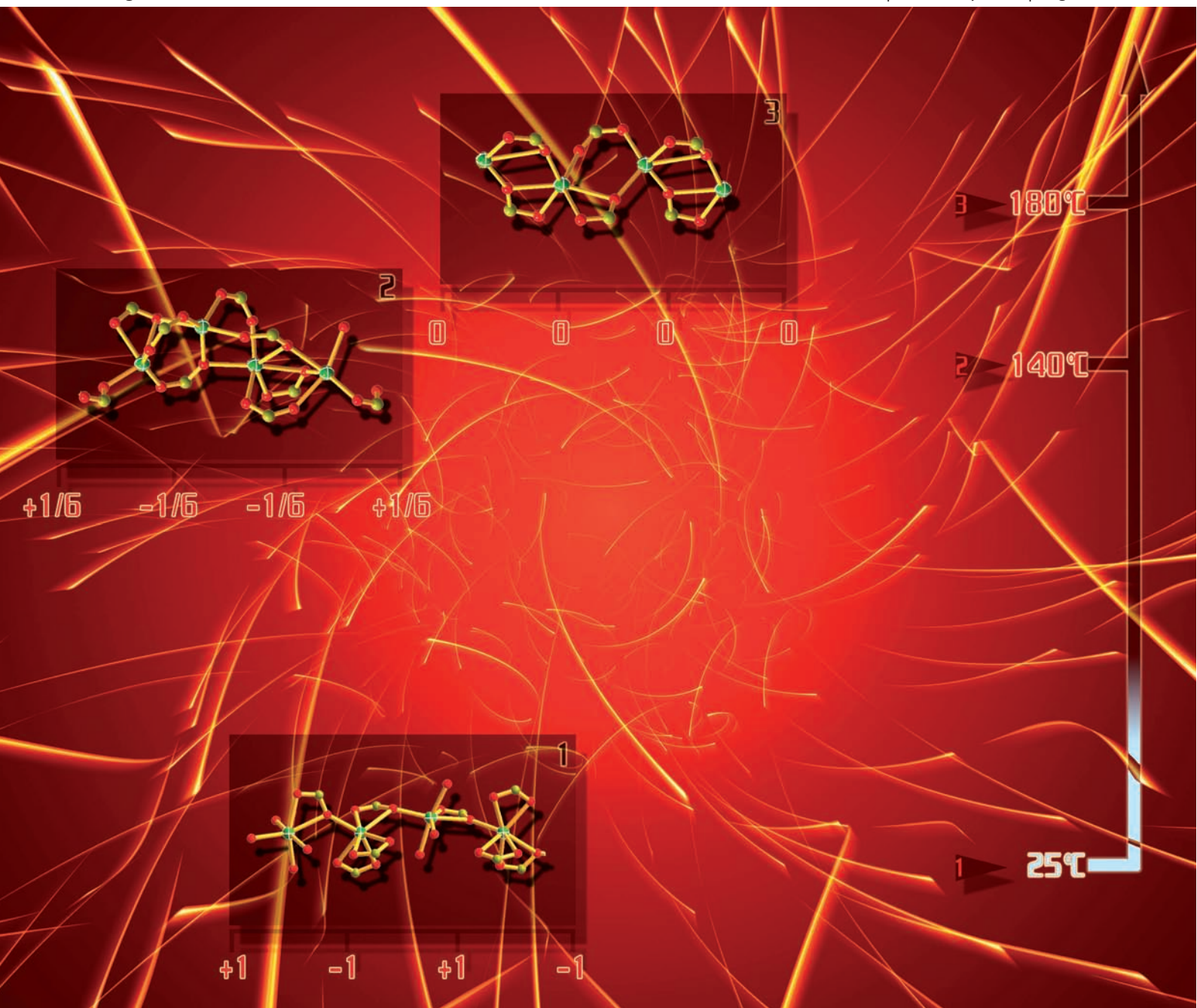


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Temperature dependent charge distribution in three-dimensional homochiral cadmium camphorates

# Temperature dependent charge distribution in three-dimensional homochiral cadmium camphorates†

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Three homochiral cadmium camphorates have been prepared through temperature-dependent synthesis; they form 3D homochiral networks without the crosslinking or pillaring functions of auxiliary neutral bipyridines and exhibit various degrees of charge separation associated with the degree of hydration and controllable by temperature.

In addition to experimental parameters such as pH and solvent, structural properties such as coordination preference (e.g., soft or hard ligands), geometry, charge, and M–L–M angles (e.g., Si–O–Al angle in zeolites) are key parameters that need to be analyzed when developing synthetic procedures for the preparation of framework materials.<sup>1,2</sup> We are particularly interested in the effect of charge distribution on the formation of three-dimensional (3D) materials and have extensively studied factors such as global- and local-charge density matching in the formation of open-framework metal phosphates, germanates, arsenates, and metal–chalcogenide-cluster based superlattices.<sup>3</sup>

Indeed, the charge distribution is such an important factor that the chemical compositions of zeolites and microporous phosphates are governed by it. For example, the well-known Lowenstein's rule (i.e., the molar Si/Al  $\geq$  1 in zeolites) is related to the fact that a structure with two adjacent negative centers (AlO<sub>2</sub><sup>−</sup>–AlO<sub>2</sub><sup>−</sup>) is unfavorable compared to other configurations with two adjacent neutral centers (SiO<sub>2</sub>–SiO<sub>2</sub>) or one negative center next to a neutral center (AlO<sub>2</sub><sup>−</sup>–SiO<sub>2</sub>). These earlier studies on metal oxides and chalcogenides have shown a tendency by stable open-framework materials to achieve a configuration towards minimal charge separation and more homogeneous charge distribution.

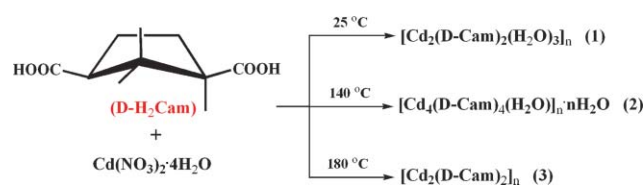
In comparison, the effect of charge distribution on the structures of metal–organic frameworks (MOFs) is less well investigated. An enhanced understanding about various possible charge distributions and how the synthetic parameters affect such charge distribution is highly desirable because it may be useful in the synthetic design and structural analysis of new framework materials.

For metal–organic frameworks, the charge distribution (or separation) can be estimated approximately by considering the local charge centered on cationic centers, taking into consideration oxidation states of metal cations, the charge of ligands, and the coordination environment of metal centers. Such an estimation of

the local charge density is essentially a variation of Pauling's second rule (the electrostatic valence rule) or Brown's valence sum rule. While this method represents a rather primitive estimation of the charge distribution compared to methods such as those based on density functional theory calculations, its usefulness to synthetic chemists has been fully demonstrated by the recent success in the synthesis of chalcogenide clusters and their superlattices.<sup>3b,4</sup>

The work reported here is a part of our systematic efforts aimed at the synthesis of new homochiral open-framework materials.<sup>5</sup> Homochiral MOFs have attracted attention due to their potential applications in asymmetric catalysis and enantioselective separation.<sup>6–8</sup> In the earlier work involving chiral dicarboxylates, a common structural mode is that divalent metal cations (or clusters) form neutral chains or sheets with deprotonated chiral dicarboxylates, which are then linked or pillared by auxiliary neutral bipyridine ligands into 3D homochiral frameworks.<sup>5,8</sup> Here we report 3D homochiral cadmium camphorate frameworks constructed without auxiliary neutral crosslinkers or pillars. Three homochiral camphorates that differ in the degree of hydration are presented here. The work demonstrates that the charge separation is favored at low temperature (room temperature in this case) and that the charge separation becomes progressively smaller when the degree of hydration is decreased (as a result of the increasing reaction temperature).

As shown in Scheme 1, compounds 1–3 were synthesized by mixing D-camphoric acid (= D-H<sub>2</sub>Cam) and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O at different temperatures.‡ The room temperature diffusion reaction gives the most hydrated, tri-aqua phase 1. There are two independent Cd(II) ions in the asymmetric unit of 1. Cd1 is coordinated to seven O atoms from four carboxylate groups while Cd2 is octahedrally coordinated by three O atoms from two carboxylate groups and three water ligands. The  $\mu_2$ -bridging carboxylate groups link the Cd centers to form a Cd–O–Cd chain along the *c* axis, with the shortest Cd···Cd separation of 4.291 Å (Fig. 1a). To estimate the charge distribution in each chain, the coordination environment of each Cd center is considered. In this case, Cd1 is surrounded by two chelate carboxylate groups and two  $\mu_2$ -bridging carboxylate groups, and the charge at this site is thus  $[(-1) \times 2 + (-1 \times \frac{1}{2}) \times 2]_{\text{COO}^-} + (+2)_{\text{Cd}} = -1$ . The Cd2

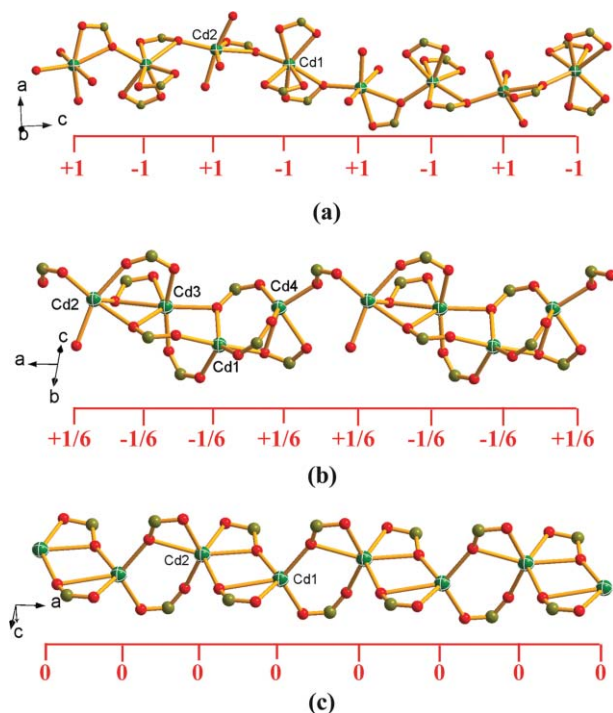


Scheme 1 Synthesis conditions for the three compounds.

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† Electronic supplementary information (ESI) available: Figures showing structural details, TGA diagrams and powder diffraction patterns. See DOI: 10.1039/b715945e





**Fig. 1** The carboxylate-bridged Cd(II) chain in **1** (a), **2** (b), and **3** (c) showing different charge distributions.

site is only surrounded by two  $\mu_2$ -bridging carboxylate groups, and the charge at this site is therefore +1. Throughout the chain, the charge distribution follows the sequence (+1, -1, +1, -1...). Such a charge distribution is comparable to microporous aluminophosphates (AlPOs) with alternating  $\text{AlO}_2^-$  and  $\text{PO}_2^+$  centers.

In the less hydrated bi-aqua phase **2**, four independent Cd(II) ions adopt the coordination number of either five (Cd1, Cd2 or Cd4) or six (Cd3), and only Cd2 is coordinated by one water ligand. The carboxylate-bridged tetranuclear Cd units are further connected into a chain along the *a* axis (Fig. 1b). The Cd...Cd

separations range from 3.257 to 4.427 Å. By considering the coordination environment of each Cd center (e.g., for Cd2 site,  $[(-1 \times \frac{1}{3}) + (-1 \times \frac{1}{2}) \times 3]_{\text{COO}^-} + (+2)_{\text{Cd}} = \frac{1}{6}$ ), the charge distribution in the chain follows the sequence (+ $\frac{1}{6}$ , - $\frac{1}{6}$ , - $\frac{1}{6}$ , + $\frac{1}{6}$ ...).

For the anhydrous phase **3**, both independent Cd(II) ions are surrounded by four carboxylate groups (Fig. 1c). The rigid Cd–O–Cd chain along the *a* axis has a charge distribution with the sequence (0, 0, 0, 0...). Such a charge distribution is comparable to silica and silicalite type structures ( $\text{SiO}_2$ ) that also carry no charge at each cationic center. The adjacent Cd...Cd distances are 3.753 and 3.811 Å, respectively, significantly shorter than that in **1**.

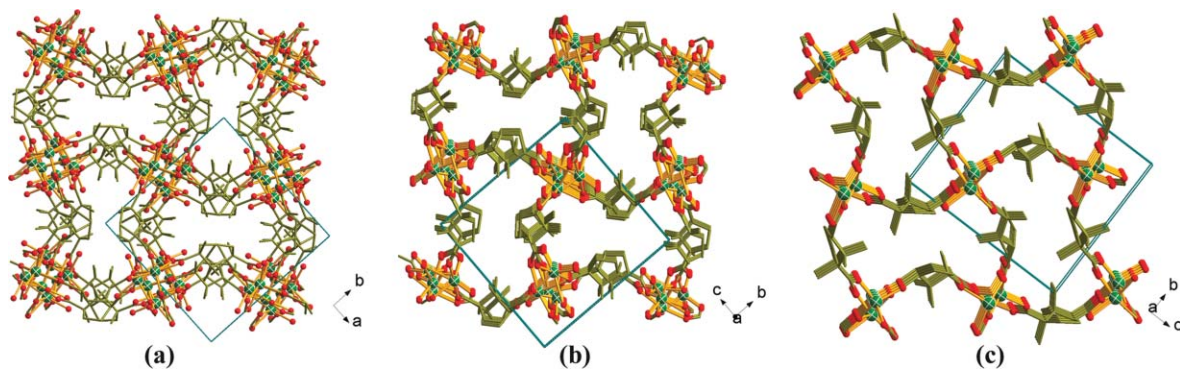
These three phases have similar 3D homochiral structures in which each carboxylate-bridged Cd chain is crosslinked to four neighboring chains by enantiopure D-Cam ligands (Fig. 2). It is therefore of interest to explore their structural relationship. As shown in Fig. 3, a trinuclear Cd unit is selected from each structure, and each unit contains three Cd centers in the same chain and four binding D-Cam ligands directed towards four adjacent chains. To transform from the tri-aqua phase **1** to the bi-aqua phase **2**, two Cd–O bonds of the seven-coordinate Cd atom in **1** need to be removed and two new Cd–O bonds are then established at the adjacent Cd atom (Fig. 3a) in **2**. Similarly, to transform from the tri-aqua phase **1** to the anhydrous phase **3**, two Cd–O bonds need to be removed from **1** and three new Cd–O bonds are formed in **3** (Fig. 3b). Accompanying such bond transformations from **1** to **2** or **1** to **3**, the charge separation at each site is reduced or eliminated.

It is worth noting that the tri-aqua phase **1** can readily dissolve in water even though it has a 3D framework structure, however, **2** and **3** cannot be dissolved in common solvents such as  $\text{H}_2\text{O}$  or DMF. The thermal analysis (Fig. S7†) of **1** shows that the first weight loss (found: 8.76%) occurs between 50 and 105 °C, which is likely due to the loss of three water molecules (calc. 8.00%). There is no obvious weight loss until 400 °C when the decomposition starts. According to the powder X-ray diffraction studies

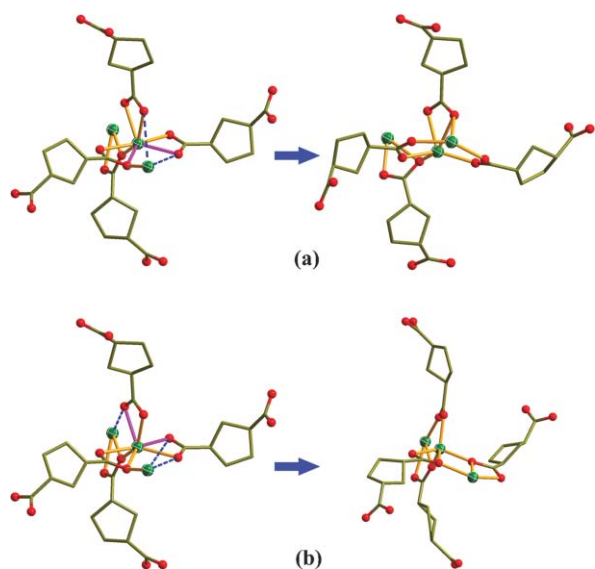
**Table 1** A summary of crystal data and refinement results<sup>a</sup>

Formula	SG	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\beta$ /°	<i>R</i> ( <i>F</i> )	Flack parameter
<b>1</b> $[\text{Cd}_2(\text{D-Cam})_2(\text{H}_2\text{O})_3]_n$	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2	13.4066(2)	13.4066(2)	32.0618(11)	90	0.0456	−0.02(7)
<b>2</b> $[\text{Cd}_4(\text{D-Cam})_4(\text{H}_2\text{O})_n] \cdot n\text{H}_2\text{O}$	<i>P</i> 2 <sub>1</sub>	12.8807(3)	13.3380(3)	13.4542(3)	104.94(1)	0.0251	−0.02(2)
<b>3</b> $[\text{Cd}_2(\text{D-Cam})_2]_n$	<i>P</i> 2 <sub>1</sub>	7.2911(4)	11.3103(7)	13.0172(9)	99.332(4)	0.0513	−0.08(9)

<sup>a</sup> D-H<sub>2</sub>Cam = D-camphoric acid; SG = space group.



**Fig. 2** A view of the 3D frameworks in **1** (a), **2** (b), and **3** (c).



**Fig. 3** (a) Schematic representation of the transformation from **1** to **2** through the rearrangement of some coordination bonds; (b) schematic representation of the transformation from **1** to **3** through the rearrangement of some coordination bonds (purple bonds: need to be removed; blue dashed lines: should be new bonds).

(Fig. S10†), the dehydrated solid obtained by heating crystals of **1** to 120 °C is amorphous. However, when this dehydrated solid is immersed in a mixed water–ethanol (1 : 3 volume ratio) solvent, it is restored to **1**. Furthermore, **1** can be transformed into **2** when treated in a mixed H<sub>2</sub>O–ethanol (1 : 3 volume ratio) solvent at 140° for 2 days. However, similar transformation from **1** to **3** (or from **2** to **3**) has not been achieved.

In conclusion, three 3D homochiral cadmium camphorates have been prepared through temperature-dependent synthesis. Unlike previously known homochiral camphorate-based frameworks, these three materials form 3D homochiral networks even without the crosslinking or pillaring functions of auxiliary neutral bipyridines. These camphorates exhibit various degrees of charge separation associated with the degree of hydration and controllable by temperature. The most hydrated phase has a charge distribution comparable to microporous aluminophosphates while the anhydrous homochiral framework has a charge distribution comparable to silicalites. The structural inter-relationship and a possible mechanism for the conversion among these phases are also illustrated.

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## Notes and references

‡ Synthesis: (a) [Cd<sub>2</sub>(D-Cam)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**): ethanol (6 ml) was layered onto Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.0815 g), Na<sub>2</sub>CO<sub>3</sub> (0.0253 g), and D-camphoric acid (0.0512 g) in distilled water (2 ml). Slow diffusion over several days yielded colorless crystals (Table 1).§ (b) [Cd<sub>4</sub>(D-Cam)<sub>4</sub>(H<sub>2</sub>O)]<sub>n</sub>·nH<sub>2</sub>O (**2**): Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.1546 g), Na<sub>2</sub>CO<sub>3</sub> (0.0528 g), D-camphoric acid (0.1075 g), distilled water (2.0240 g) and ethanol (6.1203 g) were mixed in a 23 ml Teflon cup and the mixture was stirred for 20 min. The vessel was then sealed and heated at 140 °C for 3 days. The autoclave was allowed to cool to room temperature. Transparent colorless crystals were obtained (Table 1).§ (c) [Cd<sub>2</sub>(D-Cam)<sub>2</sub>]<sub>n</sub> (**3**): Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.1507 g), Na<sub>2</sub>CO<sub>3</sub> (0.0530 g), D-camphoric acid (0.1004 g), distilled water (2.4321 g) and ethylene glycol (4.4356 g) were mixed in a 23 ml Teflon cup and the mixture was stirred for 20 min. The vessel was then sealed and heated at 180 °C for 5 days. The autoclave was allowed to cool to room temperature. Transparent colorless crystals were obtained (Table 1).§  
§ CCDC 664303–664305. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715945e

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