



# Influence of pH on the structures of two Cd phosphonate compounds

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MS received 11 December 2018; revised 8 October 2019; accepted 9 October 2019

**Abstract.** Two novel Cd-based coordination polymers Cd(H<sub>2</sub>BCP)<sub>2</sub>(phen)<sub>2</sub> **1** and {[Cd<sub>6</sub>(BCP)<sub>4</sub>(phen)<sub>3</sub>]-2H<sub>2</sub>O}<sub>n</sub> **2** (Phen=1,10-phenanthroline) have been hydrothermally synthesized from a combination of 4-(phosphonomethyl) benzoic acid 4-HOOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> (H<sub>3</sub>BCP) and 1,10-phenanthroline. The X-ray crystal structure analyses revealed that **1** is a 0D mononuclear molecular structure and **2** is a 3D structure existing the novel Cd<sub>6</sub> cluster unit. It is worth mentioning that **1** and **2** have the same constitutional units, namely the Cd ion, H<sub>3</sub>BCP ligand and second ligand- Phen. However, their structures are different and it results from the different solution pH value. In order to explore the structural characteristics, FTIR, photoluminescent and solid UV-Vis spectra are employed.

**Keywords.** Cd-based coordination polymers; Solution pH value; Photo-luminescent; FTIR.

## 1. Introduction

The scientists simulate the property of traditional zeolite and explore the excellent physics and chemistry properties of novel organic zeolite materials, in order to obtain the inorganic-organic hybrid materials with open-framework structures by means of the regulation of structures. Metal phosphonate compounds, which are one kind of inorganic-organic hybrid materials, have developed rapidly due to the extensive applications in the magnetism, ion change, catalysis, non-linear optical material, luminescence sensing, etc.<sup>1–24</sup>

The research on the synthesis and structure of metal phosphonate compounds has already developed quickly and achieved many research results,<sup>13,15,17,18</sup> the structures of metal phosphonate compounds are different from zero-dimensional clusters and one-dimensional chain to two-dimensional layer and three-dimensional open-framework architectures.<sup>25–29</sup> For the sake of further enriching the family of Metal

phosphonate compounds, we synthesize the novel organic phosphonate ligand containing benzene rings - 4-(phosphonomethyl) benzoic acid 4-HOOC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>(H<sub>3</sub>BCP). As we all know that Metal phenyl phosphonate compounds have small solubility in water and it is easy to obtain the precipitations and their crystals are difficult to be obtained from the solution. However, metal phosphonate compounds based on the H<sub>3</sub>BCP ligand may solve the problems of poor solubility and crystallinity of metal phosphonate compounds due to the existence of the carboxyl group. Furthermore, the ligand- H<sub>3</sub>BCP has more abundant coordination modes owing to contain the carboxyl group.<sup>25,26,30,31</sup>

It is well known that many factors play the important part in the synthesis of coordination compounds, for example, the choices of metal ions and the ligand,<sup>32–34</sup> the ratio of reactant,<sup>35</sup> reaction temperature,<sup>36,37</sup> reaction time,<sup>38</sup> pH<sup>39,40</sup> and so on.<sup>41–43</sup> As a hybrid ligand, H<sub>3</sub>BCP has five potential coordinating sites: two oxygen atoms of the carboxylate group and

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Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-019-1733-3>) contains supplementary material, which is available to authorized users.

three oxygen atoms of the phosphate group. At the same time, there are three protons, one from the carboxylate and two from the phosphate group in the ligand-H<sub>3</sub>BCP, which play an important role in the structure of the compounds contained the ligand-H<sub>3</sub>BCP. So, the ligand-H<sub>3</sub>BCP is a good candidate for the investigation of the relationship between the pH value and the structure of the coordination compound. In this paper, we report the syntheses and characterizations of the novel cadmium coordination polymers: Cd(H<sub>2</sub>BCP)<sub>2</sub>(phen)<sub>2</sub> **1** and {[Cd<sub>6</sub>(BCP)<sub>4</sub>(phen)<sub>3</sub>]·2H<sub>2</sub>O}<sub>n</sub> **2** built from the Organic phosphonate ligands-H<sub>3</sub>BCP and CdSO<sub>4</sub>·3H<sub>2</sub>O. Two compounds have been characterized by elemental analysis, IR spectra, UV-Vis spectra, and fluorescent spectroscopy.

## 2. Experimental

### 2.1 Materials and methods

H<sub>3</sub>BCP was synthesized by a classical Arbuzov reaction followed by acidic hydrolysis of the ester of diphosphonic acid.<sup>44</sup> Other chemicals purchased were of reagent grade or even better and were used without further purification. The IR spectrum was recorded on a Perkin-Elmer Spectrum 2000 FT-IR Fourier transform spectrometer with pressed KBr pellets in the range 400–4000 cm<sup>-1</sup>. The luminescence spectrum was reported on an Edinburgh-Instrument spectra-Fluorimeter (solid). The solid UV-Vis spectrum was reported on Perkin-Elmer Lambda 900 spectrometer. Elements analyzing C, H and N were performed with an Elemental Vario EI III elemental analyzer.

### 2.2 Synthesis of Cd(H<sub>2</sub>BCP)<sub>2</sub>(phen)<sub>2</sub> **1**

**1** was prepared by hydrothermal reaction. A mixture of CdSO<sub>4</sub>·3H<sub>2</sub>O (0.50 mmol, 0.13 g), H<sub>3</sub>BCP (0.25 mmol, 0.054 g), 1,10-Phenanthroline (0.50 mmol, 0.09 g), H<sub>2</sub>O (10 mL) were sealed into a bomb equipped with a teflon liner, the solution's pH value was adjusted to 2.1 with saturated NaOH solution and 5 M HCl solution and heated at 443 K for three days and then cooled to room temperature in 24 h. Plate crystals for **1** were obtained. (yield 30%). Anal.Calcld for C<sub>40</sub>H<sub>32</sub>N<sub>4</sub>O<sub>10</sub>P<sub>2</sub>Cd: C, 53.20; H, 3.57; N,6.20. Found (%): C,54.93; H,3.52, N,5.74. IR data (KBr pellet,  $\nu$  [cm<sup>-1</sup>]): 3045, 3063, 3661, 2918, 2783, 2430, 1687, 1620, 1515, 1428, 1281, 1222, 845, 786, 728, 700, 637.

### 2.3 Synthesis of [Cd<sub>6</sub>(BCP)<sub>4</sub>(phen)<sub>3</sub>]·2H<sub>2</sub>O **2**

The synthesis of **2** was similar to the above description for **1** except pH = 5 was used. rod like crystals for **2** were

obtained. (yield 30%). Anal.Calcld for C<sub>40</sub>H<sub>52</sub>N<sub>6</sub>O<sub>22</sub>P<sub>4</sub>Cd<sub>6</sub>: C, 38.83; H, 2.49; N,4.00. Found (%): C, 38.03; H,2.12, N,3.34. IR data (KBr pellet,  $\nu$ [cm<sup>-1</sup>]): 3405, 3048, 3002, 2914, 2852, 1576, 1515, 1493, 1425, 1252, 922, 862, 785, 729, 699, 542, 473.

### 2.4 X-ray crystallography analysis

Single crystals of **1** and **2** were obtained from the reactions described above. X-ray crystallographic data were collected using epoxy-coated crystal mounted on the glass fiber. Its measurement was carried out on a Rigaku Saturn 724 CCD area detector. Intensity data were collected by graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) using  $\omega$  scan mode at 298 k. The data sets were corrected for absorption by the multi-scan technique.<sup>45</sup> The structure of the complex was solved by direct methods, and the non-hydrogen atoms were located from the trial structures and then refined anisotropically with Shelx-97 using a full-matrix least-squares procedure based on  $F^2$  values.<sup>46</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of water molecules were located on a difference Fourier map, while other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. The relevant crystallographic data is presented in Table 1, while the selected bond lengths and angles are summarized in Tables S1 and S2 (Supplementary Information).

## 3. Results and Discussion

### 3.1 Structural description of Cd(H<sub>2</sub>BCP)<sub>2</sub>(phen)<sub>2</sub> **1**

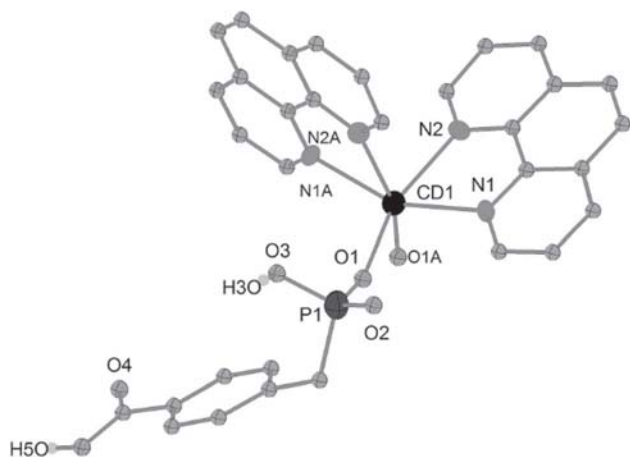
The X-ray crystal structure analysis reveals that the structure of **1** is the monoclinic system, space group  $C2/c$ . The asymmetric unit of **1** is shown in Figure 1. the Cd ion is located on the two-fold axis (the symbol of Wyckoff:  $4e$ ) and is six-coordinated by four nitrogen atoms from two phens, and two phosphonate oxygen atoms in an octahedral geometry. The Cd-O bond is 2.1797(18) Å and the Cd-N bond lengths are 2.368(2) to 2.383(2) Å, which are similar to those works previously reported.<sup>47</sup>

The structure of **1** is a 0D mononuclear molecular structure. Each molecular contains one Cd<sup>2+</sup> ion, two H<sub>2</sub>BCP<sup>-</sup> ions and two phens, as shown in Figure S1 (Supplementary Information). It is worth mentioning that the H<sub>2</sub>BCP<sup>-</sup> is a monodentate ligand and one oxygen atom of the phosphonate group coordinates with the Cd ion, the carboxyl of ligand doesn't participate in the coordination. Furthermore, the bond lengths of P(1)-O(1) and P(1)-O(2) are respectively

**Table 1.** Crystal data and structure refinement for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>40</sub> H <sub>32</sub> N <sub>4</sub> O <sub>10</sub> P <sub>2</sub> Cd	C <sub>68</sub> H <sub>52</sub> N <sub>6</sub> O <sub>22</sub> P <sub>4</sub> Cd <sub>6</sub>
Formula mass	903.06	2103.53
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a (Å)	10.075(2)	19.011(1)
b (Å)	21.665(4)	14.774(3)
c (Å)	18.594(4)	23.533(5)
α (°)	90	90
β (°)	102.30(3)	92.42(3)
γ (°)	90	90
V (Å <sup>3</sup> )	3965.4(14)	6570(2)
Z	4	8
F(000)	1832	4104
Crystal size (mm)	0.25 × 0.16 × 0.15	0.25 × 0.19 × 0.18
Goodness-of-fit on F <sup>2</sup>	1.078	1.054
Observed reflections (I > 2σ (I))	4385	7290
Final R factors (I > 2σ (I))	R <sub>1</sub> = 0.0772, R <sub>2</sub> = 0.1818	R <sub>1</sub> = 0.0365, wR <sub>2</sub> = 0.1283
Final R factors (all data)	R <sub>1</sub> = 0.0361, wR <sub>2</sub> = 0.2827	R <sub>1</sub> = 0.0342, wR <sub>2</sub> = 0.2305
Independent reflections (R <sub>int</sub> )	4490 (0.0377)	7476 (0.0375)
Largest diff. map peak and hole eÅ <sup>-3</sup>	0.23 and -0.380	0.645 and -1.116

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

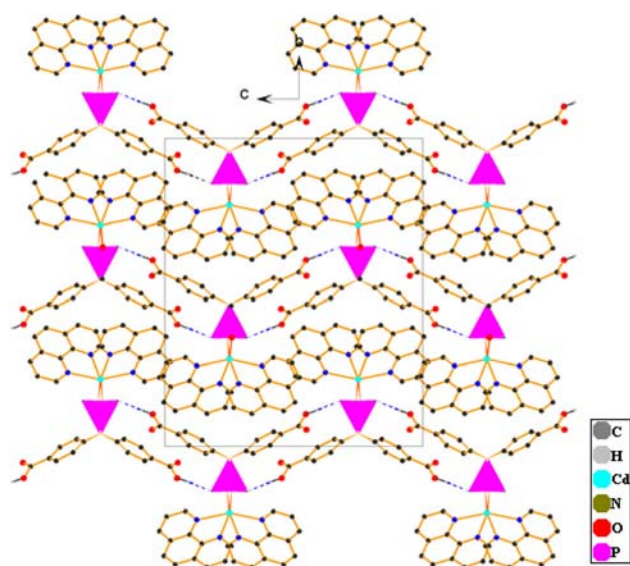
**Figure 1.** Building block of **1** with the atomic labelling scheme. The H atoms attached to C atoms were omitted for clarity. Symmetry codes for the generated atoms are as follows: A, -x, y, 0.5-z.

1.4870(18) and 1.5140(18) Å, the P(1)-O(3) length is 1.567(2) Å, a conclusion can be drawn that the H<sub>2</sub>BCP ligand is mono-protonated and the proton lies in the oxygen of the longer P(1)-O(3). In the carboxyl, the C(8)-O(4) and C(8)-O(5) lengths are 1.310(3) and 1.199(3) Å, which indicates that C(8)-O(5) is C=O double bond and C(8)-O(4) is a single bond, at the same time, the O(4) atom is protonated. As illustrated in Figure 2, the hydrogen bonds connect the adjacent molecules into the super-molecular layers. Finally, the

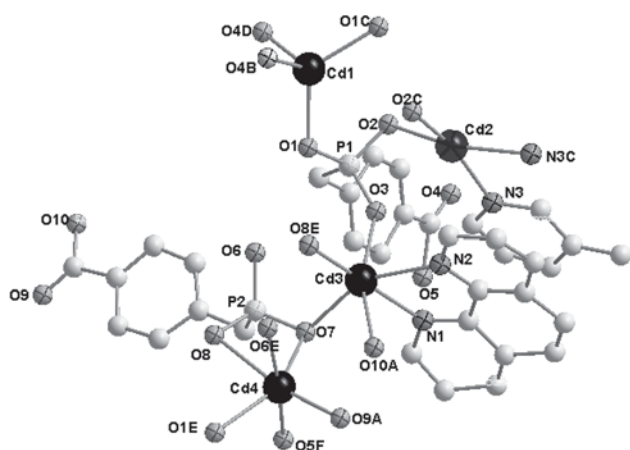
three-dimension supra-molecular framework exists by the π···π stacking interactions of the neighbouring phen molecules in the layers.

### 3.2 Structural description of [Cd<sub>6</sub>(BCP)<sub>4</sub>(phen)<sub>3</sub>]·2H<sub>2</sub>O **2**

The X-ray crystal structure analysis reveals that the structure of **2** is a 3D framework structure, crystallizing in the monoclinic system, space group C2/c. The asymmetric unit of **2** contains four Cd ions, two BCP ligands, one and a half o-phens, one water molecule. Cd1 and Cd3 (Wyckoff position: 4e) are in a particular position, the rest of the atoms are located at equivalent points. As shown in Figure 3, the Cd1 and Cd2 are four-coordinated by two carboxylic oxygen atoms and two phosphonate oxygen atoms for Cd1 and by two phosphonate oxygen atoms and two nitrogen atoms from the phen for Cd2 in distorted tetrahedron geometries. The six-coordinated Cd3 and Cd4 show a slightly distorted octahedral coordination sphere, completed by three phosphonate oxygen atoms, one carboxylic oxygen atom and two nitrogen atoms from the phen for Cd3 and by two carboxylic oxygen atoms and the remained four coordinated sites occupied by four phosphonate oxygen atoms for Cd4, respectively. The Cd-O bonds distances vary from 2.169(16) to



**Figure 2.** Two different views of the 2D supramolecular layer formed by O–H...O hydrogen bonds in **1**. Dashed lines represent the hydrogen bonds. The CPO<sub>3</sub> groups are represented in polyhedrons. Phen ligands coordinated with Cd ions and the H atoms attached to C atoms are omitted for clarity.



**Figure 3.** ORTEP representation of the coordination environment of Cd atoms in **2**. Symmetry codes for the generated atoms are as follows: A,  $0.5+x, 0.5+y, z$ ; B,  $0.5+x, -0.5+y, z$ ; C,  $2-x, y, 1.5-z$ ; D,  $1.5-x, -0.5+y, 1.5-z$ ; E,  $2-x, -y, 1-z$ ; F,  $1.5-x, 0.5-y, 1-z$ .

$2.619(12) \text{ \AA}^{48}$  and the Cd–N bond lengths vary from  $2.294(14)$  to  $2.370(13) \text{ \AA}$ , which are similar to previously reported works.<sup>49</sup>

It is interesting that there is a novel Cd<sub>6</sub> cluster unit comprised of six Cd atoms and four PO<sub>3</sub> groups in the structure, as is illustrated in Figure S2 (Supplementary Information). Six Cd atoms are located in an equatorial plane and come into being the rectangle, its long length is composed of three Cd atoms. There are two BCP ligands containing P1 and P2 atoms respectively above the Cd<sub>6</sub> cluster unit, moreover, their benzene

rings are nearly in a plane. Although there are also two containing P1 and P2 H<sub>3</sub>BCP ligands under the Cd<sub>6</sub> cluster unit, their benzene rings aren't in a plane and the dihedral angle are close to 90.

The adjacent Cd<sub>6</sub> cluster units are connected up by the communal vertexes and form the 1D cluster chain along the C direction (Figure 4(a)). The adjacent chains link to be 2D layer structure by oxygen atoms of the carboxyls which are in a plane and point to the same direction coordinating with the Cd atoms of the adjacent chain (Figure 4(b)). The adjacent layers are connected to form the 3D framework by the carboxyl of the fourth ligand (Figure 4(c)). In the meanwhile, the porous channel of the 3D framework is occupied by the phen coordinating with the Cd atoms, there is the  $\pi\cdots\pi$  packing weak interaction of the aromatic rings between the phen, due to their existence the entire crystalline architecture is more stable.

### 3.3 Influence of synthesis conditions-pH on the structure of the compounds

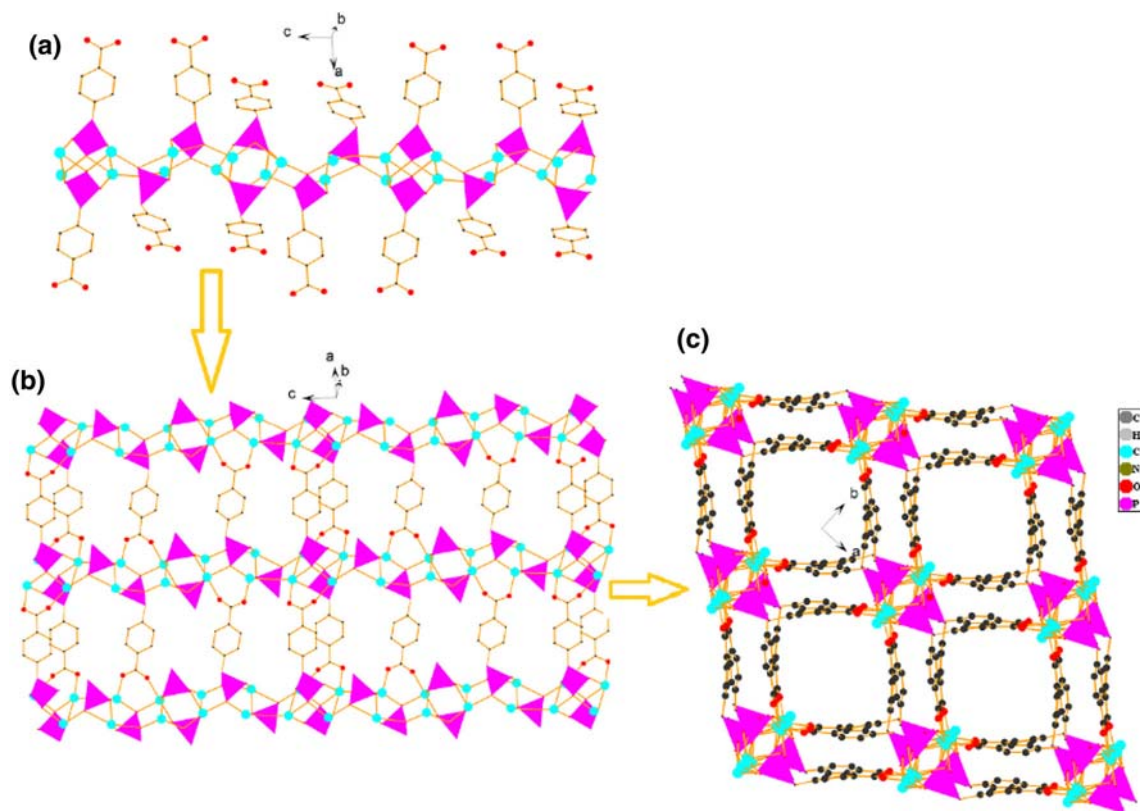
By the analysis of the above structural descriptions, we know that **1** forms a 0D mononuclear molecular structure, nevertheless **2** forms the 3D framework structure. That is because that **1** and **2** have the same synthesis conditions except for the pH, the different solution pH makes the protonation degree of carboxyl and phosphonate group in H<sub>3</sub>BCP different, the coordination modes of ligands in **1** and **2** are different, **1** and **2** finally form the respective structures. So controlling the pH of the solution plays an important role in the structure of the compound.<sup>30</sup>

### 3.4 PXRD analysis

The observed and simulated powder XRD patterns of **1** and **2** are depicted in Figure S3 (Supplementary Information). It is obvious that the measured powder XRD patterns are in good agreement with the patterns simulated from the X-ray single crystal data, indicating phase purities of the samples. The difference in reflection intensities between the simulated and experimental patterns is due to the different orientation of the crystals in the bulk powder samples.

### 3.5 IR spectra

The IR spectra of **1** and **2** are shown in Figure S4 (Supplementary Information), which gives full expression to the characteristic absorption peaks of



**Figure 4.** (a) View of the 1D chain in **2** along  $c$  axis. The  $\text{CPO}_3$  groups are represented in polyhedrons. (b) View of the 2D layer structure in **2** along  $c$  axis. (c) Schematic view the 3D structure along the  $c$  axis. Phen ligands coordinated with Cd ions and the H atoms attached to C atoms are omitted for clarity.

benzyl-phosphonic acid and carboxylic acid. Because the coordination mode of  $\text{H}_3\text{BCP}$  in **1** and **2** is different, their IR spectra are differentiated. The peaks at  $3661\text{ cm}^{-1}$  can be assigned to  $\nu(\text{PO}_3\text{-H})$  and  $\nu(\text{COO-H})$  in **1** and the peaks at  $3405\text{ cm}^{-1}$  is assigned to the coordinated water  $\nu(\text{o-H})$  in **2**, the sharp bands in  $3045\text{ cm}^{-1}$  in **1** and in the region from  $3048$  to  $3002\text{ cm}^{-1}$  in **2** belong to the aromatic C-H stretching vibrations. The strong Peaks appearing at  $1620\text{ cm}^{-1}$  in **1** and at  $1576\text{ cm}^{-1}$  in **2** should be assigned to the asymmetric stretching vibrations and at  $1428\text{ cm}^{-1}$  in **1** and at  $1425\text{ cm}^{-1}$  in **2** to the symmetric stretching vibrations of the carboxylate groups, respectively. The bands in the range of  $1222$  to  $910\text{ cm}^{-1}$  in **1** and  $1252$  to  $922\text{ cm}^{-1}$  in **2** can be assigned to the stretching vibration of  $\text{CPO}_3$  group. Peaks at  $542$  and  $473\text{ cm}^{-1}$  in **1** and at  $542$  and  $473\text{ cm}^{-1}$  in **2** are ascribed to the bending vibration of phosphonic acid.<sup>26</sup>

### 3.6 Fluorescence properties

Due to the potential applications in photochemistry, chemical sensors, electro-luminescent display and so on.<sup>50-55</sup> The luminescent behaviors of free  $\text{H}_3\text{BCP}$ , **1**

and **2** are studied in the solid state at room temperature. As the Figure S5 (Supplementary Information) shows, upon excitation at  $320\text{ nm}$  the emission showed at  $330\text{ nm}$  for free  $\text{H}_3\text{BCP}$ , which can be ascribed to the intra-ligand  $\Pi^* \rightarrow \Pi$  or  $\Pi^* \rightarrow n$  transitions. Upon excitation at  $384\text{ nm}$ , the emission showed at  $416\text{ nm}$  for **1**, which can be ascribed to the ligand to metal charge transfer transition. When excited at  $356\text{ nm}$ , there are very strong and speculate emission peaks at  $433\text{ nm}$ , the emission peak corresponds to the ligand to metal charge transfer transition in **2**.<sup>21</sup> In comparison with the free  $\text{H}_3\text{BCP}$ , the emission maxima of **1** is red-shifted  $97\text{ nm}$ , the emission maxima of **1** and **2** are red-shifted  $86\text{ nm}$  and  $103$  respectively, CP **1** and **2** may be fit for promising candidates for the exploration of red-luminescent materials.<sup>56,57</sup>

### 3.7 Solid UV-Vis spectra

In UV-Vis spectra of **1** and **2** (Figure S6, Supplementary Information), they show the intense band centered at  $275\text{ nm}$  in **1** and at  $271\text{ nm}$  in **2**, which can be assigned to  $\Pi\text{-}\Pi^*$  electron transition absorption peak of the ligand. In addition, the more intense band

centered at 330 nm in **1** can be assigned to the ligand to metal charge transfer transition.<sup>31,58</sup>

#### 4. Conclusions

In this research, the compounds **1** and **2** with the novel framework was successfully obtained from H<sub>3</sub>BCP with Cd (II) in the presence of the auxiliary ligands o-phen and H<sub>2</sub>O. Owing to only the different pH of synthesis conditions, namely, pH = 2.1 in **1** and pH = 5 in **2**, the protonation degree of carboxyl and phosphonate group in H<sub>3</sub>BCP is different. **1** a 0D mononuclear molecular structure and **2** is a very beautiful 3D framework at last. Furthermore, it is worth mentioning that in **2** the chain is formed by the rare La<sub>6</sub> cluster units connected by the communal vertexes and form the 1D cluster chain along the C direction. The adjacent chains link to be 2D layer structure by oxygen atoms of the carboxyl coordinate with the Cd atoms of the adjacent chain, the adjacent layers are connected to form the 3D framework by the carboxyl of the fourth ligand. At the same time, the IR spectra, fluorescence properties, and solid UV-Vis spectra are researched.

#### Supplementary Information (SI)

The selected bond lengths and angles, ORTEP drawing of the molecular structure of **1**, a view of the Cd<sub>6</sub> cluster unit in **2**, the observed and simulated powder XRD patterns of **1** and **2**, the IR spectra of **1** and **2**, solid-state emission spectra for **1** and **2** at room temperature, the solid UV-Vis spectra of **1** and **2** are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci). Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications CCDC reference number 1847204 and 1579731. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: + (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### References

- Mehring M 2004 Two- and three-dimensional hydrogen-bonded networks built from 1,3,5-[(HO)<sub>2</sub>(O)P]<sub>3</sub>C<sub>6</sub>H<sub>3</sub> and 4-(dimethylamino)pyridine *Eur. J. Inorg. Chem.* **16** 3240
- Li J Y, Yu J H, Yan W F, Xu Y H, Xu W G, Qiu S L and Xu R R 1999 Structures and templating effect in the formation of 2D layered aluminophosphates with Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub><sup>3-</sup> stoichiometry *Chem. Mater.* **11** 2600
- Fawcett J, Platt A W G and Vickers S 2003 Synthesis of tripodal tris-phosphonate ligands and the structure of the dimeric complex, [Ce(NO<sub>3</sub>)<sub>3</sub>{(EtO)<sub>2</sub>P(O)CH<sub>2</sub>)}<sub>2</sub>C<sub>6</sub>Me<sub>3</sub>]<sub>2</sub> *Polyhedron* **22** 1431
- Zakowsky N, Hix G B and Morris R E 2000 Synthesis of a family of aluminium benzylphosphonates *J. Mat. Chem.* **10** 2375
- Serre C, Stock N, Bein T and Ferey G 2004 Synthesis and characterization of a new three-dimensional lanthanide carboxyphosphonate: Ln<sub>4</sub>(H<sub>2</sub>O)<sub>7</sub>[O<sub>2</sub>CC<sub>5</sub>H<sub>10</sub>-NCH<sub>2</sub>PO<sub>3</sub>]<sub>4</sub>(H<sub>2</sub>O)<sub>5</sub> *Inorg. Chem.* **43** 3159
- Lai Z Z, Fu R B, Hu S M and Wu X T 2007 Syntheses, crystal structures, thermal stabilities, and magnetic and luminescent properties of 3D heterometal phosphonates: NaM[O<sub>3</sub>PCH(OH)CO<sub>2</sub>] (M = Mn, Fe, Co, Zn) *Eur. J. Inorg. Chem.* **34** 5439
- Tang S F, Song J L and Mao J G 2006 Syntheses, crystal structures, and characterizations of a series of new layered lanthanide carboxylate-phosphonates *Eur. J. Inorg. Chem.* **10** 2011
- Shanmugam M, Shanmugam M, Chastanet G, Sessoli R, Mallah T, Wernsdorfer W and Winpenny R E P 2006 Minor changes in phosphonate ligands lead to new hexa- and dodeca-nuclear Mn clusters *J. Mater. Chem.* **16** 2576
- Cao D K, Gao S and Zheng L M 2004 Syntheses, structure and magnetic properties of pillared layered diphosphonates: M<sub>2</sub>(O<sub>3</sub>PC<sub>6</sub>H<sub>4</sub>PO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub> (M=Co-II, Ni-II) *J. Solid. State Chem.* **17** 2311
- Galczyńska K, Kurdziel K, Ciepluch K et al. 2018 Synthesis, physicochemical and biological characterization of Ni(II) complex with imidazole-4-acetate anion as new antifungal agent *J. Chem. Sci.* **130** 169
- Subbiah A, Pyle D, Rowland A, Huang J, Narayanan R A, Thiyagarajan P, Zon J and Clearfield A 2005 A family of microporous materials formed by Sn(IV) phosphonate nanoparticles *J. Am. Chem. Soc.* **127** 10826
- Irran E, Bein T and Stock N 2003 Inorganic-organic hybrid materials: synthesis and crystal structure determination from powder diffraction data of Pb<sub>2</sub>(O<sub>3</sub>PCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PO<sub>3</sub>) *J. Solid. State Chem.* **173** 293
- Shakir M, Bano N, Rauf M A and Owaiset M 2017 Pharmacologically significant tetraaza macrocyclic metal complexes derived from isatin and 3,4-diaminobenzophenone: Synthesis, spectral studies and comparative in vitro biological assessment *J. Chem. Sci.* **129** 1905
- Stock N, Guillou N, Bein T and Ferey G 2003 Inorganic-organic hybrid compounds: synthesis and crystal structure determination from powder diffraction data of Sn<sub>2</sub>[O<sub>3</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PO<sub>3</sub>] *Solid. State Sci.* **5** 629
- Du Z Y, Xu H B and Mao J G 2006 Rational design of 0D, 1D, and 3D open frameworks based on tetranuclear lanthanide(III) sulfonate-phosphonate clusters *Inorg. Chem.* **45** 9780
- Dumas E, Sassoey C, Smith K D and Sevov S C 2002 Synthesis and characterization of [Mo<sub>7</sub>O<sub>16</sub>(O<sub>3</sub>PCH<sub>2</sub>-PO<sub>3</sub>)<sub>3</sub>]<sup>8-</sup> - A mixed-valent polyoxomolybdenum diphosphonate anion with octahedrally and tetrahedrally coordinated molybdenum *Inorg. Chem.* **41** 4029
- Fu R B, Wu X T, Hu S M and Wang L S 2004 Hydrothermal synthesis and crystal structure of a new

- phosphonate:  $\{[\text{Cu}(1,10\text{-phen})]_2(\text{H}_2\text{O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{PO}_3\text{H})_2 \cdot (\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{PO}_3\text{H})\}_n$  *Chin. J. Struct. Chem.* **23** 1107
18. Wu Y, Gu Z J, Luo W, Wu L, Li Y L, Xie B and Zou L K 2018 Hybrid open-frameworks. Hydrothermal synthesis and structure determination of MIL-40 or (VO)OIV(H<sub>2</sub>O){HO<sub>3</sub>PCH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>PO<sub>3</sub>H}: a lamellar vanadodiphosphonate prepared with p-xylylenediphosphonic acid *Transit. Metal. Chem.* <https://doi.org/10.1007/s11243-018-0256-y>
  19. Li Y X, Chen Y Z, Liu Y L, Jia L H and Chen Y F 2000 Hybrid open frameworks. Hydrothermal synthesis, structure determinations, and magnetic behavior of ((VO)-O-IV)<sub>2</sub>(H<sub>2</sub>O){O<sub>3</sub>P(CH<sub>2</sub>)<sub>3</sub>PO<sub>3</sub>}·2H<sub>2</sub>O: A new vanado-alkyldiphosphonate closely related to VO(HPO<sub>4</sub>)·0.5H<sub>2</sub>O *Transit. Metal. Chem.* <https://doi.org/10.1007/s11243-018-0261-1>.
  20. Cui J W, Hou S X, Li Y H and Cui G H 2017 A multifunctional Ni(II) coordination polymer: synthesis, crystal structure and applications as a luminescent sensor, electrochemical probe, and photocatalyst *Dalton Trans.* **46** 16911
  21. Li J X, Qin Z B, Li Y H and Cui G H 2018 Sonochemical synthesis and properties of two new nanostructured silver(I) coordination polymers *Ultrason. Sonochem.* **48** 127
  22. Wei X J, Liu D, Li Y H and Cui G H 2019 Two Zn(II) coordination polymers based on 5-substituted isophthalic acid: Syntheses, crystal structures, luminescence sensing properties *Polyhedron* **158** 357
  23. Wei X J, Liu D, Li Y H and Cui G H 2019 New 2D and 3D Cd(II) coordination polymers from aromatic dicarboxylate and 1,3-bis(5,6-dimethylbenzimidazol-1-yl)-2-propanol ligands: Syntheses, structures, photocatalytic, and luminescence sensing properties *J. Solid. State. Chem.* **272** 138
  24. Wei X J, Li Y H, Qin Z B and Cui G H 2019 Two zinc(II) coordination polymers for selective luminescence sensing of iron(III) ions and photocatalytic degradation of methylene blue *J. Mol. Struct.* **1175** 253
  25. Zhang C G, Zhang H H, Cao Y N, Hu J, Zhang S and Chen Y P 2009 Synthesis and Crystal Structure of a Novel Zinc Phosphonate Compound: [Zn(phen)(m-OOC<sub>6</sub>H<sub>4</sub>PO<sub>3</sub>H)] *Chin. J. Struct. Chem.* **7** 893
  26. Hu J, Zhang H H, Cao Y N, Zhang C G, Zhang S, Chen Y P and Sun R Q 2009 Synthesis and Structural Chemistry of Two Novel Transition Metal Organic Phosphonates *Chin. J. Struct. Chem.* **8** 939
  27. Kan W Q, Xu J M, Wen S Z and Yang L 2017 Metal ions directed assembly of two coordination polymers based on an organic phosphonate anion and a multi-dentate N-donor ligand *J. Mol. Struct.* **1128** 513
  28. Li Z X, Liu X F, Zhen Y L, Chen X and Zhou Y M 2017 A two-dimensional zinc Phosphonate: Synthesis, structure and photoluminescence properties *Inorg. Chem. Commun.* **84** 59
  29. Zhai F P, Deng M L, Zhen Y L, Chen X, Weng L H and Zhou Y M 2013 Syntheses, structures and magnetic properties of two isostructural metal-phosphonate frameworks *Inorg. Chim. Acta* **402** 104
  30. Lei R, Chai X C, Mei H X, Zhang H H, Chen Y P and Sun Y Q 2010 Four divalent transition metal carboxyarylphosphonate compounds: Hydrothermal synthesis, structural chemistry and generalized 2D FTIR correlation spectroscopy studies *J. Solid. State Chem.* **183** 1510
  31. Sun R Q, Hu J, Zhang H H, Cao Y N, Ye Z B, Wang Y Q and Chen Y P 2010 Syntheses and spectral study of novel metal zinc organic phosphonate *Spectrosc. Spect. Anal.* **30** 2215
  32. Wan Y H, Jin L P and Wang K Z 2003 Hydrothermal synthesis and structural characterization of two novel lanthanide supramolecular coordination polymers with nano-chains *J. Mol. Struct.* **649** 85
  33. Eddaoudi M, Kim J, Wachter J B, Chae H K, Keefe M O and Yaghi O M 2001 Porous Metal–Organic Polyhedra: 25 Å Cuboctahedron Constructed from 12 Cu<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub> Paddle-Wheel Building Blocks *J. Am. Chem. Soc.* **123** 4368
  34. Zhao L Y, Chen Y P and Zhang H H 2009 Study of structure and two-dimension correlation infrared spectroscopy on three rare-earth/3-methylbenzoic acid complexes *J. Mol. Struct.* **920** 441
  35. Zhang S, Cao Y N, Zhang H H, Chai X C, Chen Y P and Sun R Q 2008 Influence of synthesis condition on product formation: hydrothermal auto-oxidated synthesis of five copper halides with ratio of Cu(I)/Cu(II) in 1:1, 2:1, 3:1, 4:1 and 1:0 *J. Am. Chem. Soc.* **181** 3327
  36. Tong M L, Hu S, Wang J, Kitagawa S and Ng S W 2005 Supramolecular isomerism in cadmium hydroxide phases. Temperature-dependent synthesis and structure of photoluminescent coordination polymers of alpha- and beta-Cd<sub>2</sub>(OH)<sub>2</sub>(2,4-pyda) *Cryst. Growth. Des.* **5** 837
  37. Carlucci L, Ciani G and von Gudenberg D W 1997 Self-assembly of a three-dimensional network from two-dimensional layers via metallic spacers: The (3,4)-connected frame of [Ag<sub>3</sub>(hmt)<sub>2</sub>][ClO<sub>4</sub>]<sub>3</sub>·2H<sub>2</sub>O (hmt equals hexamethylenetetramine) *Chem. Commun.* **6** 631
  38. Zhao L Y, Chai X C and Chen Y P 2014 Structure, Luminescence, and Two-Dimensional Correlation Infrared Spectroscopy of Two Sm/3-Methylbenzoic Acid Complexes *Synth. React. Inorg. M* **44** 572
  39. Chai X C, Zhang H H, Zhang S, Cao Y N and Chen Y P 2009 The tunable coordination architectures of a flexible multicarboxylate N-(4-carboxyphenyl)iminodiacetic acid via different metal ions, pH values and auxiliary ligand *J. Am. Chem. Soc.* **182** 1889
  40. Guo Z G, Cao R, Li X J, Yuan D Q, Bi W H, Zhu X D and Li Y F 2007 A Series of Cadmium(II) Coordination Polymers Synthesized at different pH Values *Eur. J. Inorg. Chem.* **742**
  41. Jordi A S, Cristina S P, Daniel H A, Eduardo C E A, José Ramón G M and Pablo B 2017 A Metal–Organic Framework Based on a Tetra-Arylextended Calix[4]pyrrole Ligand: Structure Control through the Covalent Connectivity of the Linker *Cryst. Growth Des.* **17** 1328
  42. Elahi S M, Chand S, Deng W H, Pal A and Das M C 2018 Polycarboxylate-Templated Coordination Polymers: Role of Templates for Superprotonic Conductivities of up to 10<sup>-1</sup> S cm<sup>-1</sup> *Angew. Chem. Int. Ed.* **57** 6662
  43. Liu S Q, Kuroda-Sowa T and Konaka H 2005 Silver(I) coordination polymers of fluorescent

- oligo(phenylenevinylene) with pi-pi stackings: Luminescence and conductivity *Inorg. Chem.* **44** 1031
44. Bhattacharya A K and Thyagarajan G 1981 the michaelis-arbuzov rearrangement *Chem. Rev.* **81** 415
  45. G. M. Sheldrick 1996 SADABS, University of Göttingen: Göttingen, Germany.
  46. G. M. Sheldrick 1997 SHELXS 97, Program for the Solution of Crystal Structures; University of Göttingen: Göttingen, Germany.
  47. Zhong D C, Meng M, Zhu J, Yang G Y and Lu T B 2010 A highly-connected acentric organic-inorganic hybrid material with unique 3D inorganic and 3D organic connectivity *Chem. Commun.* **46** 4354
  48. Weingartz L E, Nettleman J H, Farnum G A, Staples R J and LaDuca R L 2016 Reprint of Divalent metal diphenate dipyridylamine coordination topology based on arc-like hexanuclear clusters *Polyhedron* **114** 459
  49. Tao J, Yin X, Wei Z B, Huang R B and Zheng L S 2004 Hydrothermal Syntheses, Crystal Structures and Photoluminescent Properties of Three Metal-Cluster Based Coordination Polymers Containing Mixed Organic Ligands *Eur. J. Inorg. Chem.* **2004** 125
  50. Bloch E D, Queen W L, Hudson M R, Mason J A, Xiao D J, Murray L J, Flacau R, Brown C M and Long J R 2016 Hydrogen Storage and Selective, Reversible O<sub>2</sub> Adsorption in a Metal-Organic Framework with Open Chromium(II) Sites *Angew. Chem. Int. Ed.* **55** 8605
  51. Chen B, Xiang S and Qian G 2010 Metal-organic frameworks with functional pores for recognition of small molecules *Acc. Chem. Res.* **43** 1115
  52. Li J R, Kuppler R J and Zhou H C 2009 Selective gas adsorption and separation in metal-organic frameworks *Chem. Soc. Rev.* **38** 1477
  53. Britt D, Furukawa H, Wang B, Glover T G and Yaghi O M 2009 Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites *Proc. Natl. Acad. Sci. USA* **106** 206 37
  54. Kreno L E, Leong K, Farha O K, Allendorf M, VanDuyne R P and Hupp J T 2012 Metal-organic framework materials as chemical sensors *Chem. Rev.* **112** 1105
  55. Zhou L J, Deng W H, Wang Y L, Xu G, Yin S G and Liu Q Y 2016 Lanthanide-Potassium Biphenyl-3,3'-disulfonyl-4,4'-dicarboxylate Frameworks: Gas Sorption, Proton Conductivity, and Luminescent Sensing of Metal Ions *Inorg. Chem.* **55** 6271
  56. Hu Z, Deibert B J and Li J 2014 Luminescent metal-organic frameworks for chemical sensing and explosive detection *Chem. Soc. Rev.* **43** 5815
  57. Cao L H, Wei Y L, Yang Y, Xu H, Zang S Q and Hou H W 2014 Crystal Structures and Properties of Cd(II) Coordination Polymers Supported by a New Chiral Aromatic Polycarboxylate Ligand *Cryst. Growth Des.* **14** 1827
  58. Wu X Y, Qi H X, Ning J J, Wang J F, Ren Z G and Lang J P 2015 One silver(I)/tetraphosphine coordination polymer showing good catalytic performance in the photodegradation of nitroaromatics in aqueous solution *Appl. Catal. B* **168** 98