer and JEOL JMX-SX/SX 102A Mass Spectrometer at the Instruments Center of National Chung Hsing University, Taiwan. DFT calculations were performed on the *Gaussian 03* program.<sup>6</sup> The geometry optimizations were conducted using the BP86 functional and 6-31G\*\* basis sets.

### Synthesis of precursor A and L1:

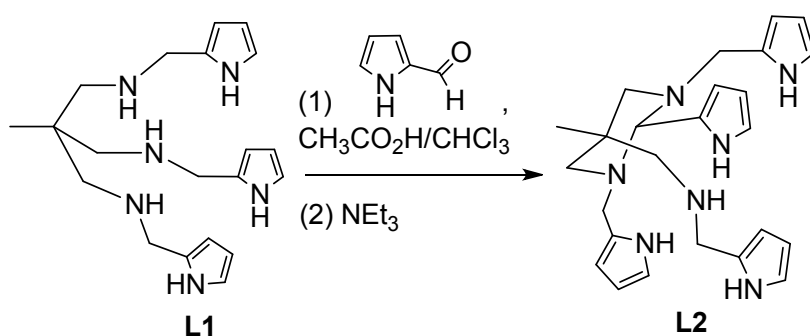


**Synthesis of precursor A:** A stirring solution containing compound 1,1,1-Tris(aminomethyl)ethane trihydrochloride (1.3 g, 5.74 mmol) and sodium hydroxide (1.5 g, 37.5 mmol) in distilled water (150 ml) was added with a solution of pyrrole-2-carboxaldehyde (3.3 g, 34.7 mmol) in ethanol (10 ml). After the resultant solution was stirred at room temperature for 12 hrs, the yellow precipitated powder (precursor A) was isolated (1.39 g, 70 %) by filtration, washed with distilled water twice, and dried under vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 300K):  $\delta$  7.84 (s, 3H, NCHC<sub>4</sub>H<sub>3</sub>NH), 6.80 (s, 3H, NHC<sub>4</sub>H<sub>3</sub>), 6.33 (t, 3H, NHC<sub>4</sub>H<sub>3</sub>), 6.20 (t, 3H, NHC<sub>4</sub>H<sub>3</sub>), 3.52 (s, 6H, CCH<sub>2</sub>N), 0.91 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 300K):  $\delta$  153.39,

129.87, 122.29, 114.83, 109.30, 65.85, 41.36, 21.11. IR (KBr,  $\nu_{\max}/\text{cm}^{-1}$ ): 1660 (C=N). HRMS Calcd for  $\text{C}_{20}\text{H}_{25}\text{N}_6$   $[\text{M}+\text{H}]^+$ :  $m/z$  349.2141. Found: 349.2138 (100).

**Synthesis of L1:** Compound A (0.70 g, 2.01 mmol) dissolved in ethanol (50 ml) was added with a batch of  $\text{NaBH}_4$  (0.38 g, 10.1 mmol), and the resultant mixture was stirred at room temperature for 12 hrs. The mixture was dried under vacuum, and extracted with  $\text{CH}_2\text{Cl}_2$  and distilled water. The combined  $\text{CH}_2\text{Cl}_2$  portions were vacuum dried to afford a light-yellow oil (0.56 g, 79%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 300K):  $\delta$  9.06 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.68 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.21 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.09 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 3.77 (s, 6H,  $\text{NHCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.60 (s, 6H,  $\text{CCH}_2\text{NH}$ ), 0.91 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 300K):  $\delta$  130.73, 117.24, 107.97, 106.00, 56.12, 46.94, 38.15, 22.06. HRMS Calcd for  $\text{C}_{20}\text{H}_{31}\text{N}_6$   $[\text{M}+\text{H}]^+$ :  $m/z$  355.2610. Found: 355.2619 (100).

### Synthesis of L2:



A stirring solution containing L1 (0.407 g, 1.148 mmol) and acetic acid (0.069 g, 1.148 mmol) in  $\text{CHCl}_3$  (30 ml) was added with a batch of pyrrole-2-carboxaldehyde (0.109 g, 1.148 mmol). After the resultant solution was stirred at room temperature for 12 hrs, the mixture was added with trimethylamine (10 ml) and stirred for another 1 hrs. The solution was extracted with distilled water three times (15 ml). The extracted  $\text{CHCl}_3$  portions were vacuum dried, washed with hexane, and vacuum dried to afford a light-yellow solid (0.288 g, 58%).  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 300 MHz, 300K):  $\delta$  11.12 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 10.44 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 9.48 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 7.04 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.84 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.74 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.29 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.14 (d, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.04 (d, 4H,  $\text{C}_4\text{H}_3\text{NH}$ ), 5.95 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 3.79 (s, 2H,  $\text{NHCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 3.74 (s, 1H,  $\text{NCHN}$ ), 3.69 (d, 2H,  $\text{NCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.95 (d, 2H,  $\text{CCH}_2\text{N}$ ), 2.84 (d, 2H  $\text{NCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.56 (s, 2H,  $\text{CCH}_2\text{NH}$ ), 2.17 (d, 2H,  $\text{CCH}_2\text{N}$ ), 0.74 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 75 MHz, 300K):  $\delta$  127.02, 126.11, 120.94, 119.92, 118.93, 112.61, 111.23, 108.43, 107.90, 107.82, 107.53, 81.93, 62.03, 57.16, 50.32, 45.17, 31.54, 23.26. HRMS Calcd for  $\text{C}_{25}\text{H}_{34}\text{N}_7$   $[\text{M}+\text{H}]^+$ :  $m/z$  432.28702. Found: 432.28699 (100).

### Synthesis and crystallization of $[\text{HL2}][\text{AcO}]$ :

A stirring solution containing L1 (0.15 g, 0.423 mmol) and acetic acid (0.026 g, 0.423 mmol) in  $\text{CHCl}_3$  (30 ml) was added with a batch of pyrrole-2-carboxaldehyde (0.04 g, 0.423 mmol). After the resultant solution was stirred at room temperature for 12 hrs, the mixture was extracted with  $\text{CHCl}_3$  and distilled water three times. The combined  $\text{CHCl}_3$  portions were vacuum dried, washed with hexane, and vacuum dried to afford a light-yellow solid (0.12 g, 60%). Yellow crystals suitable for X-ray diffraction analysis were obtained by

slow diffusion of pentane into  $\text{CHCl}_3$  solution of compound  $[\text{HL2}][\text{AcO}]$  at  $4^\circ\text{C}$  for two weeks.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 300K):  $\delta$  11.36 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 11.15 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 9.89 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.98 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.88 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.77 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.30 (s, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.15 (d, 1H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.07 (d, 4H,  $\text{C}_4\text{H}_3\text{NH}$ ), 5.98 (s, 2H,  $\text{C}_4\text{H}_3\text{NH}$ ), 3.78 (s, 2H,  $\text{N}^+\text{H}_2\text{CH}_2\text{C}_4\text{H}_3\text{NH}$ ), 3.71 (s, 1H,  $\text{NCHN}$ ), 3.62 (d, 2H,  $\text{NCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.92 (d, 2H,  $\text{CCH}_2\text{N}$ ), 2.87 (d, 2H  $\text{NCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.54 (s, 2H,  $\text{CCH}_2\text{N}^+\text{H}_2$ ), 2.15 (d, 2H,  $\text{CCH}_2\text{N}$ ), 0.73 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 300K):  $\delta$  180.69, 127.32, 126.41, 120.85, 120.48, 120.41, 118.71, 112.17, 111.01, 108.27, 107.75, 107.64, 107.45, 82.24, 62.09, 56.53, 50.42, 44.95, 31.46, 25.09, 23.54. IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3338 (NH). Elem Anal. Calcd (%) for  $\text{C}_{27}\text{H}_{37}\text{N}_7\text{O}_2$ : C, 65.96; H, 7.59; N, 19.94. Found: C, 66.00; H, 7.56; N, 19.90. ESI-MS Calcd for  $\text{C}_{25}\text{H}_{34}\text{N}_7$   $[\text{M}+\text{H}]^+$ :  $m/z$  432.29. Found: 432.3.

#### Synthesis and crystallization of $[\text{H}_2\text{L1}][\text{SO}_4]$ :

To a string solution containing **L1** (0.100g, 0.282mmol) and acetic acid (0.017g, 0.282mmol) in ethanol (15 ml), a batch of  $[\text{But}_4\text{N}][\text{HSO}_4]$  (0.096 g, 0.282 mmol) was added. After the resultant solution was stirred at RT for 30 mins, the white precipitates were separated, washed with ethanol (20 ml) three times, and vacuum dried to afford white solids (0.091 g, 71%). Colorless crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into distilled water solution of compound  $[\text{H}_2\text{L1}][\text{SO}_4]$  at  $4^\circ\text{C}$  for two weeks.  $^1\text{H}$  NMR ( $d^6$ -DMSO, 300 MHz, 300K):  $\delta$  11.60 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.72 (t, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.04 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 5.95 (q, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 3.90 (s, 6H,  $\text{NHCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.88 (s, 6H,  $\text{CCH}_2\text{NH}$ ), 0.90 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $d^6$ -DMSO, 75 MHz, 300K):  $\delta$  124.65, 118.87, 109.27, 107.41, 53.37, 44.91, 35.64, 20.91, 13.64. IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1119, 1470 (O=S=O). Elem Anal. Calcd (%) for  $\text{C}_{20}\text{H}_{32}\text{N}_6\text{O}_4\text{S}$ : C, 53.08; H, 7.13; N, 18.57. Found: C, 52.97; H, 6.72; N, 18.42.

#### Synthesis of $[\text{H}_2\text{L1}][\text{HPO}_4]$ or $[\text{HL1}][\text{H}_2\text{PO}_4]$ :

To a string solution containing **L1** (0.100g, 0.282mmol) and acetic acid (0.017g, 0.282mmol) in ethanol (15 ml), a batch of  $[\text{But}_4\text{N}][\text{H}_2\text{PO}_4]$  (0.096 g, 0.282 mmol) was added. After the resultant solution was stirred at RT for 30 mins, the white precipitates were separated, washed with ethanol (20 ml) three times, and vacuum dried to afford white solids (0.045 g, 35%).  $^1\text{H}$  NMR ( $d^6$ -DMSO, 300 MHz, 300K):  $\delta$  11.51 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 6.69 (t, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 5.98 (s, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 5.92 (t, 3H,  $\text{C}_4\text{H}_3\text{NH}$ ), 3.83 (s, 6H,  $\text{NHCH}_2\text{C}_4\text{H}_3\text{NH}$ ), 2.69 (s, 6H,  $\text{CCH}_2\text{NH}$ ), 0.84 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $d^6$ -DMSO, 75 MHz, 300K):  $\delta$  126.01, 118.89, 108.82, 107.62, 53.64, 45.22, 36.25, 21.06. IR (KBr,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1072 (P=O). Elem Anal. Calcd (%) for  $\text{C}_{20}\text{H}_{33}\text{N}_6\text{O}_4\text{P}$ : C, 53.09; H, 7.35; N, 18.57. Found: C, 53.08; H, 7.35; N, 18.58.

#### Synthesis and crystallization of $[\text{HL2}]_2[\text{SO}_4]$ :

*Method 1:* To a stirring solution of Pyrrole-2-carboxaldehyde (0.15 g, 1.58 mmol) and  $[\text{But}_4\text{N}][\text{HSO}_4]$  (0.54 g, 1.59 mmol) in 95% ethanol<sub>(aq)</sub> (15 ml), a batch of compound **L1** (0.53 g, 1.50 mmol) was added. After the solid was completely dissolved, the solution was stand aerobically at room temperature for 4 days. Light-yellow crystals of compound  $[\text{HL2}]_2[\text{SO}_4]$  suitable for X-ray diffraction analysis were obtained (0.41 g, 57 %). This product (0.40 g, 55%) in the form of white precipitates was also obtained from Pyrrole-2-

carboxaldehyde (0.15 g, 1.58 mmol), Na<sub>2</sub>SO<sub>4</sub> (0.22 g, 1.58 mmol) and **L1** (0.53 g, 1.50 mmol) in 50% ethanol<sub>(aq)</sub> (15 ml).

*Method 2:* To a stirring solution of [But<sub>4</sub>N][HSO<sub>4</sub>] (0.075 g, 0.220 mmol) in 95% ethanol<sub>(aq)</sub> (15 ml), a batch of compound **L2** (0.095 g, 0.220 mmol) was added. After the resultant solution was stirred at RT for 30 mins, the white precipitates were separated, washed with ethanol (20 ml) three times, and vacuum dried to afford white solids (0.088 g, 83%). This product (0.082 g, 78 %) in the form of white precipitates was also obtained from Na<sub>2</sub>SO<sub>4</sub> (0.065 g, 0.458 mmol) and **L2** (0.095 g, 0.220 mmol) in 50% ethanol<sub>(aq)</sub>.

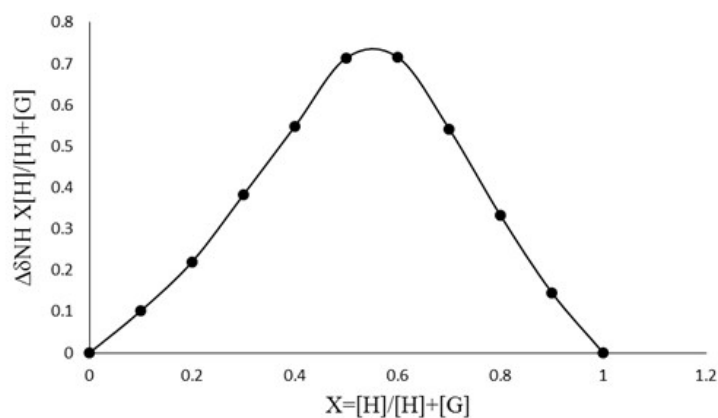
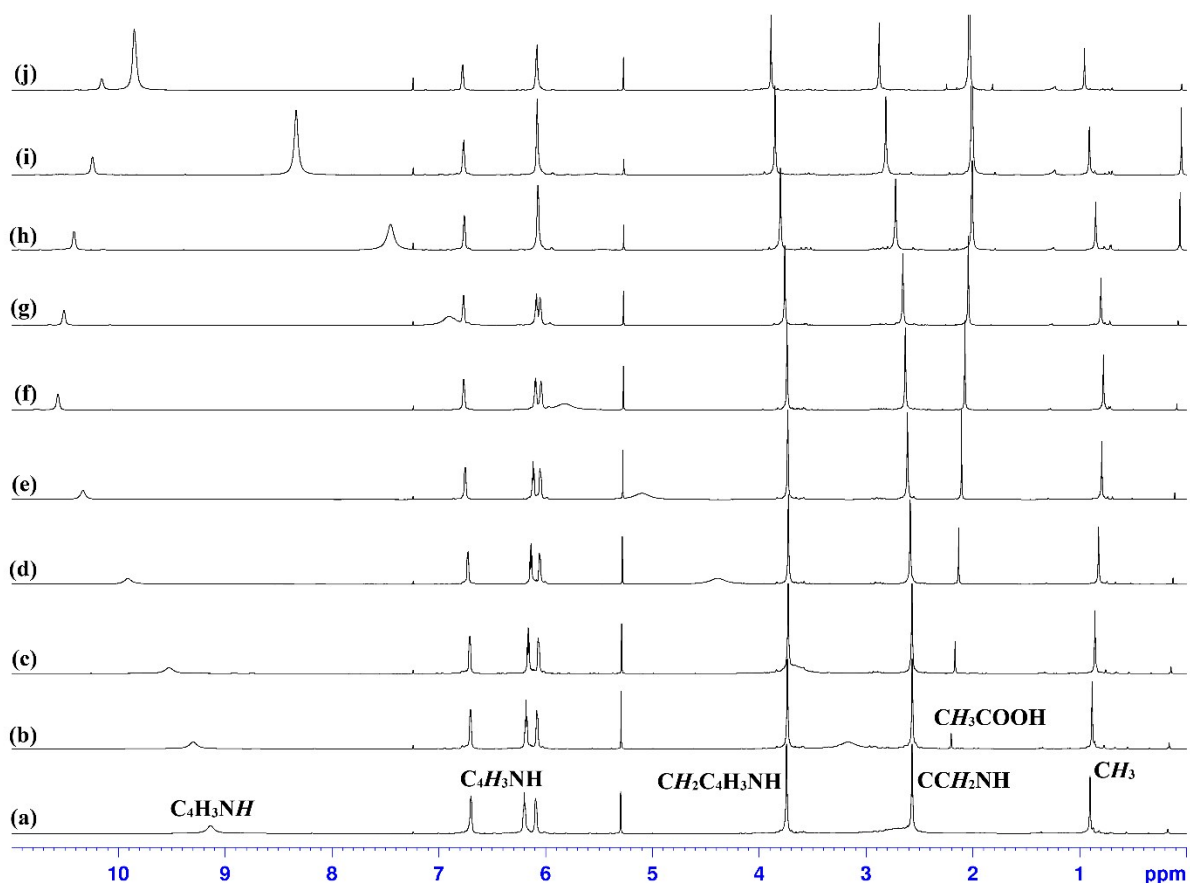
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 300K): δ 11.68 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 11.16 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 10.07 (s, 2H, C<sub>4</sub>H<sub>3</sub>NH), 6.97 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 6.75 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 6.54 (s, 2H, C<sub>4</sub>H<sub>3</sub>NH), 6.26 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 6.08 (s, 1H, C<sub>4</sub>H<sub>3</sub>NH), 6.06 (s, 2H, C<sub>4</sub>H<sub>3</sub>NH), 5.95 (s, 2H, C<sub>4</sub>H<sub>3</sub>NH), 5.92 (s, 2H, C<sub>4</sub>H<sub>3</sub>NH), 3.99 (s, 2H, NH<sup>+</sup>CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NH), 3.74 (s, 1H, CCHN<sub>2</sub>), 3.65 (d, 2H, NHCH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NH), 3.00 (d, 2H, NHCH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NH), 2.84 (d, 2H, CCH<sub>2</sub>NH), 2.60 (s, 2H, CCH<sub>2</sub>NH<sup>+</sup>), 2.18 (d, 2H, CCH<sub>2</sub>NH), 0.76 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 300K): δ 127.23, 125.87, 121.22, 120.92, 120.13, 119.11, 112.38, 111.32, 108.64, 107.94, 107.49, 107.21, 83.28, 62.42, 57.31, 50.48, 45.76, 31.52, 23.67. Elem Anal. Calcd (%) for C<sub>50</sub>H<sub>68</sub>N<sub>14</sub>O<sub>4</sub>S<sub>1</sub>: C, 62.48; H, 7.13; N, 20.40; S, 3.34. Found: C, 62.40; H, 7.13; N, 20.42; S, 3.32. IR (KBr, ν<sub>max</sub>/cm<sup>-1</sup>): 3380 (NH).

#### **Recovery of L2 from [HL2]<sub>2</sub>[SO<sub>4</sub>]<sub>(s)</sub>:**

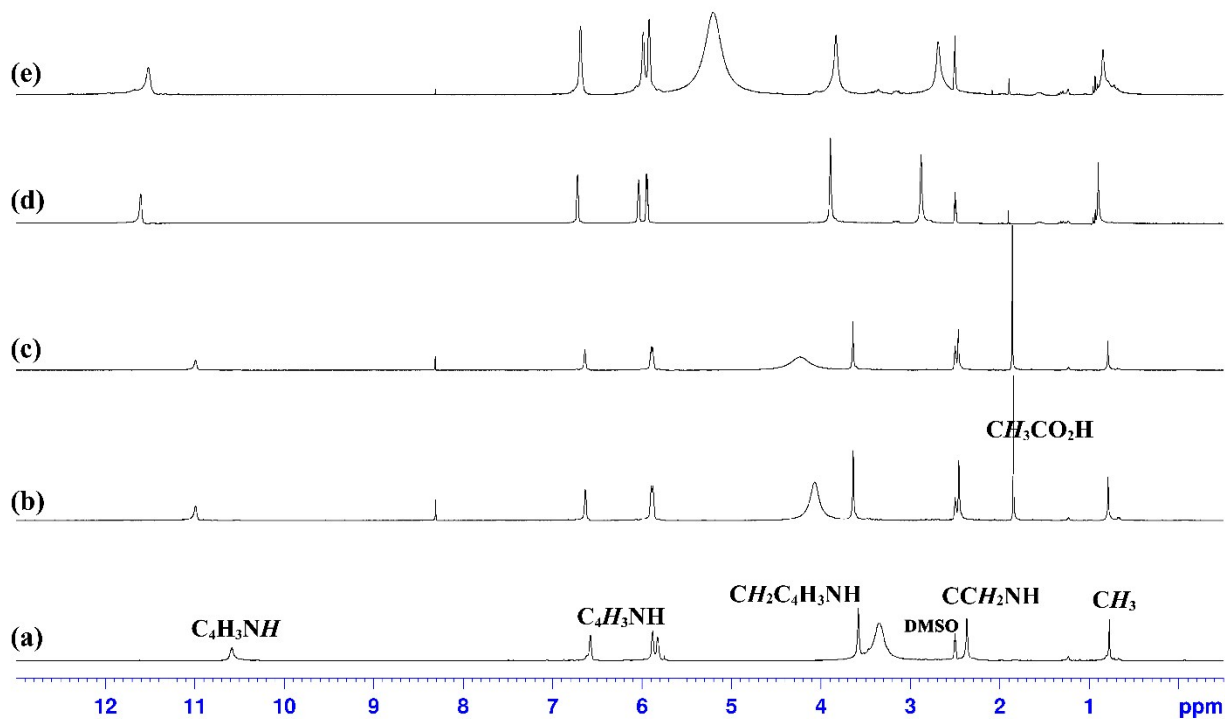
To a stirring solution of [HL2]<sub>2</sub>[SO<sub>4</sub>] (0.144 g, 0.15 mmol) in CHCl<sub>3</sub> (15 ml), a solution of 15% NaOH (15 ml) was added. After the resultant mixture was stirred for 2 hrs at room temperature, the aqueous portion was removed, and the CHCl<sub>3</sub> portion was extracted with distilled water three times. The CHCl<sub>3</sub> portion was then vacuum dried to afford a light-yellow solid **L2** (0.111 g, 86%).

#### **The liquid-liquid extraction procedure:**

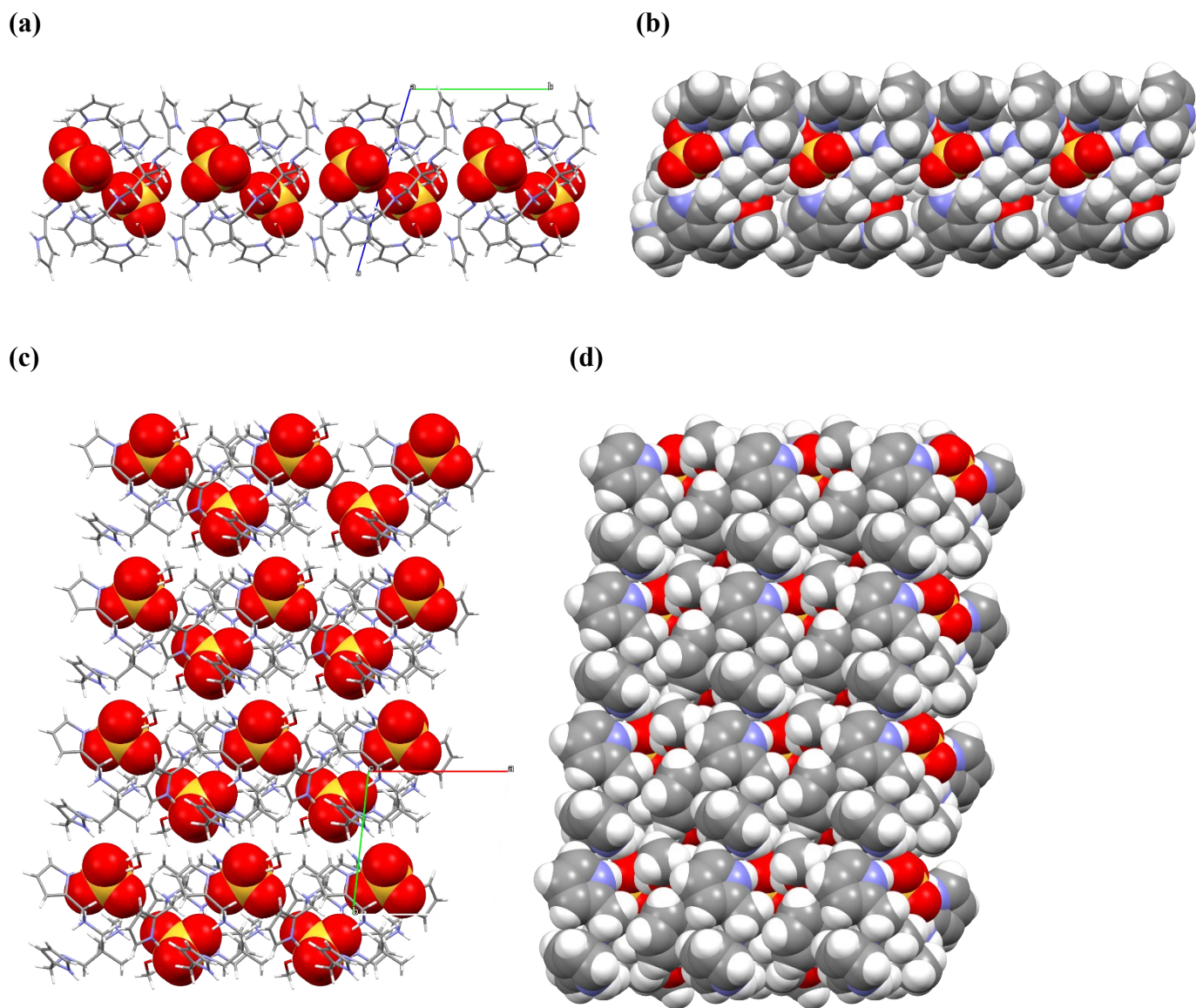
For the CHCl<sub>3</sub>-water extraction study, equal volumes (400 μl each) of the CDCl<sub>3</sub> solution ([HL2][AcO], 50 mM) and aqueous solution (MgSO<sub>4</sub>, 200 mM) were mixed and stirred for 10 mins at room temperature. The CDCl<sub>3</sub> portion, collected by a transfer pipette, was used for NMR studies.



**Fig. S1**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 300 MHz, 300K) of **L1** titrated with acetic acid (top), and the Job plot (bottom).  $X = [\text{H}]/[\text{H}]+[\text{G}]$ . (a)  $X = 1$ ; (b)  $X = 0.9$ ; (c)  $X = 0.8$ ; (d)  $X = 0.7$ ; (e)  $X = 0.6$ ; (f)  $X = 0.5$ ; (g)  $X = 0.4$ ; (h)  $X = 0.3$ ; (i)  $X = 0.2$ ; (j)  $X = 0.1$ . The broad signal that gives a downfield shifting from 2.7 to 9.9 ppm with the decrease of  $X$  value is originated from the N-H ( $\text{CCH}_2\text{NH}$  in the absence of AcOH or  $\text{CCH}_2\text{NH}_2$ ) chemical shift of **L1**. These NH protons are fast exchanged with AcOH protons.

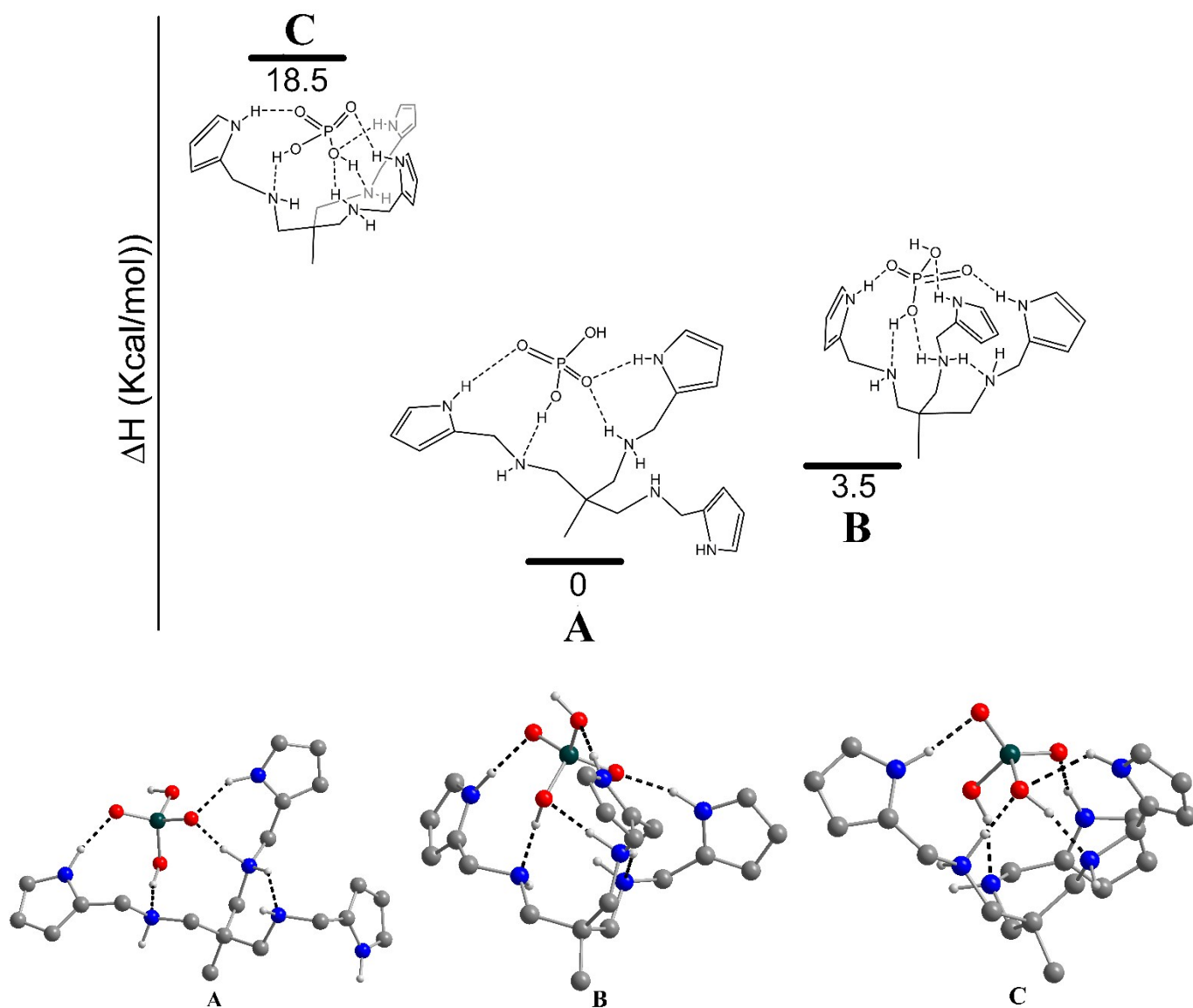


**Fig. S2**  $^1\text{H}$  NMR spectra ( $\text{d}_6\text{-DMSO}$ , 300 MHz, 300K) of (a) pure **L1** (b) **L1** reacted with 1 equiv acetic acid (c) **L1** reacted with 2 equiv acetic acid (d) isolated  $[\text{H}_2\text{L1}][\text{SO}_4]$  (e) isolated  $[\text{H}_2\text{L1}][\text{HPO}_4]$  or  $[\text{HL1}][\text{H}_2\text{PO}_4]$ .

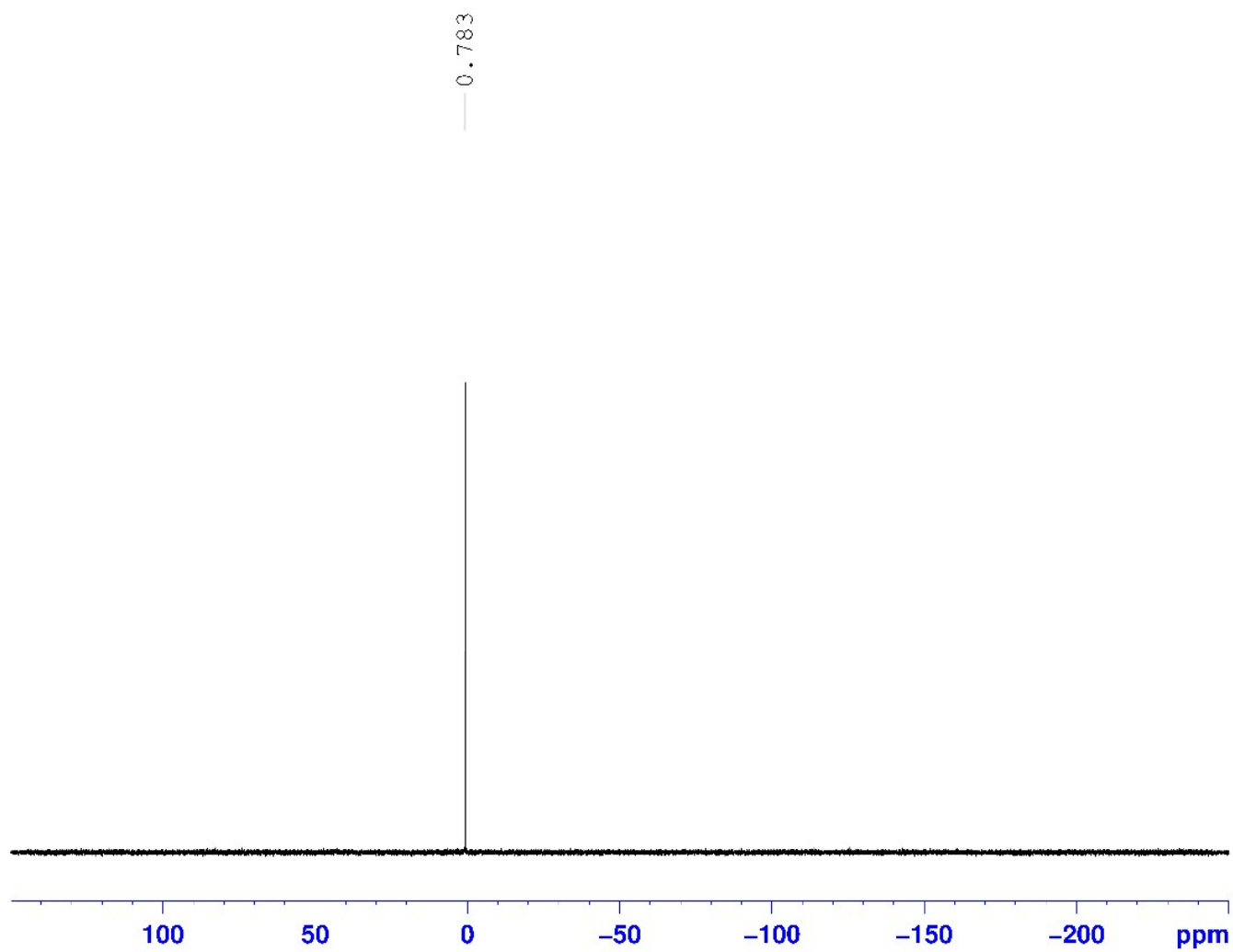


**Fig. S3** The capped sticks model and space-filling model of  $[H_2L1][SO_4] \cdot MeOH$ : (a)(b) viewed along the crystallographic  $a$  axis; (c)(d) viewed along the crystallographic  $c$  axis.

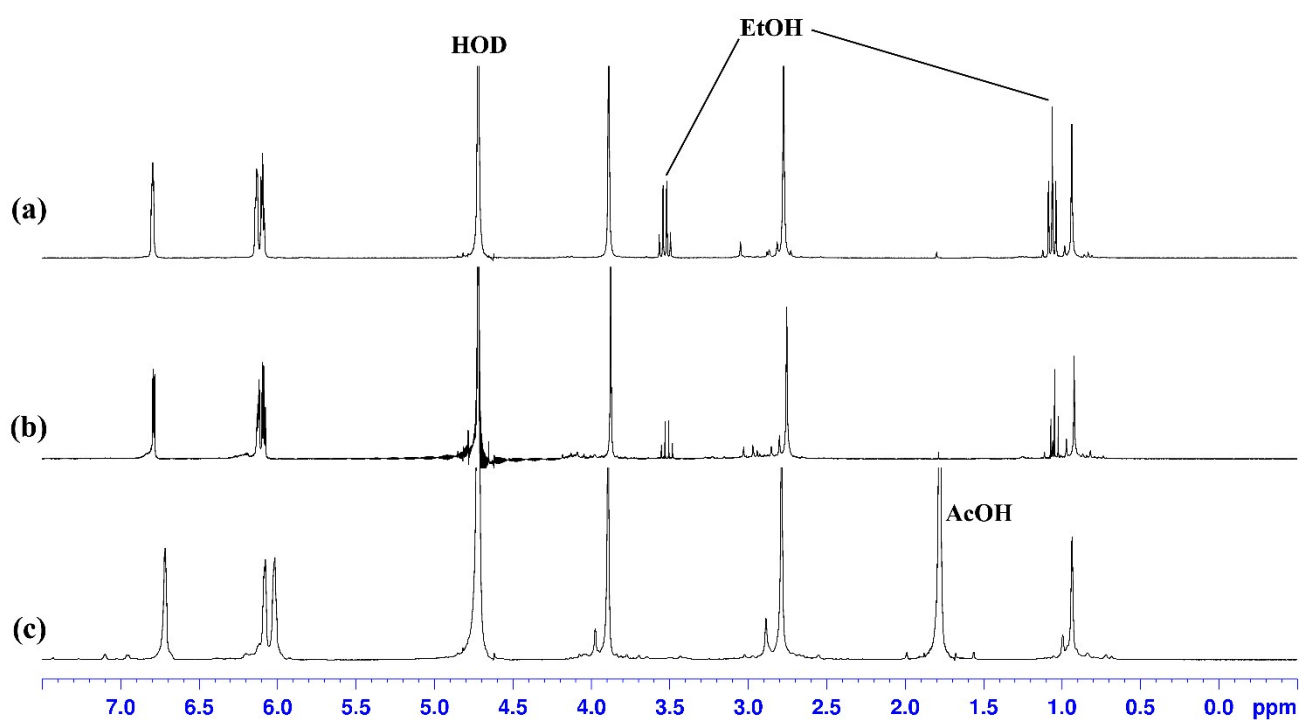




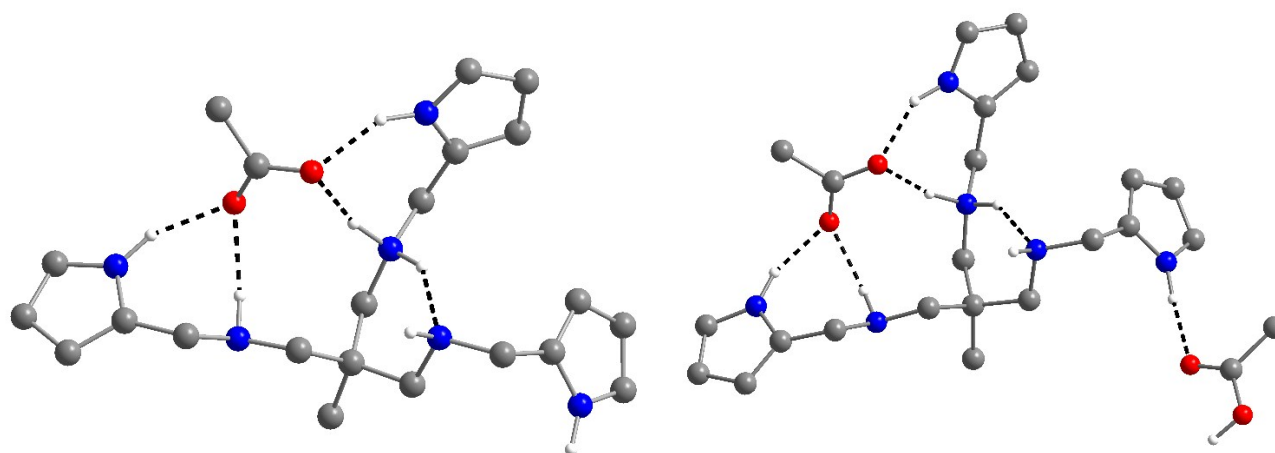
**Fig. S4** The optimized structures and relative electronic energies of three possible isomers of complex  $H_3L1(PO_4)$  from DFT theoretical calculation, initially calculated from  $[H_2L1][HPO_4]$  similar to the crystal structure of  $[H_2L1][SO_4]$ . The results showed that the most stable conformation is in the form of  $[HL1][H_2PO_4]$ . Hydrogen atoms bound on carbon atoms were omitted for clarity.



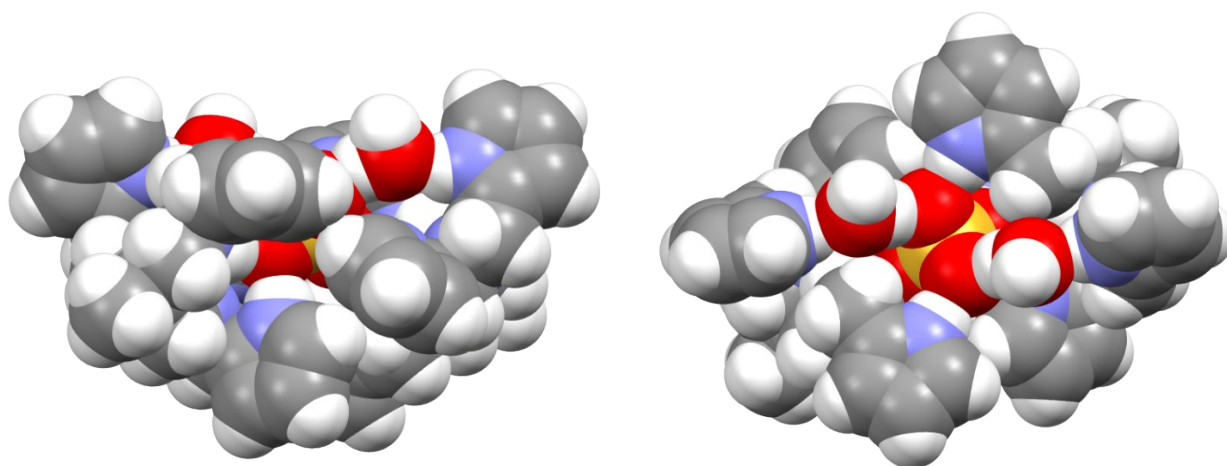
**Fig. S5**  $^{31}\text{P}$  NMR spectrum ( $\text{D}_2\text{O}$ , 300K) of isolated  $[\text{H}_2\text{L1}][\text{HPO}_4]$  or  $[\text{HL1}][\text{H}_2\text{PO}_4]$ .



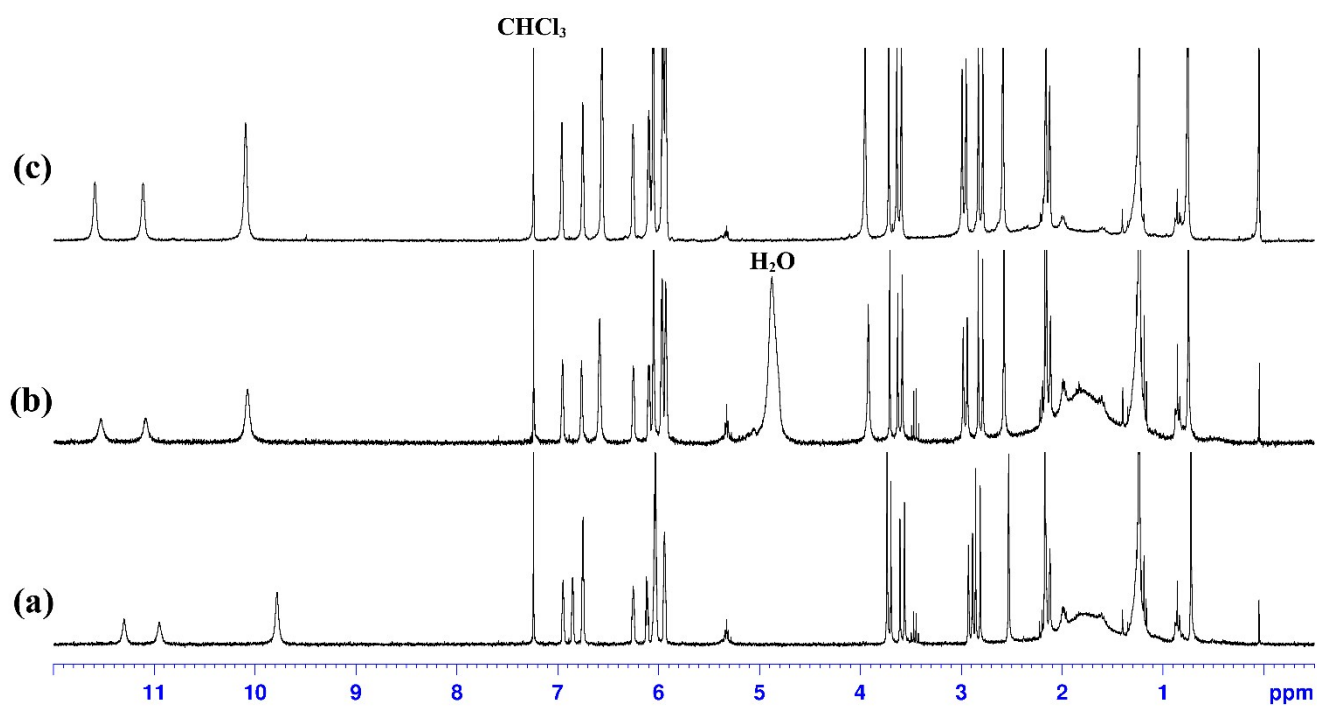
**Fig. S6**  $^1\text{H}$  NMR spectra ( $\text{D}_2\text{O}$ , 300 MHz, 300K) of (a) isolated  $[\text{H}_2\text{L1}][\text{SO}_4]$ , (b) isolated  $[\text{H}_2\text{L1}][\text{HPO}_4]$  or  $[\text{HL1}][\text{H}_2\text{PO}_4]$ , and (c) the vacuum dried mixture of **L1** reacted with 3 equiv acetic acid in EtOH.



**Fig. S7** The optimized structures of complex  $[\text{HL1}][\text{AcO}]$  (left) and  $[\text{HL1}][\text{AcO}]$  added with one molecule of AcOH (right) from DFT theoretical calculations. Hydrogen atoms bound on carbon atoms were omitted for clarity.



**Fig. S8** The space-filling model of  $[\text{HL2}]_2[\text{SO}_4]\cdot 2\text{H}_2\text{O}$ ; side view (left) and top view (right).



**Fig. S9**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 300 MHz, 300K) of purified  $[\text{HL2}][\text{AcO}]$  before (a) and after (b) the  $\text{CDCl}_3\text{-H}_2\text{O}$  extraction experiment using  $\text{MgSO}_4(\text{aq})$ , and (c) purified  $[\text{HL2}]_2[\text{SO}_4]$ .

**Table S1.** The summary of crystallographic data for [H<sub>2</sub>L1][SO<sub>4</sub>], [HL2]<sub>2</sub>[SO<sub>4</sub>], and [HL2][AcO].

Complex	[H <sub>2</sub> L1][SO <sub>4</sub> ]·MeOH	[HL2] <sub>2</sub> [SO <sub>4</sub> ]·2H <sub>2</sub> O	[HL2][AcO]
formula	C <sub>21</sub> H <sub>36</sub> N <sub>6</sub> O <sub>5</sub> S	C <sub>50</sub> H <sub>72</sub> N <sub>14</sub> O <sub>6</sub> S	C <sub>27</sub> H <sub>37</sub> N <sub>7</sub> O <sub>2</sub>
Fw	484.62	997.28	491.64
temp, K	150(2)	150(2)	150(2)
cryst syst	Triclinic	Trigonal	Monoclinic
space group	<i>P</i> -1	<i>R</i> -3 <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> , Å	9.666(7)	23.541(4)	12.605(3)
<i>b</i> , Å	9.761(6)	23.541(4)	16.671(4)
<i>c</i> , Å	14.448(11)	59.81(3)	13.147(3)
α, °	104.97(5)	90	90
β, °	108.43(5)	90	99.243(13)
γ, °	91.04(6)	120	90
Volume, Å <sup>3</sup> / <i>Z</i>	1242.0(16)/2	28705(17)/18	2726.8(9)/4
Density (cald.), Mg/m <sup>3</sup>	1.296	1.038	1.198
Absorption coefficient, mm <sup>-1</sup>	0.173	0.102	0.079
crystal size, mm	0.16×0.12×0.08	0.12×0.10×0.08	0.25×0.20×0.04
θ range, deg	2.173 to 24.250	1.209 to 24.497	1.989 to 26.000
no. of reflns collected	10403	70111	29728
no. of indep reflns	4017	5305	5362
F(000)	522	9684	992
no. of data /restraints /params	4017 / 0 / 311	5305 / 3 / 327	5362 / 10 / 327
goodness-of-fit on <i>F</i> <sup>2</sup>	0.957	0.849	0.941
final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )], <i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup>	0.0624 0.1818	0.1019 0.2621	0.0478 0.1331
<i>R</i> indices (all data), <i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup>	0.1682 0.2251	0.1417 0.2863	0.0890 0.1654
largest diff. peak and hole, e Å <sup>-3</sup>	0.213 and -0.338	0.088 and -0.009	0.323 and -0.198

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b wR_2 = [\sum [\omega(F_o^2 - F_c^2)^2] / \sum [\omega(F_o^2)^2]]^{1/2}$$

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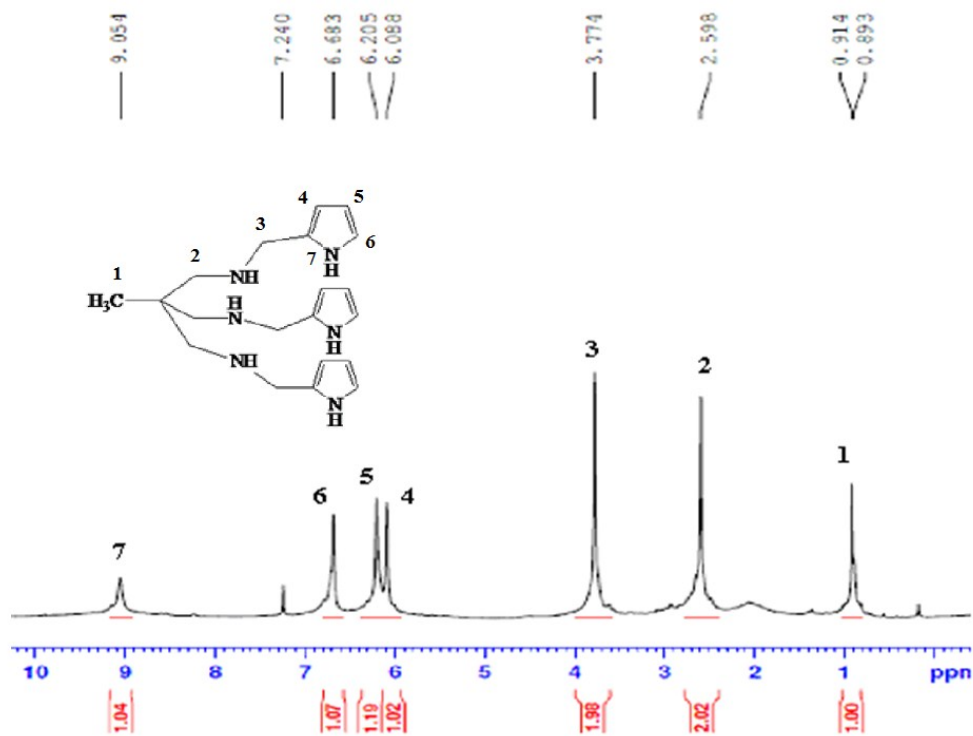


Fig. S10  $^1\text{H}$  NMR spectrum of L1 in  $\text{CDCl}_3$ .

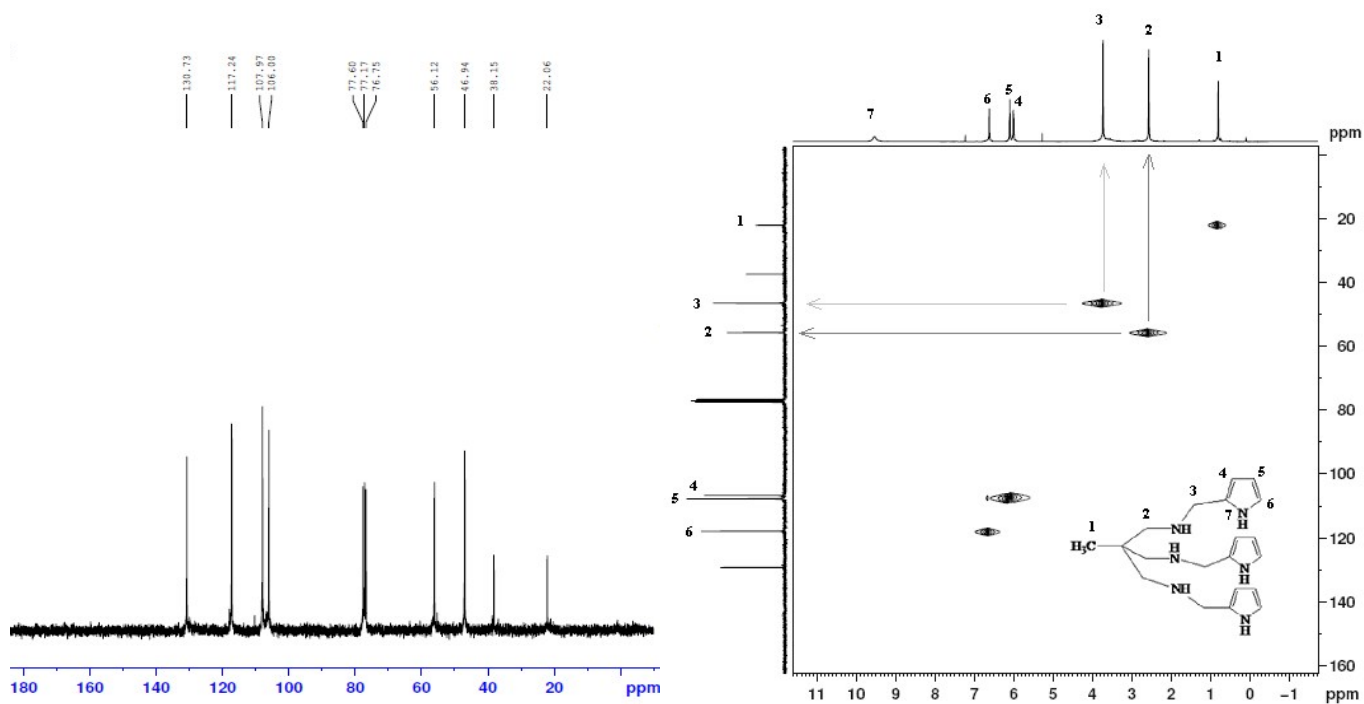


Fig. S11  $^{13}\text{C}$  NMR (left) and  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR (right) spectra of L1 in  $\text{CDCl}_3$ .



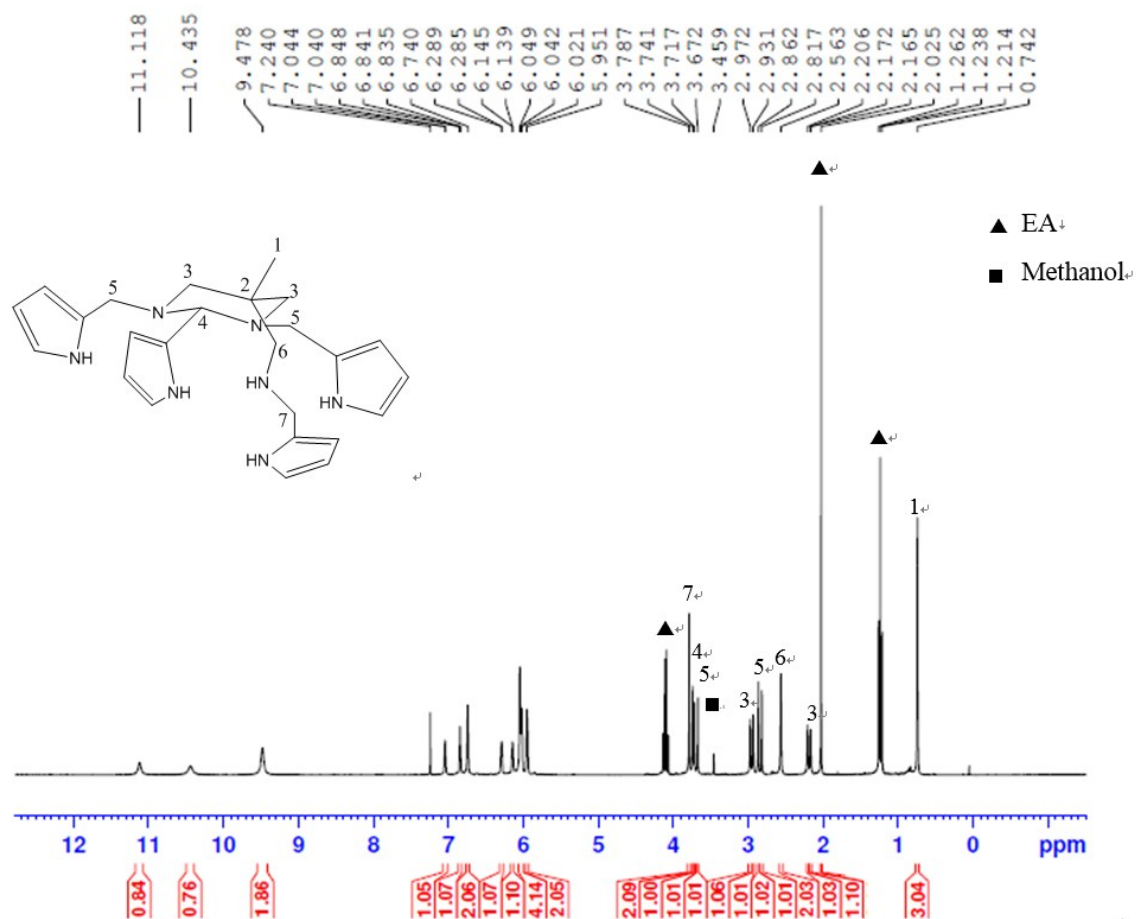


Fig. S12  $^1\text{H}$  NMR spectrum of L2 in  $\text{CDCl}_3$ .

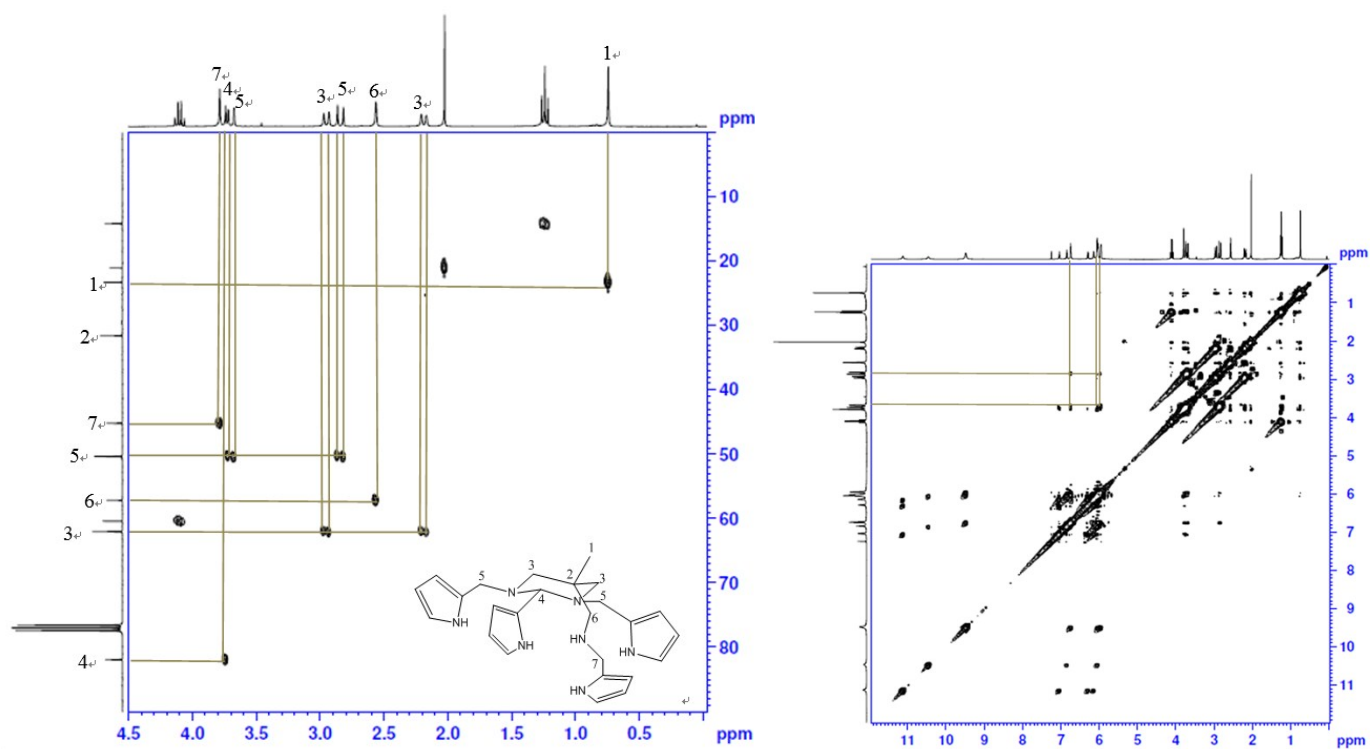


Fig. S13  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR (left) and  $^1\text{H}$ - $^1\text{H}$  COSY NMR (right) spectra of L2 in  $\text{CDCl}_3$ .

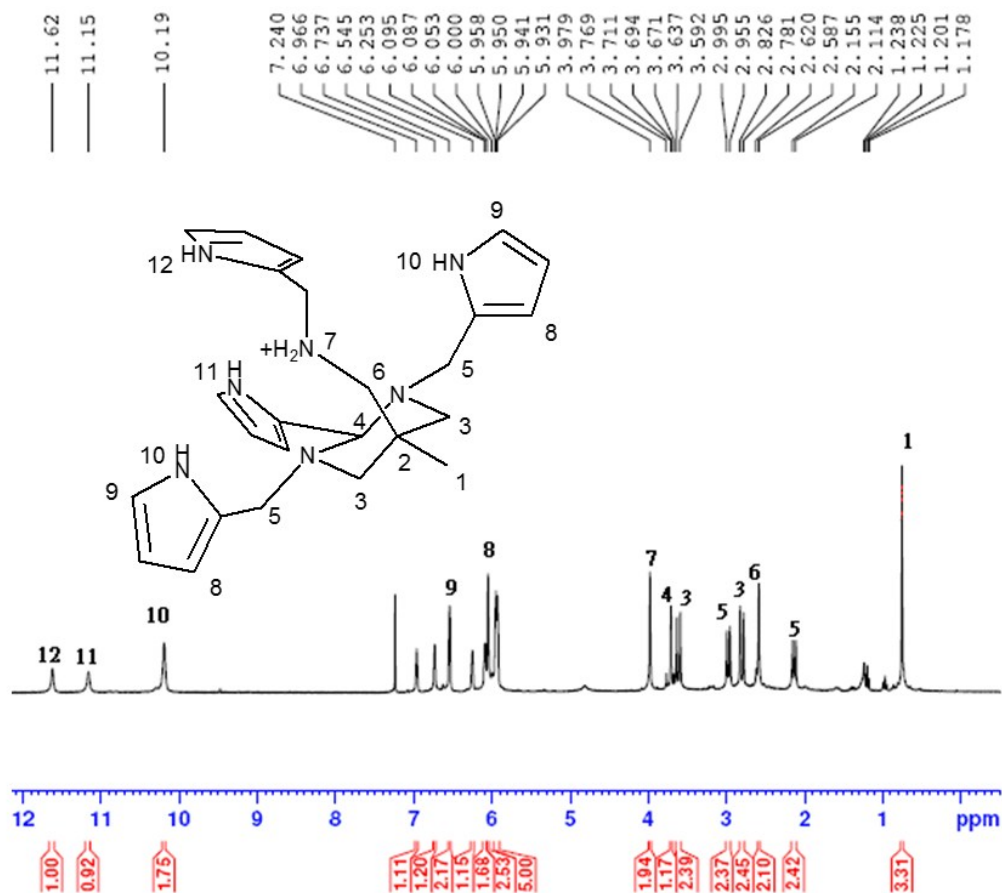


Fig. S14  $^1H$  NMR spectrum of  $[HL2]_2[SO4]$  in  $CDCl_3$ .

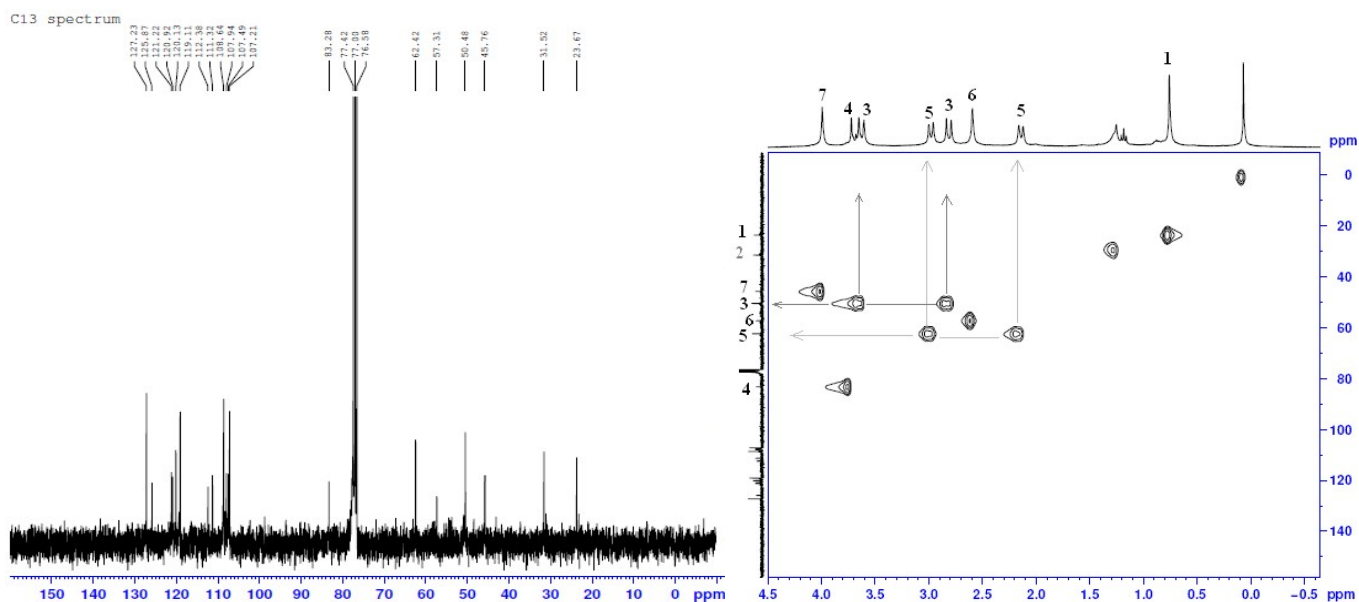


Fig. S15  $^{13}C$  NMR (left) and  $^1H$ - $^{13}C$  HSQC NMR (right) spectra of  $[HL2]_2[SO4]$  in  $CDCl_3$ .

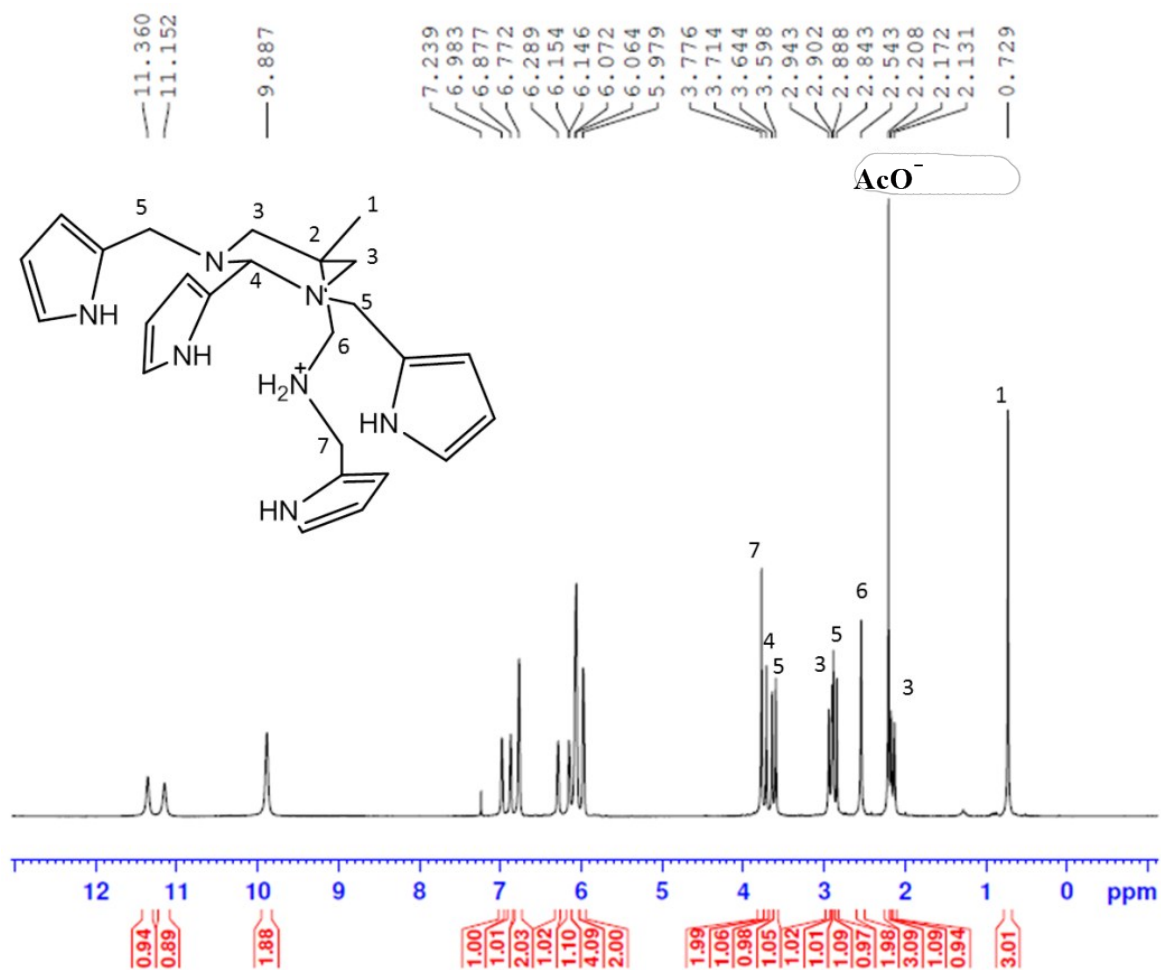


Fig. S16  $^1\text{H}$  NMR spectrum of [HL2][AcO] in  $\text{CDCl}_3$ .

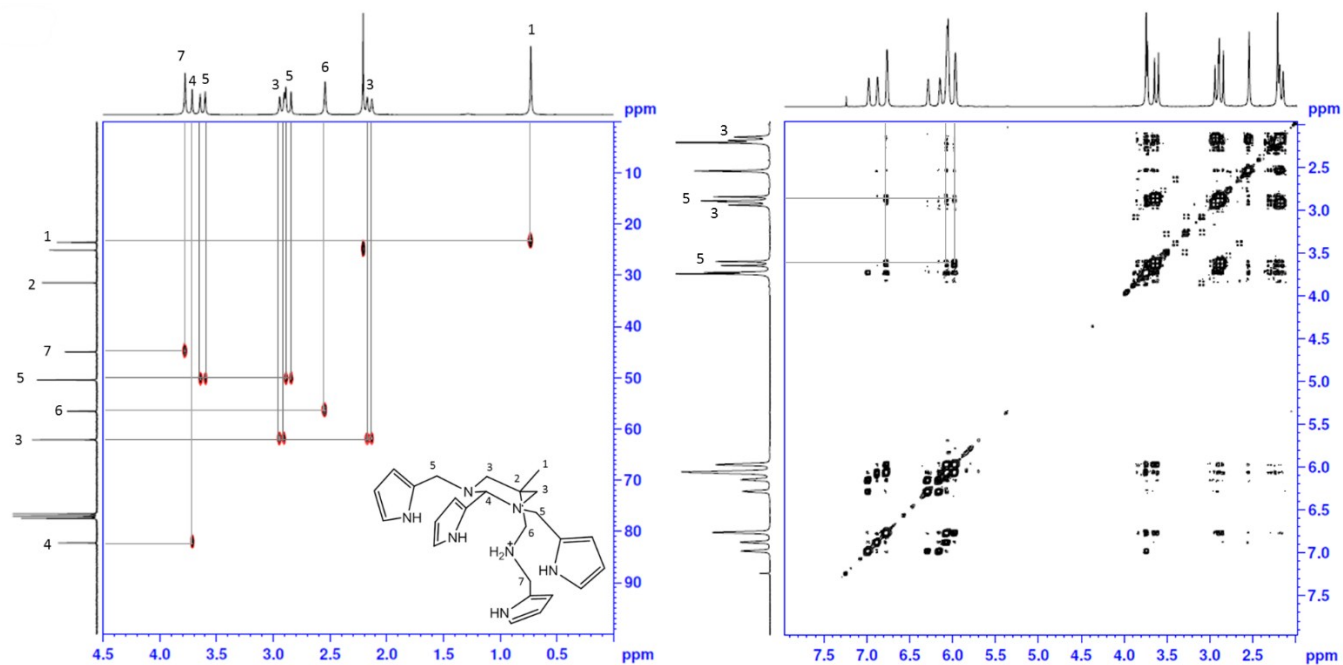


Fig. S17  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR (left) and  $^1\text{H}$ - $^1\text{H}$  COSY NMR (right) spectra of [HL2][AcO] in  $\text{CDCl}_3$ .