

## Supplementary information

### Syntheses, structures, thermal stabilities, magnetism and luminescence of two 3D metal phosphonates

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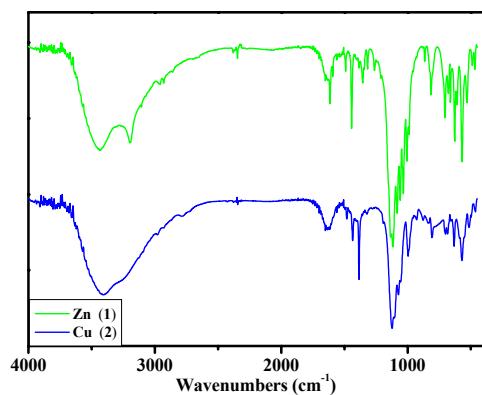


Fig. S1 IR curves of **1** and **2**.

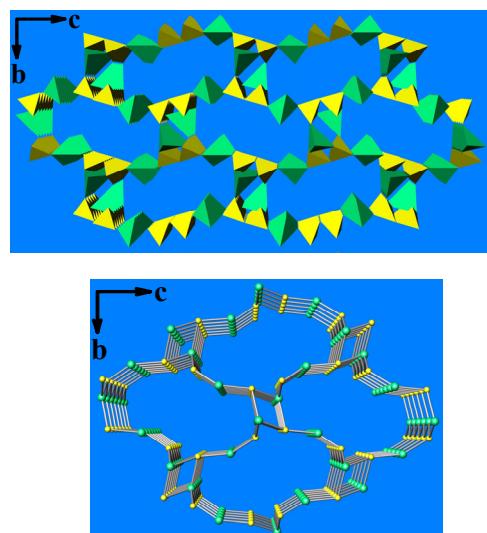
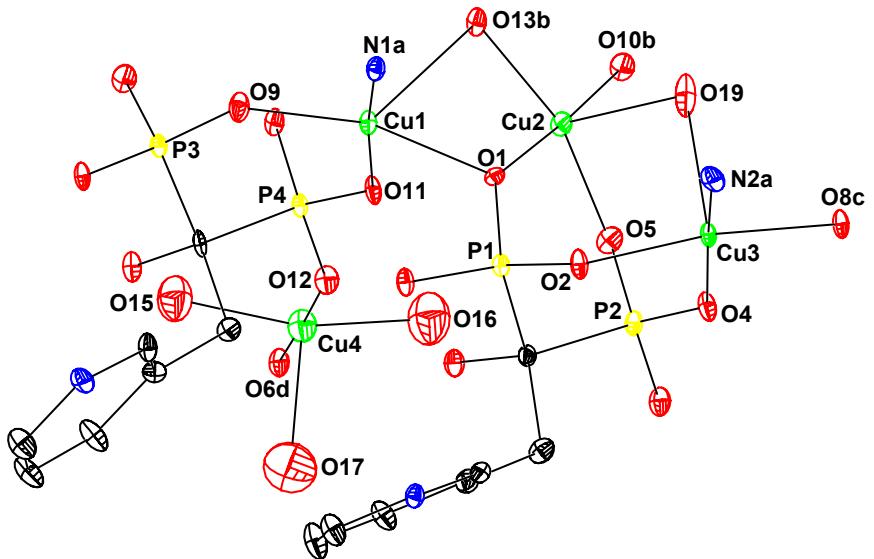
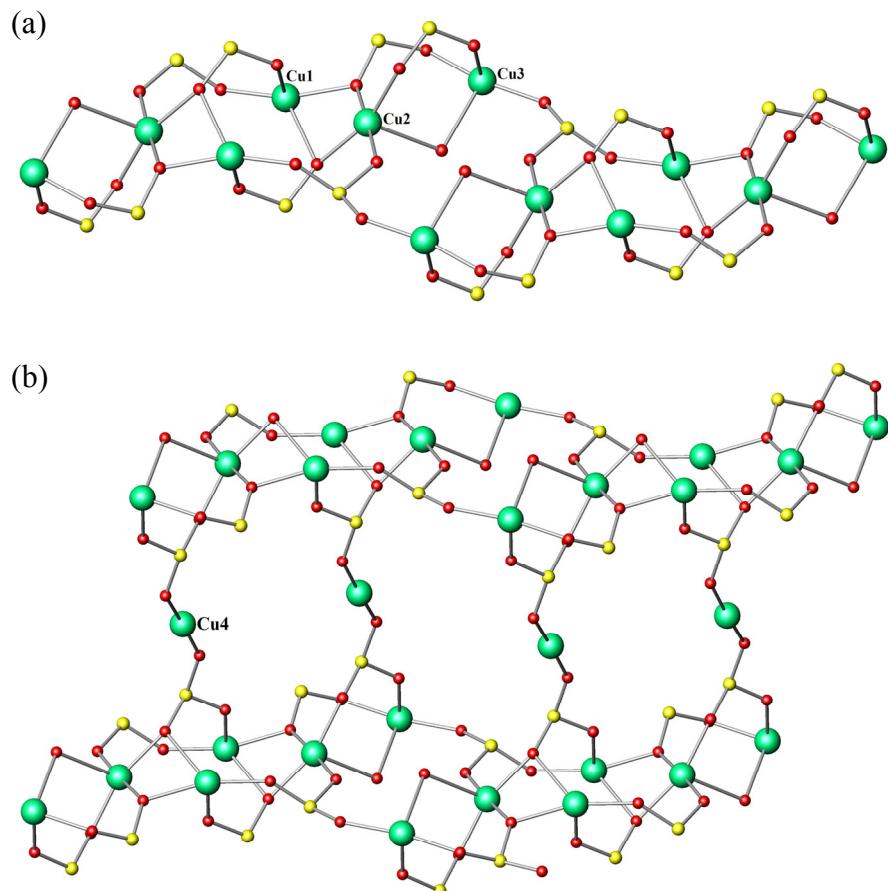


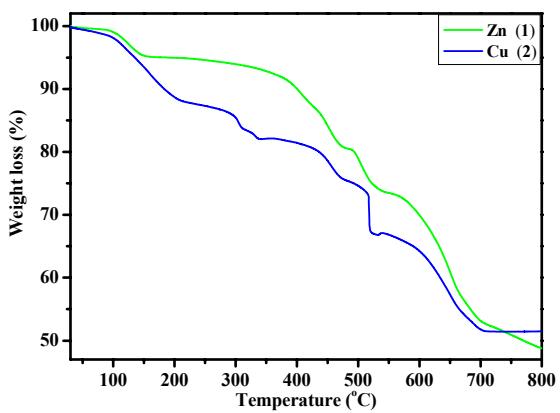
Fig. S2 Polyhedral (top) and ball-stick (bottom) view of the 3D framework for **1**.



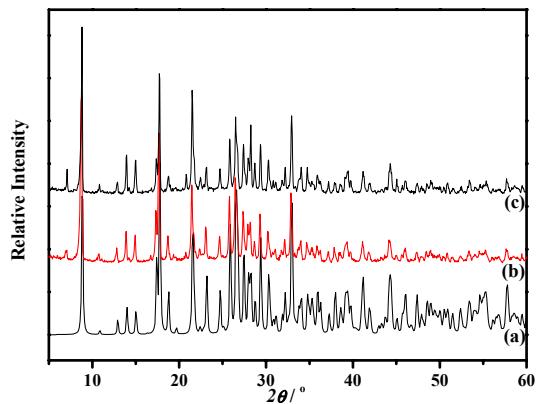
**Fig. S3** ORTEP view of the asymmetric unit (ellipsoids at 25% probability) of **2**. Unrelated atoms are omitted for clarity. Symmetry codes: *a* -  $x + 1, -y, -z + 1$ ; *b* -  $x + 1, -y, -z$ ; *c*  $x, y + 1, z$ ; *d* -  $x + 2, -y, -z$ .



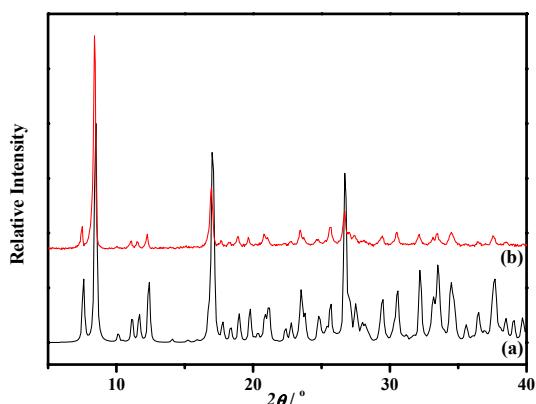
**Fig. S4** Ball-stick view of (a) the chain and the hybrid layer in **2**.



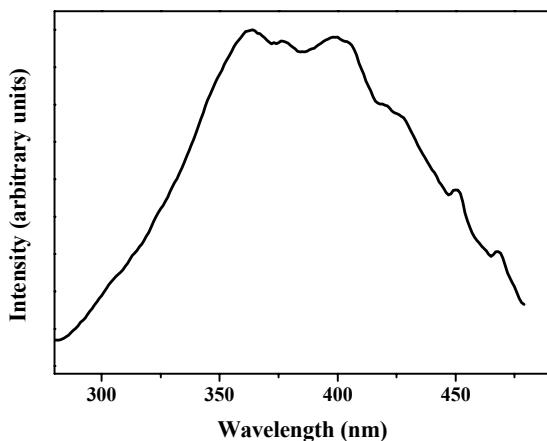
**Fig. S5** TGA curves of **1** and **2**.



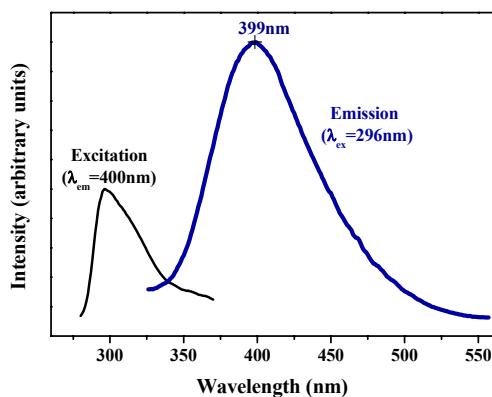
**Fig. S6** The XRD patterns of **1** (a) simulated from X-ray single crystal data, (b) polycrystalline as newly synthesized, and (c) polycrystalline annealed at 250 °C.



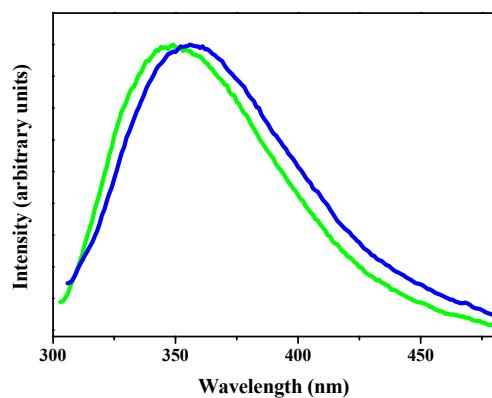
**Fig. S7** The XRD patterns of **2** (a) simulated from X-ray single crystal data, and (b) polycrystalline as newly synthesized.



**Fig. S8** Normalized fluorescent emission spectrum of  $[\text{Co}(\text{LH}_2)(\text{H}_2\text{O})]$ .

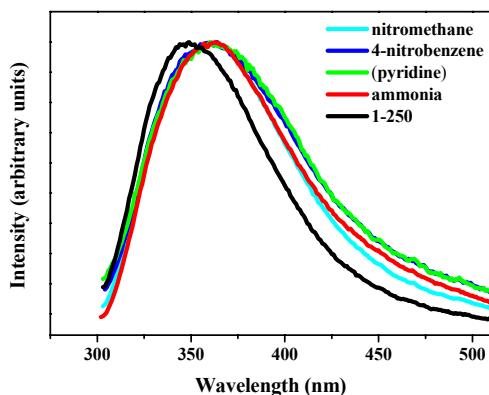


**Fig. S9** Normalized fluorescent emission and excitation spectra for  $[(\text{C}_5\text{H}_4\text{N})\text{CH}_2\text{CH}(\text{OH})(\text{PO}_3\text{H}_2)_2]\cdot\text{H}_2\text{O}$ .

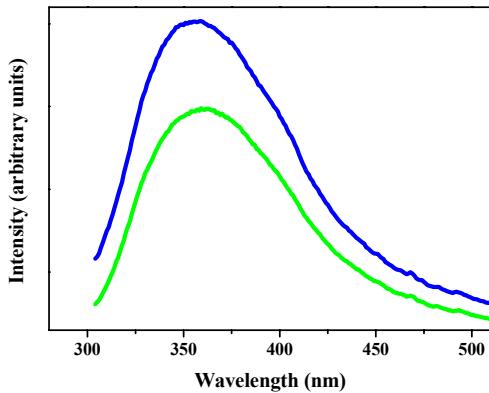


**Fig. S10** Normalized fluorescent emission spectra of as-prepared **1** (blue) and **1-250** (green).

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**Fig. S11** Normalized fluorescent emission spectra of **1-250**, as well as solid **1-250** has been exposed to nitromethane, 4-nitrotoluene, pyridine and ammonia.



**Fig. S12** Relative intensities of emission for solid **1-250** which has been exposed to the equilibrated vapors of a mixture of 2.5mmol nitrobenzene with 2.30ml water for 3 days (green), as well as briefly heating with infrared lamp for about 30 minutes (blue).