Supporting information for

A nonanuclear triangular macrocycle and a linear heptanuclear heterometallic complex based on a 2-substituted imidazole-4,5-dicarboxylate ligand

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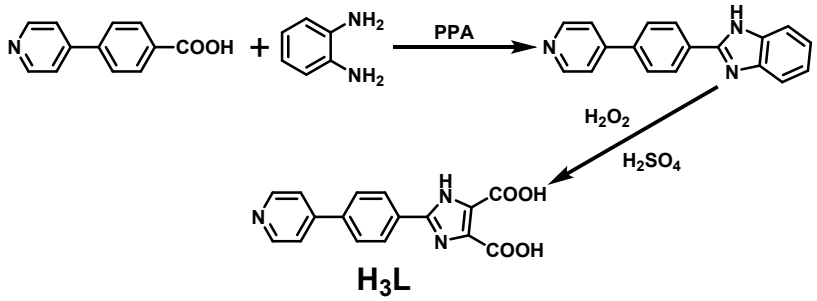
1. Ligand Synthesis



Scheme S1 Synthetic route to H_3**L** ligand.

Synthesis of 2-(4-(pyridin-4-yl)phenyl)-1*H*-imidazole-4,5-benzimidazole: A mixture of *o*-pheylenediamine (1.08 g, 10 mmol), 4-(pyridin-4-yl)benzoic acid (1.99 g, 10 mmol), and polyphosphoric acid (PPA, 30 g) was stirred at 180°C for 4 h under nitrogen. Afterwards, the mixture was cooled to 100 °C and poured into water (200 ml). After the PPA was dissolved, the resulting solution was cooled and the pH was adjusted to 7 by the addition of $NH_3 \cdot H_2O$. The precipitated solid was filtered off, washed with water and dried. The yields: 2.58 g, 95%. ^{1}H NMR (CD_3OD-D_4, 400 MHz) δ: 7.28 (q, J = 3.2 Hz, 2H), 7.62 (q, J = 3.2 Hz, 2H), 7.78 (dd, J = 1.6, 4.8 Hz, 2H), 7.95 (dd, J = 2.0, 6.4 Hz, 2H), 8.23 (dd, J = 1.6, 6.8 Hz, 2H), 8.61 (dd, J = 1.6, 4.4 Hz, 2H); IR (KBr, cm^{-1}): 3422 (s), 3154 (s), 1601 (s), 1542 (w), 1490 (w), 1478 (w), 1449 (w), 1435 (m), 1415 (m), 1317 (w), 1281 (w), 1228 (w), 1121 (w), 1072 (w), 1033 (w), 999 (w), 948 (w), 858 (w), 815 (s), 734 (s), 659 (m), 617 (w), 561 (s), 450 (w); elemental analysis calcd (%) for $C_{18}H_{13}N_3$: C: 79.68, H: 4.83, N: 15.49; found C: 79.35, H: 5.26, N: 15.25.

Synthesis of 2-(4-(pyridine-4-yl)phenyl)-1*H*-imidazole-4,5-dicarboxylic acid (H_3L): A mixture of 2-(4-(pyridin-4-yl)phenyl)-1*H*-imidazole-4,5-benzimidazole (271 mg, 1 mmol) and 98% H_2SO_4 (1 ml), then H_2O_2 solution (30%,1 ml) was added dropwise to the above solution at 100 °C. The resulting solution was then stirred for 1.5 h at 140 °C. After cooling to 40 °C and poured into water (50 ml). The precipitated product was filtered off, washed with water and dried. The yields: 192 mg, 62%.^{1}H NMR (Li_3**L**, D_2O-D_2, 400 MHz) δ: 7.69 (d, J = 6 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.51 (d, J = 6 Hz, 2H); IR (KBr, cm^{-1}): 3448 (s), 3179 (m), 3094 (m), 2131 (w), 1634 (s), 1535 (w), 1483 (s), 1369 (s), 1268 (w), 1224 (w), 1039 (w), 993 (w), 962 (w), 855 (w), 820 (m), 749 (w), 724 (w), 654 (s), 556 (w); elemental analysis calcd (%) for $C_{16}H_{11}N_3O_4$: C: 62.13, H: 3.58, N: 13.59; found C: 61.94, H: 3.26, N: 13.29.

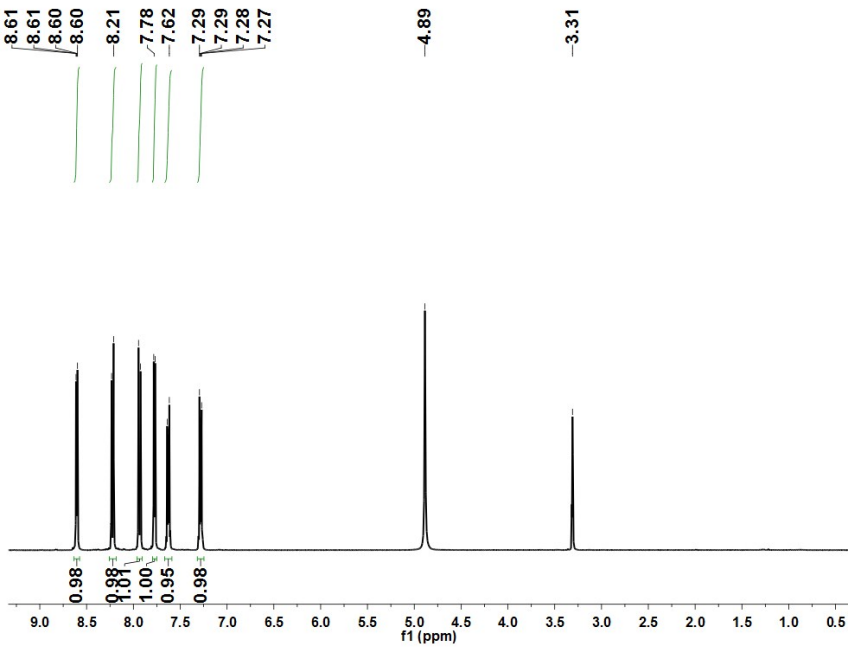


Figure. S1 [1]H NMR spectrum of 2-(4-(pyridin-4-yl)phenyl)-1*H*-benzimidazole

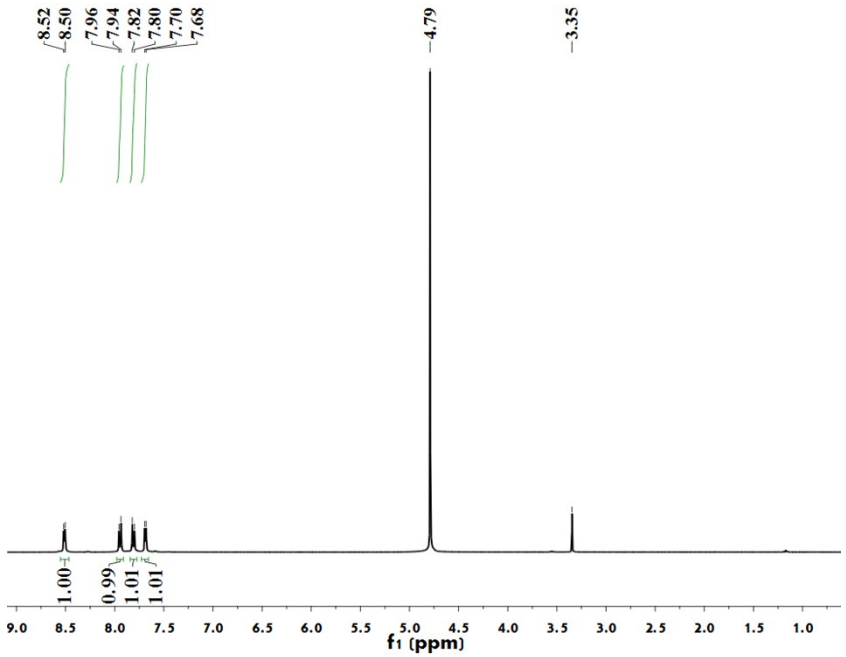


Figure. S2 [1]H NMR spectrum of 2-(4-(pyridin-4-yl)phenyl)-1*H*-benzimidazole

2. Single-Crystal Structure Determination

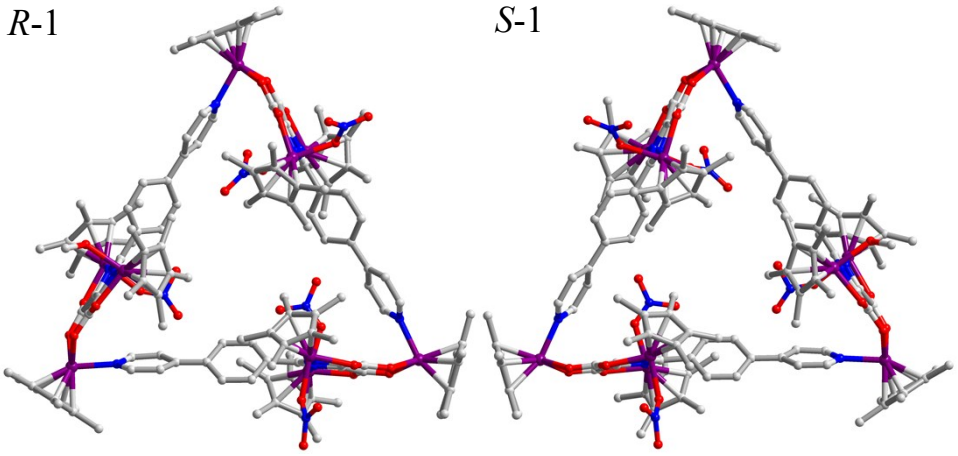


Figure. S3 Single-crystal X-ray structure of *R*-**1** and *S*-**1**

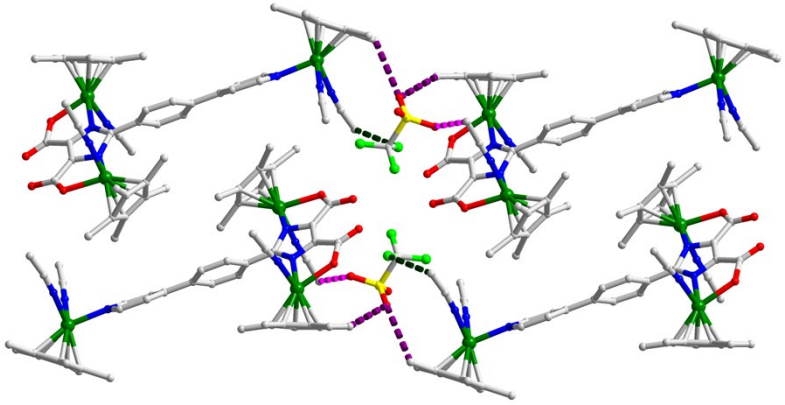


Figure. S4 view showing hydrogen bonds between the OTf^- anions and carbon atoms of **2**

3. NMR Spectra

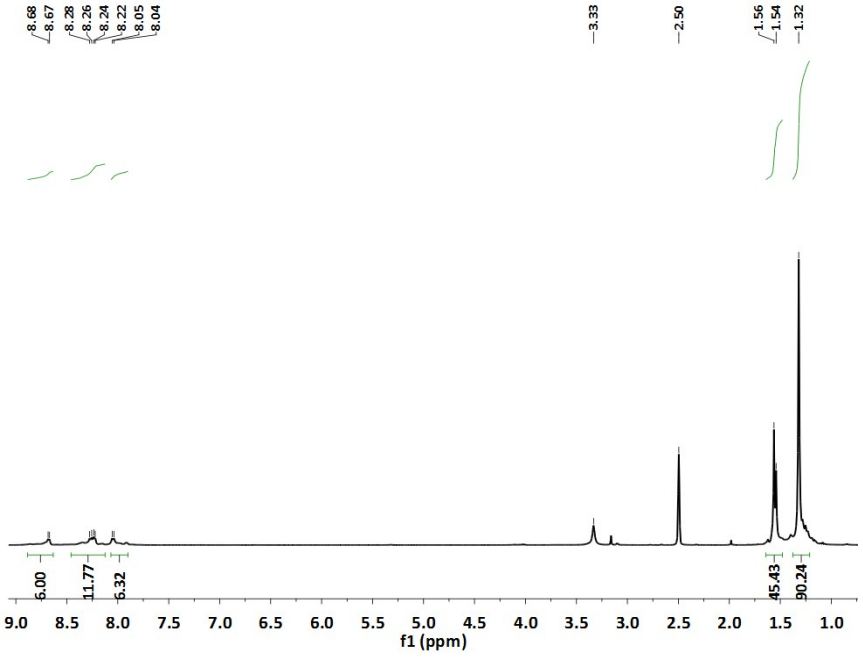


Figure. S5 ^{1}H NMR spectrum of complex **1**

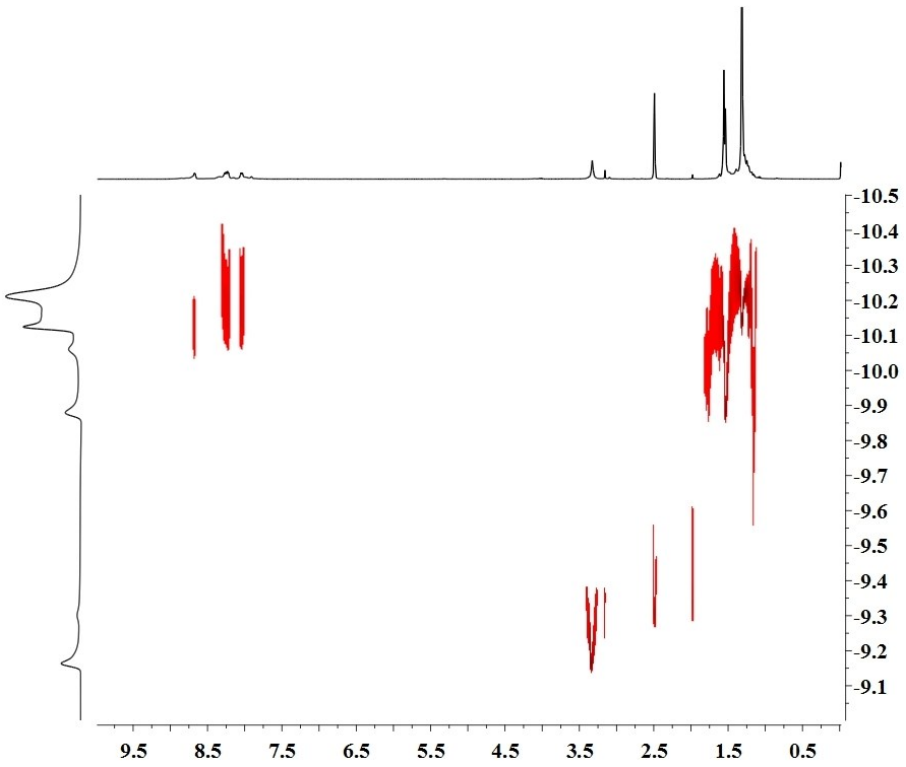


Figure. S6 DOSY NMR spectrum of complex **1**

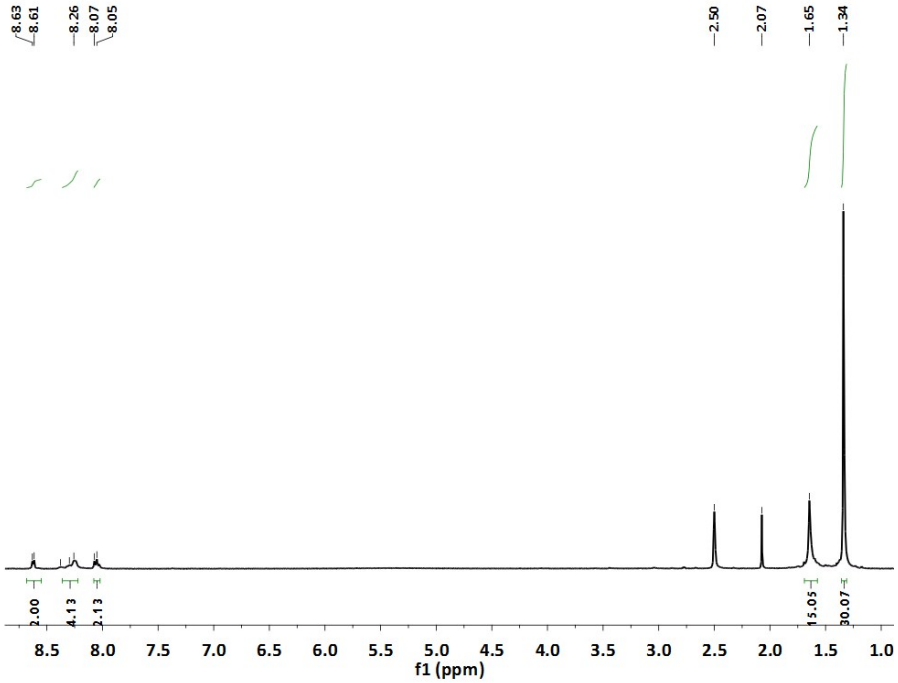


Figure. S7 ^{1}H NMR spectrum of complex **2**

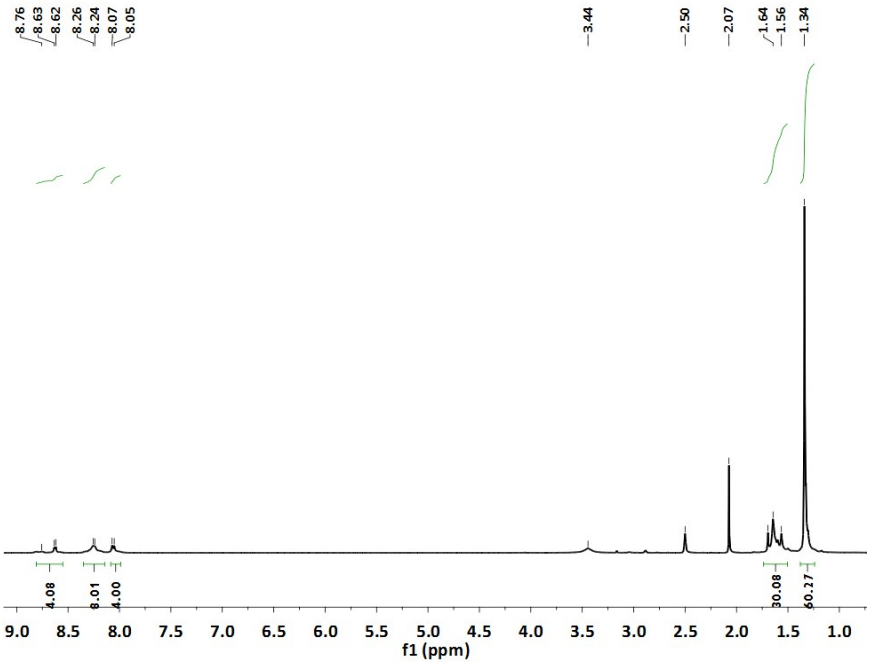


Figure. S8 ^{1}H NMR spectrum of complex **3**

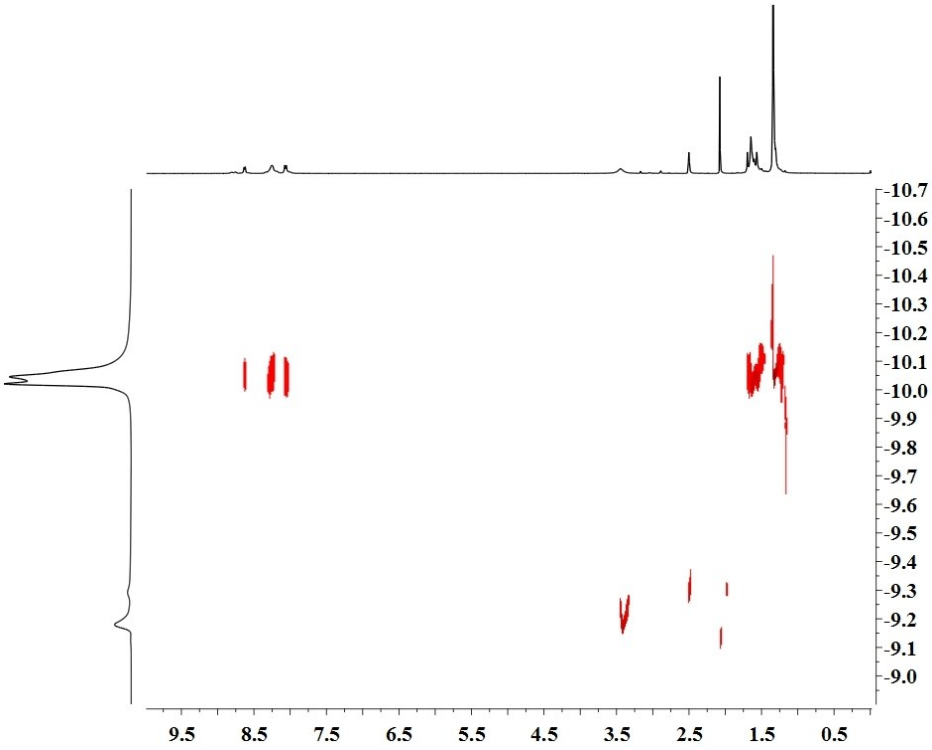


Figure. S9 DOSY NMR spectrum of complex **3**