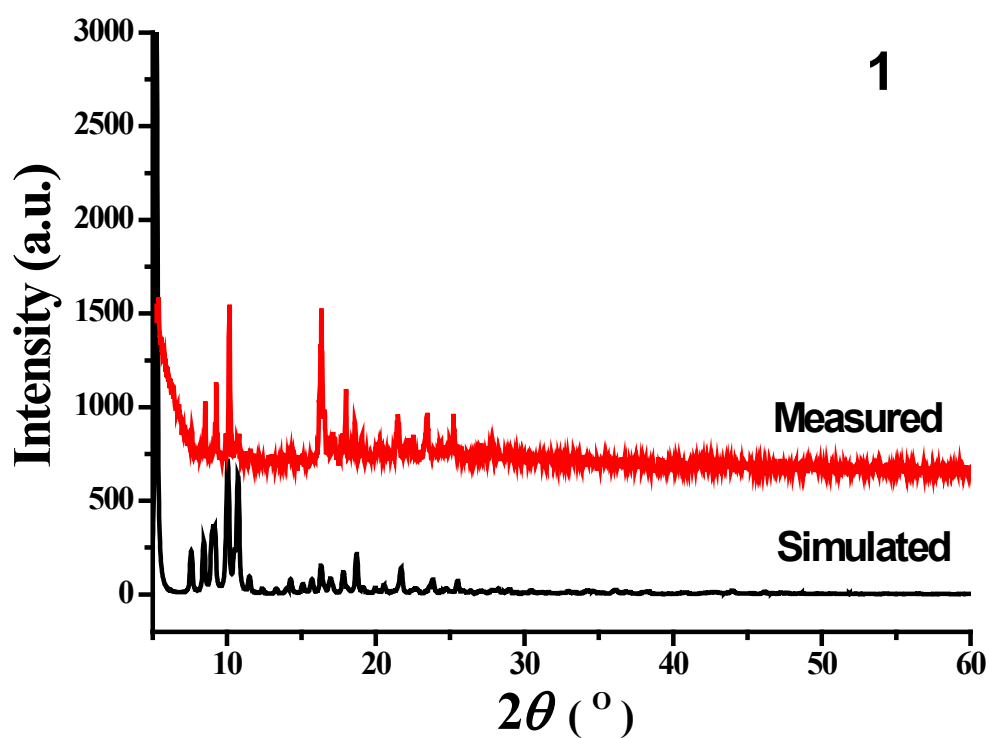


## ESI

# Construction of Porous Mn(II)-based Metal-organic Frameworks by Flexible Hexacarboxylic Acid and Rigid Coligands

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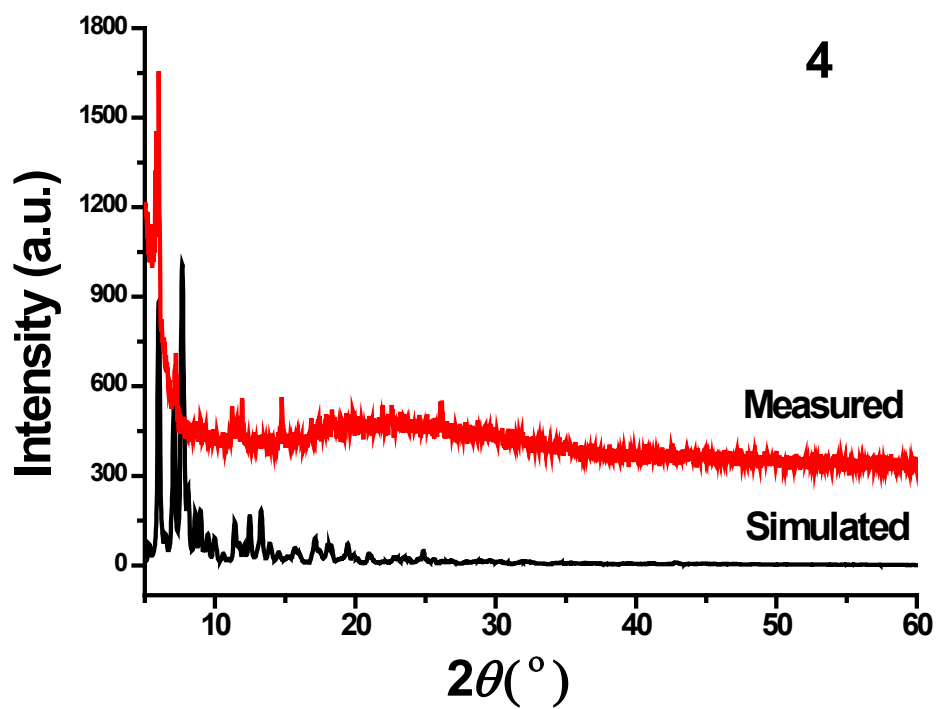
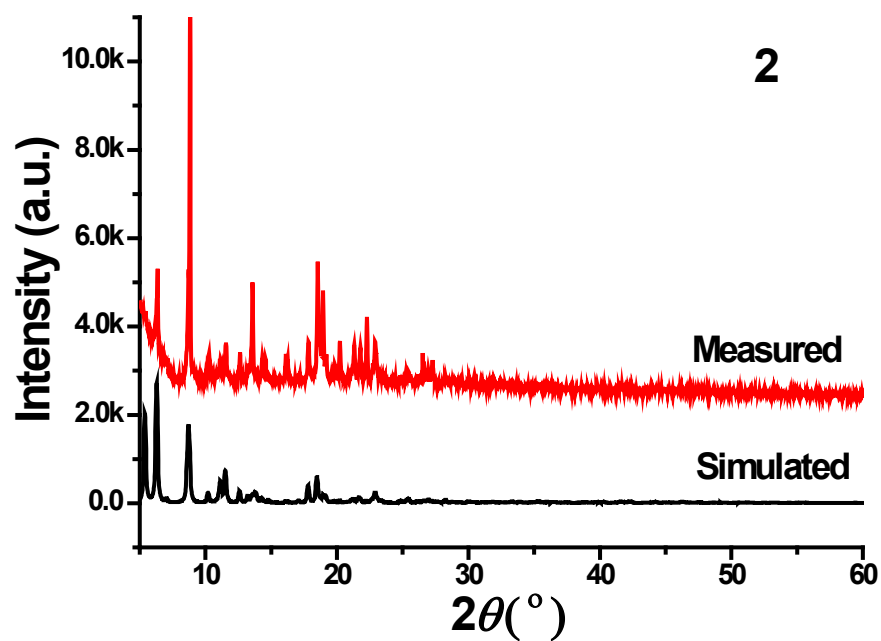
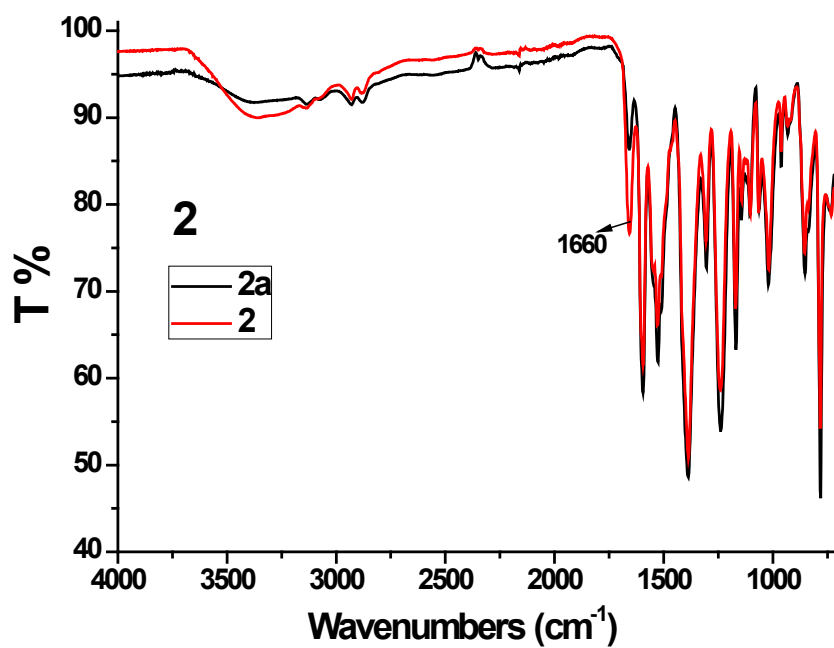
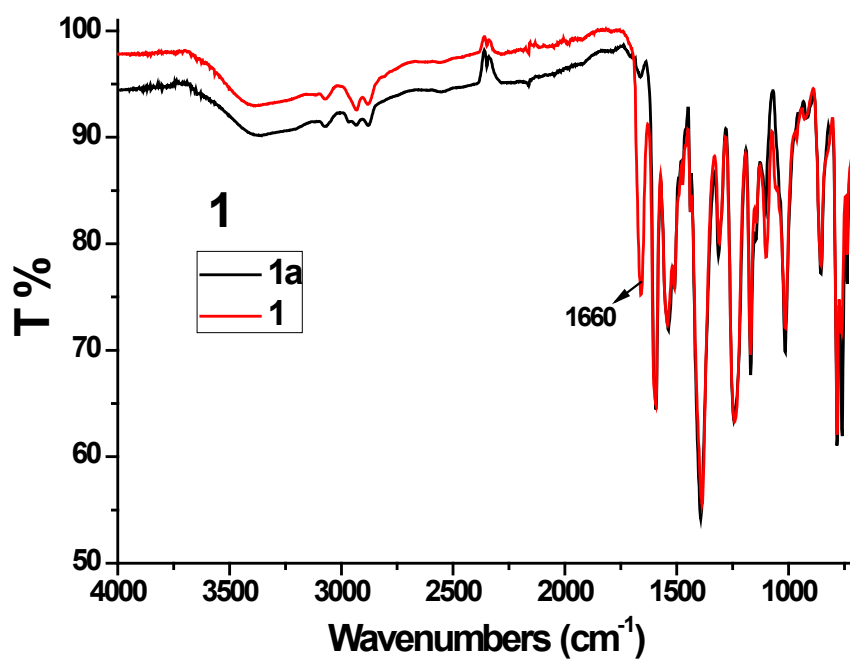


Fig. S1 Simulated and measured XRD powder patterns for compounds 1, 2 and 4.



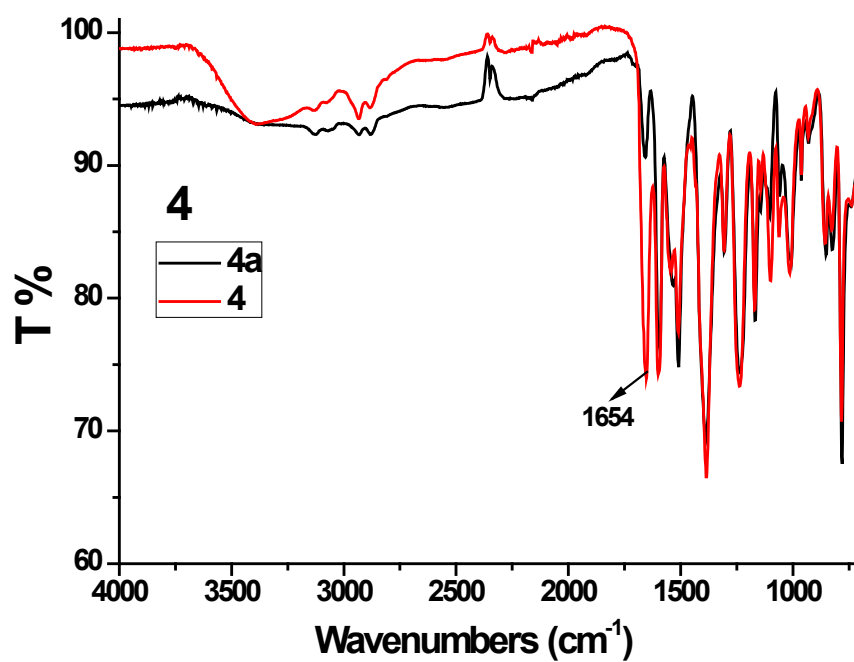
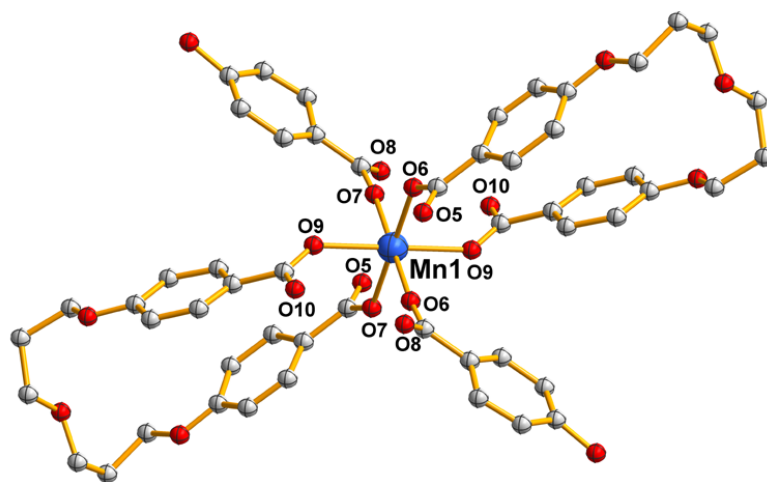


Fig. S2 The IR spectra of compounds 1, 2 and 4 (red), as well as the activated compounds 1a, 2a, and 4a (black) after thermal treatments.



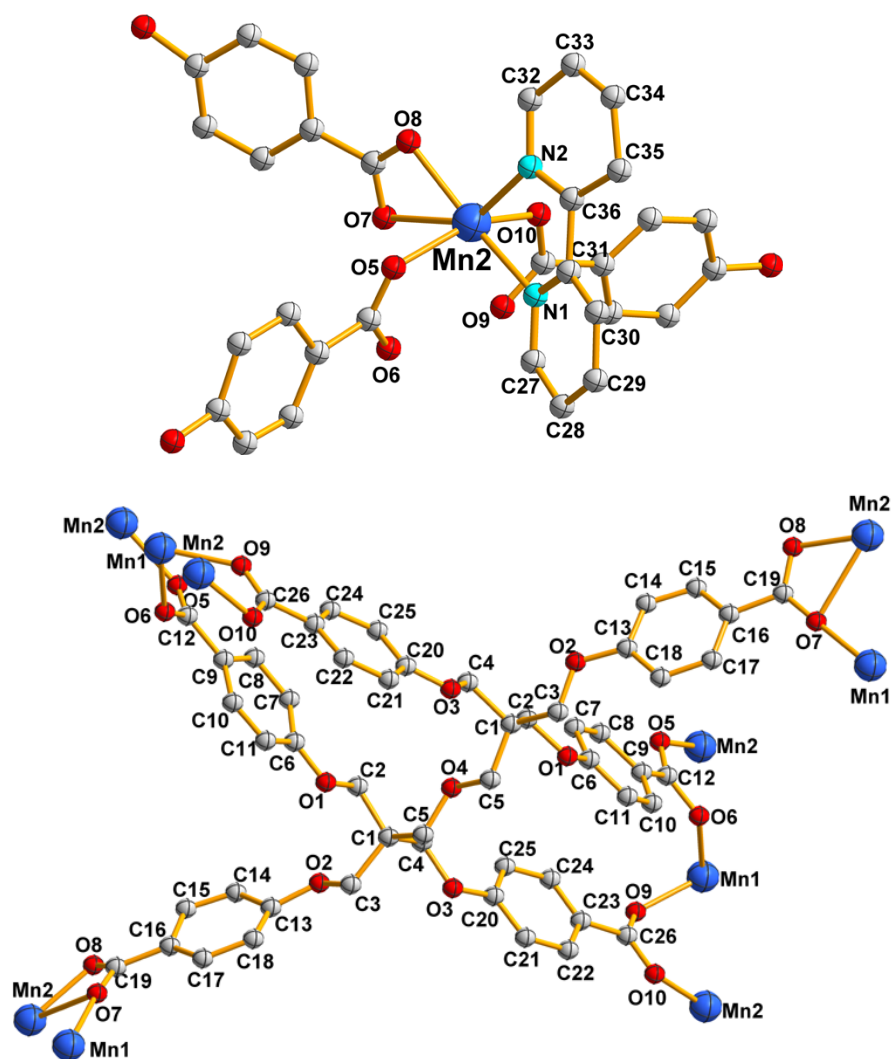


Fig. S3 The coordination modes of metal centers (Mn(1) and Mn(2)) and L ligand in **1**.

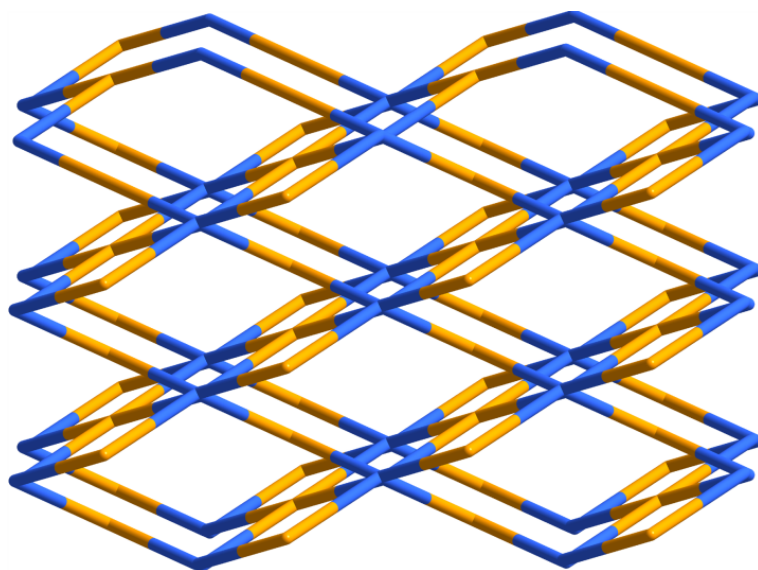


Fig. S4 Topological view of **1**.

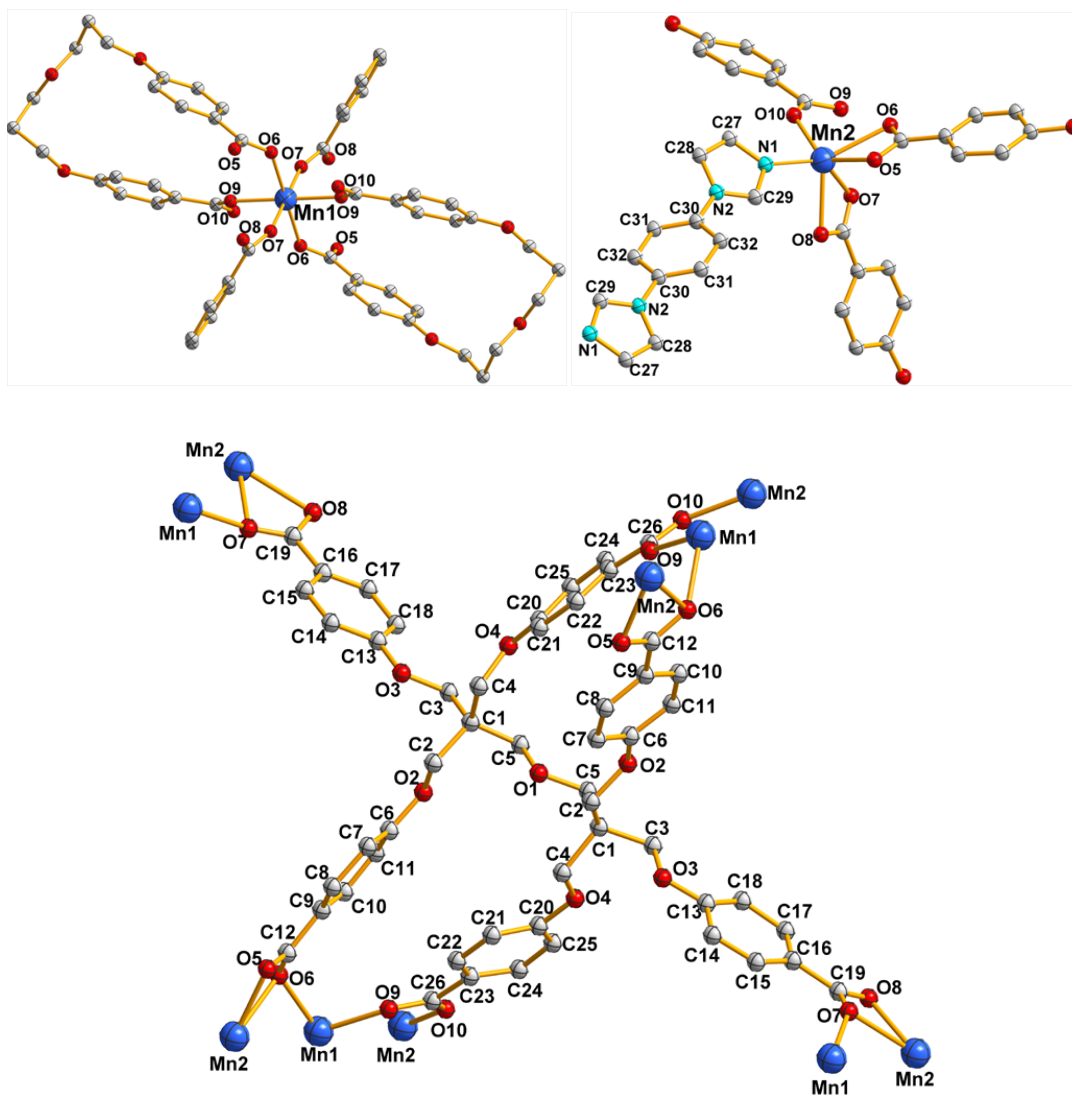
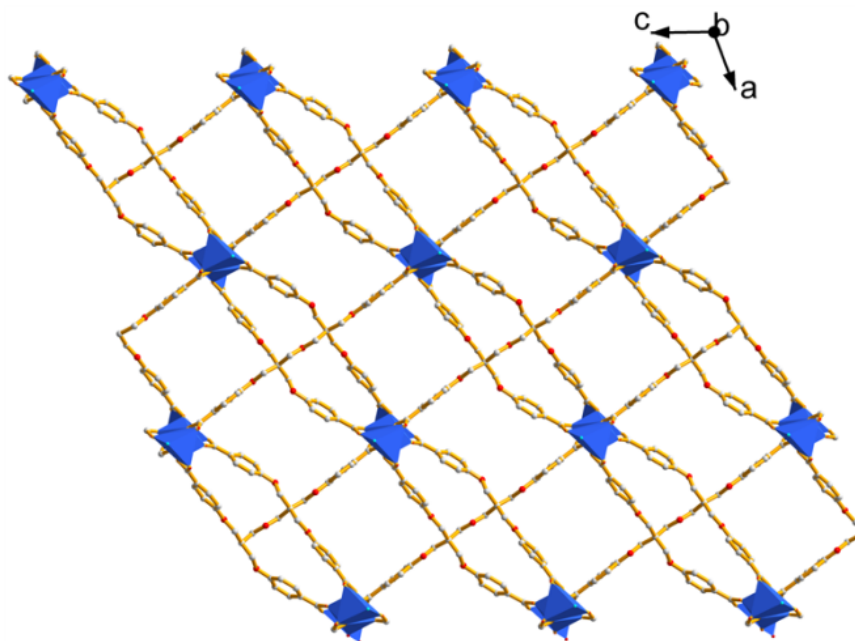


Fig. S5 The coordination modes of metal centers and L ligand in 2.



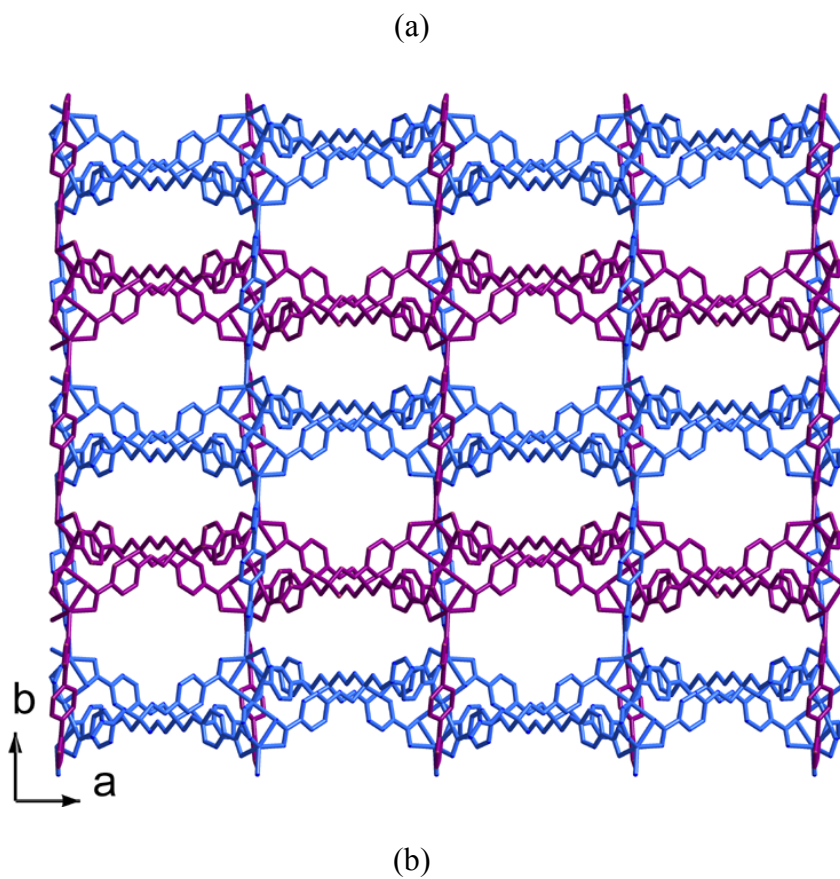
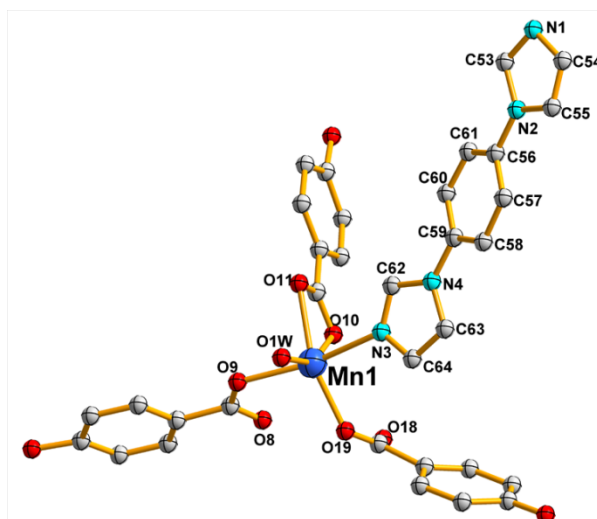
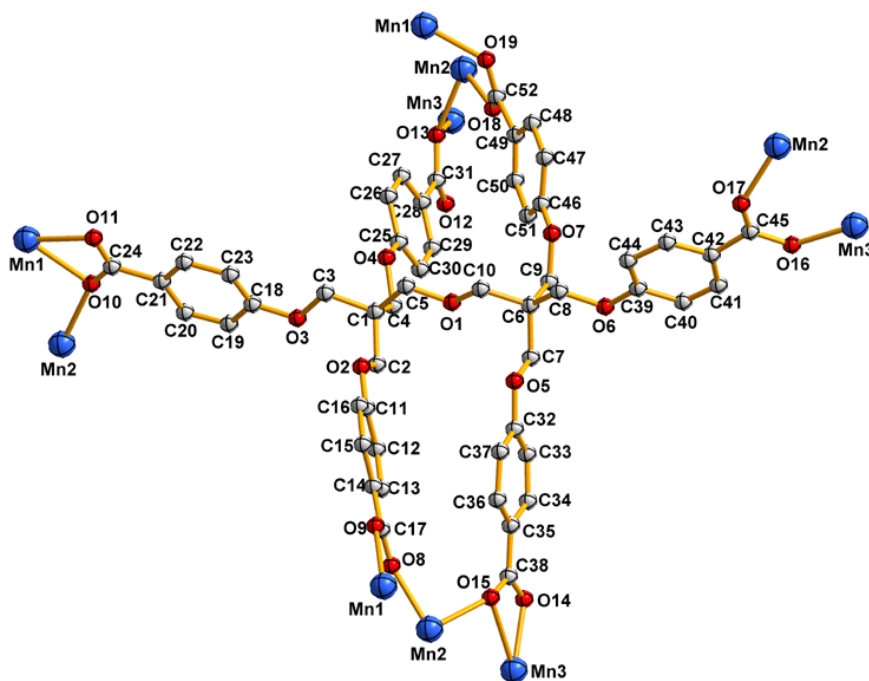
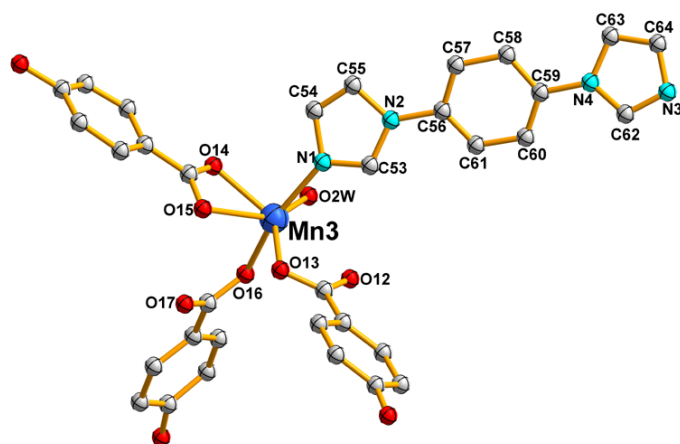
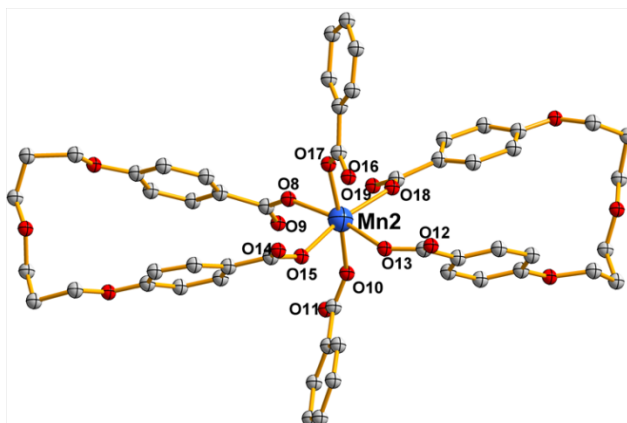


Fig. S6 View of the 2D Mn-L layer along the *b*-axis (a), and the 2-fold interpenetrating framework (b) of **2**.







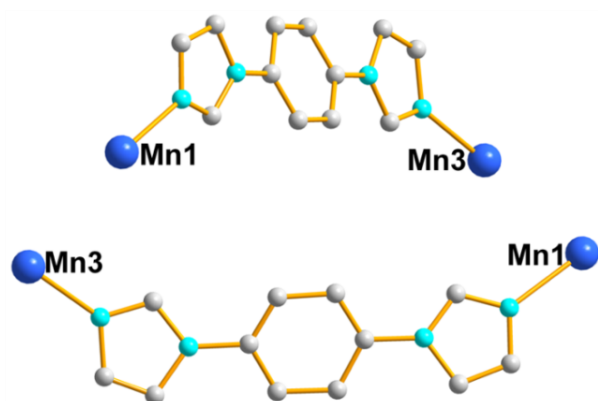


Fig. S7 The coordination modes of metal centers, L and dib ligands in **3**.

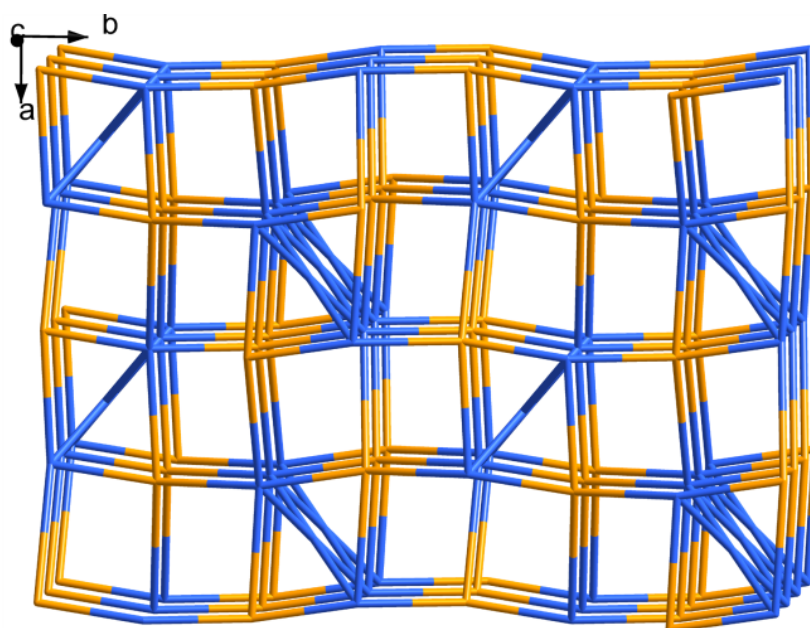
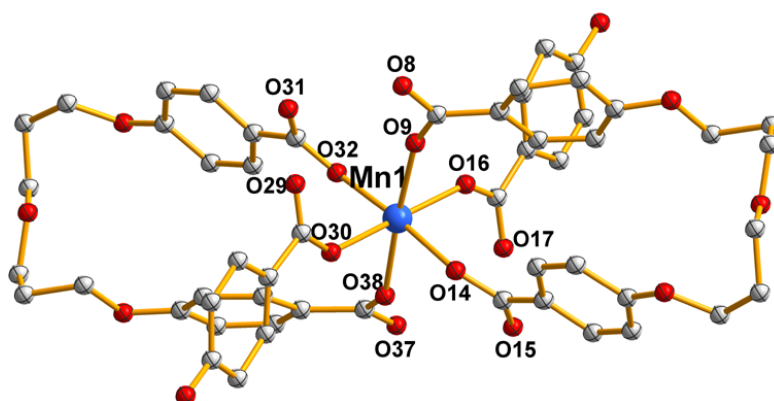
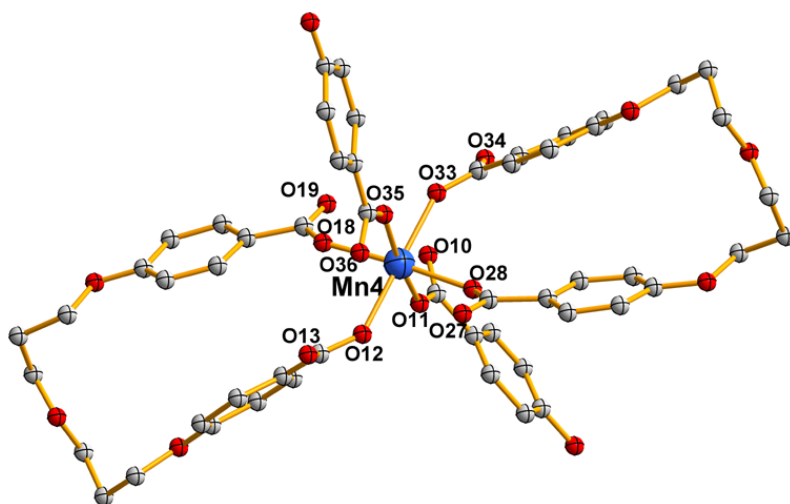
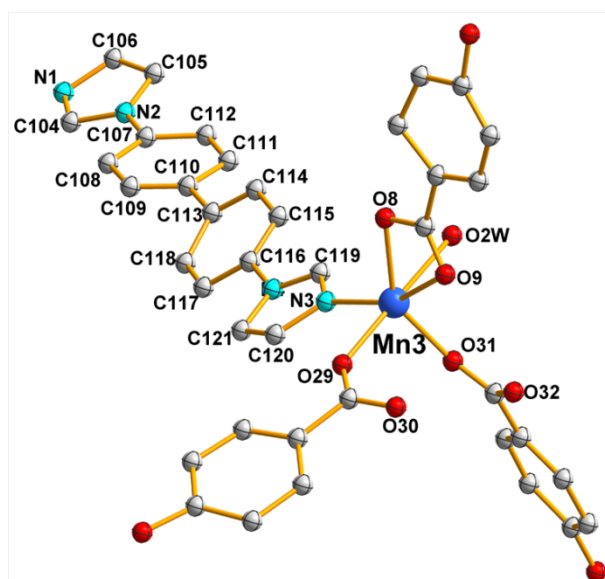
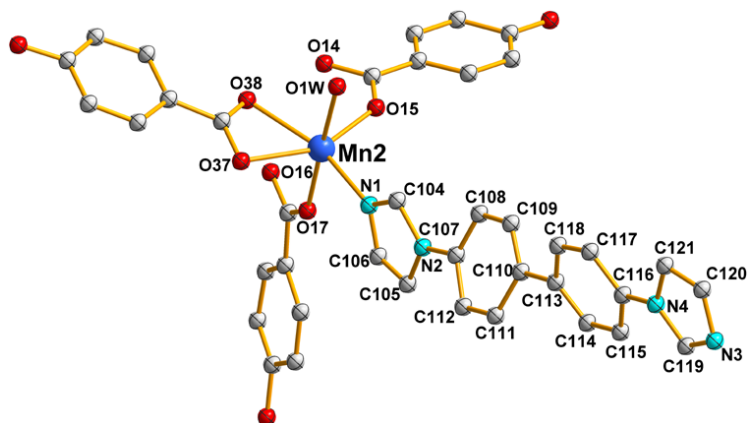
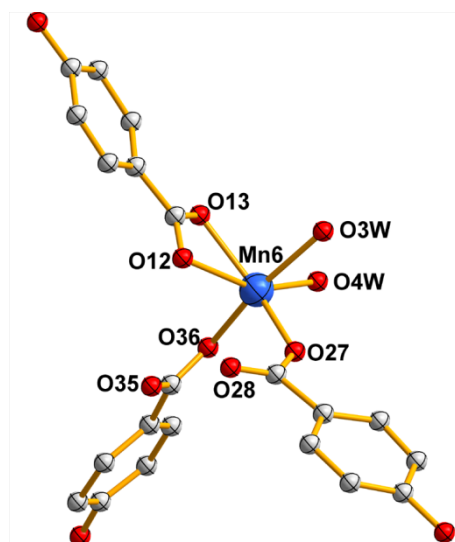
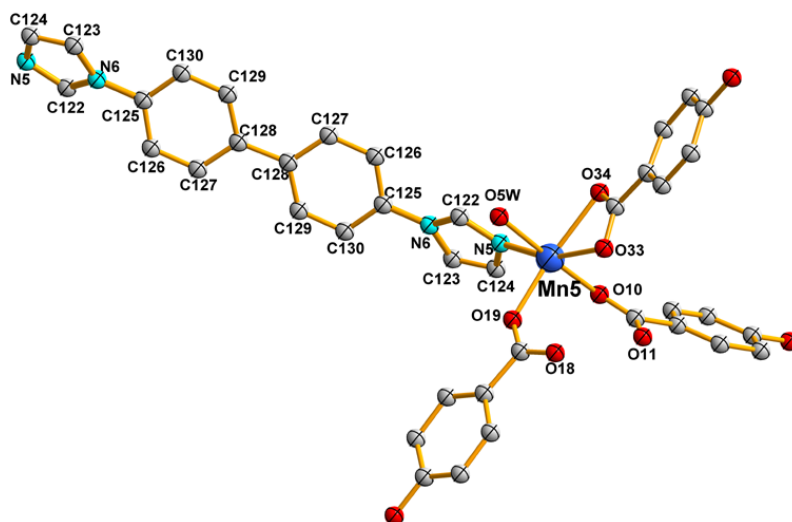


Fig. S8 The simplified net of **3**.







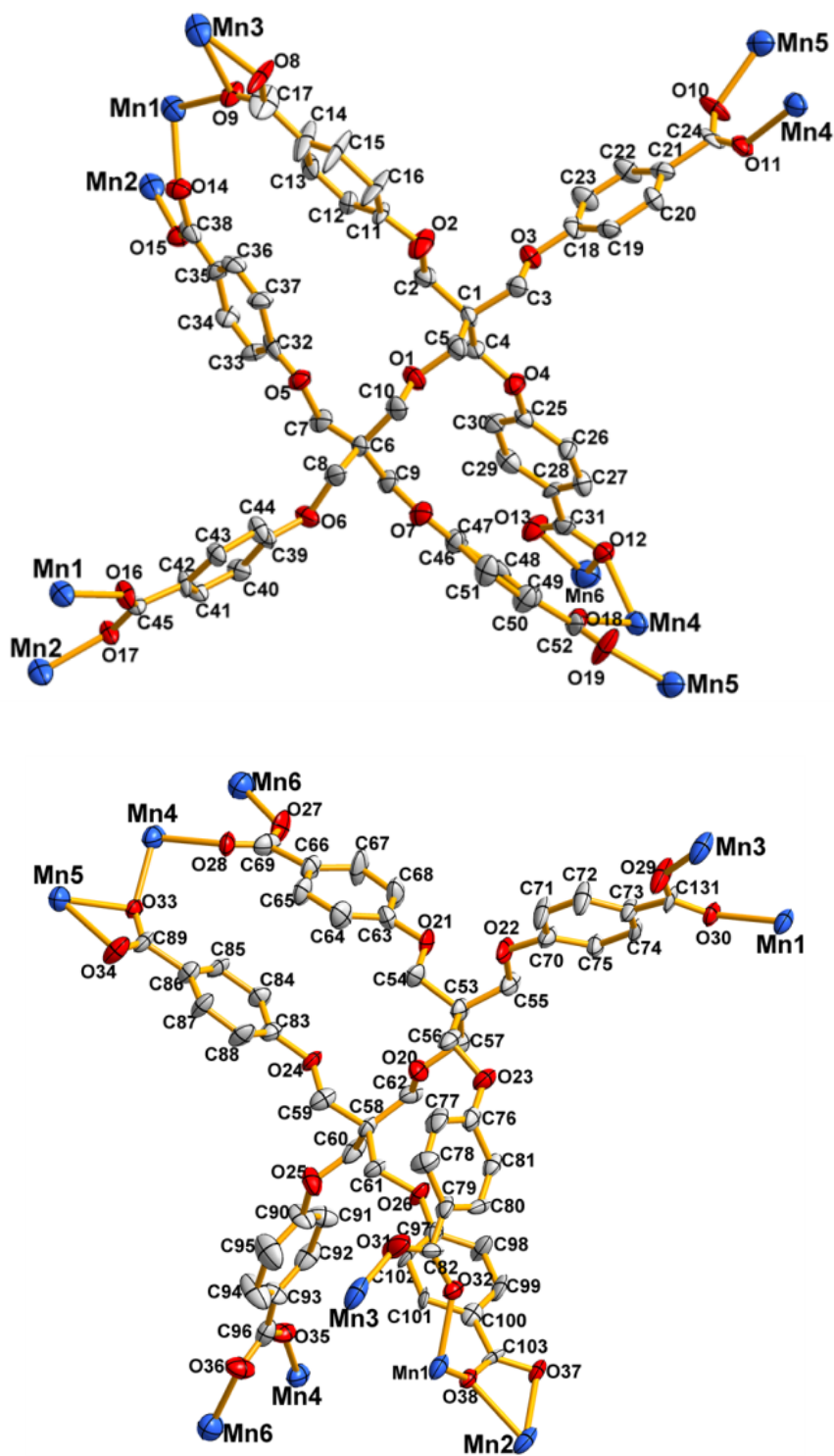


Fig. S9 The coordination modes of metal centers, and L ligands in 4.

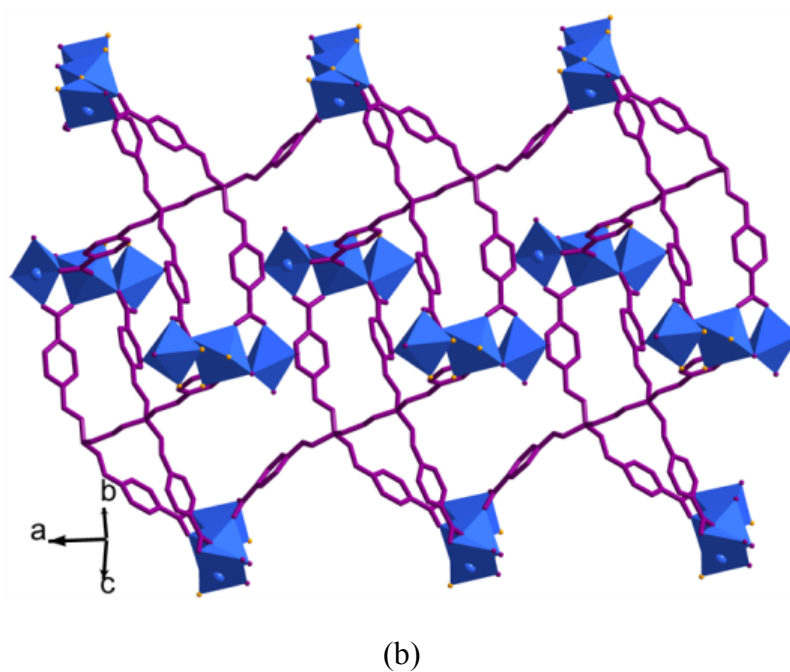
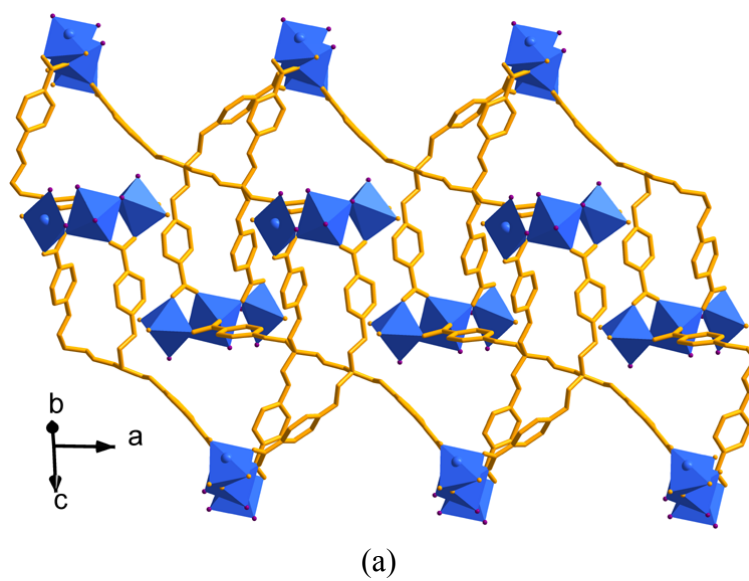


Fig. S10 The 1D chain forming between  $\text{Mn}^{\text{II}}_3(\text{A})$  and L(1) ligands (a), as well as  $\text{Mn}^{\text{II}}_3(\text{B})$  and L(2) ligands (b) in **4**. The ligands  $\text{L}_1(\text{O}(1))$  and  $\text{L}_2(\text{O}(20))$  are shown as gold, and violet sticks, respectively.

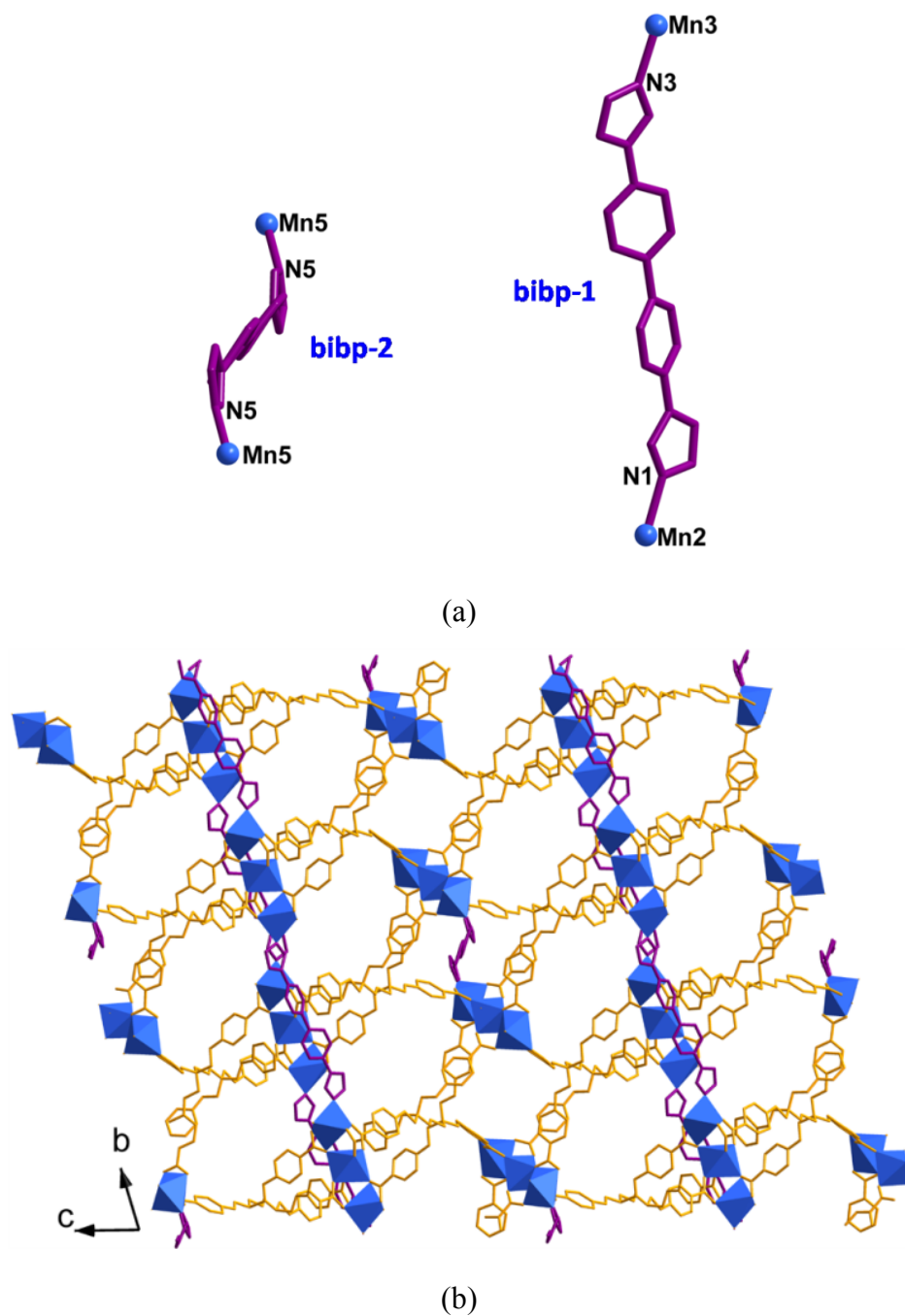


Fig. S11 (a) The coordination modes of two unique bibp ligands. (b) The 3D porous framework of 4. Metal polyhedra are shaded in blue. L and bibp ligands are shown as gold, violet sticks, respectively.

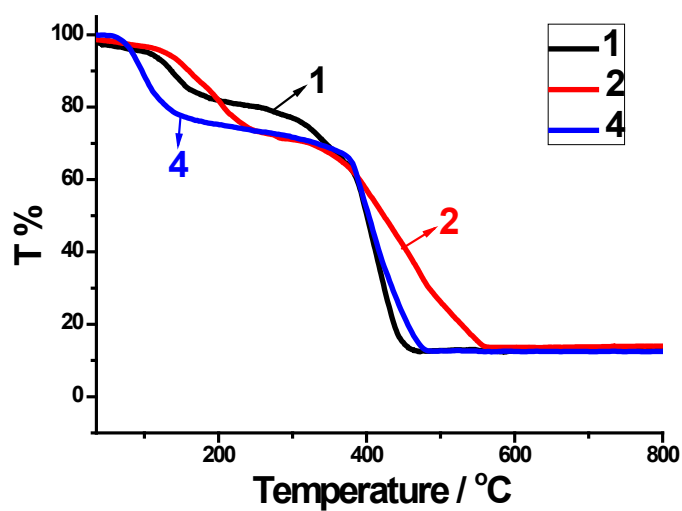


Fig. S12 TGA curves of complexes 1, 2 and 4.

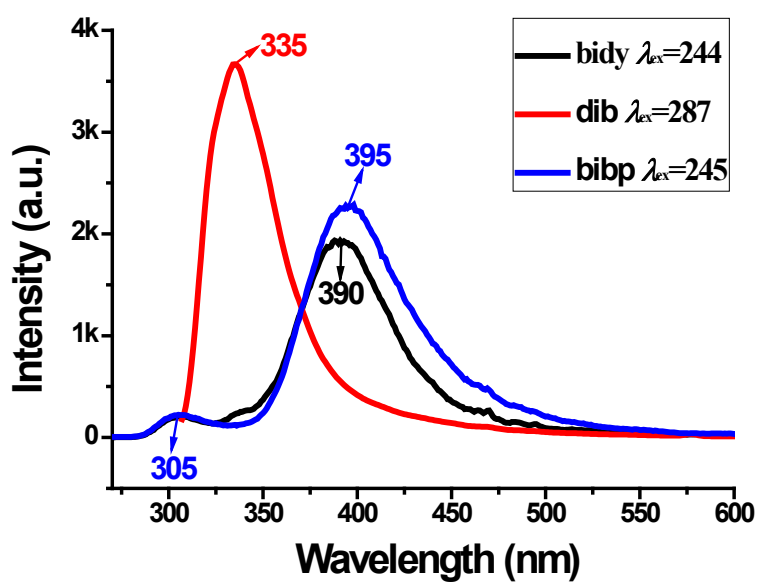


Fig. S13 Solid-state photoluminescent spectra of bipy (black), dib (red) and bibp (blue).