

# The Role of Spacers between Carboxylate Groups in Self-Assembly Process: Syntheses and Characterizations of Two Novel Cadmium(II) Complexes Derived from Mixed Ligands

Ruihu Wang,<sup>[a]</sup> Maochun Hong,<sup>\*[a]</sup> Daqiang Yuan,<sup>[a]</sup> Yanqiong Sun,<sup>[a]</sup> Lijin Xu,<sup>[b]</sup> Junhua Luo,<sup>[a]</sup> Rong Cao,<sup>[a]</sup> and Albert S. C. Chan<sup>[b]</sup>

**Keywords:** Cadmium / Bridging ligands / X-ray diffraction / Polymers / Self assembly

Two novel cadmium(II) coordination polymers,  $[\text{Cd}_2(\text{bpda})_2(\text{dpe})]_n$  (**1**) and  $[\text{Cd}_2\{(R)\text{-Hdmpa}\}_2\{(S)\text{-Hdmpa}\}_2(\text{dpe})_3]_n$  (**2**), [ $\text{H}_2\text{bpda}$  = 1,1'-biphenyl-3,3'-dicarboxylic acid,  $\text{H}_2\text{dmpa}$  = 6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxylic acid, and  $\text{dpe}$  = 1,2-di(4-pyridyl)ethylene] have been prepared by hydrothermal reactions of both  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{dpe}$  with  $\text{H}_2\text{bpda}$  and  $\text{H}_2\text{dmpa}$ , respectively. **1** is a threefold interpenetrating three-dimensional coordination network

composed of paddle-wheel tetracarboxylate dicadmium(II) units bridged by  $\text{dpe}$ . **2** affords an example of ligand self-discrimination in an assembly process, in which  $\text{dpe}$  connects the  $[\text{Cd}\{(R)\text{-Hdmpa}\}\{(S)\text{-Hdmpa}\}]$  building units to generate a one-dimensional ladder structure.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

## Introduction

The prospect of generating new materials with interesting structures and technologically useful functions provides significant motivation for the recent surge of research interest in organic-inorganic supramolecular frameworks.<sup>[1,2]</sup> The construction of metal-organic polymeric networks has achieved considerable progress in supramolecular chemistry and material science due to their intriguing structural diversities and potential applications in molecular adsorption, ion exchange, molecular recognition and heterogeneous catalysis.<sup>[2–5]</sup> Molecular self-assembly based on the principle of crystal engineering has proved to be efficient for the formation of these architectures. Some structural motifs with specific topologies and functions can, to a certain extent, be predicted through dominating the assembly and orientation of individual building blocks. For example, the groups of Yaghi,<sup>[3]</sup> Zaworotko,<sup>[4]</sup> and others<sup>[5]</sup> have developed a strategy to construct extended porous structures using rigid dicarboxylate ligands with different spacers and metal clusters of known geometries. However, the mecha-

nism of molecular self-assembly is still unclear, and predictability and tinability of the exact structures of the assembly products are difficult. Thus, understanding the factors that govern the assembly process is crucial to technological development. Such factors include: the role of spacers between coordination sites in organic bridging ligands and the coordination geometry of metal ions;<sup>[6]</sup> the formation and role of the reaction precursors;<sup>[7]</sup> the formation of interpenetration and/or interdigitation lattices vs. the inclusion of solvent or guest molecules;<sup>[8]</sup> and the formation of the convergent products and the divergent products.<sup>[9]</sup>

It is well-known that the design and synthesis of bridging ligands containing appropriate coordination sites linked by spacers with specific orientations are especially crucial to the construction of desirable frameworks. By closely controlling the properties of the spacers, such as the shape, functionality, flexibility, length, and symmetry, a remarkable class of materials containing diverse architectures and functions can be obtained.<sup>[2–6]</sup> The coordination of multi-pyridine and multi-carboxylate ligands to metal centers has proved to be an excellent tool in the assembly process and has been highly influenced by the structural characterizations of linker groups. Moreover, as the length of organic spacer increases, interpenetration and/or interdigitation has been commonly adopted by nature in order to avoid the formation of large open channels or cavities.<sup>[10]</sup> The combination of metal ions and mixed bridging ligands containing carboxylate and pyridyl groups can allow for the formation of coordination networks possessing different structures and functional properties.<sup>[11,12]</sup> The exo-bidentate pyridyl

<sup>[a]</sup> State Key Laboratory of Structural Chemistry Fujian Institute of the Research on the Structure of Matter Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China  
Fax: (internat.) +86-591-3714946  
E-mail: hmc@ms.fjirsm.ac.cn

<sup>[b]</sup> Open Laboratory of Chirotechnology Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Hum, Hong Kong  
Fax: (internat.) +852-23649932  
E-mail: bcachan@polyu.edu.hk

derivative, *trans*-1,2-di(4-pyridyl)ethylene (dpe), possesses several peculiar characteristics when used in the construction of the extended networks: 1) the double bond in the ligand can result in conformational rigidity;<sup>[13]</sup> 2) the delocalized  $\pi$ -system can be applied as potential electron propagating components;<sup>[14]</sup> 3) the long spacer between coordination sites can result in interpenetration and/or interdigitation;<sup>[14,15]</sup> and 4) this ligand may be used as a reaction precursor.<sup>[7a,16]</sup> However, supramolecular architectures constructed by dpe, and ligands with di- or multi-carboxylate groups, have seldom been reported to date.<sup>[16,17]</sup> Very recently, we have reported a three-dimensional pillared compound consisting of dodecanuclear cadmium(II) macrocycles  $\{[\text{Cd}_2(\text{dpa})(\text{pya})]_6(\text{pya})_6(\text{dpe})_3\}_n$  ( $\text{H}_2\text{dpa}$  = diphenic acid and  $\text{Hpya}$  = isonicotinic acid),<sup>[16]</sup> in which dpe not only serves as a  $\mu$ -bridge, but also acts as the precursor of pya. To systematically investigate the effects of the steric hindrance of the spacers between the carboxylate coordination sites on dpe and the assembly products, we have designed two new ligands, 1,1'-biphenyl-3,3'-dicarboxylic acid ( $\text{H}_2\text{bpda}$ ) and 6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxylic acid ( $\text{H}_2\text{dmpa}$ ). The steric hinderance between the two carboxylate groups of Bpda is smaller than for  $\text{H}_2\text{dpa}$ , and this provides a greater degree of freedom for the twisting of the two phenyl rings in Bpda relative to that in  $\text{H}_2\text{dpa}$  can be more freely twisted than  $\text{H}_2\text{dpa}$ . However, not only is the steric hinderance between the two carboxylate groups of racemic dmpa greater than for  $\text{H}_2\text{dpa}$ , but dmpa can also form products of ligand self-discrimination or self-recognition. Herein, we wish to report the syntheses and characterizations two novel cadmium(II) complexes,  $[\text{Cd}_2(\text{bpda})_2(\text{dpe})]_n$  (**1**), and  $[\text{Cd}_2\{(R)\text{-Hdmpa}\}_2\{(S)\text{-Hdmpa}\}_2(\text{dpe})_3]_n$  (**2**).

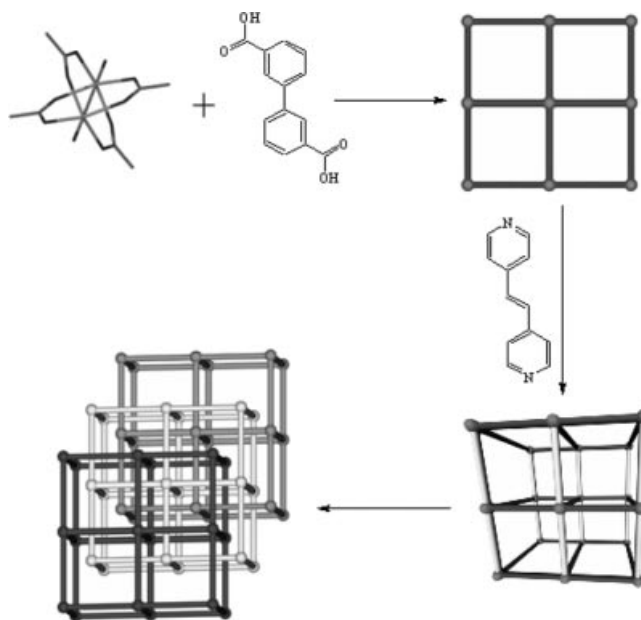
## Result and Discussion

### Synthesis and Characterization

Diphenic acid ( $\text{H}_2\text{dpa}$ ) is an excellent bridging ligand for the construction of metallomacrocyclic and helical frameworks<sup>[16,18]</sup> owing to the steric hindrance between the 2,2'-positioned carboxylate groups in the assembly process, which results in a great distortion of the two phenyl rings about the central bond in dpa. Bpda and dmpa are dicarboxylate ligands that are similar to dpa. In bpda, the two carboxylate groups in the 3,3'-positions have a smaller effect on the distortion of the diphenyl spacer about the central bond in the assembly process. Dmpa is an axially chiral ligand, in which two phenyl rings cannot freely rotate about the central bond and therefore can produce two different conformations, (*R*)-dmpa and (*S*)-dmpa. Hence, it is interesting to investigate the assembly process of  $\text{H}_2\text{bpda}$  or  $\text{H}_2\text{dmpa}$  with dpe and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  under the same reaction conditions as those used in the formation of  $[\{\text{Cd}_2(\text{dpa})(\text{pya})\}_6(\text{pya})_6(\text{dpe})_3]_n$ .<sup>[16]</sup>

The hydrothermal reaction of  $\text{H}_2\text{bpda}$ , dpe,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and NaOH, with a molar ratio of 2:2:2:3, in  $\text{H}_2\text{O}$  at 180 °C for 3 days, produced a threefold interpen-

etrating three-dimensional coordination polymer consisting of the dimeric cadmium–tetracarboxylate secondary building units (SBUs) bridged by dpe. Dpe has not been hydrolyzed and only serves as the axis linkers of the SBUs so as to extend the two-dimensional  $[\text{Cd}_2(\text{bpda})_2]_n$  layer into a three-dimensional framework (Scheme 1). The hydrothermal reaction of dpe, the racemic mixture of (*R*)- $\text{H}_2\text{dmpa}$  and (*S*)- $\text{H}_2\text{dmpa}$ , and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  under the same conditions as those used in the preparation of **1** afforded the colorless crystals of **2**, in which Hdmpa undergoes ligand self-discrimination and acts as a chelating mono-bidentate ligand in the formation of the building units of  $[\text{Cd}\{(R)\text{-Hdmpa}\}\{(S)\text{-Hdmpa}\}]$ .



Scheme 1. Construction of the threefold interpenetrating three-dimensional framework in **1**

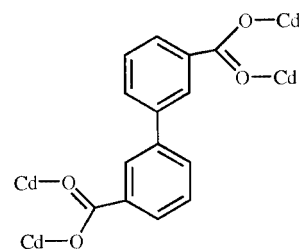
Thermogravimetric analysis (TGA) was performed on polycrystalline samples under a nitrogen atmosphere. No chemical decomposition was observed up to 390 °C and 300 °C for **1** and **2**, respectively. The two most significant weight losses occurred between 440 and 730 °C for **1**, and between 350 and 430 °C for **2**, and are attributed to the complete decomposition of the samples to cadmium(II) oxide. Considering the formation of stoichiometric amounts of  $\text{CdO}$ , this conclusion is supported by 29.7% (above 820 °C) and 13.2% (above 540 °C) of the residues for **1** and **2**, respectively, which are in accordance with the expected values (28.9% for **1** and 13.9% for **2**).

### Structural Description

#### $[\text{Cd}_2(\text{bpda})_2(\text{dpe})]_n$ (**1**)

Single crystal X-ray diffraction analysis reveals that compound **1** is a threefold interpenetrating three-dimensional coordination network and crystallizes in the monoclinic

space group  $P2_1/c$ . As shown in Figure 1(a), the geometry around the  $\text{Cd}^{\text{II}}$  center is square-pyramidal and the metal center is coordinated by four oxygen atoms from different bpda ligands in the equatorial plane and a nitrogen atom from dpe at the axial position. Four carboxylate groups from different bpda ligands form a bridge between the two cadmium(II) centers in a *syn-syn* bidentate mode, forming a paddle-wheel secondary building unit (SBU). The  $\text{Cd}-\text{Cd}$  distance of 3.0428(14) Å suggests that there is no significant  $\text{Cd}^{\text{II}}-\text{Cd}^{\text{II}}$  interaction in the SBU (the sum of the van der Waals radii of  $\text{Cd}^{\text{II}}$  is 3.04 Å<sup>[19]</sup>); however, this distance is significantly shorter than those in discrete dimeric cadmium–tetracarboxylate complexes (3.278–3.452 Å).<sup>[20]</sup>



Scheme 2. Coordination mode of bpda in **1**

Bpda acts as a bis-bidentate bridging ligand by coordinating to four different  $\text{Cd}^{\text{II}}$  centers (Scheme 2). The dihedral angle between the two phenyl rings in bpda is 34.8°. The

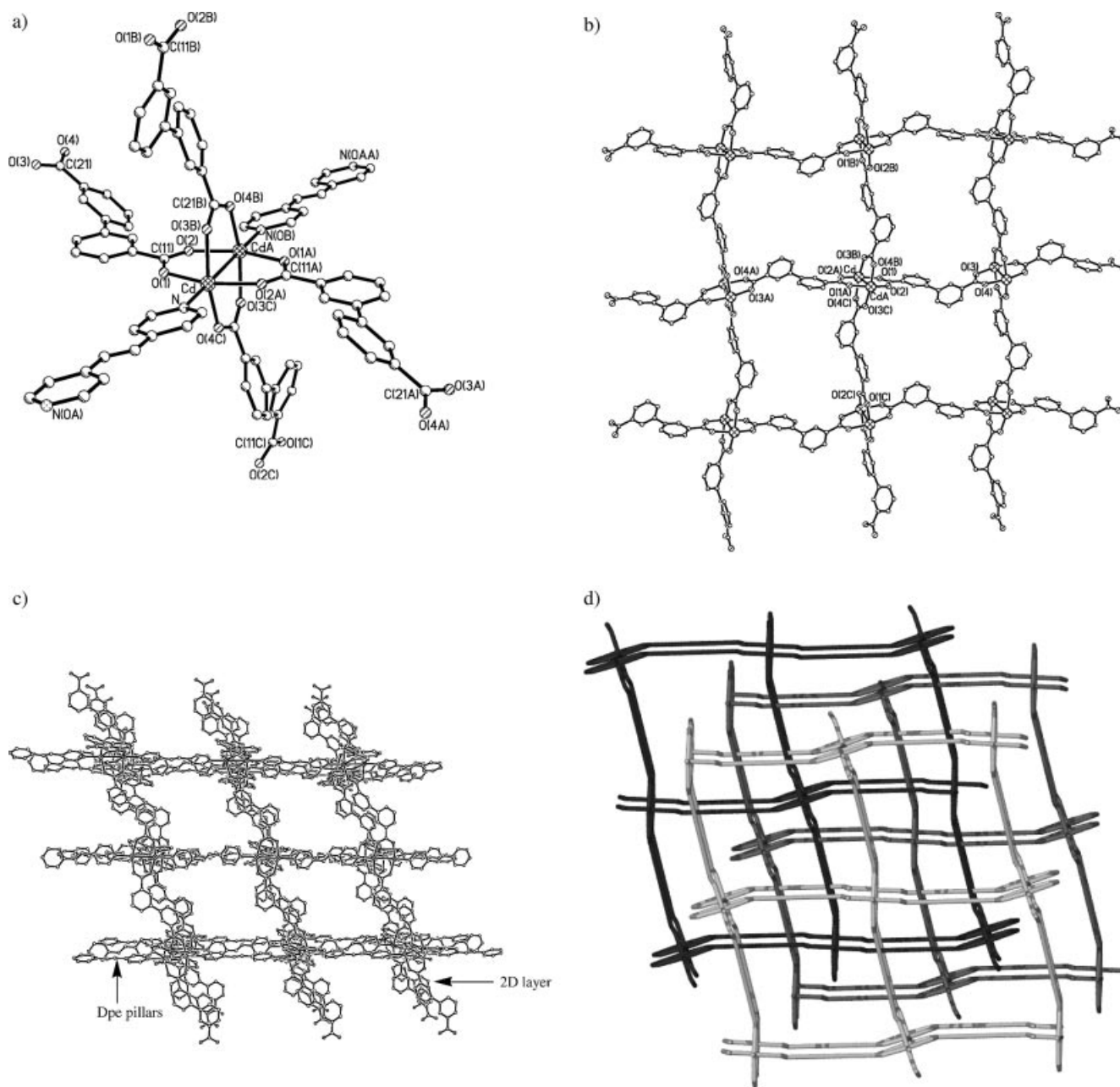


Figure 1. a) ORTEP drawing of the dinuclear cadmium(II) unit with the atom numbering scheme in **1**, b) view of the two-dimensional layer in **1** with dpe omitted, c) view of the three-dimensional layer-pillar in **1**, d) view of the threefold interpenetrating three-dimensional framework in **1**

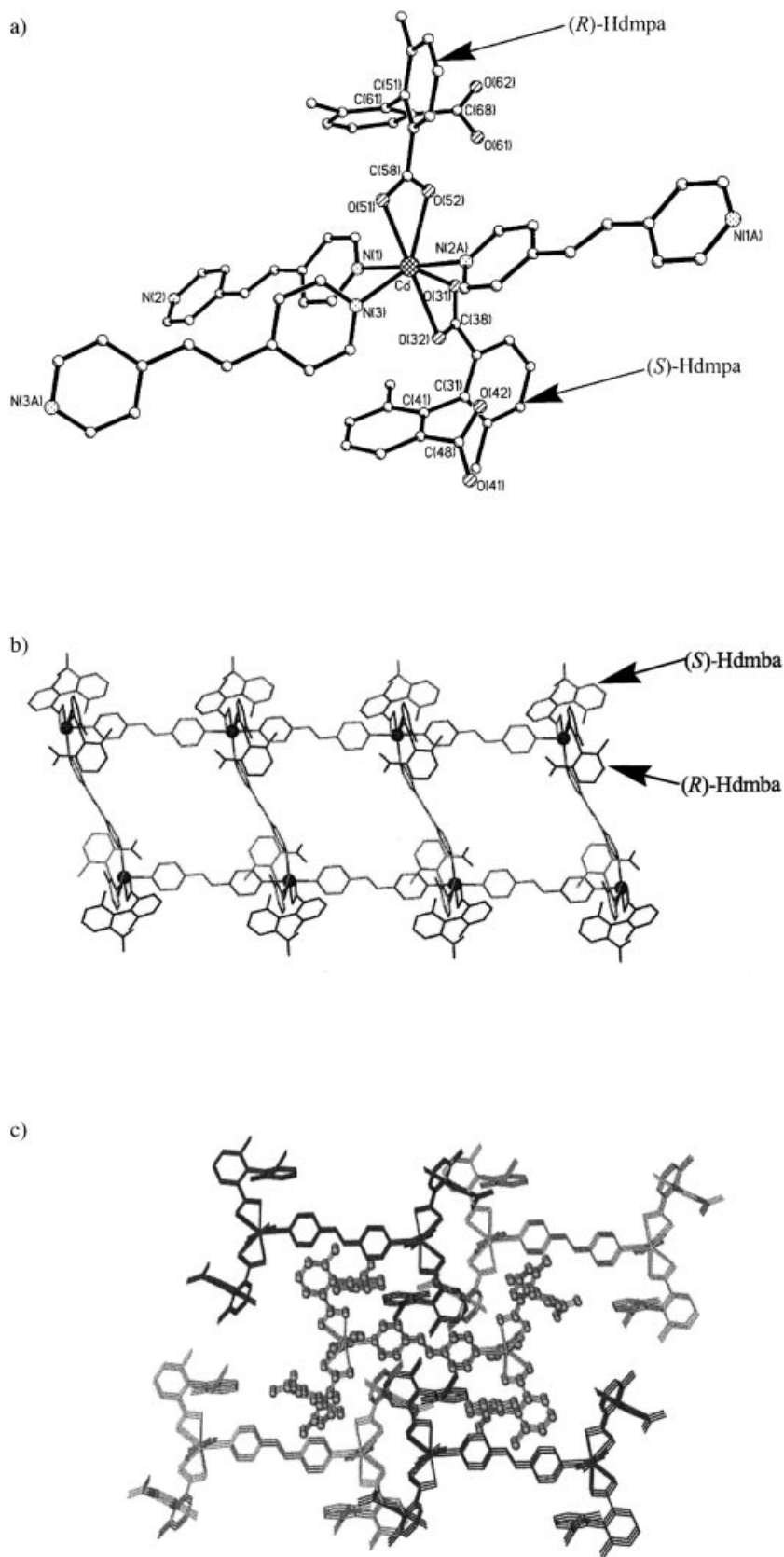


Figure 2. a) ORTEP drawing around the cadmium(II) center with atom numbering scheme in **2**, b) view of the one-dimensional ladder in **2**, c) pack diagram along the *b* axis exhibiting the interdigitation between the chains in **2**

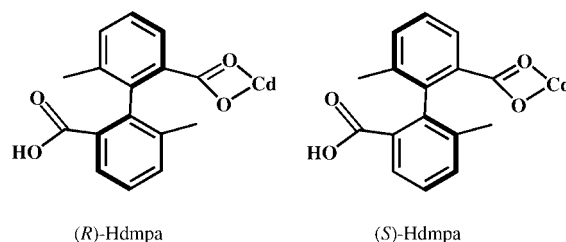


dihedral angles of 3.6 and 14.5° between the carboxylate groups and the linking phenyl rings allow for the formation of paddle-wheel SBUs.<sup>[21]</sup> The SBUs are inter-connected by bpda forming a two-dimensional layer with a Cd...Cd separation across bpda of 13.481 Å. To the best of our knowledge, this is the first extended structure constructed from cadmium–tetracarboxylate SBUs. The dpe ligands are *trans*-coordinated to the SBUs and form axis linkers with a Cd–N distance of 2.237(9) Å and Cd–Cd–N angle of 178.0(3)°. Thus, dpe can serve as a pillar between two adjacent two-dimensional layers thus generating a three-dimensional open framework (Figure 1, b). The Cd...Cd separation across dpe is 13.809 Å. It should be emphasized that there is a large void within the cuboidal units owing to the longer spacers between the coordination sites in dpe and bpda, but no enclathration of solvent or guest molecules is observed within the larger units. Thus, two identical frameworks fill the void in another framework, which results in the formation of a threefold interpenetrating framework (Figure 1, c).

It is worthy noting that the cuboidal units in **1** are not regular due to the fact that the coordination sites are off-axis in dpe and bpda. Klinowski et al.<sup>[11a]</sup> has recently reported a threefold interpenetrating three-dimensional modular coordination network using the more flexible biphenyl-4,4'-dicarboxylate and 1,2-bis(4-pyridyl)ethane mixed ligands, in which the cuboidal units are highly distorted owing to the high flexibility of spacers between the coordination sites. However, Chen et al.<sup>[11b]</sup> has reported a twofold interpenetrating three-dimensional structure using the mixed ligands 4,4'-bipyridine and terephthalate, in which the cuboidal units are regular due to the rigidity of the bridging ligands. This shows that the spacers between coordination sites have an important effect on the construction of the structural framework.

### $[\text{Cd}_2\{(R)\text{-Hdmpa}\}_2\{(S)\text{-Hdmpa}\}_2(\text{dpe})_3]_n$ (**2**)

Compound **2** is a one-dimensional ladder structure and crystallizes in the monoclinic space group  $P2_1/c$ . As shown in Figure 2(a), the Cd<sup>II</sup> center has a distorted pentagonal bipyramidal geometry, and is coordinated by two chelating carboxylate groups from different conformational Hdmpa and three nitrogen atoms from different dpe ligands. The ligands (*R*)-Hdmpa and a (*S*)-Hdmpa are coordinated by the Cd<sup>II</sup> center, which suggests an assembly process of ligand self-discrimination, therefore, no optical activity is expected in this structure. Three dpe ligands form a slightly distorted T-shaped arrangement at the seven-coordinate Cd<sup>II</sup> center [N(1)–Cd–N(3) 85.0(2)°; N(2A)–Cd–N(3) 96.4(2)°; N(1)–Cd–N(2A) 177.5(2)°], in which two nitrogen atoms (N1 and N2) stand at the apical positions, the remaining nitrogen atom (N3) and four carboxylate oxygen atoms (O31, O32, O51, and O52) occupy the equatorial positions. The Cd<sup>II</sup> center lies in the plane defined by the equatorial atoms, with a deviation of 0.0155 Å. Hdmpa



Scheme 3. Coordination modes of (*R*)-Hdmpa and (*S*)-Hdmpa in **2**

(Scheme 3) serves as a chelating mono-bidentate ligand which is coordinated through the carboxylate group to the Cd<sup>II</sup> center; carboxylic groups do not take part in coordination and do not interact with the metal centers or other ligands, therefore, this is an unusual feature of di- or multicarboxylic ligands. The dihedral angles between the two phenyl rings in (*R*)-Hdmpa and (*S*)-Hdmpa are 85.6 and 85.1°, respectively, and hence they are approximately perpendicular to each other. However, the dihedral angles between the carboxylate groups and the linking phenyl rings in (*R*)-Hdmpa and (*S*)-Hdmpa are 58.8 and 59.4°, and 29.2 and 56.1°, respectively, which are significantly larger than those in **1** and are unfavorable for the formation of the paddle-wheel SBU.<sup>[21]</sup> Dpe acts as a *trans* exo-bidentate ligand and links the [Cd{(R)-Hdmpa}{(S)-Hdmpa}] building units to form an infinite ladder structure (Figure 2, b). The methyl groups in Hdmpa prevent the formation of an extended motif. The adjacent Cd...Cd distances along the side dpe and the inner dpe are 14.069 and 13.893 Å, respectively. Owing to a longer spacer in the dpe ligand, there is a large void within the rhombohedral grids, which have been effectively filled by interdigitation of Hdmpa from the adjacent one-dimensional ladders in the *ac* plane (Figure 2, c).

## Conclusions

The hydrothermal reactions of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 1,2-di(4-pyridyl)ethylene (dpe) with dicarboxylic ligands with different steric properties, 1,1'-biphenyl-3,3'-dicarboxylic acid (H<sub>2</sub>bpda) and 6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxylic acid (H<sub>2</sub>dmpa), under the same reaction conditions, produced two novel cadmium(II) coordination polymers [Cd<sub>2</sub>(bpda)<sub>2</sub>(dpe)]<sub>n</sub> (**1**) and [Cd<sub>2</sub>{(*R*)-Hdmpa}<sub>2</sub>{(*S*)-Hdmpa}<sub>2</sub>(dpe)<sub>3</sub>]<sub>n</sub> (**2**), respectively. In **1**, bpda and dpe link the dimeric cadmium–tetracarboxylate secondary building units (SBUs) to form a threefold interpenetrating three-dimensional coordination network. **2** is a one-dimensional ladder structure constructed from [Cd{(R)-Hdmpa}{(S)-Hdmpa}] building units and dpe bridges, and exhibits a ligand self-discrimination in an assembly process. The large void in **1** and **2** has been efficiently filled through the interpenetration and inter-interdigitation of adjacent frameworks, respectively. The results show that the steric hindrance of spacers between the carboxylate coordination sites has an important effect on the coordination modes of the carboxylate groups, and different spacers between the carboxylate coordination sites can result in supramolecular architectures with different structures and functions.

## Experimental Section

1,1'-Biphenyl-3,3'-dicarboxylic acid and 6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxylic acid were synthesized according to literature methods, using 3-aminobenzoic acid and 2-amino-3-methylbenzoic acid, respectively, as starting materials.<sup>[22]</sup> 1,2-di(4-pyridyl)ethylene and 2-amino-3-methylbenzoic acid were purchased from Aldrich and used without further purification, all the other reagents were commercially available and used as purchased. The IR spectra as KBr discs were recorded on a Magna 750 FT-IR spectrophotometer. C, H, and N elemental analyses were determined on an Elementary Vario ELIII elemental analyzer. Thermal analyses were performed using a Thermal Analyst 2100 TA Instrument and a SDT 2960 Simultaneous TGA-DTA Instrument.

**Synthesis of  $[\text{Cd}_2(\text{bpda})_2(\text{dpe})]_n$  (**1**):** A mixture of  $\text{H}_2\text{bpda}$  (0.12 g, 0.5 mmol),  $\text{dpe}$  (0.09 g, 0.5 mmol),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.15 g, 0.5 mmol) and  $\text{NaOH}$  (0.03 g, 0.75 mmol), with a molar ratio of about 2:2:2:3 in  $\text{H}_2\text{O}$  (15.0 mL), was placed in a Parr Teflon-lined stainless steel vessel and heated to 180 °C for 72 h. The reaction system was then cooled at room temperature for 24 hours. A large amount of colorless crystals were obtained and collected by filtration, washed with water and dried in air. Yield: 0.06 g (54%). Elementary analysis: calcd. for  $\text{C}_{20}\text{H}_{13}\text{CdNO}_4$  (444.71): calcd. C 54.13, H 2.93, N 3.16; found C 54.07, H 2.89, N 3.18%. IR (KBr pellet):  $\tilde{\nu} = 3469 \text{ cm}^{-1}$  (w), 3057 (w), 1686 (w), 1622 (s), 1610 (s), 1593 (s), 1568 (s), 1433 (m), 1408 (s), 1385 (s), 1301 (vw), 1263 (w), 1169 (vw), 1024 (w), 835 (w), 758 (s), 690 (m), 623 (vw), 552 (w).

**Synthesis of  $\{\text{Cd}_2[(R)\text{-Hdmpa}]_2[(S)\text{-Hdmpa}]_2(\text{dpe})\}_n$  (**2**):** The procedure was similar to the synthesis of compound **1**, except that  $\text{H}_2\text{dmpa}$  (0.13 g, 0.5 mmol) was used instead of  $\text{H}_2\text{bpda}$ . Yield: 0.05 g (43% based on  $\text{H}_2\text{dmpa}$ ). Elementary analysis: calcd. for  $\text{C}_{50}\text{H}_{39}\text{CdN}_3\text{O}_8$  (922.24): calcd. C 65.11, H 4.23, N 4.55; found C 65.05, H 4.18, N 4.57%. IR (KBr pellet):  $\tilde{\nu} = 3051 \text{ cm}^{-1}$  (vw), 2922 (vw), 2872 (vw), 1738 (m), 1722 (m), 1606 (s), 1560 (s), 1504 (w), 1421 (s), 1406 (s), 1389 (s), 1375 (m), 1290 (w), 1142 (vw), 1070 (vw), 1012 (w), 835 (w), 775 (w), 721 (w), 554 (w).

**X-ray Crystallographic Study:** Intensity data for **1** and **2** were measured on a Siemens Smart CCD diffractometer with graphite-monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. All empirical absorption corrections were applied using the SADABS program.<sup>[23]</sup> The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using the SHELXL-97 program package.<sup>[24]</sup> The positions of the H atoms were generated geometrically (C–H bond fixed at  $0.96 \text{ \AA}$ ), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The summary of the crystal data and structure determination for **1** and **2** are listed in the Table 1. The selected bond lengths and angles for **1** and **2** are listed in the Table 2.

Crystallographic data (excluding structure factors) for the two structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-212589 and -212590. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

This work was supported by the National Nature Science Foundation of China, Nature Science Foundation of Fujian

Table 1. Summary of the crystal data and structure determination for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{20}\text{H}_{13}\text{CdNO}_4$	$\text{C}_{50}\text{H}_{39}\text{CdN}_3\text{O}_8$
Formula mass	443.71	922.24
Crystal size [mm]	$0.47 \times 0.35 \times 0.28$	$0.30 \times 0.26 \times 0.14$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a$ [Å]	9.9943(8)	14.0695(3)
$b$ [Å]	19.7593(16)	14.0633(4)
$c$ [Å]	10.3333(8)	22.2760(4)
$\beta$ [°]	111.893(2)	92.4430(10)
$V$ [Å <sup>3</sup> ]	1893.5(3)	4403.60(18)
$Z$	4	4
$D_c$ [g cm <sup>-3</sup> ]	1.557	1.391
$\mu$ [mm <sup>-1</sup> ]	1.176	0.554
$T$ [K]	293(2)	293(2)
$\lambda$ (Mo- $K_\alpha$ ) [Å]	0.71073	0.71073
Reflections collected	6022	13408
Unique reflections	3336	7726
$R_{\text{int}}$	0.0585	0.0573
Parameters	235	559
$S$ on $F^2$	1.111	1.187
$R_1$ [ $I > 2\sigma(I)$ ] <sup>[a]</sup>	0.0781	0.0767
$wR_2$ (all data) <sup>[b]</sup>	0.1717	0.1491
$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ [e/Å <sup>3</sup> ]	1.203 and -1.525	0.706 and -0.624

<sup>[a]</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>[b]</sup>  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

Table 2. Selected bond lengths [Å] and angles [°] for **1** and **2**

Compound 1			
Cd–O(2A) <sup>[a]</sup>	2.209(8)	Cd–N	2.237(9)
Cd–O(1)	2.210(8)	Cd–O(3B)	2.240(8)
Cd–O(4C)	2.218(8)	Cd–CdA	3.043(2)
O(2A)–Cd–O(1)	158.0(4)	O(2A)–Cd–O(3B)	87.7(3)
O(2A)–Cd–O(4C)	86.7(4)	O(1)–Cd–O(3B)	86.2(3)
O(1)–Cd–O(4C)	91.5(4)	O(4)–Cd–O(3B)	159.1(4)
O(2A)–Cd–N	101.8(4)	N–Cd–O(3B)	100.1(3)
O(1)–Cd–N	100.1(4)	N–Cd–CdA	178.0(3)
O(4C)–Cd–N	100.7(3)		
Compound 2			
Cd–N(1)	2.341(5)	Cd–O(31)	2.416(5)
Cd–N(2A)	2.349(6)	Cd–O(51)	2.429(5)
Cd–O(32)	2.399(5)	Cd–O(52)	2.474(5)
Cd–N(3)	2.406(5)		
N(1)–Cd–N(2A)	177.5(2)	N(2A)–Cd–O(51)	82.3(2)
N(1)–Cd–O(32)	96.70(19)	O(32)–Cd–O(51)	163.05(17)
N(2A)–Cd–O(32)	85.4(2)	N(3)–Cd–O(51)	84.65(18)
N(1)–Cd–N(3)	85.0(2)	O(31)–Cd–O(51)	139.44(17)
N(2A)–Cd–N(3)	96.4(2)	N(1)–Cd–O(52)	91.57(19)
O(32)–Cd–N(3)	85.15(18)	N(2A)–Cd–O(52)	86.01(19)
N(1)–Cd–O(31)	82.6(2)	O(32)–Cd–O(52)	137.36(16)
N(2A)–Cd–O(31)	97.8(2)	N(3)–Cd–O(52)	137.34(18)
O(32)–Cd–O(31)	53.96(16)	O(31)–Cd–O(52)	86.12(16)
N(3)–Cd–O(31)	135.08(18)	O(51)–Cd–O(52)	53.34(16)
N(1)–Cd–O(51)	95.87(19)		

<sup>[a]</sup> Symmetry code: **1** (A)  $-x+2, -y, -z$ ; (B)  $-x+3, y+1/2, -z+1/2$ ; (C)  $x-1, -y-1/2, z-1/2$ ; **2** (A)  $x, y-1, z$ .

Province, the Key Project of Chinese Academy of Science and Open Laboratory of Chirotechnology of the Hong Kong Polytechnic University.

- [1] [1a] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**. [1b] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons: New York, **2000**. [1c] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier: New York **1989**.
- [2] [2a] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908. [2b] P. J. Hagrman, D. Hagrman, J. Zubietta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684. [2c] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 173–303.
- [3] [3a] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472. [3b] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330.
- [4] [4a] S. A. Bourne, J. Lu, A. Mondal, B. Moulton, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2001**, *40*, 2111–2113. [4b] J. Lu, A. Mondal, B. Moulton, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2001**, *40*, 2113–2116.
- [5] [5a] S. I. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* **2000**, *39*, 2081–2084. [5b] S. Dalai, P. S. Mukherjee, E. Zangrando, F. Lloret, N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2002**, 822–823. [5c] A. Grirrane, A. Pastor, A. Galindo, A. Ienco, C. Mealli, P. Rosa, *Chem. Commun.* **2003**, 512–513.
- [6] [6a] O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522. [6b] H. W. Roesky, M. Andruh, *Coord. Chem. Rev.* **2003**, *236*, 91–119. [6c] D. A. McMorran, P. J. Steel, *Chem. Commun.* **2002**, 2120–2121. [6d] S. Banfi, L. Carlucci, E. Caruso, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **2002**, 2714–2721. [6e] E. Lindner, R. Zong, K. Eichele, U. Weisser, M. Ströbele, *Eur. J. Inorg. Chem.* **2003**, 705–712.
- [7] [7a] A. J. Blake, N. R. Champness, S. S. M. Chung, W. S. Li, M. Schröder, *Chem. Commun.* **1997**, 1675–1676. [7b] H. K. Fun, S. S. S. Raj, R. G. Xiong, J. L. Zuo, Y. Zhi, X. Z. You, *J. Chem. Soc., Dalton Trans.* **1999**, 1915–1917.
- [8] [8a] W. Lin, O. R. Evans, R. G. Xiong, Z. Wang, *J. Am. Chem. Soc.* **1998**, *120*, 13272–13273. [8b] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986. [8c] D. K. Chand, K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 1652–1653. [8d] T. J. Prior, M. J. Rosseinsky, *Inorg. Chem.* **2003**, *42*, 1564–1575.
- [9] [9a] A. J. Blake, N. R. Champness, A. N. Khlobystov, S. Parsons, M. Schröder, *Angew. Chem. Int. Ed.* **2000**, *39*, 2317–2320. [9b] S. A. Barnett, A. J. Blake, N. R. Champness, J. E. B. Nicolson, C. Wilson, *J. Chem. Soc., Dalton Trans.* **2001**, 567–573.
- [10] [10a] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494. [10b] L. Carlucci, G. Ciani, D. Proserpio, *Chem. Commun.* **1999**, 449–450. [10c] M. J. Plater, M. R. S. J. Foreman, E. Coronado, C. J. Gómez-García, A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.* **1999**, 4209–4216. [10d] Z. Y. Fu, X. T. Wu, J. C. Dai, S. M. Hu, W. X. Du, H. H. Zhang, R. Q. Sun, *Eur. J. Inorg. Chem.* **2002**, 2730–2735.
- [11] [11a] F. A. A. Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowski, *Eur. J. Inorg. Chem.* **2002**, 2823–2828. [11b] J. Tao, M. L. Tong, X. M. Chen, *J. Chem. Soc., Dalton Trans.* **2000**, 3669–3674.
- [12] [12a] S. M.-F. Lo, S. S.-Y. Chui, L.-Y. Shek, Z. Lin, X. X. Zhang, G. H. Wen, I. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 6293–6294. [12b] Z. Shi, S. H. Feng, Y. Sun, J. Hua, *Inorg. Chem.* **2001**, *40*, 5312–5313.
- [13] [13a] K. D. Benkstein, J. T. Hupp, C. L. Stern, *J. Am. Chem. Soc.* **1998**, *120*, 12982–12983. [13b] D. Hagrman, R. D. Haushalter, J. Zubietta, *Chem. Mater.* **1998**, *10*, 361–365.
- [14] [14a] J. A. Real, E. Andres, M. C. Munoz, M. Julve, T. Granier, A. Boussekou, F. Varret, *Science* **1995**, *268*, 265–269. [14b] G. De Munno, R. Ruiz, F. Lloret, J. Faus, R. Sessoli, M. Julve, *Inorg. Chem.* **1995**, *34*, 408–411.
- [15] [15a] A. J. Blake, N. R. Champness, S. S. M. Chung, W. S. Li, M. Schröder, *Chem. Commun.* **1997**, 1005–1006. [15b] M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, A. L. Realf, S. J. Teat, M. Schröder, *J. Chem. Soc., Dalton Trans.* **2000**, 3261–3268.
- [16] R. H. Wang, M. C. Hong, J. H. Luo, R. Cao, J. B. Weng, *Chem. Commun.* **2003**, 1018–1019.
- [17] F. A. Cotton, C. Lin, C. A. Murillo, *Chem. Commun.* **2001**, 11–12.
- [18] [18a] J.-M. Rueff, S. Pillet, N. Clauser, G. Bonaventure, M. Souhassou, P. Rabu, *Eur. J. Inorg. Chem.* **2002**, 895–900. [18b] H. Kumagai, K. Inoue, M. Kurmoo, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1283–1289. [18c] R. H. Wang, M. C. Hong, J. H. Luo, R. Cao, J. B. Weng, *Eur. J. Inorg. Chem.* **2002**, 2082–2085.
- [19] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press: London, **1962**, p. 984.
- [20] [20a] T. Allman, R. Goel, N. K. Jha, A. L. Beauchamp, *Inorg. Chem.* **1984**, *23*, 914–918. [20b] S. L. Li, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1995**, 1519–1524.
- [21] M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen, O. M. Yaghi, *Chem. Commun.* **2001**, 2532–2533.
- [22] [22a] S. E. Denmark, H. Matsuhashi, *J. Org. Chem.* **2002**, *67*, 3479–3486. [22b] R. Curci, M. Fiorenino, M. R. Serio, *J. Chem. Soc., Chem. Commun.* **1984**, 155–156.
- [23] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen: Göttingen, **1996**.
- [24] G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen: Göttingen, **1997**.

Received June 18, 2003

Early View Article

Published Online October 31, 2003