

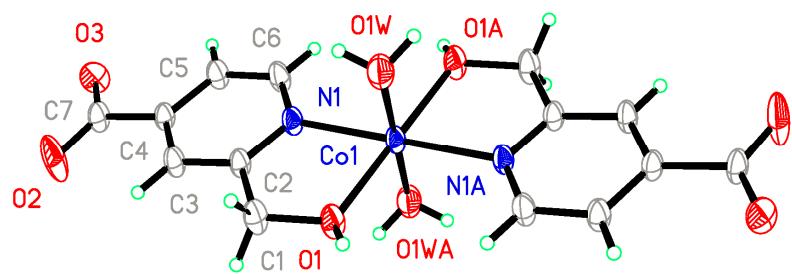
Electronic Supplementary Information

Isolation of First Row Transition Metal–Carboxylate Zwitterions

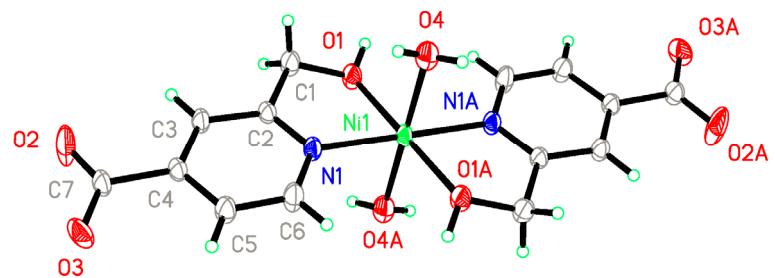
Mahsa Armaghan, W. Y. James Lu, Di Wu, Yao Wei, Feng-Ling Yuan, Seik Weng Ng, Mostafa M. Amini, Wen-Hua Zhang,* David J. Young,* T. S. Andy Hor* and Jian-Ping Lang

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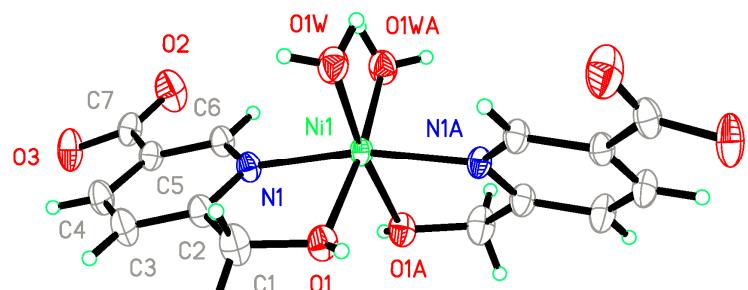
Fig. S1 Structure of <i>trans</i> -Co(<i>iso</i> -hmnnH) ₂ (H ₂ O) ₂ (3) (a), <i>trans</i> -Ni(<i>iso</i> -hmnnH) ₂ (H ₂ O) ₂ (4) (b), <i>cis</i> -Ni(hmnnH) ₂ (H ₂ O) ₂ (5) (c), <i>trans</i> -Co(3,2,4-hpbH)(H ₂ O) ₂ (15) (d) and <i>trans</i> -Ni(3,2,4-hpbH)(H ₂ O) ₂ (16) (e) with labeling schemes. Selected C–O bond distances: O ₂ –C7 1.244(1) Å, O ₃ –C7 1.246(1) Å (3); O ₂ –C7 1.238(1) Å, O ₃ –C7 1.244(1) Å (4); O ₂ –C7 1.230(2) Å, O ₃ –C7 1.271(1) Å (5); O ₂ –C13 1.249(4) Å, O ₃ –C13 1.262(4) Å (15) and O ₂ –C13 1.267(5) Å, O ₃ –C13 1.249(5) Å (16).	3
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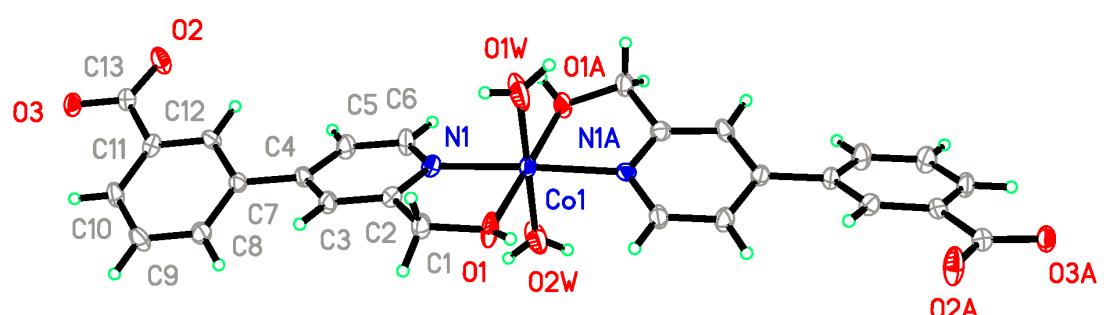
(a)



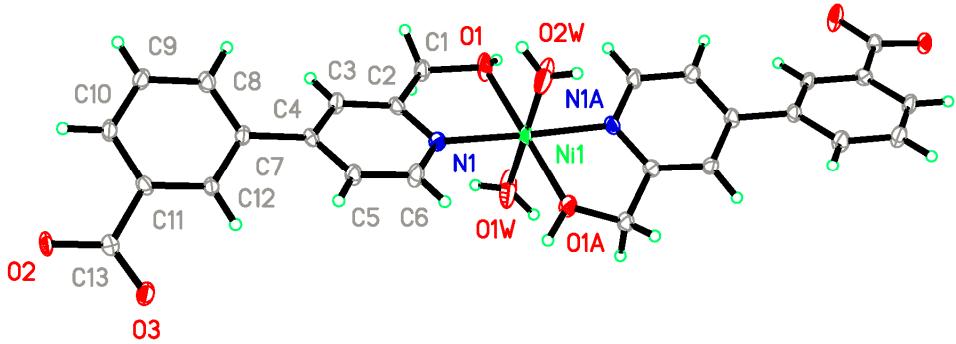
(b)



(c)



(d)



(e)

Fig. S1 Structure of *trans*-Co(iso-hmnH)₂(H₂O)₂ (**3**) (a), *trans*-Ni(iso-hmnH)₂(H₂O)₂ (**4**) (b), *cis*-[Ni(hmnH)₂(H₂O)₂]·2H₂O (**5**) (c), *trans*-Co(3,2,4-hpbH)(H₂O)₂ (**15**) (d) and *trans*-Ni(3,2,4-hpbH)(H₂O)₂ (**16**) (e) with labeling schemes. Selected C–O bond distances: O2–C7 1.244(1) Å, O3–C7 1.246(1) Å (**3**); O2–C7 1.238(1) Å, O3–C7 1.244(1) Å (**4**); O2–C7 1.230(2) Å, O3–C7 1.271(1) Å (**5**); O2–C13 1.249(4) Å, O3–C13 1.262(4) Å (**15**) and O2–C13 1.267(5) Å, O3–C13 1.249(5) Å (**16**).

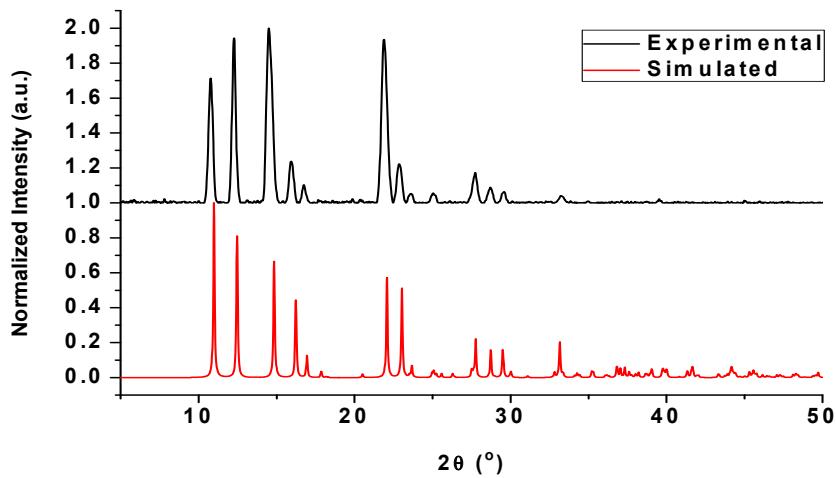


Fig. S2 Experimental (black) and simulated (red) powder X-ray diffraction (PXRD) pattern for $[\text{Cu}(\text{hmnh})_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}]_n$ (**8**).

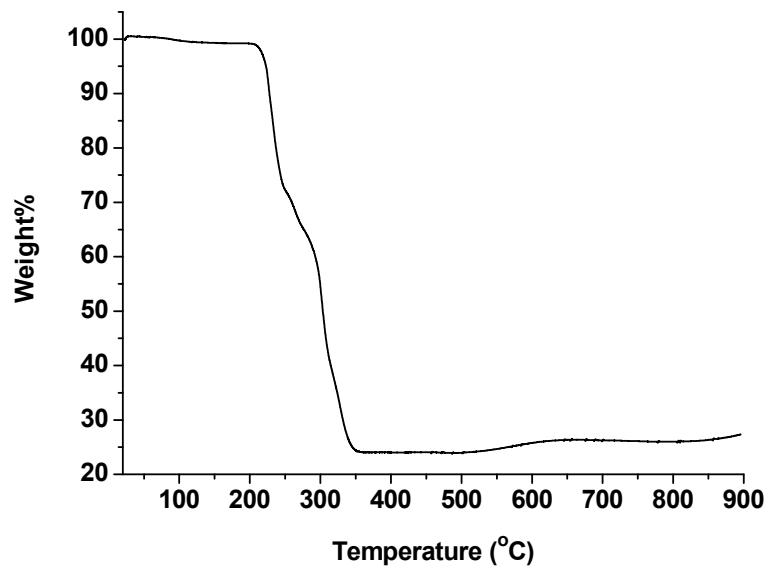
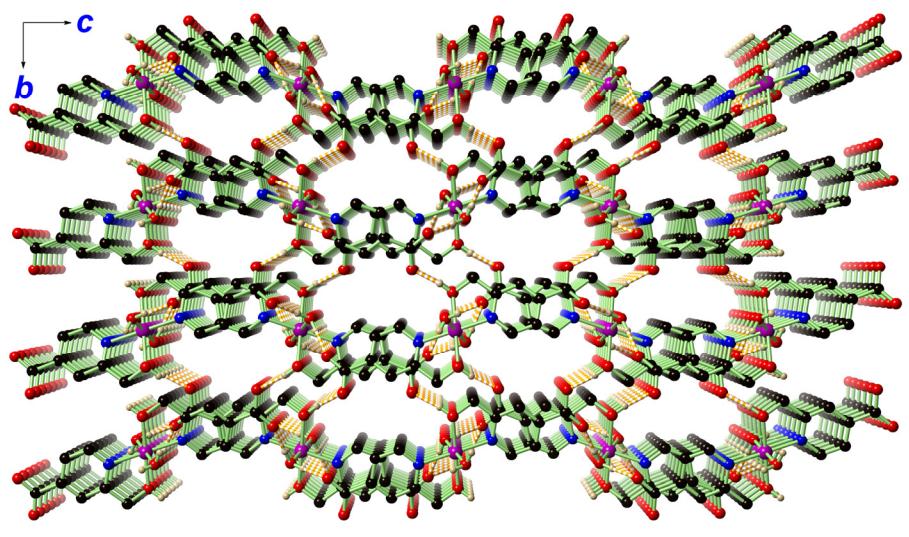
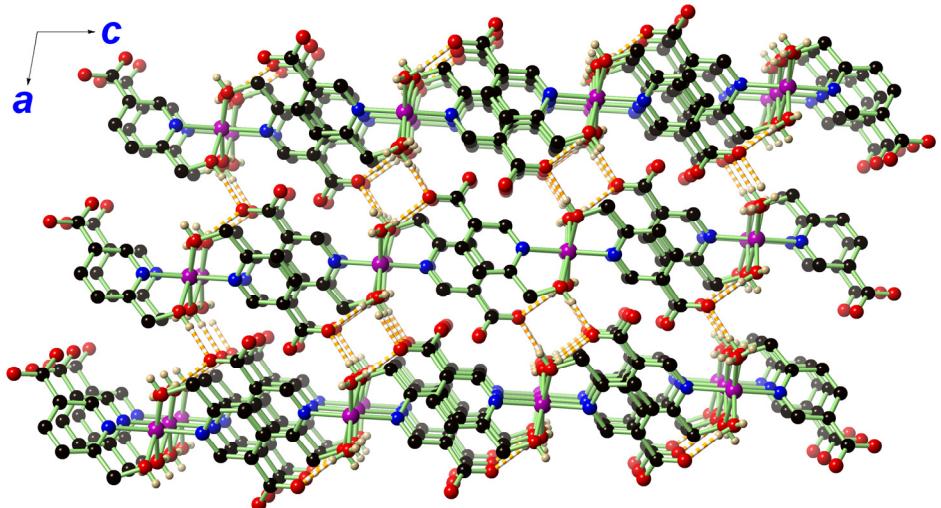


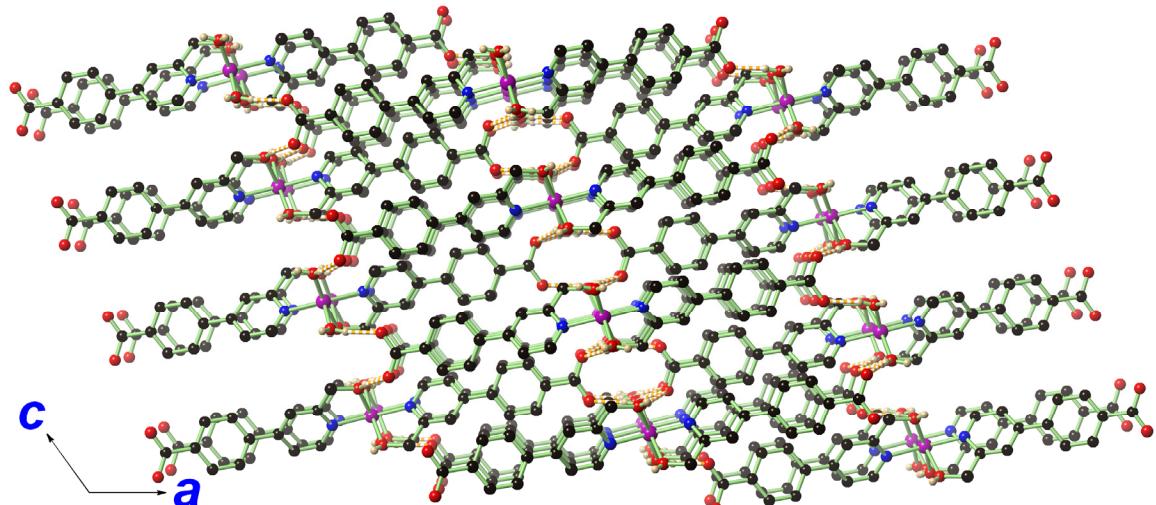
Fig. S3 TGA curves for $[\text{Cu}(\text{hmnh})_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}]_n$ (**8**).



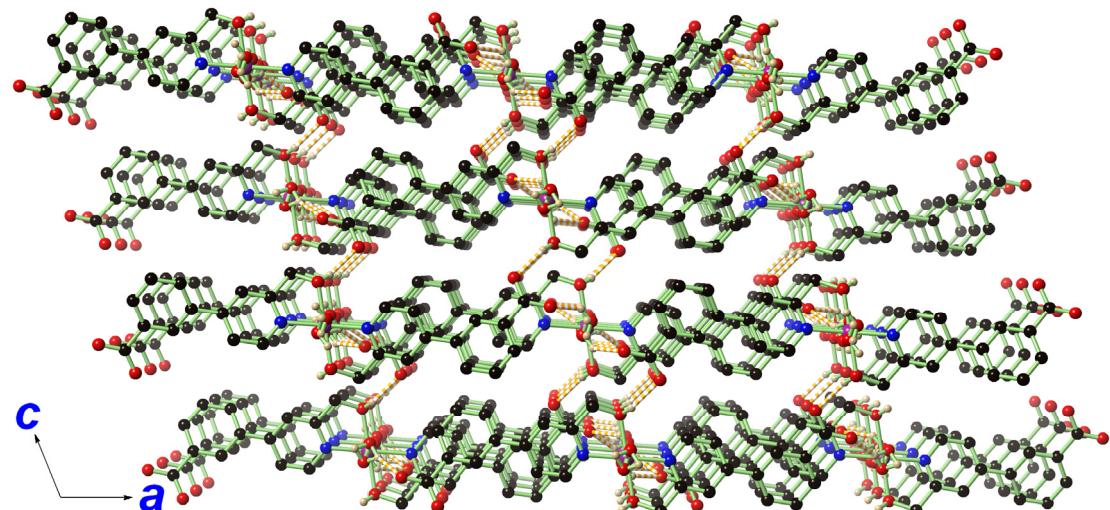
(a)



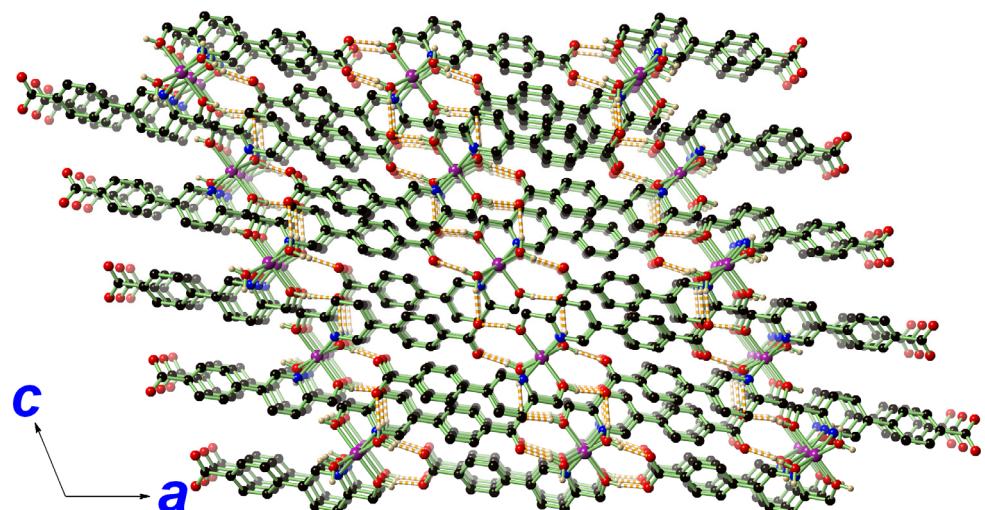
(b)



(c)

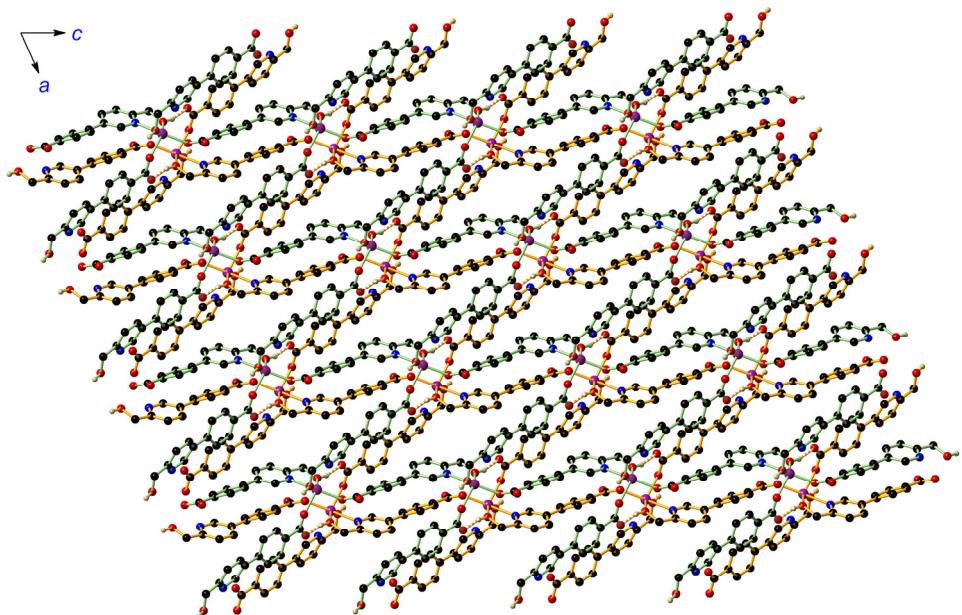


(d)

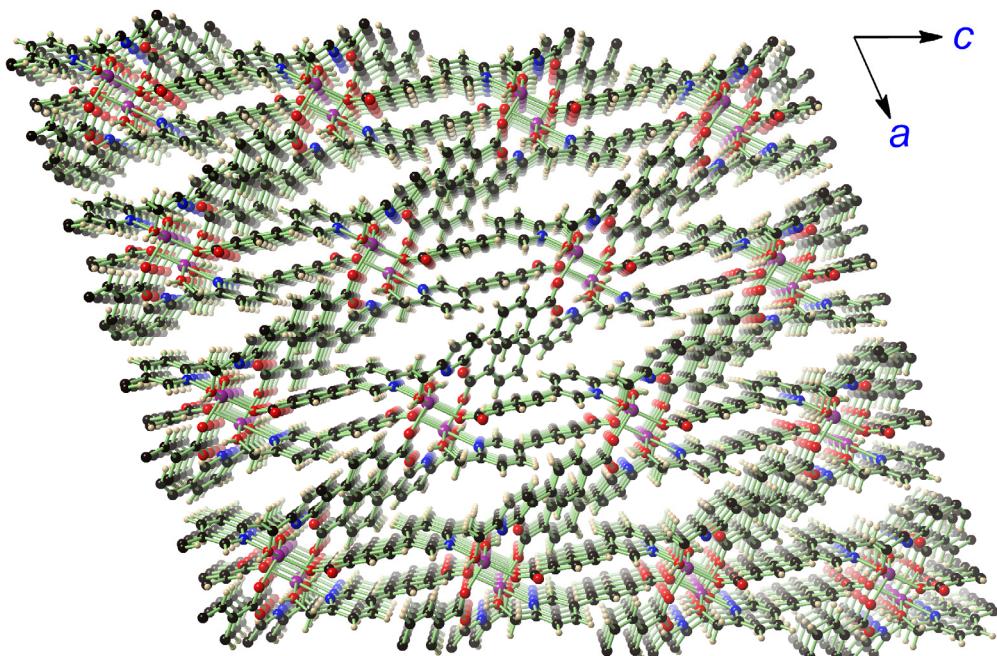


(e)

Fig. S4 Cell packing diagrams of *trans*-Zn(*iso*-hmnh)₂(H₂O)₂ (**1**) (a), *cis*-[Zn(hmnh)₂(H₂O)₂] · 2H₂O (**2**) (b), *cis*-Zn(4,2,4-hpbH)₂(H₂O)₂ (**12**) (c), *trans*-Zn(3,2,4-hpbH)₂(H₂O)₂ (**13**) (d) and *cis*-Zn(4,6,3-hpbH)₂(H₂O)₂ · H₂O (**14**) (e) showing intensive hydrogen bonding interactions among these zwitterions.



(a)



(b)

Fig. S5 Crystal structure of $[\text{Mn}(4,6,3\text{-hpBH})_2]_n$ (17) looking along the b direction showing, a) two adjacent layers (orange and bamboo) associated by hydrogen bonding interactions and b) cell packing diagrams.