

Structure and Near Infrared Luminescence of Unique 4d-4f Heterometal-Organic Frameworks (HMOF)

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Crystallographic studies: Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.^[1,2] Hydrogen atoms were located geometrically and refined isotropically. See the CIF file for details.

(1) Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.

(2) Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

Physical measurements: Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. The thermal gravimetric analysis (under oxygenated atmosphere, heating rate of 10°C/min) for **2** was completed on a Labsys NETZSCH TG 209 Setaram apparatus. Luminescence spectra in the near-infrared (NIR) region of **1** and **2** were recorded by a homemade apparatus based on an Edinburgh CD900 spectrofluorimeter, which uses a Xenon lamp as the excitation source and a liquid nitrogen cooled hyperpure germanium crystal as a detector.

Detailed report on TGA of 2: Thermal gravimetric analysis (TGA) was performed on crystalline samples of **2** in the range of 18 to 800°C (SI-5). The TGA results reveal that the weight loss of 1.84% for **2** between 214 and 320°C corresponds to the loss of all coordinated water molecules (calcd. 2.07%).

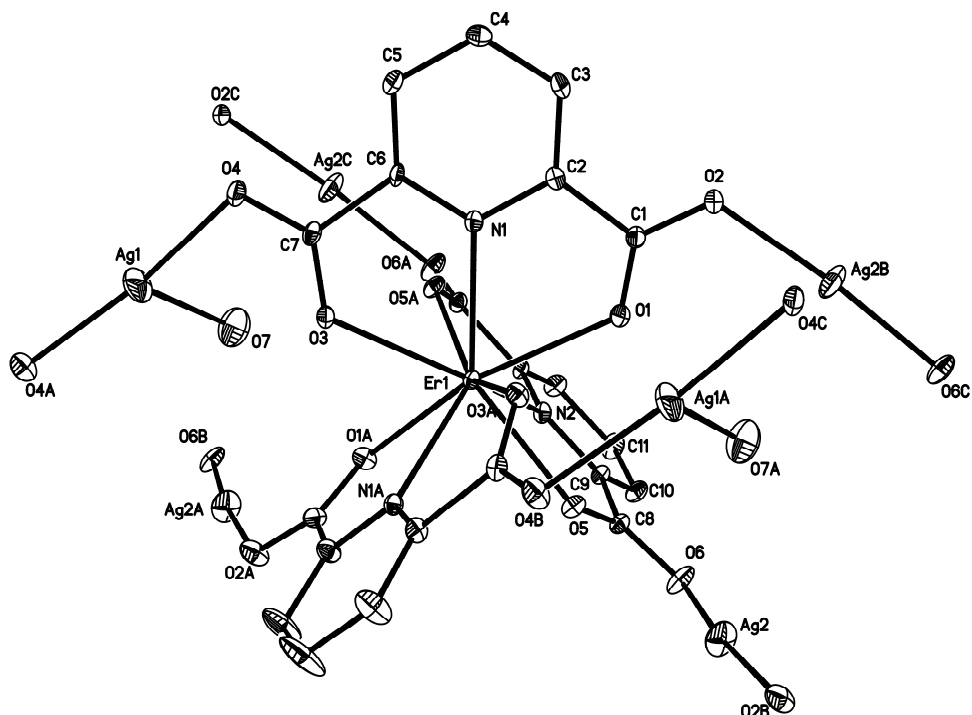


Figure S1. The molecular structure of **1**, showing the coordination environments of Er^{3+} and Ag^+ ions. H atoms were omitted for clarity.

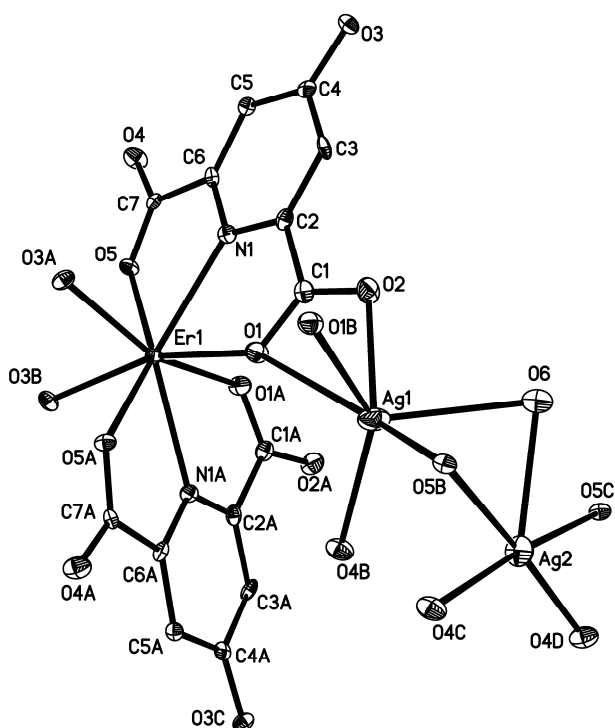


Figure S2. The molecular structure of **2**, showing the coordination environments of Er^{3+} and Ag^+ ions. H atoms were omitted for clarity.

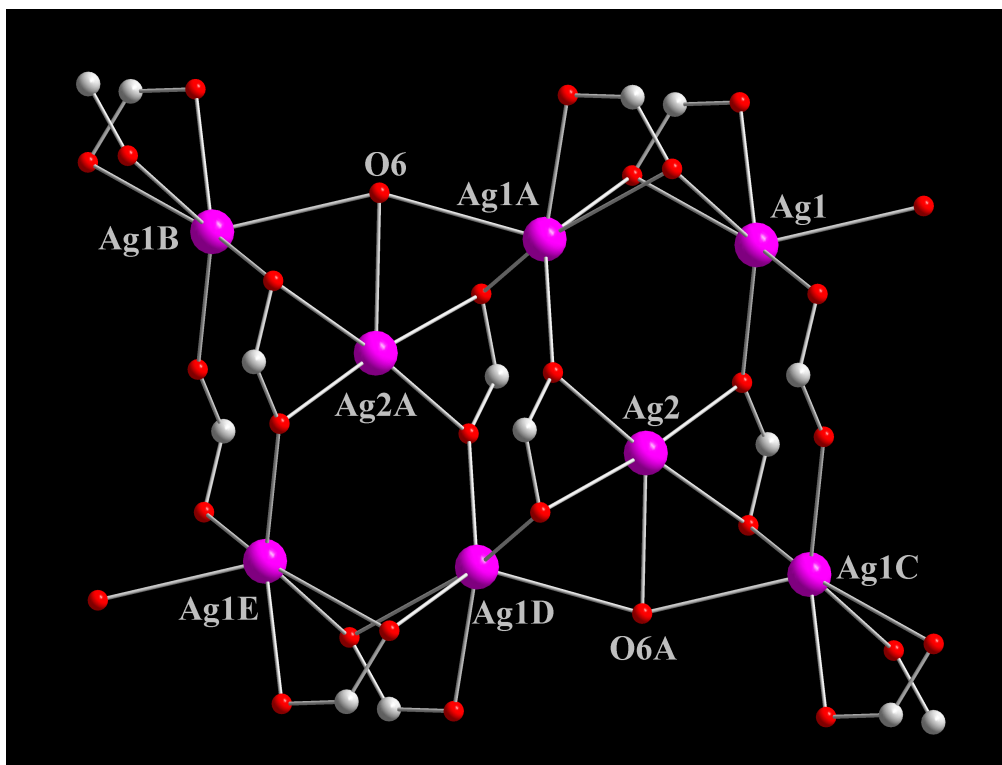


Figure S3. In **2**, the structure of the Ag_8 cluster as a repeat unit in 1D Ag-belt. Color codes: C, gray; Ag, purple; O, red.

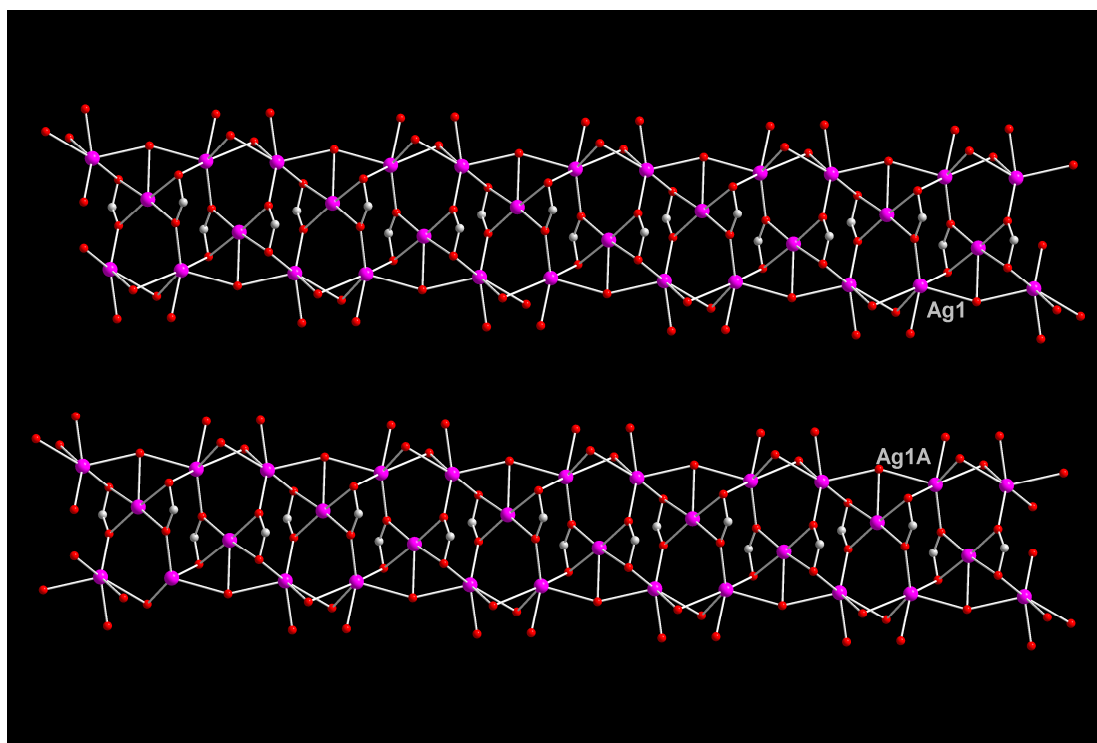


Figure S4. The separation between adjacent 1D Ag-belt in *ac* plane with about 8.8 Å (defined by the separation between Ag1 and Ag1A).

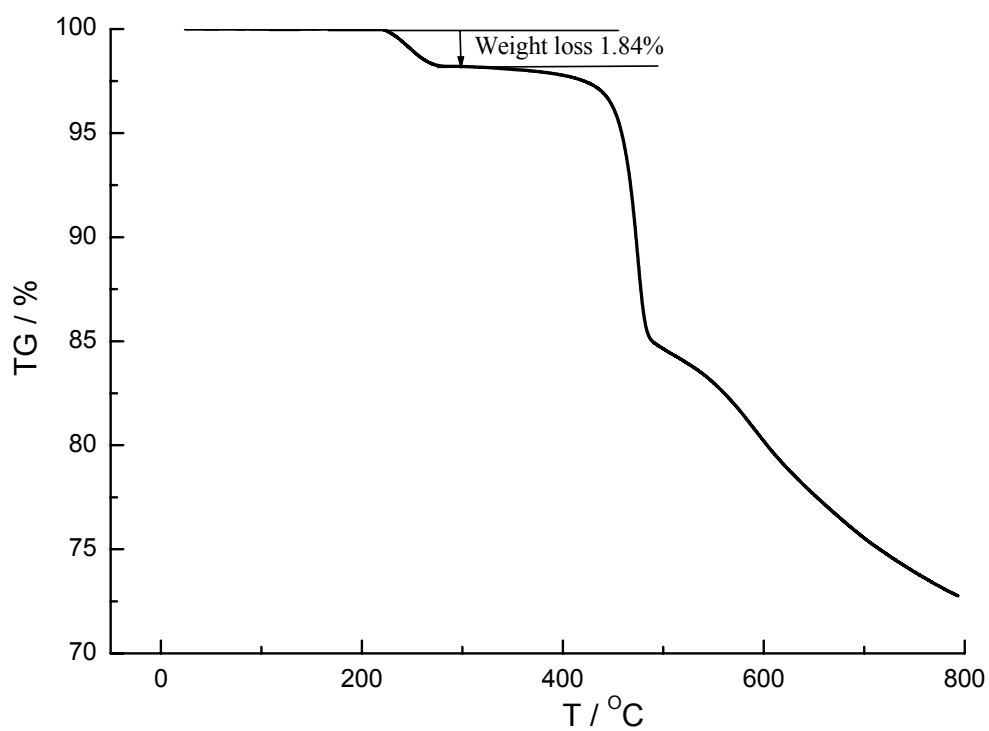


Figure S5. TGA curves of **2**.

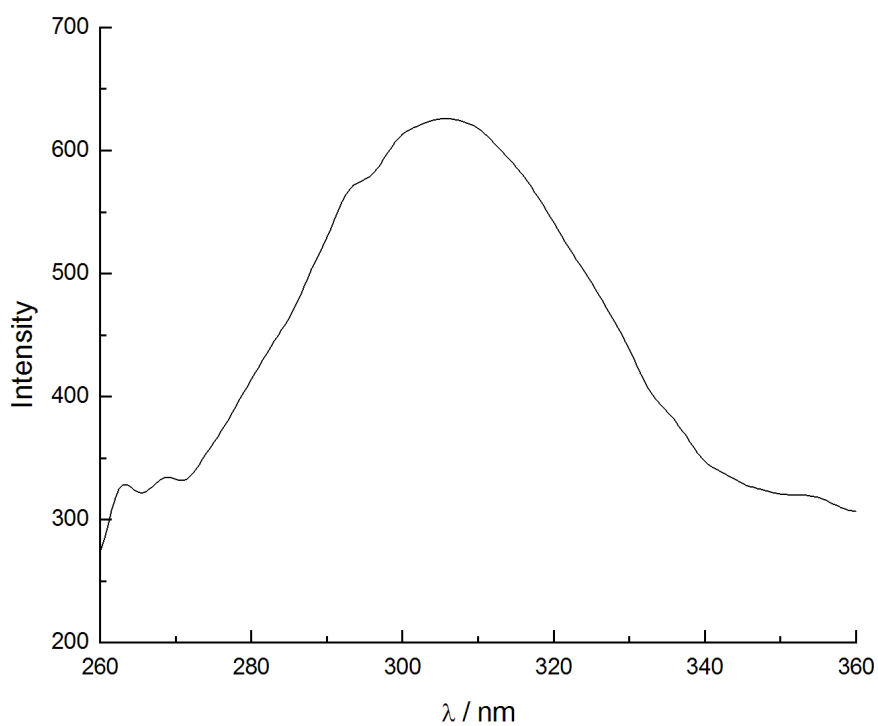


Figure S6. The excitation spectrum of **1** (emission at 1540 nm).

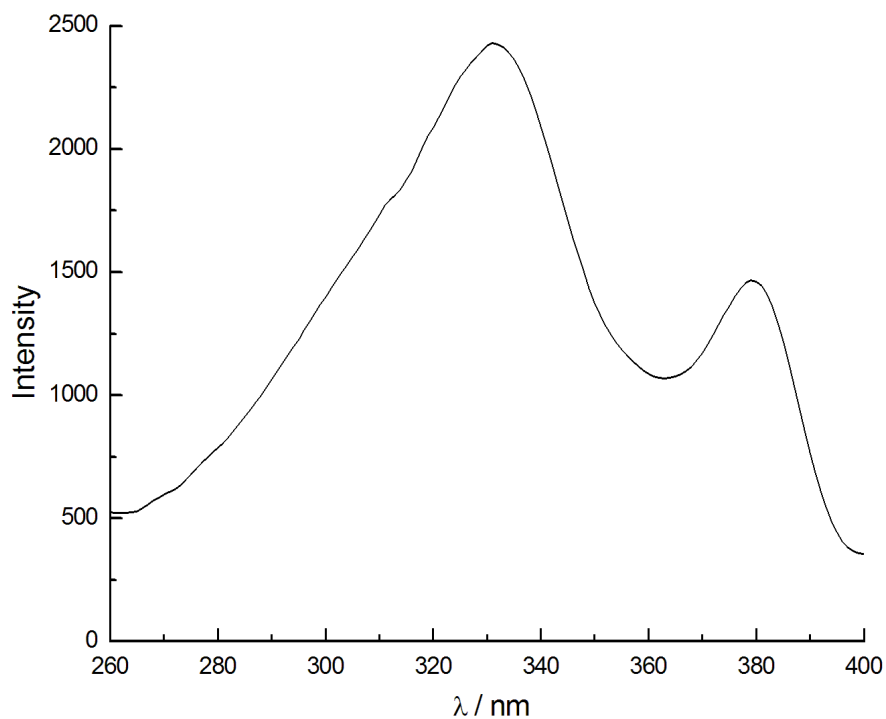


Figure S7. The excitation spectrum of **2** (emission at 1540 nm).

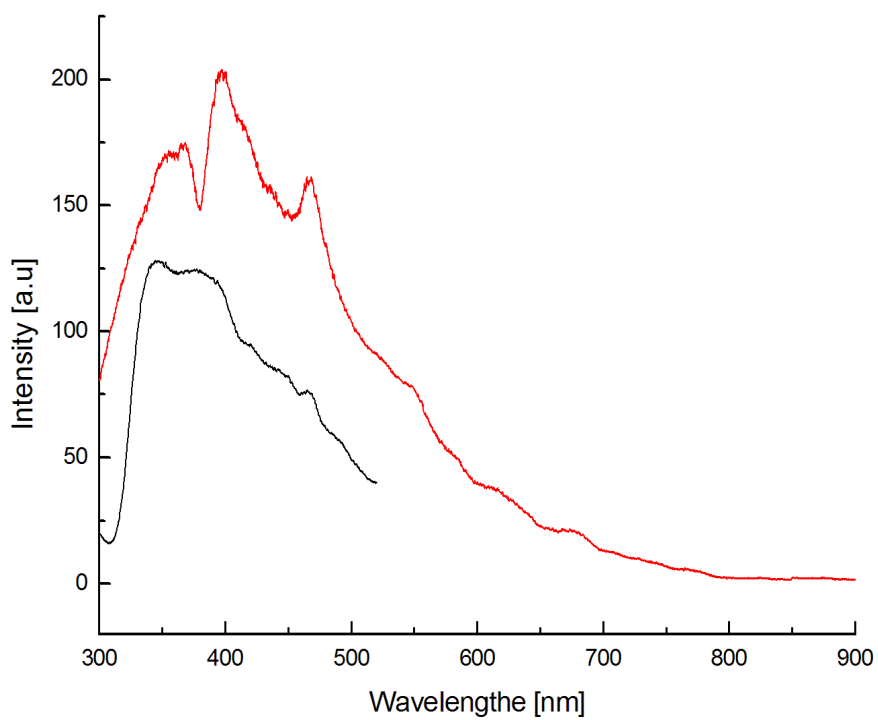


Figure S8. The emission spectra of H₂PDA (black) and **1** (red) (excited at 260 nm).

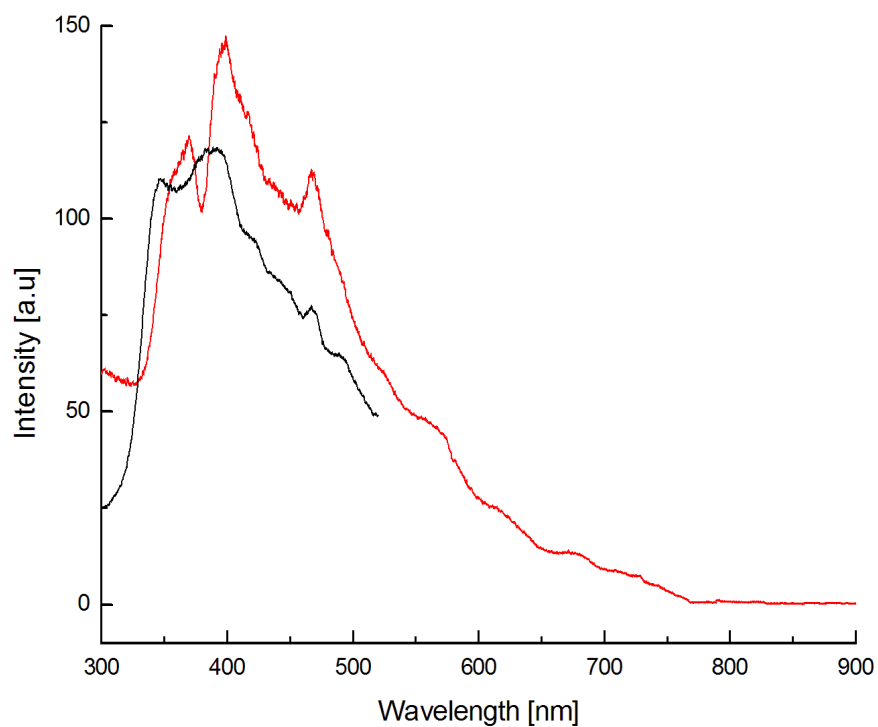


Figure S9. The emission spectra of H₃CAM (black) and 2 (red) (excited at 260 nm).