

Supporting information

Luminescence Behaviour of Pb²⁺-Based Cage-Containing and Channel-Containing Porous Coordination Polymers

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Experimental

Materials and measurements

The ligand quinoline-2-carbonitrile (**QCN**), was bought from purchased from Acros Organics. 2-cyano-1,10-phenanthroline (**PhenCN**) was synthesized according to literature procedures.^[1] The other materials, which were of reagent grade, or were obtained from commercial sources and used without further purification. Elemental analysis was performed with an ElementarVario MICRO Cube elemental analyzer. IR spectra of the solid samples as KBr discs were obtained within the range 4000–400 cm⁻¹ with an AVATAR 360 FTIR spectrometer. Luminescent spectra were measured at room temperature with a Horiba JobinYvon Fluorolog-3-TCSPC spectrofluorometer. Thermogravimetric analyses were performed using a Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C min⁻¹ in flowing nitrogen atmosphere. X-ray powder diffraction measurements were measured by using a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator.

X-ray Crystal Structure Determination: The crystal structures were determined with an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer by using graphite-monochromated Cu-K α radiation ($\lambda = 1.5417$). The structures were solved by using direct methods with the SHELXS-97 program.^[2] The Pb atoms and many of the non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were located after refinement by full-matrix least-squares by using the SHELXL-97 program.^[3] In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by using the SHELXL-97 program. The positions of the H atoms were calculated based on the riding model with 521 thermal parameters that were 1.2 times that of the associated C atoms and participated in the calculation of the final *R* indices. For the refinement of crystal structure of **2**, there was disordered associated with solvent molecules. There were extensive areas of residual electron density that could not sensibly be modeled as solvent or anions, which were removed via application of the Squeeze function in PLATON.^[4]

Synthesis of $[\text{Pb}_5(\text{L}_1)_6(\text{N}_3)_2(\text{OH})_2]_n$ (**1**). A mixture of quinoline-2-carbonitrile (QCN) (20 mg, 0.13 mmol), $\text{Pb}(\text{NO}_3)_2$ (66.2 mg, 0.2 mmol), NaN_3 (13 mg, 0.2 mmol) and EtOH/ H_2O (15 mL, v/v = 1/2) was sealed in a 15 mL Teflonlined stainless-steel reactor, heated at 120 °C for 72 hours under autogenous pressure, and then slowly cooled to room temperature at a rate of 6 °C h⁻¹. Colorless block crystals of **1** were collected by filtration and washed with ethanol several times. Yield 35.6 mg, 58.4 % (based on QCN). Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{38}\text{N}_{36}\text{O}_2\text{Pb}_5 \cdot \text{H}_2\text{O}$: C, 30.68, H, 1.72, N, 21.46. Found: C, 30.60, H, 1.85, N, 21.33%. IR (KBr, v/cm^{-1}): 3431(s), 2046(s), 1618(w), 1599(m), 1561(w), 1493(m), 1394(w), 1160(w), 836(w), 769(m), 596(w).

Synthesis of $[\text{Pb}(\text{L}_2)(\text{N}_3)]_n$ (**2**). A mixture of 2-cyano-1,10-phenanthroline (PhenCN) (20.5 mg, 0.1 mmol), $\text{Pb}(\text{NO}_3)_2$ (49.7 mg, 0.15 mmol), NaN_3 (9.8 mg, 0.15 mmol) and EtOH/ H_2O (15 mL, v/v = 1/2) was sealed in a 15 mL Teflonlined stainless-steel reactor, heated at 120 °C for 72 hours under autogenous pressure, and then slowly cooled to room temperature at a rate of 6 °C h⁻¹. Colorless block crystals of **2** were collected by filtration and washed with ethanol several times. Yield 32.4 mg, 60.9 % (based on QCN). Elemental analysis calcd (%) for $\text{C}_{13}\text{H}_7\text{N}_9\text{Pb} \cdot 2\text{H}_2\text{O}$: C, 29.32, H, 2.08, N, 23.67. Found: C, 29.21, H, 2.15, N, 23.59%. IR (KBr, v/cm^{-1}): 3430(s), 2035(s), 1618(m), 1589(m), 1418(m), 1368(w), 860(w), 731(s).

References:

- [1] E. J. Corey, A. L. Borrer, T. Foglia, *J. Org. Chem.* **1965**, 30, 288.
- [2] G. M. Sheldrick, *SHELX-97: Programs for Crystal Structure Analysis*, release 97-2, University of Gottingen, Germany, **1997**.
- [3] A. Altomare, G. Casciarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, 27, 435.
- [4] Spek, A. L. *J. Appl. Crystallogr.* **2003**, 36, 7.

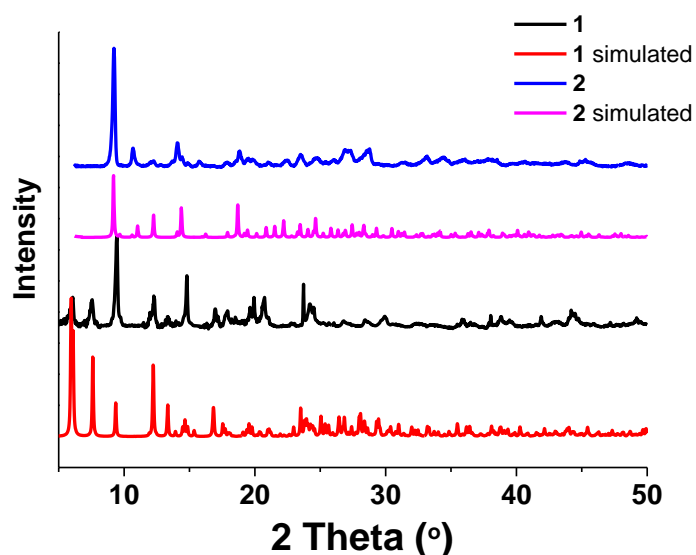


Figure S1. Experimental PXRD patterns of as-synthesized **1** and **2** and the simulated diffraction pattern from its single-crystal X-ray data.

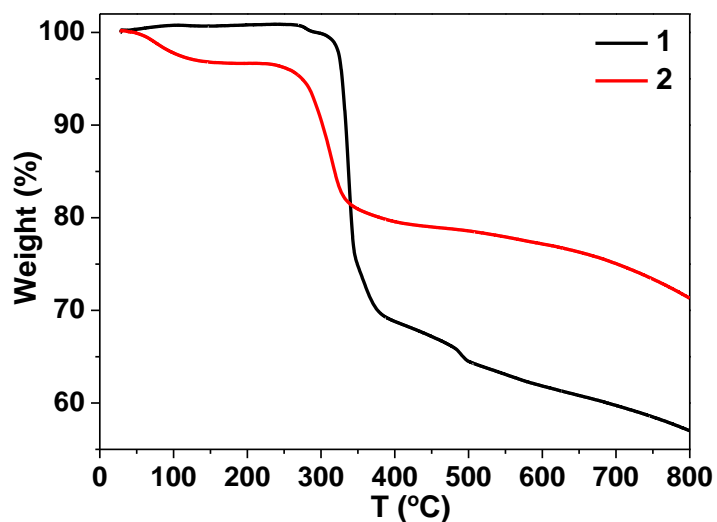


Figure S2. TGA of **1** and **2**.

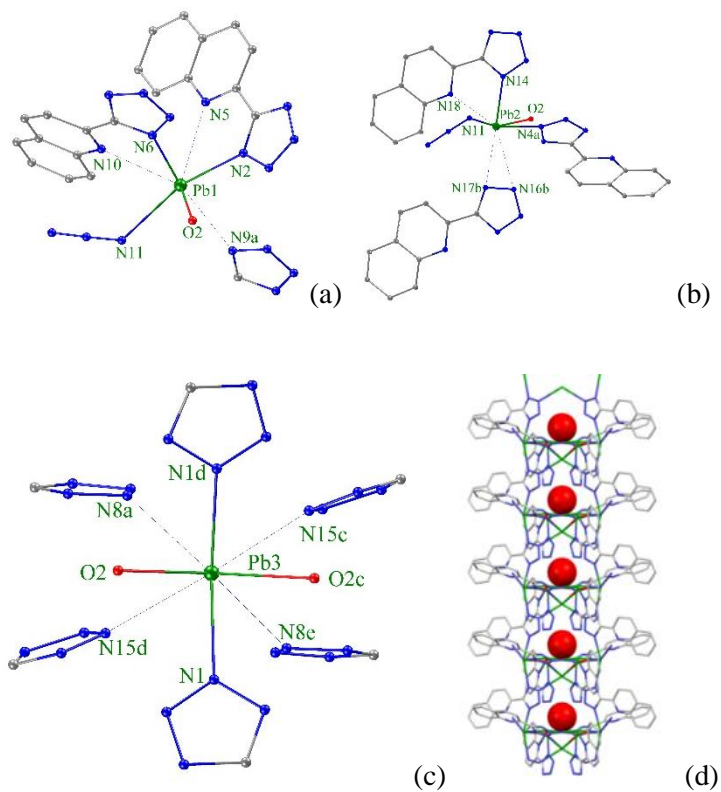


Figure S3. (a-c) different coordination environment of each Pb^{2+} ions; (d) the extended 1-D chain cage structure. (a) 0.500-X, 0.500-Y,0.500-Z; (b)-0.500+X, 1.500-Y, -1.000+Z; (c) -0.500+X, 1.500-Y,-1.000+Z; (d) 0.500-X,1.500-Y,0.500-Z; (e) -0.500+X,0.500-Y,-1.000+Z.

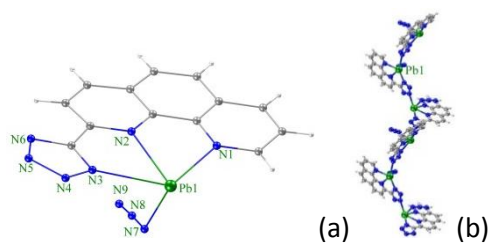


Figure S4. (a) The asymmetric unit of **2**; (b) 1-D helical chain of **2**.

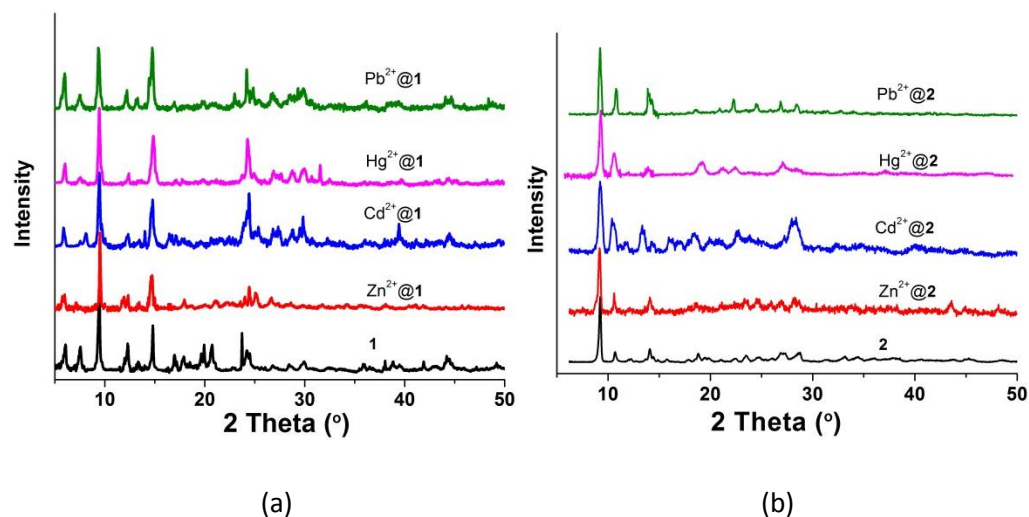


Figure S5. Experimental PXRD patterns: (a) **1** and samples $M^{2+}@1$ after uptaking different metal ions; (b) **2** and samples $M^{2+}@2$ after uptaking different metal ions.

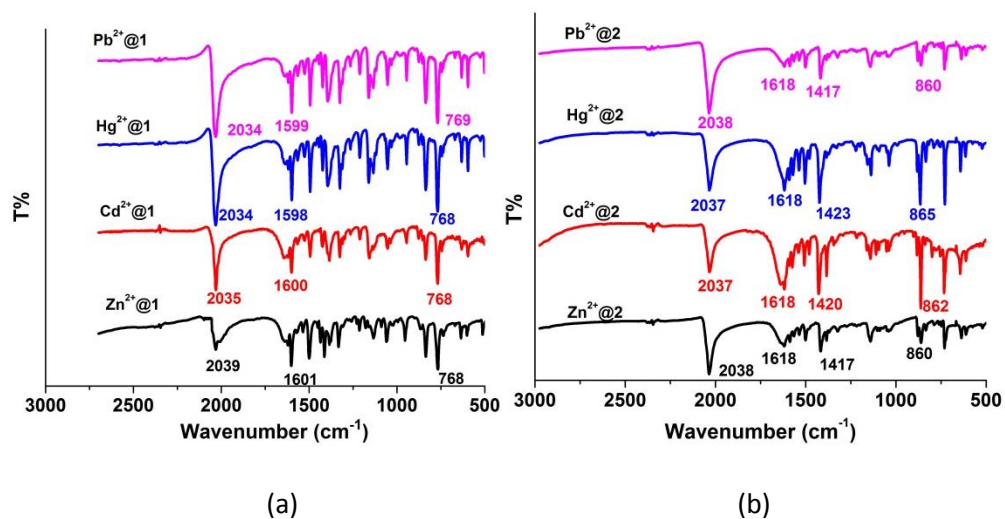


Figure S6. IR spectra of $M^{2+}@1$ (a) and $M^{2+}@2$.

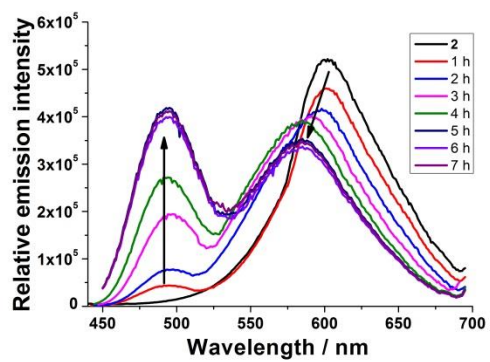


Figure S7. Emission spectral changes of **2** suspended in the aqueous solution of 0.005 *M* ZnCl₂ as a function of time.