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A novel organic-inorganic hybrid material with fluorescent emission: $[Cd(PT)(H_2O)]_n$ (PT = phthalate)†

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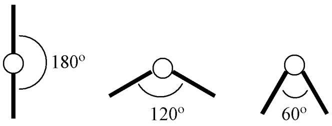
The novel organic-inorganic hybrid material $[Cd(PT)(H_2O)]_n$ (**1**; PT = phthalate) has been hydrothermally synthesized. The X-ray diffraction study reveals that **1** exhibits an interesting two-dimensional (2D) honeycomb framework constructed from $[CdO_7]$ single helical chains linked *via* oxygen atoms of the PT ligands, which adopt the μ_6-bridging coordination mode. A study of the physical properties of **1** demonstrates that it exhibits a strong fluorescent emission in the solid state at room temperature.

Organic-inorganic hybrid compounds with extended structures are currently of considerable interest owing to their intriguing structural motifs and unique electro-conductive, optical and magnetic properties, as well as three-dimensional (3D) porosity.[1–10] This kind of hybrid materials combines the unique characteristics of both inorganic and organic subunits; furthermore, the extended structures improve and/or strengthen some interesting physical properties. In this family, metal carboxylates have been extensively studied.[3] By selecting suitable bi-, tri- and tetracarboxylic ligands and metal ions, clusters, or other building blocks, chemists have obtained some exciting results.[4,5,8–10] The research on metal benzene dicarboxylic ligands is one of the most active areas. Generally, benzene dicarboxylic ligands can be of three structural types (see Scheme 1): (i) linear (180°) 1,4-dicarboxylic ligand; (ii) 1,3-dicarboxylic ligand with a large angle (*ca.* 120°) between the two carboxyl groups; (iii) 1,2-dicarboxylic ligand with a small angle (*ca.* 60°) between the two carboxyl groups. It is noteworthy that many reports are concerned with the multi-dimensional compounds constructed by metal ions and 1,4-dicarboxylic ligands, while the extended compounds composed of 1,3- and 1,2-dicarboxylic ligands have rarely been reported. The possible reason may lie in the differences in stereo orientation of these ligands. However, the variety of coordination modes[11–14] of phthalate may also provide the possibility to prepare new metal phthalate with diverse topological structures and potentially interesting physical properties.

Cadmium compounds with organic acids show interesting optical properties, especially fluorescence. Recently, cadmium carboxylates with extended frameworks have received much attention because of their excellent fluorescent properties, besides their interesting structural topologies. A series of open-framework cadmium oxalates and succinates have been observed,[15] however, few cadmium benzene dicarboxylates with extended structures are known to date.[16] To the best of our knowledge, no cadmium phthalate with a multi-dimensional structure has been synthesized hitherto. In this paper, we report a novel two-dimensional (2D) cadmium phthalate, $[Cd(PT)(H_2O)]_n$ (**1**; PT = phthalate), which exhibits a strong fluorescent emission in the solid state at room temperature.



Scheme 1 Schematic representation of three structural types of benzene dicarboxylic ligands.

Experimental

Materials and general methods

All chemicals were commercially available and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240 CHN elemental analyzer. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric data were collected on a Perkin–Elmer TGA7 instrument in flowing nitrogen at a heating rate of 10 °C·min^{-1}. The diffuse reflectance UV-vis spectrum ($BaSO_4$ pellet) was obtained with a Varian Cary 500 UV-vis NIR spectroscopy. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a SPEX 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source. All measurements were performed at room temperature.

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† Electronic supplementary information (ESI) available: figures showing the metal-oxygen framework of **1** and its XPS, IR, UV-vis spectra and the decay of the luminescence, as well as the fluorescent excitation and emission spectra of PT. See http://www.rsc.org/suppdata/nj/b2/b211358a/

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Hydrothermal synthesis

The title compound **1** was hydrothermally synthesized under autogeneous pressure. An aqueous mixture (7 cm^3) containing KH(PT) (0.204 g, 1 mmol), Cd(NO$_3$)$_2$·4H$_2$O, (0.462 g, 1.5 mmol), and oxalic acid (0.126 g, 1 mmol) was neutralized to pH 6.5 with 2 M KOH aqueous alkali under continuous stirring and then sealed in a Parr teflon-lined stainless steel vessel (15 mL), which was heated to 160 °C for 120 h. After slowly cooling at 5 °C·h^{-1} to ambient temperature, colorless block-like crystals of the complex [Cd(PT)(H$_2$O)]$_n$ (**1**) were mechanically separated from the white powder and washed by water (yield: *ca.* 40% based on Cd). Anal. calcd for C$_8$H$_6$CdO$_5$: C: 32.62; H: 2.06%; found: C: 32.57; H: 2.19%. FT-IR (cm^{-1}): 3439(m), 3348(s), 3248(m), 1643(m), 1580(vs), 1550(vs), 1491(s), 1446(m), 1417(s), 1290(w), 1158(w), 1087(w), 1039(w), 967w, 877(m), 842(m), 798(m), 764(m), 735(m), 703(m), 657(m), 553(w), 453(w).

X-Ray crystallography

The crystal determination for compound **1** was performed on a Bruker Smart Apex CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range of $2.80° < \theta < 28.04°$ using the ω-scan technique. An empirical absorption correction was applied. The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 program package.[17] All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were located from difference maps. The two H atoms of the water molecule could not be located on the difference Fourier maps owing to the presence of the very heavy Cd atoms. The large peak near the Cd atom is caused by the "truncated tail" effect. Crystal data are summarized in Table 1.

CCDC reference number 195535. See http://www.rsc.org/suppdata/nj/b2/b211358a/ for crystallographic files in CIF or other electronic format.

Results and discussion

Description of the crystal structure

The single crystal X-ray diffraction study reveals that compound **1** consists of a 2D covalently bonded honeycomb framework built-up from cadmium(II), phthalate and water molecules. There is only one crystallographically unique Cd center in the asymmetric unit. As shown in Fig. 1, the local coordination environment around the Cd(II) ion in **1** exhibits a distorted pentagonal bipyramid geometry with two bidentate chelating carboxylates and one monodentate carbonate in the equatorial plane and with the other monodentate carbonate and one water molecule in the axial positions. In detail, the seven-coordination environment of Cd is as follows: four oxygen atoms of the different PT ligands coordinate with the Cd(II) ion in different bidentate chelating modes. The Cd–O distances (2.327–2.435 Å) are quite similar to normal Cd–OCO distances (2.251–2.879 Å).[18] The Cd–O (2.253 Å) and the Cd–OW (2.327 Å) distances in the apical positions are slightly shorter than those in the equatorial positions, indicating that Cd(II) ions display an oblate pentagonal bipyramidal coordination geometry.

Table 1 Crystal data and structure refinement of **1**

Molecular formula	C$_8$H$_6$CdO$_5$
M	294.53
T/K	293(2)
λ/Å	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	9.2775(8)
b/Å	7.7207(6)
c/Å	23.449(2)
U/Å^3	1679.6(2)
Z	8
μ/mm^{-1}	2.590
Reflections collected	9197
Independent reflections	1981
R_1 [$I \geq 2\sigma(I)$]	0.0322
R_{int}	0.0686
wR_2 [$I \geq 2\sigma(I)$]	0.0814
R_1 (all data)	0.0363
wR_2 (all data)	0.0840

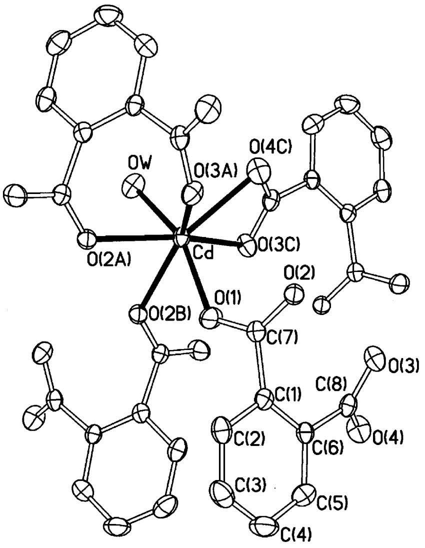
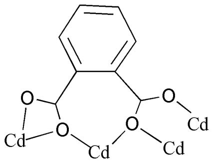


Fig. 1 ORTEP drawing of **1** showing the local coordination environment of Cd(II) with thermal ellipsoids at 50% probability.

It is noteworthy that each PT ligand adopts the uncommon μ$_6$-bridging mode[16] to connect with 4 Cd(II) ions. Overall, the two carboxyl groups of the PT ligands exhibit three coordination modes with the Cd atoms, as shown in the Scheme 2. One carboxyl group adopts a bidentate 1,3-chelating mode; the other one exhibits a bidentate bridging mode. Furthermore, both carboxyl groups show the bidentate 1,6-chelating mode. Based on these coordination modes of PT, an interesting 2D Cd–O–Cd inorganic framework is formed (see Fig. 2). It is also notable that the 2D inorganic layer consists of Cd–O–Cd single helix chains [see Fig. S1 in the Electronic Supplementary Information (ESI)†] *via* corner-sharing oxygen atoms. (CdO$_7$) pentagonal bipyramids connect to each other alternately *via* shared corners and shared edges to form left-hand single helix chains. Furthermore, oxygen atoms (O3) of the phthalate ligand link the single helices to produce a Cd–O–Cd inorganic layer. As a result, these layers show a honeycomb framework with cavity dimensions of 9.49 × 5.79 Å, filled with coordinated water molecules.

In the packing arrangement of **1** (see Fig. 3), the adjacent 2D undulated layers are parallel to each other and construct a 3D structure *via* short C–H···C interactions between aromatic



Scheme 2 The coordination modes of the phthalate ligands in **1**.

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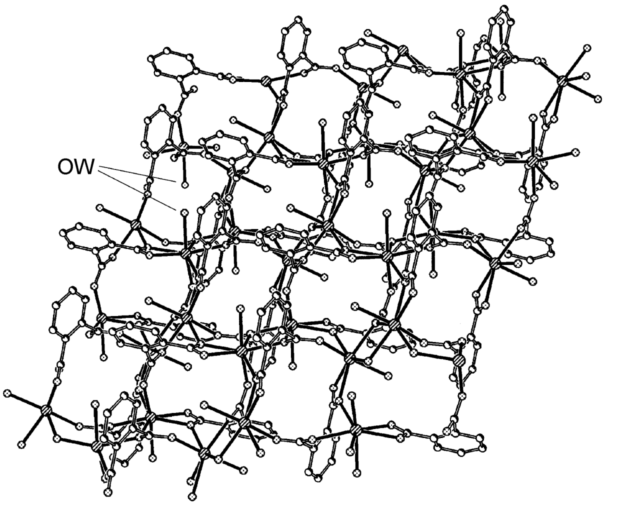

Fig. 2 A ball-and-stick representation of the 2D honeycomb structure of **1**, showing water molecules OW filling in the cavities (the longest distance between opposite Cd atoms is 9.492 Å and the shortest distance is 5.788 Å).

groups of the phthalate ligands projecting perpendicularly beyond the inorganic layers (the distance and angle of C–H···C is 2.836 Å and 153.27°, respectively) instead of the ordinary π-π interactions observed in other layered structures.[7a] Both benzene motifs between adjacent phthalates are not parallel (the angle is *ca.* 70°). Short C–H···C interactions are also found between intra-layer neighboring aromatic groups (the distance of C–H···C is 2.858 Å and the angle is 153.47°). These short interactions enhance the stability of the compound and lead to a higher dimensional structure with tunnels parallel to the *b* axis.

Bond valence calculations (Cd, 1.73) suggested that all Cd atoms are in the +2 oxidation state.[19] This result is also supported by the XPS measurement of the compound. The XPS spectrum (Fig. S2 in ESI†) in the energy region of Cd3d$^{3/2}$ and Cd3d$^{5/2}$ shows one peak at 405.6eV, attributable to Cd^{2+}.

IR, TG and fluorescence properties

The IR spectrum of **1** (Fig. S3 in ESI†) shows several bands in the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ region at 1643, 1580, 1491 cm^{-1} and 1446, 1417 cm^{-1}, respectively. The absence of strong peaks around 1720 cm^{-1} indicates that all carboxyl groups are deprotonated.[20a] The absorptions at lower frequencies (1643–1491 cm^{-1}) can be attributed to deformation vibrations of the chelating and bridging carboxylate groups. The values of $\Delta\nu$ for **1** suggest that the carboxylate groups coordinate to the metal atoms in multiple monodentate (197 cm^{-1}) and bidentate (45 cm^{-1}) fashions,[20b] consistent with the results of the X-ray analysis.

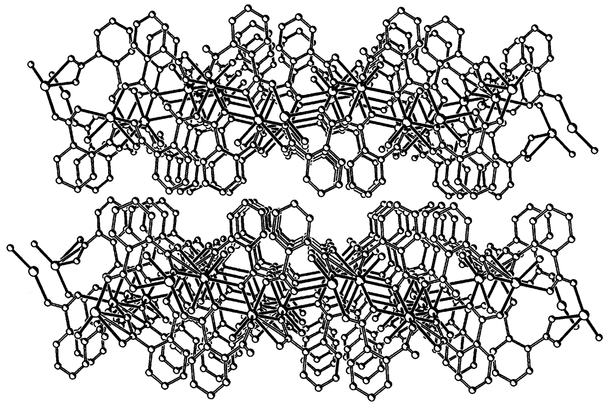

Fig. 3 View along the *b* axis of **1**. Phthalate ligands project above and below into the interlamellar region and there regularly exists some small cavities along the *b* axis direction. All H atoms are omitted for clarity.

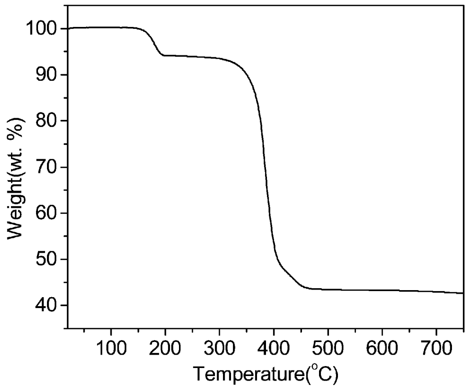

Fig. 4 The TG curve of **1**.

The TG curve of compound **1** (see Fig. 4) can be divided into two weight loss steps. The first step occurs in the range 150–220 °C, attributed to the removal of coordinated H_2O. The observed weight loss (5.94%) is in agreement with the calculated value (6.11%). The second step occurs in the range 280–500 °C, corresponding to the decomposition of PT ligands. The observed weight loss in this step (50.23%) compares well with the calculated value (50.32%). The residue is CdO.

Compound **1** exhibits a strong fluorescent emission (see Fig. 5). The solid state diffuse reflectance UV-vis spectrum (Fig. S4 in ESI†) of **1** shows two intense bands at 243 and 274 nm, assigned to the intraligand π-π* transitions of phthalate ligand. The emission of **1** [$\lambda_{max} = 407$ nm, $\tau = 0.021$ ms (see Fig. S6 in ESI†); the short luminescence should be assigned to fluorescence] is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature and can probably be assigned to intraligand fluorescent emission, since free phthalic acid exhibits a similar fluorescent emission at $\lambda_{max} = 345$ nm (Fig. S5 in ESI†). In comparison to the free phthalic acid molecule, a bathochromic shift in **1** was observed, undoubtedly owing to the deprotonation of the ligand during the formation of the 2D honeycomb framework.[21]

In conclusion, the successful isolation of **1** provides the first example of a cadmium phthalate with an extended structure, in which the phthalate ligands show interesting coordination modes. Compound **1** exhibits strong fluorescent emission and may be an excellent candidate for potential photoactive materials. Further research is going on to prepare novel metal

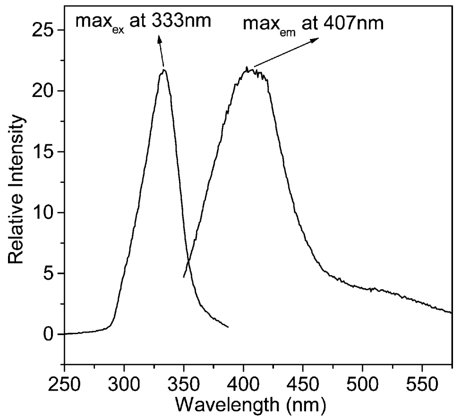

Fig. 5 Fluorescent excitation and emission spectra of **1** in the solid state at room temperature.

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phthalates with extended structures and explore their various physical properties.

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