1. X-ray crystallographic study

Single crystal X-ray diffraction was performed on an Oxford Xcalibur Eos CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. The data were corrected for Lorentz and polarization effects as well as for absorption. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedure on F^2 with SHELXL-97. Some of the C, O and N atoms in the 1,10-phen, 2-MepyH and TDC ligands in compound 1 were refined with 667 restraints (DFIX, SIMU, DELU and ISOR) to obtain the chemical-reasonable models and reasonable atomic displacement parameters. In compound 1, there still exist a few large isolated residual density peaks (< 2.233 eÅ^-3) in the difference Fourier-maps that should be assigned for the oxygen atoms of highly disordered lattice water molecules. However, it was difficult to locate all the disordered water molecules according to the D-F maps. Therefore, finally only one lattice water molecule per asymmetric unit was added and refined. The empirical formula of 1 was determined to include 20 water molecules according to the EA and TGA analyses. In compound 2, 1219 restraints (DFIX and SIMU) were applied for some of the C and N atoms in the 2-MepyH cations so that their bond geometries and atomic displacement parameters were reasonable. A few large residual density peaks (< 1.693 eÅ^-3) are present close to the metal atoms due to the smearing effect of the heavy metals which shows no feature.
2. More Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex II diffractometer using CuKα radiation. C, H and N analyses were performed on a German Elementary Vario EL III instrument. IR spectrum was recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range of 4000~450 cm⁻¹. Thermogravimetric (TG) analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 10 °C/min under a nitrogen atmosphere. Optical diffuse reflectance spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer. A BaSO₄ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectrum by using the Kubelka–Munk function: \( a/S = (1-R)^2/2R \), where \( a \) is the absorption coefficient, \( S \) is the scattering coefficient which is practically independent of wavelength when the particle size is larger than 5 μm, and \( R \) is the reflectance. Photoluminescence spectrum was recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a R928 red-sensitive photomultiplier without correction.

Fig. S2 Comparison of the powder X-ray diffraction patterns of compounds 1 (left) and 2 (right) with that simulated from the single-crystal X-ray diffraction data (bottom).
Fig. S3 IR Spectra of 1 (left) and 2 (right).

Fig. S4 TG curve of compounds 1 (left) and 2 (right).

Fig. S5 Variations of $(\alpha h\nu)^{1/2}$ as function of photon energy for 1 (left) and 2 (right).
Fig. S6 Solid-state emission spectra of compounds 1 (left) and 2 (right).

3. More structural Figures

Fig. S7 Clusters A (left) and B in 1.

Fig. S8 Prospective view of the two-fold interpenetrating anionic network of 1 (right) along the c-axis and a fragment of the double-helical chains (left) along the c-axis, with the [Fe(1,10-phen)₃] cations labeled.
Fig. S9 Topological view of the two-fold interpenetrating nets in 1.

Fig. S10 [Pr$_2$Sb$_{12}$O$_{18}$(OH)Cl$_{14}$] cluster in 2.