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A magnesium phosphonate metal-organic framework showing excellent performance for lead(II) sensing and removal from aqueous solution

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Experimental

Materials and methods

The ligand H_3PCD was synthesized according to the literature method. All of the other reagents and chemicals were of analytical grade and obtained from commercial sources. Elemental analyses were performed on a Perkin Elmer 2400II elemental analyzer. The solid-state luminescent spectra were recorded via the Hitachi F7000 fluorescence spectrophotometer. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-2200 X-ray diffractometer. Thermogravimetric analyses (TGA) were carried out with a NETZSCH STA449F3C analyzer. X-ray photoelectron spectra was carried out on a Thermo Fisher Nexsa X-ray photoelectron spectroscopy. Simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES) on a PerkinElmer Optima 8000 instrument was used to determine the metal ion concentration in aqueous solution.

Synthesis

$Mg(NO_3)_2 \cdot 6H_2O$ (5.1 mg, 0.02 mmol), H_3PCD (3.9 mg, 0.01 mmol), 1 mL CH_3CN and 1 mL H_2O were placed in a 5 mL glass tube. The pH value was adjusted to 2 with dilute HCl. The tube was fused and heated at 120 °C for 48 h. Colorless needle crystals were obtained, washed with H_2O, and dried at room temperature. Yield: 2.6 mg (60%, based on ligand). Anal. Calcd for $C_{36}H_{42}MgN_2O_{18}P_2$: C, 49.30; H, 4.83; N, 3.19. Found: C, 49.04; H, 4.55; N, 3.15. The thermal stability was examined via thermal gravimetric analysis under N_2 atmosphere, the loss of lattice water (4.1%) happened from room temperature to 50 °C. The presence of platform from 50 to 300 °C indicates the highly stable of the framework (Fig. S11)

Adsorption measurement

Before measurement, the solvent-exchanged sample (about 100 mg) was prepared by immersing the as-synthesized samples in methanol to remove nonvolatile solvents. The completely activated sample was obtained by heating the solvent-exchanged sample at 120 °C under reduced pressure ($<10^{-2}$ Pa) for more than 20 h.

Gas adsorption isotherms were obtained using a Belsorp-max adsorption instrument from BEL Japan Inc. using the volumetric technique.

X-ray data crystallographic analysis

Single crystal X-ray diffraction data were collected on a Bruker APEX II DUO CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares cycles using SHELXL. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. The diffused electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. The crystal data for Mg-MOF are summarized as follows: $C_{36}H_{38}MgN_2O_{16}P_2$, $M_r = 840.93$, monoclinic, space group $C2/c$, $a = 42.963(4)$ Å, $b = 4.7896(5)$ Å, $c = 28.280(3)$ Å, $\beta = 125.691(2)^o$, $V = 4726.3$ Å^3, $Z = 4$, $D_c = 1.182$ g cm^{-3}, $F(000) = 1752$ and $\mu = 0.168$ mm^{-1}, 50838 reflections collected, 5494 unique ($R_{int} = 0.0838$). $R_1 = 0.028$, $wR_2 = 0.1336$ and $S = 1.074$. Crystallographic data have been submitted to the Cambridge Structural Database with the deposition number CCDC 2341935.

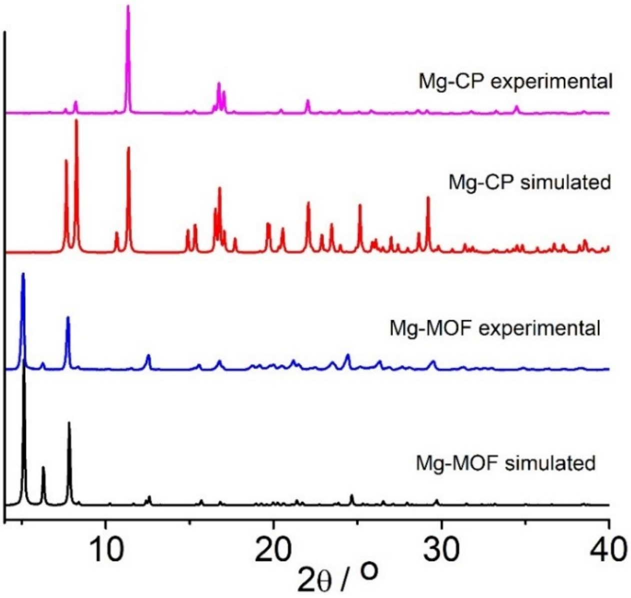

Fig. S1 PXRD patterns of Mg-MOF and Mg-CP for simulated, as-synthesized samples.

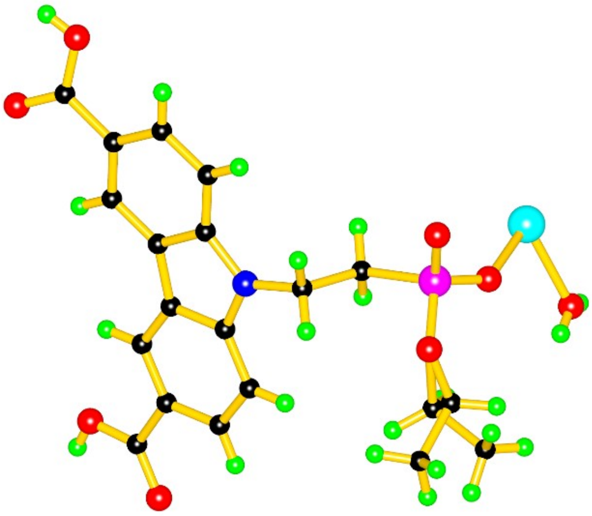

Fig. S2 Coordination environment of Mg^{2+} in Mg-MOF. The disordered ethyl group was drawn.

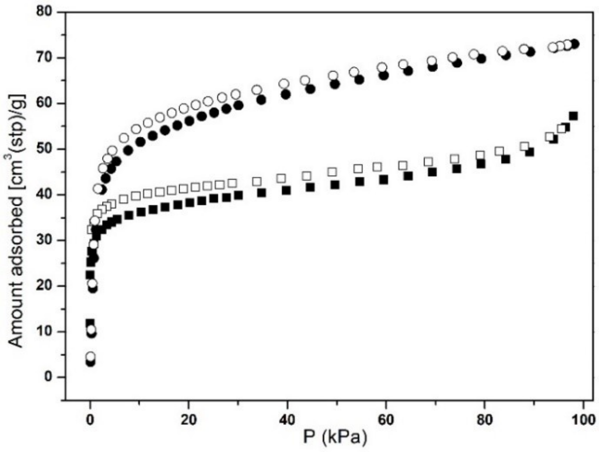

Fig. S3 CO_2 (●, ○) and N_2 (■, □) adsorption isotherms for Mg-MOF at 195 and 77 K. Adsorption and desorption profiles are shown in closed and open symbols.

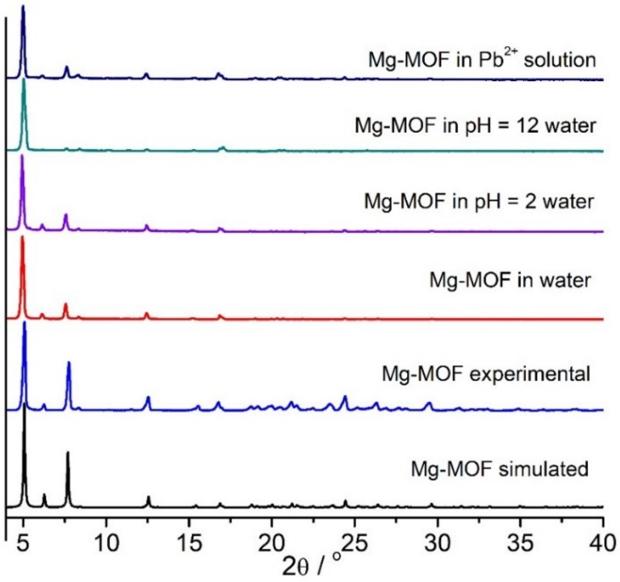

Fig. S4 PXRD patterns for Mg-MOF after treatment in water, acidic, basic and Pb^{2+} solutions for 5 h at ambient temperature.

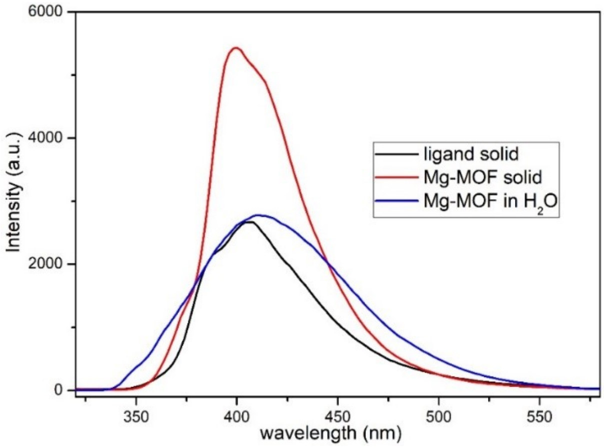

Fig. S5 Emission spectra for Mg-MOF (red, solid state; blue, aqueous suspension with the concentration of 50 mg/L) and free ligand (black) at room temperature.

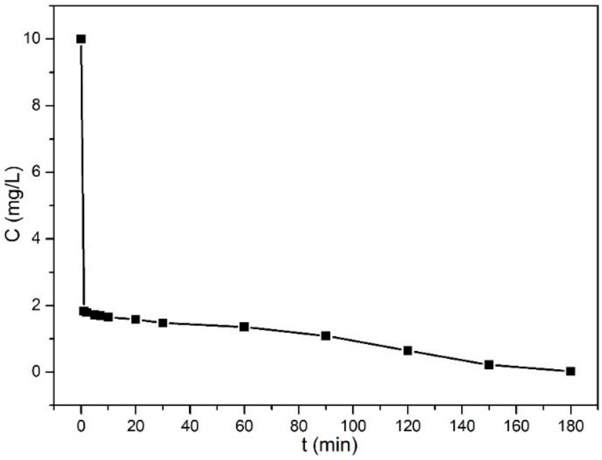

Fig. S6 The kinetics and efficiency of Mg-MOF for Pb^{2+} removal.

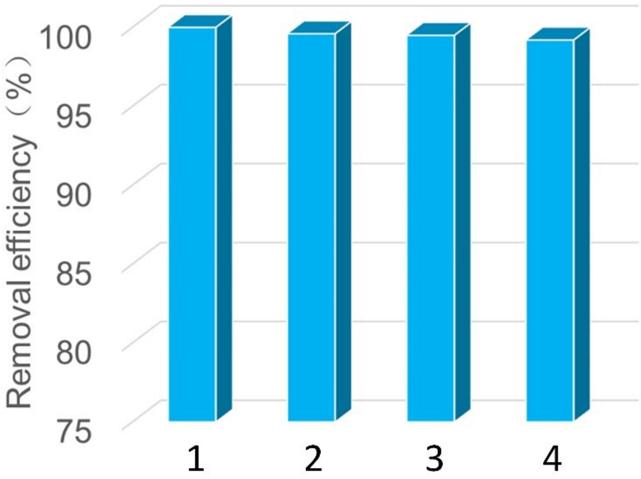

Fig. S7 Reusability of Mg-MOF for Pb^{2+} adsorption.

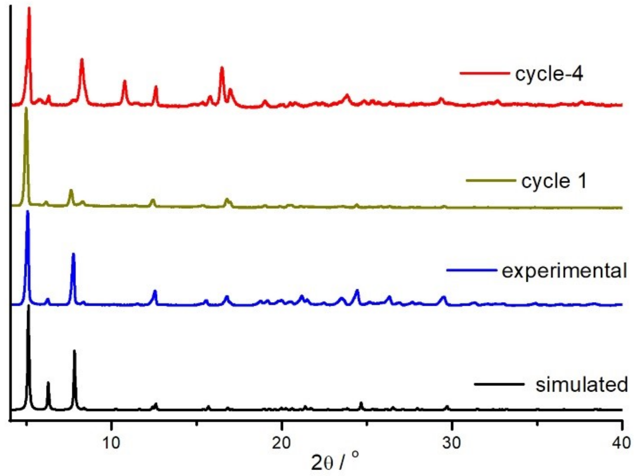

Fig. S8 PXRD patterns for Mg-MOF after four cycles.

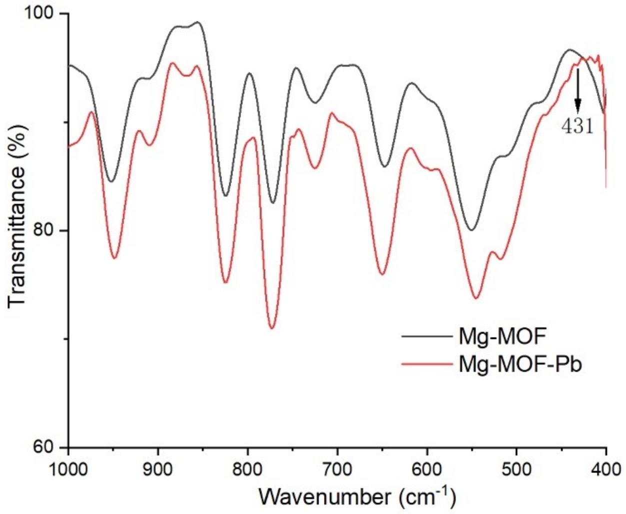

Fig. S9 IR spectra for Mg-MOF and Mg-MOF-Pb.

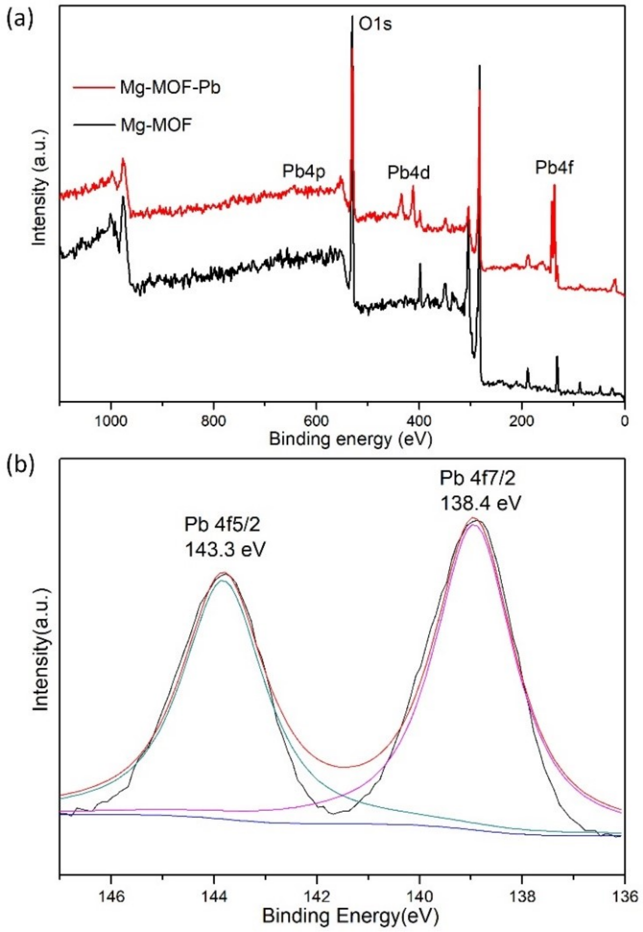

Fig. S10 (a) XPS survey spectra of Mg-MOF and Mg-MOF–Pb. (b) Pb 4f XPS spectrum of Mg-MOF–Pb.

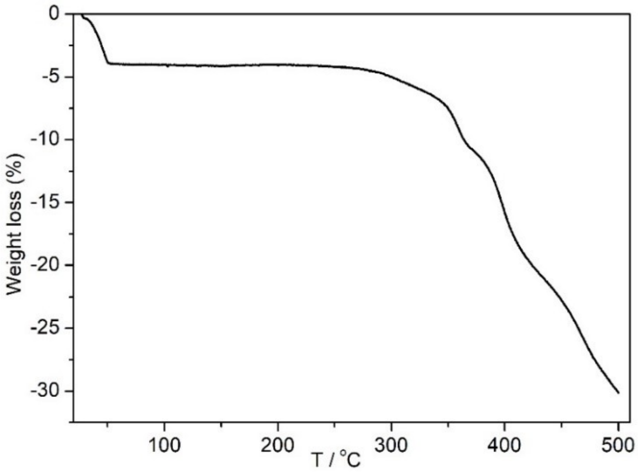

Fig. S11 Thermogravimetric analysis curve of Mg-MOF for as-synthesized sample.