

Two novel cadmium(II) carboxyphosphonates with 3D framework structure: synthesis, crystal structures, luminescence and molecular recognition properties

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Supplementary Materials

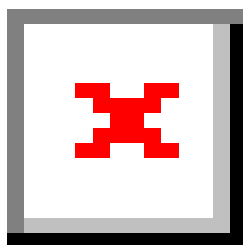


Fig. S1 The experimental powder XRD patterns and the simulated XRD patterns of compound **1**.

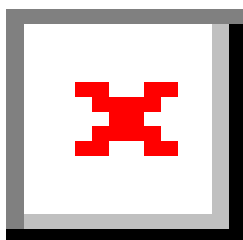


Fig. S2 The experimental powder XRD patterns and the simulated XRD patterns of compound **2**.

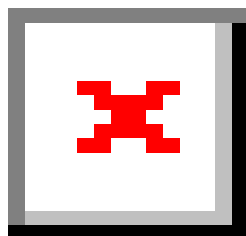


Fig. S3 The IR spectrum of compound **1**.

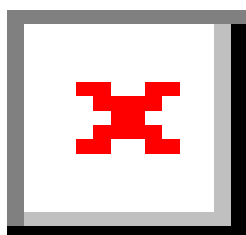


Fig. S4 The IR spectrum of compound **2**.

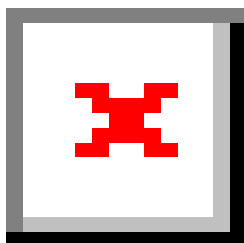


Fig. S5 The FIR spectrum of compound **1**.

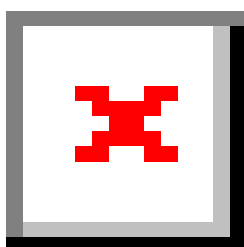


Fig. S6 The FIR spectrum of compound **2**.

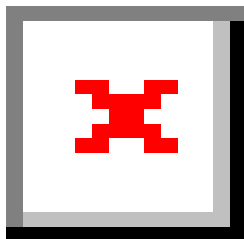


Fig. S7 The TGA curve of compound 1.

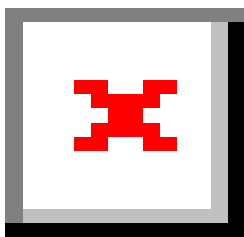


Fig. S8 The TGA curve of compound 2.

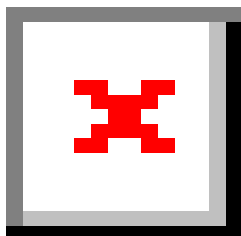


Fig. S9. The X-ray power diffraction patterns of the final products in the thermal decomposition for compounds
2. The final products is $\text{Cd}_3(\text{PO}_4)_2$ at 950 °C (JCPDS 00-031-0234)

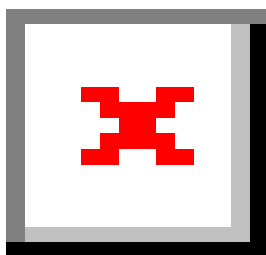


Fig. S10. The emission spectra of compound **1** introduces into various pure solvents when excited at 400 nm.

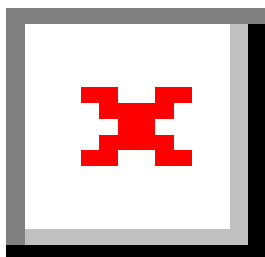


Fig. S11. The fluorescence properties of compound **2** emulsion in the presence of various contents of 1-butanol.
(by the frequency of 10 percent every time, from 10 percent to 100 percent)

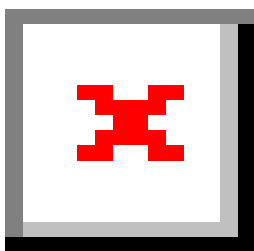


Fig. S12. The fluorescence properties of compound **2** emulsion in the presence of various contents of 1-pentanol.
(by the frequency of 10 percent every time, from 10 percent to 100 percent)

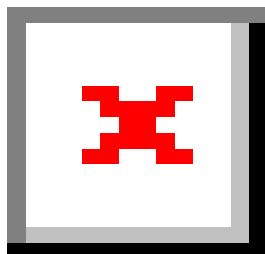


Fig. S13. The fluorescence properties of compound **2** emulsion in the presence of various contents of 1-propanol.
(by the frequency of 10 percent every time, from 10 percent to 100 percent)

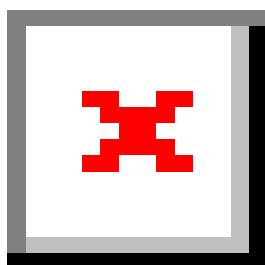


Fig. S14. The fluorescence properties of compound **2** emulsion in the presence of various contents of butanone.
(by the frequency of 10 percent every time, from 10 percent to 100 percent)

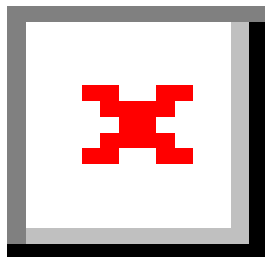


Fig. S15. The fluorescence properties of compound **2** emulsion in the presence of various contents of ethanol. (by the frequency of 10 percent every time, from 10 percent to 100 percent)

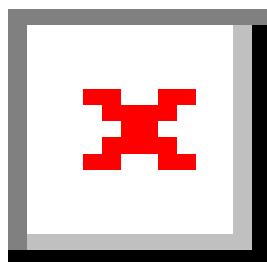


Fig. S16. The fluorescence properties of compound **2** emulsion in the presence of various contents of N,N-Dimethylacetamide. (by the frequency of 10 percent every time, from 10 percent to 100 percent)

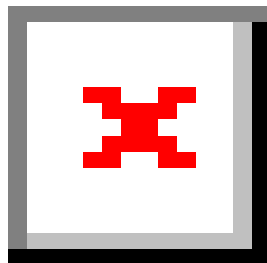


Fig. S17. The fluorescence properties of compound **2** emulsion in the presence of various contents of DMF. (by the frequency of 10 percent every time, from 10 percent to 100 percent)

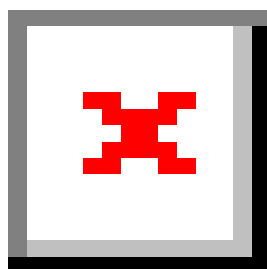


Fig. S18. The powder X-ray diffraction of compound **2** into various pure solvent after aging.

IR and FIR spectra

The IR spectra for compounds **1** and **2** were recorded in the region from 4000–400 cm^{-1} (Fig. S3 and S4, ESI), and the FIR spectra for compounds **1** and **2** were recorded in the region 400–100 cm^{-1} (Fig. S5 and S6, ESI). The bands in the range of 3500–3100 cm^{-1} and the medium bands at around 1670 cm^{-1} confirm the presence of water molecules in compounds **1** and **2**. For compound **1**, the band centered at 2928 cm^{-1} corresponds to the stretching vibration of N–H.^{1a} There are two strong bands (1618 and 1440 cm^{-1}), which are the expectative value of coordinated carboxylic acids.^{1b} The IR spectrum of compound **2** exhibits two bands at 3450 cm^{-1} and 2929 cm^{-1} , corresponding to the stretching vibration of N–H. The bands at 1636, 1549, and 1428 cm^{-1} are observed, which are assigned to the antisymmetrical and symmetrical stretching vibrations of C–O bonds of the carboxylate groups.^{1c} It is attributed to the carboxylate groups coordinated to the metal, thus showing that also the carboxylate groups are in agreement with structural results. Sharp bands located at about 3000 cm^{-1} are due to the C–H stretching vibrations for compounds **1** and **2**. The set of bands between 1200 and 900 cm^{-1} are assigned to stretching vibrations of the P–O for two title compounds.^{1d} Additional weak bands at low energy for compounds **1** and **2** are found. These bands are probably due to bending vibrations of the tetrahedral CPO_3 groups. As shown in ESI (Fig. S5 and S6, ESI), the absorption bands at 440, 384 cm^{-1} for **1** and 436, 362 cm^{-1} for **2** can be assigned to the Cd–O stretching vibrations. The band at 295 cm^{-1} for **1** can be assigned to the Cd–N stretching vibrations. The band at 282 cm^{-1} for **2** can be assigned to the Cd–Cl stretching vibrations.²

Thermal analyses

Thermogravimetric analyses of compounds **1** and **2** have been performed in the temperature range of 50–1100 $^{\circ}\text{C}$ in static air atmosphere. (Fig. S7 and S8, ESI). The TG diagram of compound **1** reveals one main continuous and complicated weight loss, which can be attributed to the release of one coordinated water molecule and the combustion of the organic ligands (Fig. S7, ESI). The weight loss started at about 50 $^{\circ}\text{C}$ and ended at 927 $^{\circ}\text{C}$. The total weight loss is 64.3 %. Above 950 $^{\circ}\text{C}$, the further decomposition of the organic groups results in an amorphous phase that was not characterized. Compound **2** indicates two main steps of weight loss. It shows no weight loss from room temperature to 218 $^{\circ}\text{C}$, suggesting that the framework is thermally stable. The first step between 218 and 280 $^{\circ}\text{C}$ corresponds to the

release of one coordinated water molecules. The weight loss of 3.9 % is close to the calculated value (4.1 %). The second step from 320 to 905 °C, which corresponds to the release of hydrogen chloride and the combustion of organic groups. The final product is $\text{Cd}_3(\text{PO}_4)_2$ based on XRD powder diffraction (Fig. S9, ESI). The total weight loss at 905 °C is 42.6%, which is basically close to the calculated value 40.5%.

Notes and references

1. (a) H. S. Martínez-Tapia, A. Cabeza, S. Bruque, P. Pertierra, S. García-Granda and M. A. G. Aranda, *J. Solid State Chem.*, 2000, **151**, 122; (b) B. Mena, I. J. Shannon, *J. Mater. Chem.*, 2002, **12**, 350; (c) A. Cabeza, M. A. G. Aranda, S. Bruque, *J. Mater. Chem.*, 1998, **8**, 2479; (d) A. Cabeza, X. Ouyang, C. V. K. Sharma, M. A. G. Aranda S. Bruque and A. Clearfield, *Inorg. Chem.*, 2002, **41**, 2325.
2. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, Wiley, New York., 2009, 63.