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Two Novel 2D Cadmium Compounds with Noncentrosymmetric or Symmetric Network Dependent on Different pH Values[1]

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Abstract—Hydrothermal reaction of cadmium chloride and 2-carboxyethyl(phenyl)phosphinic acid (H_2L) under pH 2.69 or 5.00 afforded two novel Cd(II) compounds with the formula of $[Cd(HL)_2]_n$ (**I**) and $[Cd_3(L)_2(OH)_2]_n$ (**II**), respectively. Both compounds were well characterized by elemental analysis, IR spectroscopy, power X-ray diffraction, fluorescence and single-crystal X-ray diffraction (CIF files CCDC nos. 1049809 (**I**), 1049810 (**II**)). Compound **I** crystallizes in a $Pca2_1$ space group and presents a two-dimensional (2D) layered noncentrosymmetric structure, in which slight difference of the two Cd–O(phosphinico) distances leads to the formation of the chiral phosphorus atom in HL^- ligand. Compound **II** adopts a centrosymmetric $P2_1/c$ space group and exhibits a 2D network. Both compounds show violet fluorescence, assigned as an intraligand emission.

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INTRODUCTION

The design and construction of metal-organic coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, not only by the particular beauty and intriguing structural diversity of architectures, but also by the potential applications in magnetism, molecular adsorption, catalysis, electrical conductivity, nonlinear optics, and photoluminescence [1–4]. However, it still remains a great challenge to rationally assemble the desired compounds by controlling various factors which can influence the structures, such as metal ion, organic ligand, pH value, solvent, reaction temperature, metal-to-ligand ratio and so on [5–8]. Among these factors, the suitable reaction pH value has already been proved to be a strong influence on the self-assembly synthesis [9–12]. Although alteration of the pH value in one reaction system resulted in different dimensionality [13–16], topology [17, 18] and/or symmetries [19] of coordination polymers under certain circumstances has been discovered, to be our knowledge to now, there is few noncentrosymmetric polymers obtained by pH-dependent in document [20, 21]. Nevertheless, the preparation of multi-dimensional noncentrosymmetric frameworks from symmetrical moieties by controlling the pH value is still a great challenge.

In our previous work, we synthesized two novel 2D sliver compounds exhibited symmetric or noncentrosymmetric architecture by controlling the metal-ligand ratio with a bifunctional ligand of 2,2'-phosphinico-dibenzoic acid, that has two formally analogous carboxylate and phosphinate moieties [22]. As part of our ongoing interest in study the influence of factors on the construction of noncentrosymmetric structures from the bifunctional ligands, the system of cadmium chloride and 2-carboxyethyl(phenyl)phosphinic acid (H_2L) has been investigated. Fortunately, we obtained two 2D cadmium compounds with noncentrosymmetric or symmetric architecture by adjustment of the reaction pH values. Herein, we report the syntheses, crystal structures and luminescence of $[Cd(HL)_2]_n$ (**I**) and $[Cd_3(L)_2(OH)_2]_n$ (**II**) in details.

EXPERIMENTAL

Materials and methods. All reagents and solvents used were of analytical grade as obtained from commercial sources without further purification. FT-IR spectra were carried on KBr pellets in the range from 400 to 4000 cm^{-1} on a Nicolet A370 spectrophotometer. Elemental analyses for C, H were performed on a Vario EL-III elemental analyzer. Powder X-ray diffraction (PXRD) data were collected on a DX-2700 diffractometer with (CuK_α) radiation (λ = 1.5406 Å) over the 2θ range of 5°–30° at room temperature. Luminescence spectra of the solid samples were measured on a Shimadzu RF-5310 fluorescence spectrophotometer.

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Table 1. Crystal data and structural refinement details for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	538.68	795.48
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$
a, Å	15.578(6)	5.8450(17)
b, Å	5.546(2)	6.825(2)
c, Å	23.101(9)	29.379(8)
β, deg	90	99.945(5)
V, Å^3	1995.7(13)	1154.4(6)
Z	4	2
ρ_{calcd}, g/cm^3	1.793	2.289
μ, mm^{-1}	1.299	2.929
F(000)	1080	764
Reflections collected/unique	10517/3375	5571/1833
R_{int}	0.0238	0.0301
Limiting indices	$-18 \leqslant h \leqslant 16$, $-6 \leqslant k \leqslant 6$, $-27 \leqslant l \leqslant 27$	$-6 \leqslant h \leqslant 6$, $-7 \leqslant k \leqslant 8$, $-27 \leqslant l \leqslant 34$
Data/restraints/parameters	3491/1/265	2011/0/151
Flack	0.0(17)	
GOOF (all reflections)	1.097	1.058
R_1, wR_2 ($I > 2\sigma(I)$)	0.0220, 0.0506	0.0401, 0.1302
R_1, wR_2 (all data)	0.0231, 0.0519	0.0434, 0.1329
Largest diff. peak/hole, e Å^{-3}	0.217/–0.313	2.070/–1.534

Synthesis of compound I. A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.2 mmol) with H_2L (0.1 mmol) in 8 mL H_2O was stirred at room temperature for half an hour and then sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 160°C for 3 days. After cooling to room temperature at a rate of 10°C h^{-1}, colorless crystals of **I** were obtained in 68% yield based on H_2L.

For $C_{18}H_{20}O_8P_2Cd$

anal. calcd., %:	C, 40.06;	H, 3.65.
Found, %:	C, 40.10;	H, 3.71.

IR (KBr; ν, cm^{-1}): 3438, 1662, 1350, 1274, 1201, 1040, 799.

Synthesis of compound II was carried out by the similar method described for **I** with the same components in the same molar ratio. The pH value of the solution was adjusted to 5.00 by addition of 24 μL triethylamine. Colorless crystals of **II** were isolated by filtration and washed by water in 87% yield based on H_2L.

For $C_{18}H_{20}O_{10}P_2Cd_3$

anal. calcd., %:	C, 26.80;	H, 2.48.
Found, %:	C, 27.15;	H, 2.51.

IR (KBr; ν, cm^{-1}): 3623, 1408, 1297, 1145, 1124, 1031, 951.

X-ray crystallography. Single-crystal X-ray diffraction data for compounds **I** and **II** were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromatized MoK_α radiation (λ = 0.71073 Å) at room temperature using the φ and ω scan technique. Data reduction was conducted with the Bruker SAINT package. Absorption correction was performed using the SADABS program. The structures were solved by the direct methods and refined on F^2 by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model. Crystallographic data and structural refinement results are summarized in Table 1. Important bond distances for the two compounds are given in Table 2.

Crystallographic data for the structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1049809 (**I**), 1049810 (**II**); www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Compounds **I** and **II** were obtained by hydrothermal reactions of $CdCl_2 \cdot 2.5H_2O$ and H_2L under pH values of 2.69 or 5.00. In compound **I**, only the phosphinico group of ligand H_2L is deprotonated (*vide infra*), whereas both the phosphinico and carboxyl groups are fully deprotonated in **II** (*vide infra*). To obtain compounds in pure form, the optimization of the experimental procedure was conducted by modulating the pH values of reaction with triethylamine. The PXRD patterns of the products were displayed with different pH, from 2.69 to 6.68. Compound **I** was obtained with the pH values ranging from 2.69 to 4.71, whereas compound **II** was harvested with the limited pH value of 5.00. Therefore, the pH value of 2.69 and 5.00 were selected, respectively, for the synthesis of **I** and **II**.

Infrared spectra of **I** and **II** show strong characteristic bands of P=O in the region from 1350 to 1014 cm^{-1} and middle peaks of P–O around 1050–850 cm^{-1} [23, 24]. There is a strong peak at 1662 cm^{-1} in compound **I**, which indicates the existence of –COOH group. No strong absorption peak occurring in the range of 1600–1500 cm^{-1} further proves that the carboxyl group still keeps protonated, which are in accordance with the crystal structure of **I**. While in the IR spectrum of **II**, no peak is observed near 1700 cm^{-1} for –COOH group, but two strong peaks are observed around 1560–1345 cm^{-1}, which are characteristic for expected absorption of asymmetric and symmetric vibrations of coordinated carboxylate groups [25].

The single crystal X-ray analysis reveals that compound **I** displays an extended 2D layered structure. The asymmetric unit contains one Cd^{2+} ion and two HL^- anions. As shown in Fig. 1a, Cd^{2+} ion has a distorted octahedral environment and is surrounded by four phosphinic oxygen atoms and two carboxylate oxygen atoms from six HL^- ligands. The Cd–O distances are in the range of 2.170(2)–2.381(3) Å (Table 2), which are falling in normal values reported in literature [26–28]. Each HL^- ligand bridges three Cd^{2+} ions via its two oxygen atoms of phosphinic group and one of carbonyl group. Due to somewhat difference of the two Cd–O (phosphinic) bond distances (Fig. 1b), the four groups around the phosphorus atom in each HL^- ligand are different, which leads to the formation of the chiral P atomic center.

The Cd^{2+} ions are interconnected by double phosphinic groups of two HL^- anions into a two-fold symmetrical chiral inorganic chain along the *y* axis (Fig. 2a), which was observed in a lead(II) compound [29]. Furthermore, the neighboring 1D inorganic chain is connected through the organic piece ($-CH_2CH_2COOH$) of HL^- to form a complicated noncentrosymmetric 2D hybrid layer paralleled to the *xy* plane (Fig. 2b). Phenyl groups project outwards from the 2D layer. Moreover, the 2D layers are parallel arranged. The supramolecular 3D structure can be described as layers stacking along the *z* axis, with the phenyl groups oriented toward the interlayer space (Fig. 3).

Table 2. Selected bond distances (Å) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Cd(1)–O(4)	2.173(2)	Cd(1)–O(6)	2.170(2)
Cd(1)–O(5)[a]	2.313(2)	Cd(1)–O(3)[b]	2.338(2)
Cd(1)–O(2)[c]	2.354(3)	Cd(1)–O(7)[d]	2.381(3)
P(1)–O(3)	1.516(2)	P(2)–O(5)	1.515(2)
P(1)–O(4)	1.491(3)	P(2)–O(6)	1.507(3)
II			
Cd(1)–O(2)	2.281(5)	P(1)–O(3)	1.498(5)
Cd(1)–O(4)	2.346(4)	Cd(2)–O(4)	2.347(4)
Cd(1)–O(5)	2.254(4)	Cd(2)–O(5)	2.189(4)
Cd(1)–O(1)[c]	2.348(5)	Cd(2)–O(1)[e]	2.324(5)
Cd(1)–O(3)[a]	2.243(5)	P(1)–O(4)	1.519(4)
Cd(1)–O(5)[b]	2.298(4)		

* Symmetry codes: [a] *x*, *y* – 1, *z*; [b] *x*, *y* + 1, *z*; [c] *x* + 1/2, –*y* + 1, *z*; [d] *x* – 1/2, –*y* + 2, *z* (**I**); [a] *x* – 1, *y*, *z*; [b] –*x* + 1, –*y* + 2, –*z* + 2; [c] –*x* + + 1, –*y* + 1, –*z* + 2; [e] –*x* + 2, –*y* + 1, –*z* + 2 (**II**).

Increasing reaction pH value, an extended 2D network of **II** was prepared, in which H_2L ligands are fully deprotonated. Asymmetric unit of **II** with atoms labeling is depicted in Fig. 4a. The asymmetric unit is composed of one and a half crystallographically independent Cd^{2+} ions, one L^{2-} anion and one hydroxyl group. Although the Cd(1) center sits on an inversion center, the coordination geometries around Cd(1) and Cd(2) are both distorted octahedron, which is composed of two phosphinic oxygen atoms and two carboxyl oxygen atoms from four L^{2-} ligands as well as two μ_3-OH^- groups. The Cd–O bond distances range

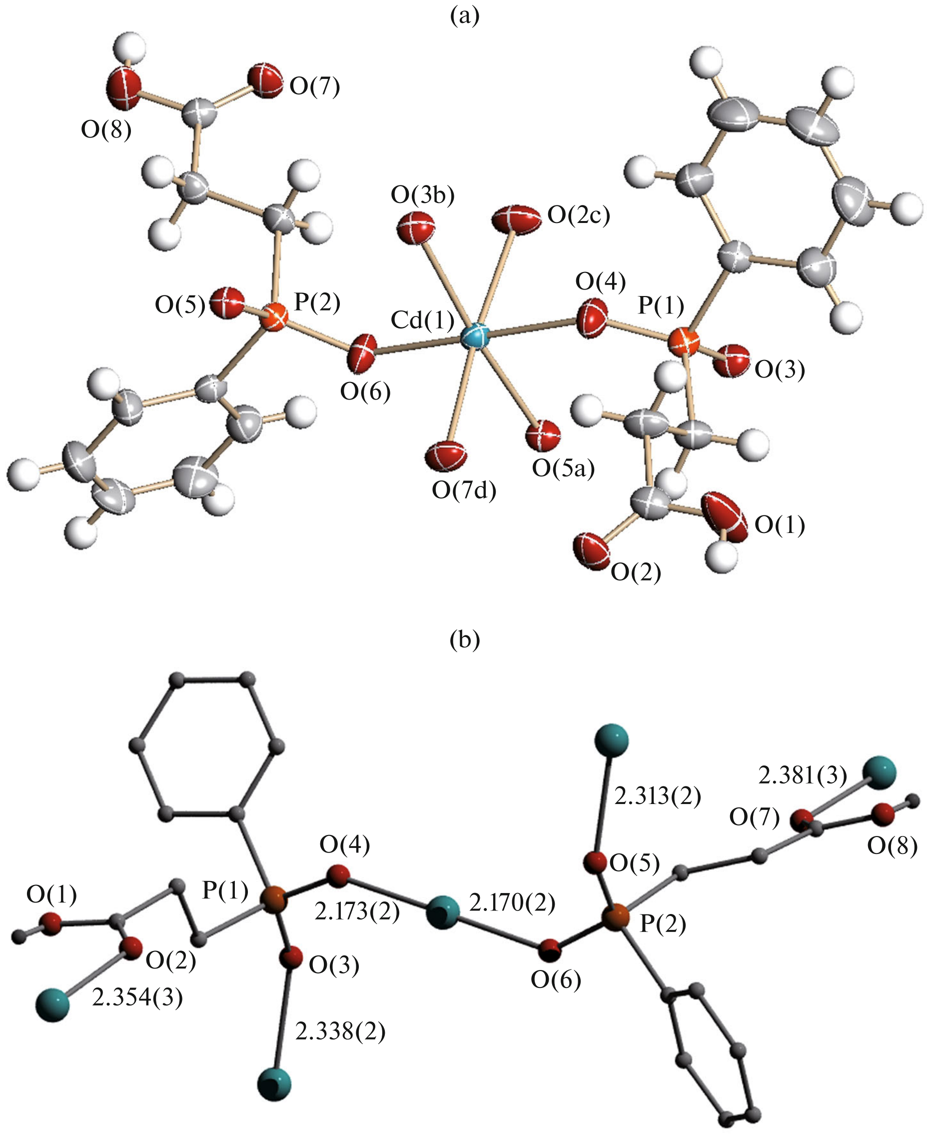

Fig. 1. Asymmetric unit of **I** with 50% probability displacement ellipsoids (a); environment of the four groups around the phosphorus atom in HL^- ligand (b). Hydrogen atoms are omitted for clarity.

from 2.187(6) to 3.349(6) Å, which are comparable to those in **I**.

In compound **II**, the L^{2-} ligand exhibits obviously different coordination mode from its compounds in literature [30, 31]. Each L^{2-} anion bridges three Cd(1) and two Cd(2) ions via monodentate phosphinic O(3) and carboxylate O(2) atoms, and monodentate-bridging phosphinic O(4) and carboxylate O(1) atoms (Fig. 4). Meanwhile, each μ_3-OH^- group connects three Cd^{2+} ions to form an inorganic chain array along the *x* axis, which is also strengthened by phosphinico groups (Fig. 5a). The neighboring 1D chain is bridged by the moieties ($CH_2CH_2COO^-$) of L^{2-} anions to form a complicated 2D hybrid layer in the *xy* plane (Fig. 5b).

The solid-state luminescent spectra of **I** and **II** have been investigated at room temperature. Compounds **I** and **II** both display a broad violet fluorescent emission band centered at λ_{max} = 368 nm (λ_{ex1} = 340 nm, λ_{ex2} = 342 nm). The bands are attributed to an intraligand emission, which are similar to the previously reported Cd(II) compounds [32].

The thermal stabilities of **I** and **II** have been examined by thermogravimetric analysis (TGA) in a nitrogen atmosphere from 35 to 800°C. The TGA curves show that compounds **I** and **II** both are stable up to 300°C and then decompose completely until 533 and

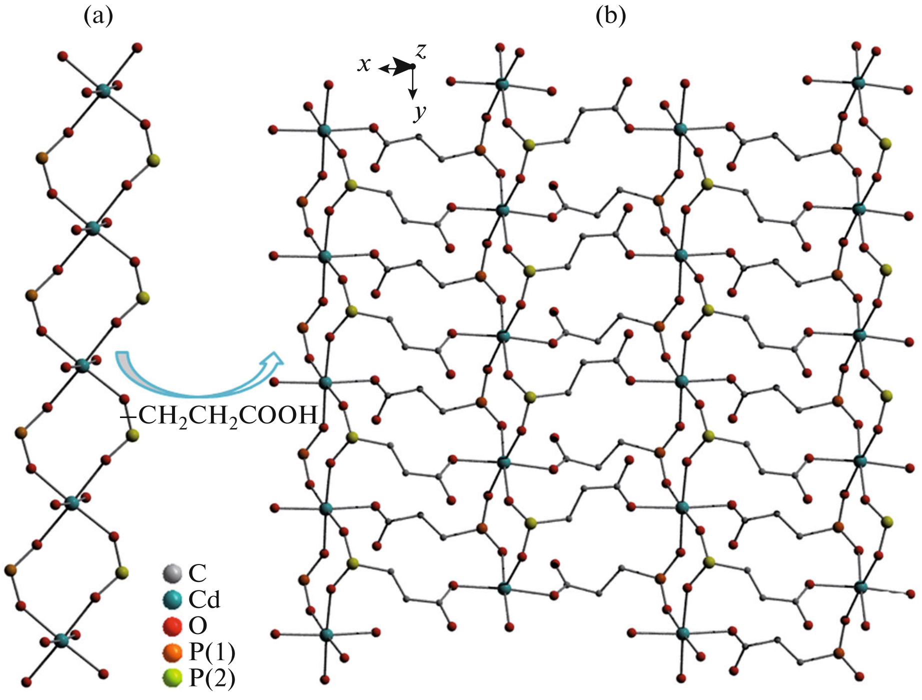

Fig. 2. A view of the 1D inorganic chain array along the *y* axis for **I** (a); their assembly into 2D network through CH_2CH_2COOH groups, the phenyl groups are omitted for clarity for **II** (b).

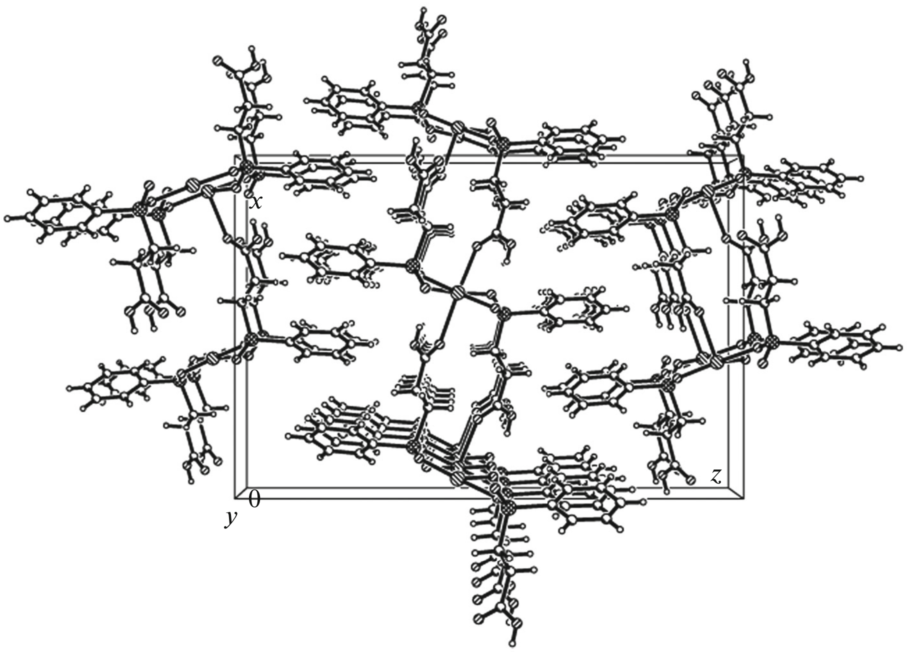

Fig. 3. The packing structure of **I** along the *y* axis.

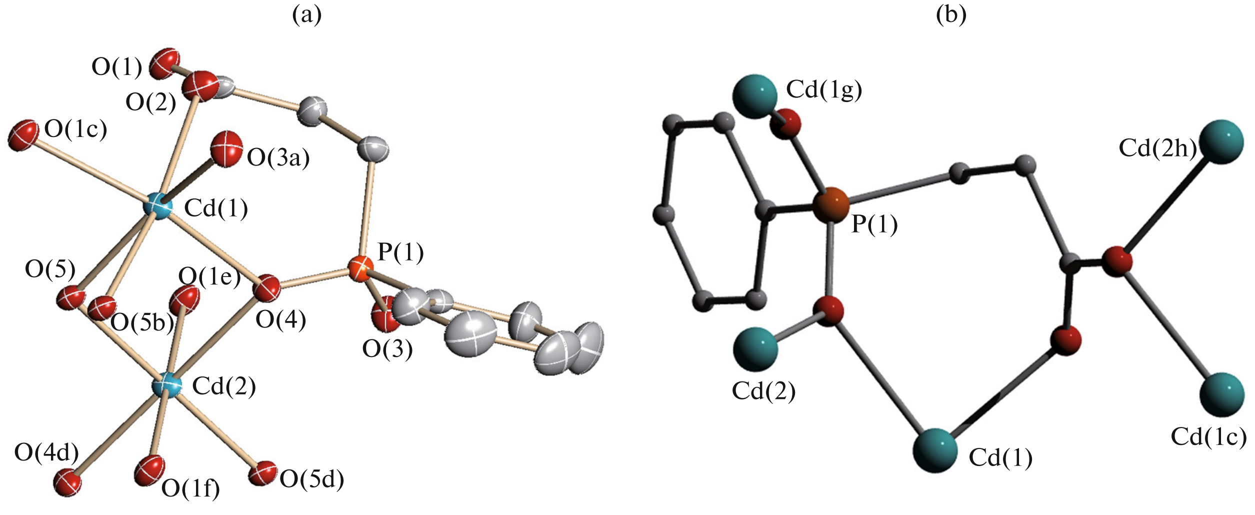

Fig. 4. Asymmetric unit of **II** with 50% probability displacement ellipsoids (a); coordination mode of L^{2-} ligand (b). Hydrogen atoms are omitted for clarity. Symmetry code: $^{c}\,-x + 1, -y + 1, -z + 2$; $^{g}\,x + 1, y, z$; $^{h}\,x, y - 1, z$.

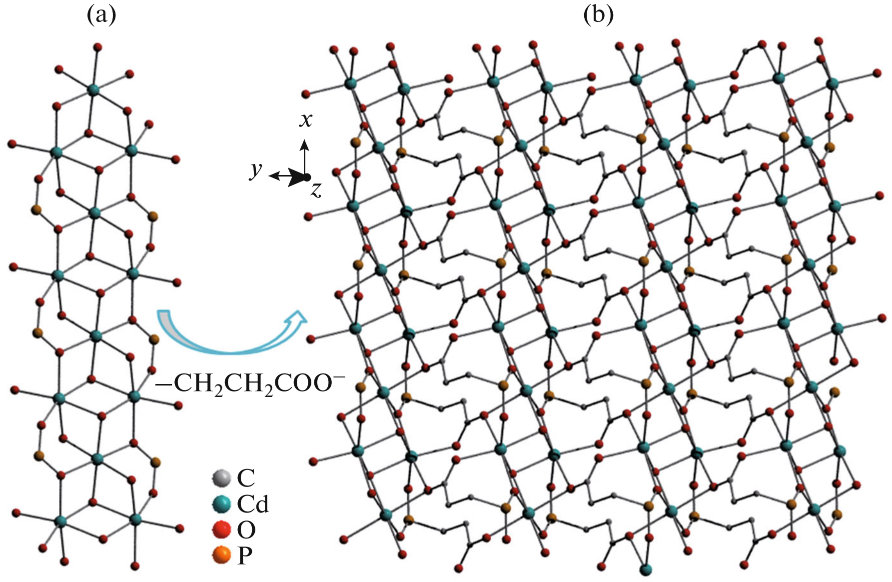

Fig. 5. A view of 1D inorganic chain array along the x axis for **II** (a); their assembly into 2D network through $CH_2CH_2COO^-$ groups (b). The phenyl groups and hydrogen atom sare omitted for clarity.

513°C, with total weight loss of 54.76 and 50.1%, respectively.

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