Electronic Supplementary Information for MS:

An unprecedented eight-connected self-penetrating network based on pentanuclear zinc clusters as building blocks

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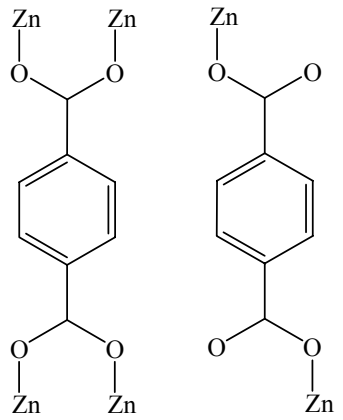
The synthesis of compound 1:

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (149mg, 0.5mmol), H_2bdc (66mg, 0.4mmol), phen (40mg, 0.2mmol), and water (10mL) in a 23ml Teflon reactor, under autogenous pressure at 140 ^oC for 5 days and then cooled to room temperature at a rate of 10 $^oC\ h^{-1}$. Colorless crystals of **1** were obtained (yield: 50mg, 36% based on Zn). Elemental analysis calcd (%) for $C_{56}H_{34}Zn_5N_4O_{18}$: C 48.82, H 2.49, N 4.07; found: C 48.93, H 2.32, N 4.15.

Luminescent properties of 1:

The solid-state luminescent property of **1** was investigated at room temperature. While the free H_2bdc ligand displays weak luminescence in the solid state at room temperature (λ_{ex} = 350 nm, λ_{em} = 390 nm) attributable to a $\pi^* \rightarrow n$ transition, compound **1** exhibits an intense emission maximum at $\lambda \approx 462$ nm upon excitation at λ = 381 nm (Fig. S2†). The enhancement of luminescence may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay. The lifetime of **1** is about 15 ns, which is significantly longer than for those without metal-hydroxy clusters. This fact may be ascribed to the presence of the metal clusters, since the μ_3–OH ligand may tighten the whole skeleton, resulting in much weaker vibrations.



Scheme S1 Coordination modes of the bdc ligands in the structure of **1**. I: bis(bidentate), II: bis(monodentate).

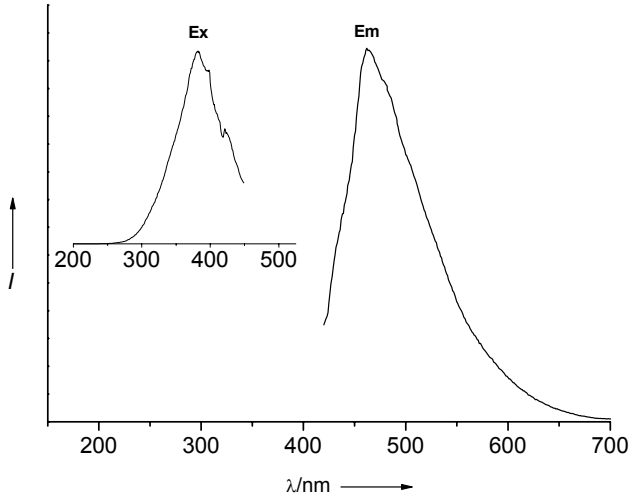


Fig. S1 Photoluminescent spectra of **1** in the solid state at room temperature. Ex = excitation, Em = emission

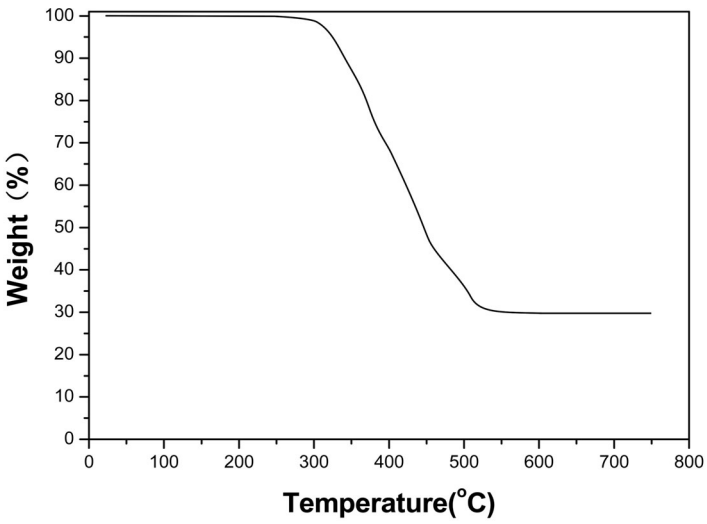


Fig. S2 TG curve of **1**.

The framework is stable up to 280 ^{o}C where the decomposition starts and ends above 550 ^{o}C. The one-step weight loss (found: 70.69%) corresponds to the loss of organic components (calcd: 70.47%). The remaining weight of 29.31% corresponds to the percentage (29.53%) of Zn and O components, indicating that the final product is ZnO.