

SYNTHESIS, STRUCTURE, THERMAL STABILITY AND FLUORESCENCE OF A NEW CADMIUM(II) COORDINATION POLYMERS AS PRECURSOR FOR PREPARATION OF CdO MICRO-CRYSTAL

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ABSTRACT

A new complex $[Cd(btca)_{0.5}(H_2O)_3]$ (**1**) (H_4btca : 1,2,4,5-benzenetetracarboxylic acid) has been synthesized and characterized by single crystal X-ray diffraction studies, elemental analysis and FT-IR. In compound **1**, Cd(II) center atoms coordinate to three ligand $btca^{4-}$ anions and three water molecules with a six-coordinated distorted octahedral geometry. Four carboxyl groups of $btca^{4-}$ adopt $\mu_2-\eta^2-\eta^0$ and $\mu_1-\eta^1-\eta^0$ two different coordination modes. The whole anion $btca^{4-}$ acts as a hexadentate bridge to connect adjacent Cd(II) atoms, resulting in 2D layer structure. Further, these two-dimensional layers are linked together by O-H...O to give rise to three-dimensional structure. Thermal stability and luminescent property of **1** are investigated. CdO micro-crystalline particles are then produced by calcination of compound **1** at 580 °C. The obtained CdO is characterized by XRD and SEM analyses.

Keywords: Cd(II) complex; carboxyl group; thermal stability; luminescent property

INTRODUCTION

Design and construction of metal-organic frameworks (MOFs) formed by joining the metal centers with organic linkers has attracted considerable attention because of their intriguing structural topologies and versatile applications in the areas of photoluminescence, ion exchange, redox catalysis, adsorption, separation, magnetism and sensors [1-6]. In these search, Carboxylic acids with aromatic rings owing to rigidity of aromatic rings are widely used in the construction of high-dimensional metal coordination polymers, for example, 1,3,5-benzenetricarboxylic acid, 1,4-naphthalenedicarboxylic acid, and so on, because these anions are able to act as bridging ligands in various ligating modes, resulting in abundant structural motifs [7]. 1,2,4,5-benzenetetracarboxylic acid also has been extendedly used to synthesized complexes because of its high symmetry and rigidity [8-10]. A great number of carboxylate bridged MOFs have been produced and reported because of the fascinating structures of metal-carboxylate clusters, potential applications, and fantastic topological networks [11-14]. On the other hand, cadmium shows few of the characteristic properties of transition metals because it does not have partially filled d orbital, and prefers the 2+ oxidation state in most of its complexes. More significantly, its spherical d^{10} configuration makes it particularly suited for the construction of coordination polymers and networks, and also facilitates diverse coordination geometries that allow the formation of multi-form metallo supramolecular materials [15]. A series of topological types of one, two, and three-dimensional coordination polymers have been synthesized and reported [16-22].

In addition, The IIB binary compound semiconductors are technologically important materials for optoelectronic applications. Cadmium oxide (CdO) has high optical transmittance and high electrical conductivity properties in the visible region of the solar spectrum, and a moderate refractive index. It is well known that cadmium oxide (CdO) is a semiconductor with direct band gap of 2.2 eV (520 nm). This material has various applications including solar cells, transparent electrodes, photodiodes, photodiodes and gas sensors, which make this material very suitable for modern technologies [23, 24]. Therefore, synthesis of nanoparticles or micro-crystal of CdO has attracted more and more attention in recent years. Many methods have been used and reported in the literature, including sol-gel [25], hydrothermal and solvothermal synthesis [26], microemulsion method [27], microwave-solvothermal synthesis, surfactant-ligand co-assisting solvothermal [28, 29] and so on [30, 31]. Considerable effort and methods have been dedicated and used to synthesis of nano-scale or micro-crystal particles of metals, metal oxides, metal sulfides, and other nano-materials, such as nano-ceramic materials, however, little attention and effort was focused on using coordination polymers to synthesize nano-particles or micro-crystal particles [32, 33]. In this paper we report the preparation and crystal structure of the new Cd(II) coordination polymer, $[Cd(btca)_{0.5}(H_2O)_3]$ (**1**), and describe a simple synthetic preparation, study of structures and properties of this coordination compound and its use in the preparation of CdO micro-crystalline particles.

EXPERIMENTAL

Materials and physical measurements: All reagents commercially available were of reagent grade and used without further purification. C, H elements analyses were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer by using KBr pellet in the range of 4000–400 cm^{-1} . The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width is 5.0 nm. Thermogravimetric analyses (TGA) were carried out with a SDT Q600 instrument under 100.0 mL/min flowing nitrogen, and ramp rate of 20.00 °C / min from 30 to 800°C. X-ray powder diffraction (XRD) measurements are performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu-K α 1 monochromatized radiation at 40 kV and 40 mA. The sample is characterized with a scanning electron microscope (SEM) (JEOL JSM 5600LV) with gold coating.

*Preparation and analysis of $[Cd(btca)_{0.5}(H_2O)_3]$ (**1**):* The mixture of 1, 2, 4, 5-benzenetetracarboxylic acid 25.4 mg (0.1 mmol) and CdCO₃ 8.6 mg (0.05 mmol) in 10 mL distilled water was heated for about 30 min in boiling water bath. Then 20.0 mg (0.25 mmol) pyrazine was added. The mixture was cooled to room temperature, colorless block crystals were produced (8.2 mg). C₅H₄CdO₄ (291.52): Anal. Calcd. for C₅H₄CdO₄ (%): C, 20.60; H, 2.42. Found: C, 20.56; H, 2.44. FT-IR spectrum (cm^{-1}): 3465(bs), 1610(s), 1585(s), 1502(s), 1392(s), 1307(m), 1268(m), 1256(m), 1138(m), 1121(m), 876(m), 835(m), 811(m), 771(m), 588(m). The micro-crystalline powder sample of **1** was synthesized as follows:

The mixture of 1, 2, 4, 5-benzenetetracarboxylic acid 50.8 mg (0.2 mmol) and CdCO₃ 17.2 mg (0.1 mmol) in 15 mL distilled water was heated for about 12 h in boiling water bath. Then 40.0 mg (0.5 mmol) pyrazine and 40 mL CH₃CH₂OH were added. The mixture was cooled to room temperature, and white powder was produced (13.4 mg). Elements analyses (%) Found: C, 20.62; H, 2.51. FT-IR spectrum (cm^{-1}): 3400(bs), 1605(s), 1590(s), 1508(s), 1395(s), 1312(m), 1262(m), 1260(m), 1143(m), 1115(m), 873(m), 830(m), 808(m), 769(m), 578(m).

X-Ray Crystallography: The crystal data collection for complex **1** was carried out on Bruker CCD ApexII diffractometer at room temperature, using graphite-monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). An empirical absorption correction was made by a multi-scan type. Out of the 1819 total reflections collected in the $2.36 \leq \theta \leq 24.99^\circ$ range, 1276 were independent with $R_{int} = 0.0189$, of which 1163 were considered to be observed ($I > 2\sigma(I)$) and used in the succeeding refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques with SHELXL-97 program [34, 35]. Anisotropic displacement parameters were refined for all non-hydrogen

atoms. The hydrogen atoms were added in the riding model. The crystal parameters, data collection and refinement results for the compounds are listed in table 1. The selected bond lengths and bond angles are listed in Table 2.

Table 1: Crystallographic data for complex **1**.

| | |
|---|--|
| Empirical formula | C ₅ H ₇ CdO ₇ |
| F. w. | 291.52 |
| Crystal system | triclinic |
| Space group | <i>P</i> -1 |
| <i>a</i> (Å) | 5.5924(9) |
| <i>b</i> (Å) | 7.7594(13) |
| <i>c</i> (Å) | 9.6750(16) |
| <i>α</i> (deg) | 111.921(2) |
| <i>β</i> (deg) | 101.810(2) |
| <i>γ</i> (deg) | 98.277(2) |
| <i>V</i> (Å ³) | 369.84(11) |
| <i>Z</i> | 2 |
| Temperature / K | 296(2) |
| D _c (g cm ⁻³) | 2.618 |
| μ (mm ⁻¹) | 2.958 |
| Crystal dimension / mm | 0.32×0.26×0.23 |
| Crystal color | colorless |
| θ range / (°) | 2.36 - 24.99 |
| Goodness of fit | 1.004 |
| Reflections collected | 1819 |
| Independent reflns | 1276 |
| Obsd. Reflns. (<i>I</i> > 2σ(<i>I</i>)) | 1163 |
| <i>F</i> (000) | 282 |
| Parameters refined | 118 |
| <i>R</i> , <i>wR</i> (<i>I</i> > 2σ(<i>I</i>)) | 0.0355, 0.1064 |
| <i>R</i> , <i>wR</i> (all reflections) | 0.0400, 0.1083 |

Preparation of micro-crystalline cadmium oxide particles: Cadmium oxide micro-crystalline particles were synthesized from powder sample through calcination. The amount of this sample (about 25 mg) was heated to 580 °C for 1 h in air. After cooling, white powder was obtained, which was directly used to study the morphology and size of the sample by means of SEM.

RESULTS AND DISCUSSION

IR and Crystal Structure of 1: In complex **1**, the IR spectra of this complex show broad strong bands at the region 3500–3000 cm⁻¹, which may be related to the existence of O–H···O hydrogen bonding between water molecules. The all carboxyl groups of the H₄btcac are completely deprotonated, in good agreement with the IR spectral data since strong band around 1690–1730 cm⁻¹ for –COOH was not observed [36,37]. The IR spectrum of **1** shows characteristic bands of carboxyl groups at 1,585 cm⁻¹ for the asymmetric stretching and at 1,392 cm⁻¹ for symmetric stretching. The volve of ν(v_{as}(–COO–)–ν_s(–COO–)) indicate that the carboxylate groups coordinate to the metal atoms bridging (Δν value: 193 cm⁻¹) fashion [38]. The spectrum also exhibits a strong broad band at 1610 cm⁻¹ indicative of COO_{as} stretching mode, while a peak corresponding to COO_s vibration appeared at 1392 cm⁻¹ [34–36]. The difference of ν(v_{as}(–COO–)–ν_s(–COO–)) is 218 cm⁻¹ characteristic of a unidentate carboxylato group [39,40]. All those are consistent with the results of the X-ray analysis.

The X-ray diffraction study for **1** reveals that the material crystallizes in the triclinic space group *P*-1. The asymmetric unit contains one Cd(II) atom, a half of btcac⁴⁻ anion and three coordinated water molecules. Selected bond lengths for **1** are listed in Table 2. As shown in Figure 1, the Cd1 ion, which is in the

center of a distorted octahedral geometry, is surrounded by three carboxylic oxygen atoms from three btcac⁴⁻ ligands and three oxygen atoms from three terminal coordinated water molecules. Cd–O bond distances are in the range of 2.245(5) – 2.401(5) Å, and the angles of O–Cd–O range from 76.10(19) to 170.87(16) °. Selected bond lengths and angles are listed in Table 2.

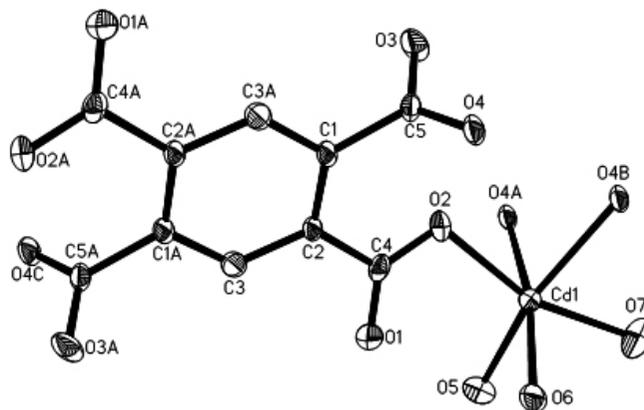


Figure 1: Coordination environment around the Cd(II) atom of **1** with 50% probability displacement, the hydrogen atoms omitted for clarity; Symmetry code: C1A, C2A, C3A, C4A, C5A, O1A, O2A, O3A, O4C: 2 - *x*, -*y*, -*z*; O4B: 2 - *x*, 1 - *y*, 1 - *z*; O4A: *x* - 1, *y*, *z*.

Table 2: Selected bond lengths (Å) and angles (deg) for complex **1**.

| Bond | Dist. | Bond | Dist. |
|-------------|------------|---------------|-----------|
| Cd1-O2 | 2.245(5) | Cd1-O5 | 2.280(5) |
| Cd1-O4#1 | 2.312(5) | Cd1-O6 | 2.338(5) |
| Cd1-O4#2 | 2.351(4) | Cd1-O7 | 2.401(5) |
| Angle | (°) | Angle | (°) |
| O2-Cd1-O5 | 114.64(19) | O2-Cd1-O4#1 | 87.48(17) |
| O5-Cd1-O4#1 | 150.44(19) | O2-Cd1-O6 | 90.94(18) |
| O5-Cd1-O6 | 86.31(19) | O4#2-Cd1-O7 | 85.14(18) |
| O4-Cd1-O6#1 | 113.97(17) | O2-Cd1-O4#2 | 84.80(18) |
| O5-Cd1-O4#2 | 88.12(17) | O4#1-Cd1-O4#2 | 73.99(17) |
| O6-Cd1-O4#2 | 170.87(16) | O2-Cd1-O7 | 162.6(2) |
| O5-Cd1-O7 | 79.2(2) | O4#1-Cd1-O7 | 76.10(19) |
| O6-Cd1-O7 | 100.9(2) | | |

Symmetry codes: #1: 2 - *x*, 1 - *y*, 1 - *z*; #2: *x* - 1, *y*, *z*.

In complex **1**, the carboxylate groups are not coplanar with centre benzene ring. The angles between benzene ring with carboxylate groups are 78.64° (O4-C5-O3, O4C-C5A-O3A), 15.87° (O1-C4-O2, O1A-C4A-O2A), respectively. In anion btcac⁴⁻, four carboxylate groups take two coordination modes (Figure 2). Two carboxylate groups take μ¹-η¹:η⁰, the other two take μ²-η²:η⁰ mode (Figure 2). The whole anion btcac⁴⁻ acts as a hexadentate bridge to connect adjacent Cd(II) atoms, resulting in 2D layer structure (Figure 2). It is noticeable that there are Cd₂(COO)₄ clusters in (secondary building block) **1**, which act as four connection nodes, while the btcac⁴⁻ anions act as four connection linker, resulting in a two-dimensional grid-like layer with (4,4) topological net (Figure 2).

There are rich O–H···O hydrogen bonds in complex **1** (Table 3). These two-dimensional layers are linked together by O5–H5C···O1, O6–H6B···O1, O6–H6C···O3, O6–H6C···O3 with a R₁²(6)⁰¹¹ hydrogen bond pattern to give rise to three-dimensional structure (Figure 3, Table 3).

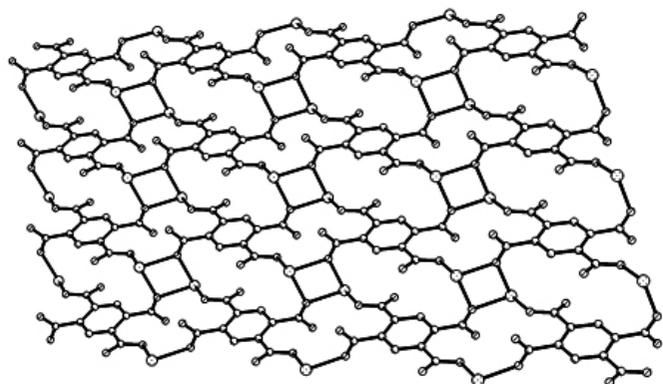


Figure 2: Figure 2 two-dimensional structure of **1**, hydrogen atoms and coordinated water molecules omitted for clarity.

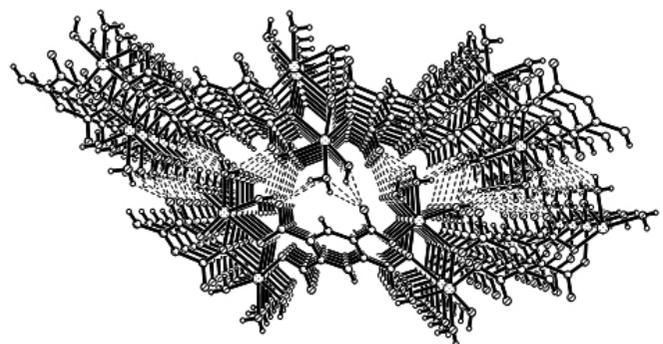


Figure 3: Figure 3 Crystal packing diagram of **1**, hydrogen bonds indicated by dashed lines..

Table 3: Distance (Å) and angles (deg) of hydrogen bonds for the complex **1**.

| D-H...A | $d(\text{D-H})$ / Å | $d(\text{H...A})$ / Å | $d(\text{D...A})$ / Å | $\angle(\text{DHA})$ / (°) |
|---------------|------------------------|--------------------------|--------------------------|-------------------------------|
| O5-H5B...O6#1 | 0.81 | 2.32 | 3.015(8) | 144 |
| O5-H5C...O1#2 | 0.81 | 2.16 | 2.778(8) | 132 |
| O6-H6B...O1#2 | 0.85 | 2.12 | 2.803(7) | 138 |
| O6-H6C...O3#3 | 0.85 | 1.98 | 2.743(8) | 149 |
| O6-H6C...O3#4 | 0.85 | 2.52 | 3.051(7) | 122 |
| O7-H7A...O2#5 | 0.85 | 2.33 | 3.058(8) | 144 |
| O7-H7A...O3#5 | 0.85 | 2.27 | 2.814(9) | 122 |
| O7-H7B...O3#4 | 0.85 | 2.47 | 3.215(9) | 147 |

Symmetry transformations are used to generate equivalent atoms: #1: $-1 + x, y, z$; #2: $1 - x, 1 - y, -z$; #3: $x, 1 + y, z$; #4: $2 - x, 1 - y, 1 - z$; #5: $1 - x, 1 - y, 1 - z$.

Luminescent Property of 1: The solid-state photoluminescent spectrum of complex **1** was measured at room temperature and excited at 250 nm, complex **1** shows one maximum emission spectrum centered at 426 nm (Figure 4). To ascertain the adsorption of emission spectra, the photoluminescence of pure H_2btc was measured under the same conditions. However, the free H_2btc ligand emission peak almost was not observed. The emission band of compound **1** may be assigned to $\pi\text{-}\pi^*$ intraligand fluorescence.

Thermogravimetric Analyses: Complex **1** was subjected to thermogravimetric analysis (TGA) in a N_2 atmosphere to ascertain their thermal stability, and the TGA curve of **1** was recorded from room temperature to 800 °C (Figure 5). In the TGA curve of complex **1** there is a weight loss of 18.99 % within the temperature range of 117–142 °C, corresponding to the release of three coordinated water molecules (calcd 18.54%), and a continuous

weight loss (calcd 43.59%) starting at 410 °C. In this process, weight loss between 410 to 506 °C of ca.45.34% (calcd. 43.59%), corresponding to the loss of a half benzene molecule and two carbon dioxide per formula unit, from the decomposition of btc^{4-} , accompanied by the subsequent decomposition of the framework. The final residues may be CdO.

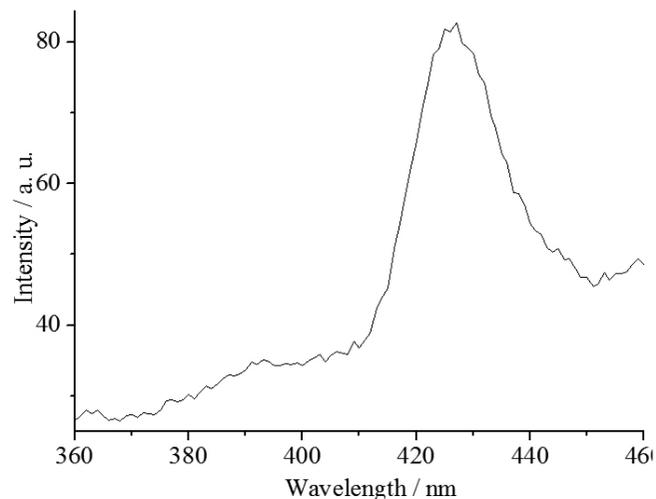


Figure 4: Emission spectrum of complex **1** in solid state at room temperature.

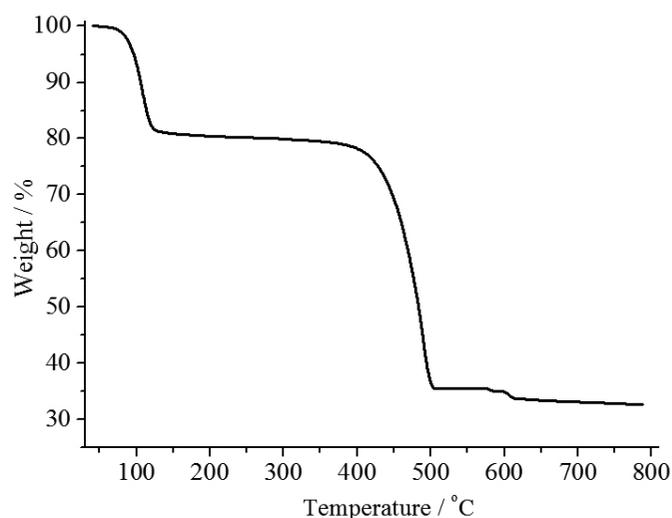


Figure 5: TG curve of **1**.

Figure 6 shows the XRPD pattern calculated from the single crystal data of **1** in compared to the XRPD pattern of the typical belt sample of **1** prepared by a solvothermal process (Figure 7). Acceptable matches, with slight differences in 2θ and differences in intensity, are observed. This suggests that the compound obtained has a single crystalline phase and that structure of this phase is identical to that obtained by single crystal diffraction. Figure 7 is the SEM of the micro-crystalline belt produced from solvothermal process. The SEM (Figure 7) indicates that average length, width and thickness of belts are 1.37, 0.38, 0.07 μm , respectively.

CdO micro-crystalline particles were synthesized from the decomposition of the precursor **1** at 580 °C under air atmosphere. The phase purity of the as-prepared orange yellow orthorhombic CdO microparticles are completely obvious and all diffraction peaks are perfectly indexed to the cubic CdO structure with the lattice parameters of $a = 4.695$ Å, $b = 4.695$ Å, $c = 4.695$ Å, $Z = 4$ and S.G = $Fm\bar{3}m$ which are in JCPDS card file no. 05-0640. No

characteristic peaks of impurities are detected in the XRD pattern (Figure 8).

Figure 9 is the SEM of as prepared CdO. Compared with Figure 7, we found that the shape of CdO particles is not same as that of its precursor. But the shape is still belt. The SEM (Figure 9) indicates that average length, width and thickness of CdO belts are 1.19, 0.31, 0.065 μm , respectively.

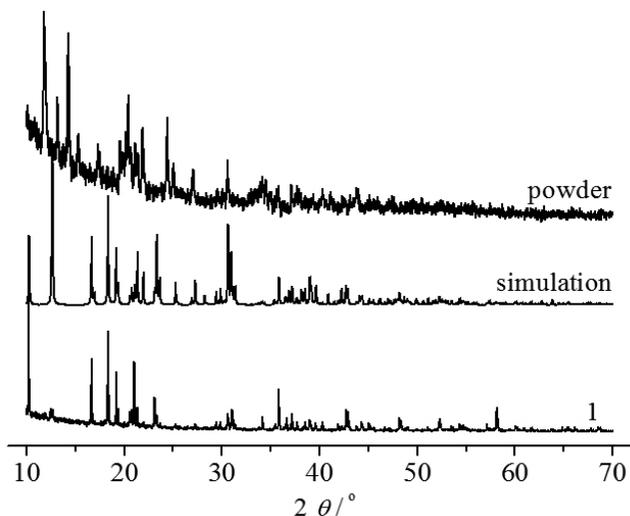


Figure 6: The XRD patterns of a simulated from single crystal X-ray data of complex, **1** and the powder sample.

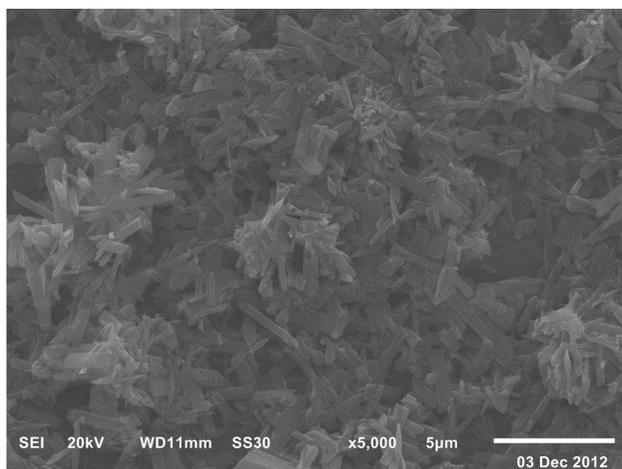


Figure 7: The SEM photographs of micro-crystalline sample.

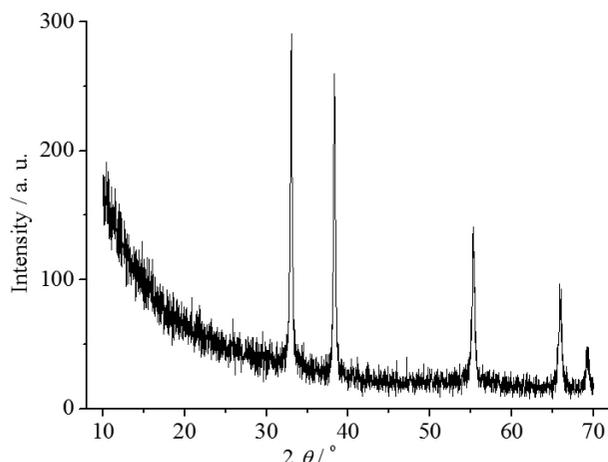


Figure 8: XRD pattern of CdO prepared from thermolysis of powder sample.

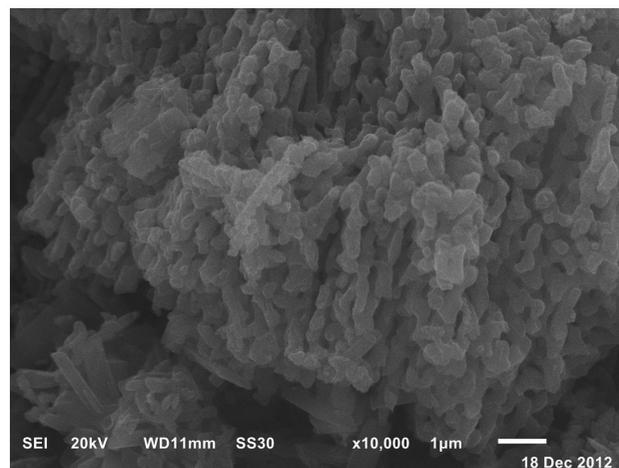


Figure 9: SEM photograph of as-prepared CdO produced by calcinating precursor at 580 °C.

CONCLUSIONS

In summary, the syntheses, crystal structures, thermal stability and luminescent properties of a new Cd(II) polymer have been described. Compound feature a 2D network. The btca^+ anions act as four connection linker connect $\text{Cd}_2(\text{COO})_4$ clusters, which adopt four connection nodes, resulting in a two-dimensional grid-like layer with (4,4) topological net. Thermal stability of three complexes and luminescent property of **1** are investigated. The CdO belt micro-crystalline particles were obtained by thermolysis of powder sample at 580 °C. The scanning electron microscopy shows that the thickness of the CdO and its precursor particles is $\sim 0.07\mu\text{m}$.

Supplementary material

Crystallographic data for the compound have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 913621 for **1**. This information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; website: <http://www.ccdc.cam.ac.uk>).

ACKNOWLEDGMENTS

The authors are grateful to grateful to An Hui Province Natural Science Foundation (1208085MB31) and Student Creative Project of Chuzhou University for financial support of this work.

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