Ligand-controlled Assembly of Cd(II) Metal-Organic Coordination Polymers Based on 3,5-Dinitrobenzoate and Flexible Bis(imidazole) Derivatives

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Three new Cd(II) metal-organic coordination polymers, $[Cd(bbi)(DNBA)_2]$ (**1**), $[Cd(bbbi)(DNBA)_2]$ (**2**), and $[Cd(dmbbbi)(DNBA)Cl]\cdot 0.38H_2O$ (**3**) [HDNBA = 3,5-dinitrobenzoic acid, bbi = 1,1-(1,4-butanediyl)bis(imidazole), bbbi = 1,1-(1,4-butanediyl)bis(benzimidazole), and dmbbbi = 1,1-(1,4-butanediyl)bis(5,6-dimethylbenzimidazole)], have been obtained from hydrothermal reactions of cadmium(II) chloride with the mixed ligands HDNBA and the three structurally related flexible bis(imidazole) derivatives. Single-crystal X-ray diffraction analyses have revealed that the dinuclear cadmium clusters acting as nodes interlinked by two μ_2-carboxylic groups, are connected to four other clusters through bridging bbi (for **1**) and bbbi (for **2**) units to generate two extended two-dimensional (2-D) networks. Compound **3** features a 1-D zigzag chain structure. A systematic structural comparison of the title compounds indicates that the conformations and the steric hindrance of flexible bis(imidazole) derivatives each play an important role in the formation of the Cd(II) coordination polymers. The thermal stability of **1** and **2**, and the luminescence behavior of **3** were also investigated.

Key words: Coordination Polymer, Hydrothermal Synthesis, Crystal Structure, Photoluminescent Property, Bis(imidazole) Derivative

Introduction

The rational design and synthesis of new metal-organic coordination polymers is of current interest in the field of crystal engineering, stemming from their potential applications as functional materials along with their intriguing variety of architectures [1 – 4]. However, one of the obvious challenges to chemists is the rational and controllable preparation of the target compounds in this area [5], the formation of which is greatly affected by the coordination ability, the coordination modes and the conformations as well as by the rigidity and stability of the ligands, and other factors [6, 7]. As an important family of multidentate N-donor ligands, flexible bis(imidazole) derivatives seem to be excellent building blocks as bridging ligands with outstanding coordination ability, versatile coordination conformations, as well as remarkable stability for constructing one-dimensional (1-D), 2-D and 3-D metal-organic coordination polymers [8, 9]. On the other hand, 3,5-dinitrobenzoic acid (HDNBA) is also an excellent ligand to construct metal-organic coordination polymers, because it has one carboxylic group for generating metal oxygen clusters as secondary building units (SBUs), two nitro-groups for H-bonding and an

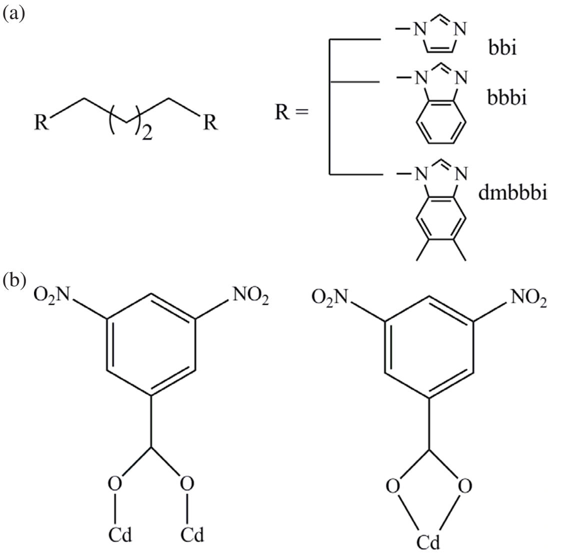


Fig. 1. (a) The N-ligands used and (b) the coordination modes of DNBA in this report.

aromatic ring for π-π-stacking interactions to diversify the supramolecular architectures [10 – 14].

In the work reported in this paper, we selected DNBA and Cd(II) to construct metal oxygen clusters and used three structurally related flexible bis(imidazole) derivatives [1,1-(1,4-butanediyl)bis(imidazole) (bbi), 1,1-(1,4-butanediyl)bis(benzimidazole) (bbbi), and 1,1-(1,4-butanediyl)bis(5,6-dimethylbenzimidazole) (dmbbbi)] as linkers (Fig. 1a). By modulating the substituents and the steric hindrance of the bis(imidazole) derivatives, three new Cd(II) coordination polymers, the 2-D grids [Cd(bbi)(DNBA)$_2$] (**1**) and [Cd(bbbi)(DNBA)$_2$] (**2**), and the 1-D zigzag chains [Cd(dmbbbi)(DNBA)Cl]·0.38H$_2$O (**3**), have been successfully obtained under hydrothermal conditions.

Results and Discussion

*Crystal and molecular structure of [Cd(bbi)(DNBA)$_2$] (**1**)*

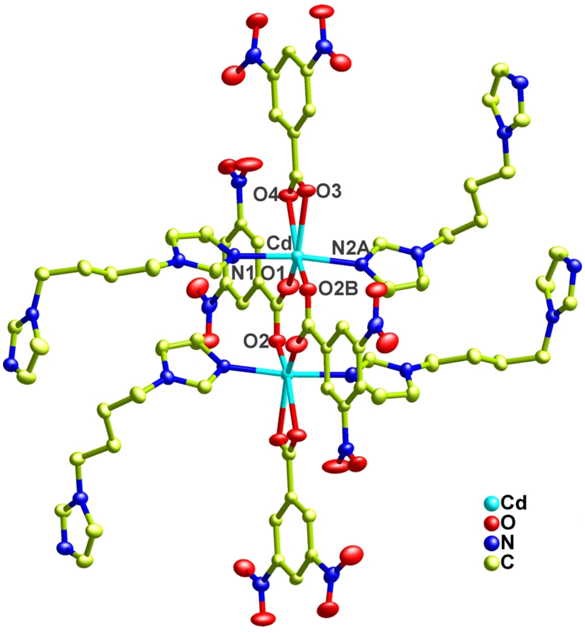


Fig. 2 (color online). Coordination environment of the Cd(II) centers in **1** (displacement ellipsoids are drawn at the 30 % probability level).

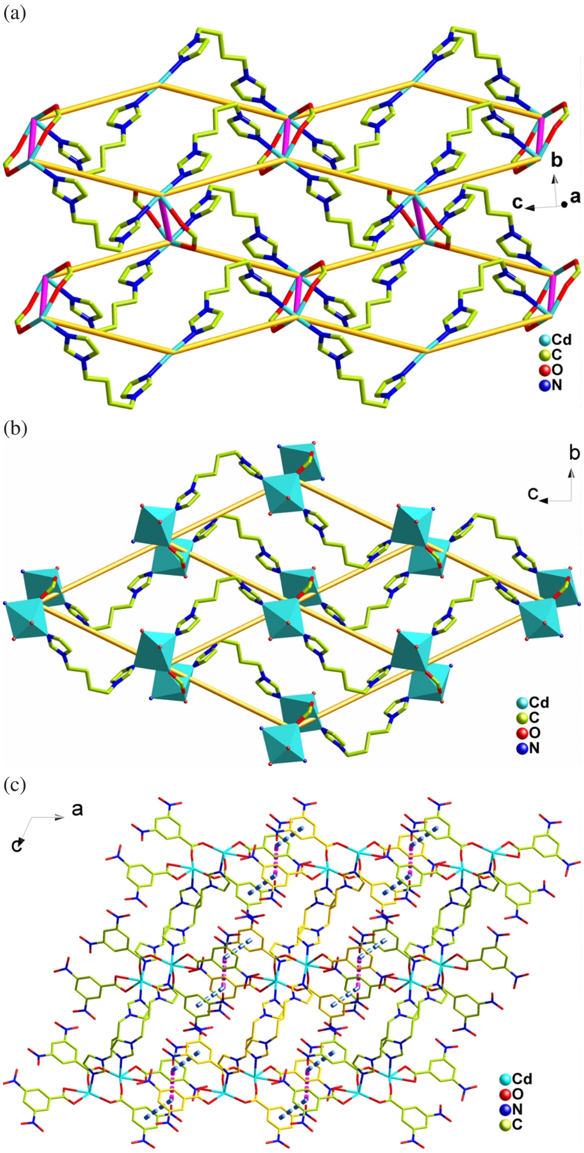


Fig. 3 (color online). (a) View of the 2-D coordination framework of **1** with (3,6) topology based on mononuclear cadmium cores; (b) view of the 2-D coordination framework of **1** with (4,4) topology based on binuclear cadmium clusters; (c) 3-D supramolecular network of **1** through intermolecular π-π interactions.

Single-crystal X-ray structural analysis of **1** has revealed that a 2-D coordination polymer with a (3,6) network based on a mononuclear cadmium center, or (4,4) grids based on binuclear cadmium units are formed by DNBA and bbi ligands lying in the crystallographic *bc* plane. Each Cd(II) in the dinuclear motif is six-coordinate by two oxygen atoms from two carboxylate groups (in a bridging monodentate fashion, Fig. 1b left) of different DNBA units (Cd–O 2.285(3), 2.296(2) Å), two oxygen atoms from one carboxylate group with chelating coordination (Fig. 1b right) of another DNBA (Cd–O 2.425(3), 2.480(3) Å), and two nitrogen atoms from two bbi ligands (Cd–N 2.246(3), 2.251(3) Å) in *trans* positions (Fig. 2). In the coordination octahedron, the bond angles of the cadmium atom with nitrogen and oxygen atoms vary from 53.26(9)° (O(3)–Cd–O(4)) to 173.36(11)° (N(1)–Cd–N(2)(A)), indicating that the octahedron is distorted. Two crystallographically equivalent Cd atoms are bridged by two μ_2-carboxylic groups forming a bimetallic SBU ($Cd_2N_4O_6$) with a Cd···Cd distance of 4.235 Å.

From further analysis of the structure of compound **1**, two kinds of 2-D topology features are apparent. Considering each six-coordinated Cd atom as a 3-connected node, and keeping every bbi ligand and the bridging carboxylate groups as spacers, the whole structure of **1** can be considered to be a (3,6) network with the distances of 11.922 and 4.235 Å based on the adjacent Cd atoms (Fig. 3a); Considering each bimetallic SBU as a 4-connected node, and keeping every bbi ligand as a linker, the whole structure of **1** can be considered to be a (4,4) grid (12.760 × 12.760 Å^2, based on the distances between the cores of SBUs) (Fig. 3b). Moreover, there are interlayer π-π-stacking interactions of the aromatic rings of the DNBA ligands between adjacent layers, which extend the 2-D layers into a 3-D supramolecular network (face-to-face distances of about 3.679(2) and 3.697(3) Å, dihedral angles of 0.0 and 1.75° (Fig. 3c)).

Crystal and molecular structure of [Cd(bbbi)(DNBA)$_2$] (2)

Single-crystal X-ray structural analysis of **2** has revealed that a 2-D coordination polymer with a (3,6) network based on mononuclear cadmium centers, or (4,4) grids based on binuclear cadmium units is formed by DNBA and bbbi ligands, which is similar to that of compound **1**. Each Cd(II) center in the dinuclear clusters is coordinated in a bridging monodentate fashion by two oxygen atoms from two carboxylate groups of different DNBA ligands (Cd–O 2.222(2), 2.383(2) Å), two oxygen atoms from one carboxylate group with chelating coordination of another DNBA ligand (Cd–O 2.416(3), 2.418(3) Å), and two nitrogen atoms from two bbbi ligands (Cd–N 2.294(3), 2.302(3) Å) in *cis* position to furnish a distorted octahedral geometry (Fig. 4). Two Cd atoms related by a center of inversion are bridged by a pair of μ_2-carboxylic groups of different DNBA ligands forming a bimetallic SBU ($Cd_2N_4O_6$), with a Cd···Cd distance of 4.583 Å.

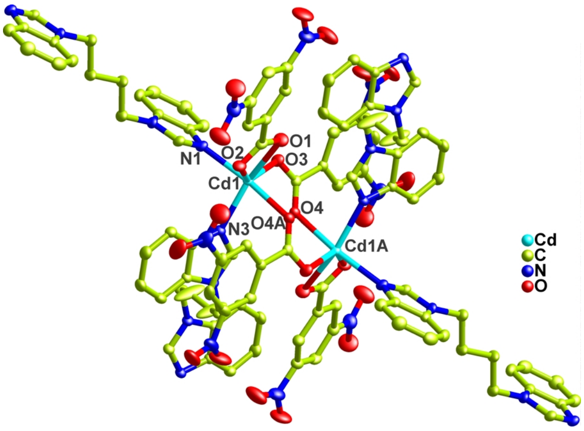


Fig. 4 (color online). Coordination environment of the Cd(II) centers in **2** (displacement ellipsoids are drawn at the 30 % probability level).

Considering each Cd atom as a 3-connected node, and keeping all bbbi ligands and bridging carboxylate groups as spacers, the whole structure of **2** can be considered to be a (3,6) network with distances of 4.583, 12.774 and 14.418 Å based on the adjacent Cd atoms (Fig. 5a); considering each bimetallic SBU as a 4-connected node, and keeping all bbbi ligands as linkers, the whole structure of **2** can be considered to be a (4,4) grid (18.997 × 11.779 Å, based on the distances between the cores of the SBUs) (Fig. 5b). In addition, the intralayer π-π-stacking interactions of the aromatic rings of the DNBA and bbbi ligands (face-to-face dis-

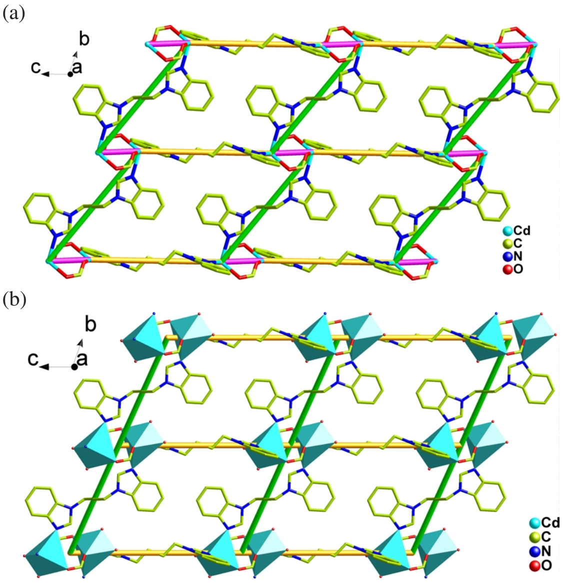


Fig. 5 (color online). (a) View of the 2-D coordination framework of **2** with (3,6) topology based on mononuclear cadmium cores; (b) view of the 2-D coordination framework of **2** with (4,4) topology based on binuclear cadmium clusters.

tance 3.550(3) Å, dihedral angle 3.8055°) stabilize the 2-D network of **2**.

*Crystal and molecular structure of [Cd(dmbbbi)(DNBA)Cl]·0.38H_2O (**3**)*

The single-crystal X-ray structural analysis shows that **3** contains 1-D zigzag chains. The asymmetric unit consists of one Cd^{2+} cation, a chloride anion, a DNBA anion and two dmbbbi ligands. The coordination sphere around the five-coordinated Cd(II) center is composed of two oxygen atoms from a DNBA with a chelating coordination mode (Cd–O 2.3354(19), 2.3995(19) Å), two nitrogen atoms from two dmbbbi ligands (Cd–N 2.2389(19), 2.2580(19) Å), and a chloride anion (Fig. 6). Two adjacent Cd atoms are linked by dmbbbi ligands with distances of 14.562 and 11.913 Å to form a 1-D zigzag chain structure (Fig. 7). Moreover, there are π-π-stacking interactions between the aromatic rings of the dmbbbi ligands from the adjacent chains, which extend the 1-D chains into a 2-D supramolecular network (face-to-face distances 3.465(2) to 3.786(2) Å, dihedral angle 0.00°, Fig. 7).

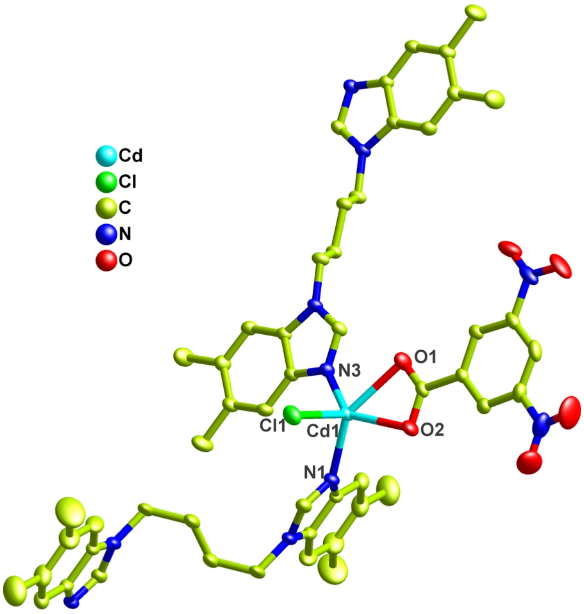


Fig. 6 (color online). Coordination environment of the Cd(II) center in **3** (displacement ellipsoids are drawn at the 30 % probability level).

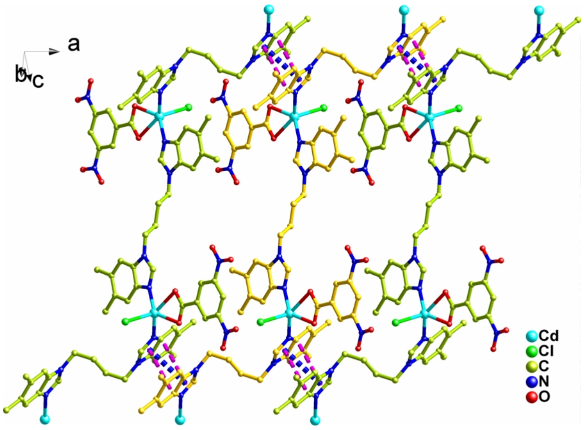


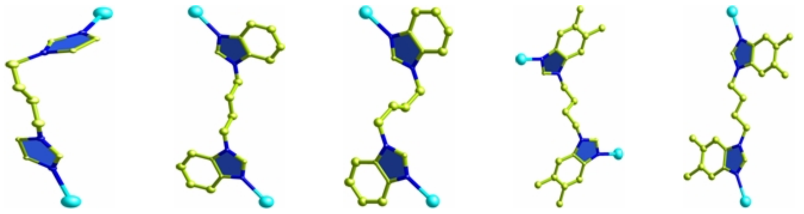
Fig. 7 (color online). (a) Structure of the 1-D "zigzag" chain of **3**; (b) view of a 2-D layer in **3** formed *via* π-π stacking interactions between dmbbbi ligands.

Structural discussion of the title compounds

Three new Cd(II) coordination polymers have been synthesized from the appropriate combinations with flexible bis(imidazole) ligands, which further enrich the coordination chemistry of these components. From a comparison of the title compounds, the effects of the flexible bis(imidazole) ligands with different conformations and steric hindrance on the coordination polymer structures become apparent. The flexible nature of the -CH_2-spacers allows the bis(imidazole)-derived ligands to bend and rotate when they coordinate to Cd atoms, resulting in numerous possible conformations. In **1**, bbi ligands adopt two kinds of conformations, *viz. cis*···*trans* and *trans*···*trans*. In **2** and **3**, all the flexible bis(imidazole) derivatives adopt a *trans*···*trans* conformation. Furthermore, it is evident that the distance between the two coordinating nitrogen atoms (8.68 to 10.41 Å) and the dihedral angles between the two imidazolyl groups (0 to 84.30°) in the ligand are quite variable, resulting in two grids with different sizes for **1** and **2**, and different separation distances for **3** (Fig. 8). Although the bis(imidazole) ligands exhibit only bridging coordination modes, they are quite different due to the different coexistent groups in the imidazolyl ring (Fig. 1a). The existence of these groups can provide different spatial effects in the construction of the architectures even though they are not involved in coordination with the metal centers. Thus, considering coexistent non-coordinated groups besides coordinated functional units may be a feasible way to design various architectures.

IR spectra

The main features in the IR spectra of the title compounds concern the nitro and carboxylate groups and



	a	b	c	d	e
N···N (Å)	8.86	10.39	8.80	8.79	10.41
Cd···Cd (Å)	11.9	14.4	12.8	11.9	14.6
Dihedral angle	84.3	0	0	0	0
Conformation	*cis...trans*	*trans...trans*	*trans...trans*	*trans...trans*	*trans...trans*

Fig. 8 (color online). The N···N distances and the conformations of the ligands in the title compounds.

the N-ligands. The bands at about 725 cm^{-1} may be attributed to the $\nu_{\mathrm{C-N}}$ stretching of the imidazol ring [9]. No strong absorption peaks around 1700 cm^{-1} for carboxylate groups are observed, indicating that all carboxylic groups in **1**, **2**, and **3** are deprotonated. The absorption bands at about 1348 and 1539 cm^{-1} arise from the nitro-groups of DNBA [10–14]. For **1**, the asymmetric and symmetric vibrations of carboxylate groups appear at 1635, 1581 and 1386 cm^{-1}. The Δ values, which represent the separation between ν_{asym}(-COO) and ν_{sym}(-COO), are 249 and 195 cm^{-1}. These values are consistent with the coordination modes of this complex. For **2**, carboxylate group bands appear at 1608, 1568 and 1390 cm^{-1} for the asymmetric and symmetric vibrations. The Δ values are 218 and 178 cm^{-1}, which is in agreement with the results of the crystal structure analysis. For **3**, the characteristic bands of the carboxylate groups appear at 1612 cm^{-1} for asymmetric vibrations and at 1392 cm^{-1} for symmetric vibrations. The Δ value of 220 cm^{-1} indicates that the carboxylate groups adopt a chelating coordination mode [15, 16].

TG analyses

The TG curves of **1** and **2** exhibit two weight loss stages in a range of 25 to 600 °C, as shown in Fig. 9. The TGA curve of **1** indicates that the network is stable from r. t. to about 280 °C, after which decomposition of the framework occurs. The complete decomposition is finished at 530 °C with the defined decomposition product CdO (calcd. 17.71 %; found 17.8 %). In comparison with **1**, compound **2** is slightly more stable up to 300 °C, where the decomposition of the framework starts leading to a rapid and significant weight loss in the temperature range of 300 to 550 °C, the resulting residue being CdO (observed 15.50, calcd. 15.6 %). The framework of compound **3** begins to collapse at about 290 °C and kept decomposing until 720 °C. The different decomposition temperature for the frameworks may be due to the difference of their structures [8].

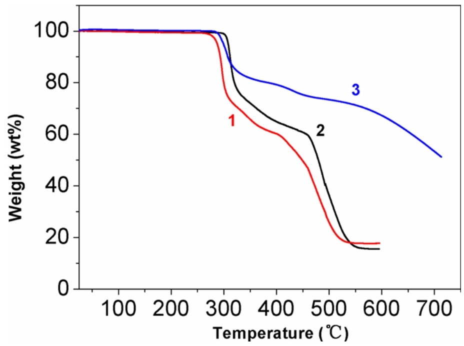


Fig. 9 (color online). TG curves of **1** and **2**.

Photoluminescence

Metal-organic framework compounds based on aromatic amine ligands have been shown to exhibit interesting photoluminescent properties [17, 18]. In the present work, we have examined the photoluminescent properties of the title compounds in the solid state at r. t. (Fig. 10). However, only compound **3** has shown weak a photoluminescent emission at 470 nm upon excitation at 344 nm. **1** and **2** do not exhibit such an emission, which may due to the quenching effects of Cd(II) [19]. For the emission band of **3**, the main peak has a red-shifted position, compared with that of dmbbbi (λ_{ex} = 406, λ_{ex} = 323). The emission bands for **3** can be assigned mainly to a $\pi^* \rightarrow \pi$ transition of the coordinated dmbbbi ligands [20, 21]. The photolumines-

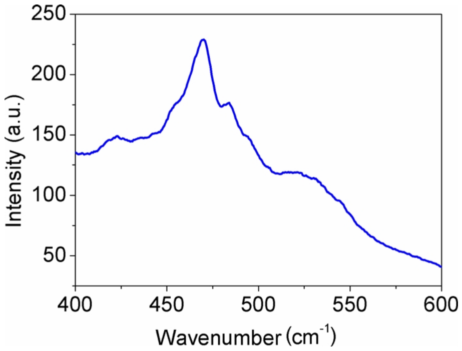


Fig. 10 (color online). Photoluminescence spectrum of **3**.

cence intensity of **3** is higher than those of **1** and **2**, which may due to larger conjugative effects of dmbbbi in **3** than in bbi and bbbi in **1** and **2** [19].

Conclusions

In summary, the successful isolation of the title compounds has not only provided some new examples of Cd coordination polymers with bis(imidazole) ligand spacers but also further confirms the conformational diversity of flexible ligands. An increasing steric hindrance on the flexible bis(imidazole) derivatives was achieved by the rational design of the substituting groups in the imidazolyl ring, which suggests that this synthetic strategy used for the title compounds may open a new perspective to generate new types of metal-organic coordination polymers with transition metals.

Experimental Section

Materials and measurements

The flexible bis(imidazole) derivatives (bbi, bbbi and dmbbbi) were prepared according to the published method [22]. All other reagents were readily available from commercial sources and were used as received without further purification. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Fluorescence spectra were performed on an F-4500 fluorescence/phosphorescence spectrophotometer at r. t., and elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric data for the title compounds were collected on a Pyris Diamond thermal analyzer with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

*Synthesis of [Cd(bbi)(DNBA)$_2$] (**1**)*

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.1 mmol), bbi (0.1 mmol), DNBA (0.2 mmol), NaOH (0.2 mmol), H_2O (12 mL), stirred for 20 min, was sealed in a Teflon-lined stainless-steel autoclave (25 mL) and kept at 150 °C for 3 d. After the mixture was slowly cooled to r. t., yellow block-shaped crystals of **1** suitable for X-ray diffraction were obtained in 40 % yield (based on the Cd(II) salt). Anal. for $C_{24}H_{20}CdN_8O_{12}$: calcd. C 39.76, H 2.78, N 15.46; found C 39.72, H 2.82, N 15.50 %. – IR (KBr, cm^{-1}): ν = 1635(s), 1616(s), 1581(m), 1539(s), 1456(m), 1386(s), 1348(s), 1089(m), 1072(w), 842(w), 725(s).

*Synthesis of [Cd(bbbi)(DNBA)$_2$] (**2**)*

The reaction was carried out with a method similar to that for **1**, using bbbi (0.1 mmol) instead of bbi. Yellow block-shaped crystals suitable for X-ray diffraction were obtained in 36 % yield (based on the Cd(II) salt). Anal. for $C_{32}H_{24}CdN_8O_{12}$: calcd. C 46.58, H 2.93, N 11.58; found: C 46.60, H 2.95, N 11.61 %. – IR (KBr, cm^{-1}): ν = 1622(m), 1608(s), 1568(m), 1539(s), 1458(m), 1390(m), 1342(s), 1089(m), 1072(w), 858(w), 731(s).

*Synthesis of [Cd(dmbbbi)(DNBA)Cl]·0.38H$_2$O (**3**)*

The reaction was carried out with a method similar to that for **1**, using dmbbbi (0.1 mmol) instead of bbi. Yellow block-shaped crystals suitable for X-ray diffraction were obtained in 32 % yield (based on the Cd(II) salt). Anal. for $C_{29}H_{29.76}ClCdN_6O_{6.38}$: calcd. C 48.85, H 4.18, N 11.79; found C 48.80, H 4.14, N 11.89 %. – IR (KBr, cm^{-1}): ν = 1612(s), 1573(m), 1531(s), 1460(m), 1392(s), 1348(s), 1083(w), 1072(w), 921(w), 723(s).

X-Ray crystallography

All diffraction data were collected using a Bruker P4 diffractometer (MoK_α radiation, graphite monochromator, λ = 0.71073 Å). The structures were solved by Direct Methods with SHELXS-97, expanded by Fourier techniques and refined by full-matrix least-squares methods on F^2 with SHELXL-97 [23, 24]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the ligands were generated theoretically on their specific atoms and refined isotropically. All the crystal data and structure refinement details for the three compounds are given in Table 1.

CCDC 727905–727907 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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Table 1. Crystal data and structure refinement summary for **1**–**3**.

Compound	**1**	**2**	**3**
Formula	$C_{24}H_{20}CdN_8O_{12}$	$C_{32}H_{24}CdN_8O_{12}$	$C_{29}H_{29.76}ClCdN_6O_{6.38}$
M_r	724.88	824.99	712.28
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	12.736(4)	10.8376(15)	9.3670(6)
b, Å	10.319(3)	11.4051(16)	12.2846(8)
c, Å	23.340(5)	16.100(2)	14.0589(9)
α, deg	90	108.275(2)	75.799(1)
β, deg	114.836(12)	92.589(2)	84.896(1)
γ, deg	90	116.108(2)	87.815(1)
V, Å^3	2783.7(13)	1657.2(4)	1561.88(17)
Z	4	2	2
D_{calcd}, g cm^{-3}	1.73	1.65	1.52
$\mu(MoK_\alpha)$, cm^{-1}	0.9	0.7	0.8
$F(000)$, e	1456	832	724
θ range, deg	2.20–25.02	2.07–25.00	1.98–25.00
Data collect. / unique / R_{int}	21385 / 4912 / 0.069	8323 / 5737 / 0.020	7945 / 5417 / 0.013
Data with $I \geq 2\ \sigma(I)$	3308	4956	4983
Restraints / ref. param.	0 / 406	1 / 482	2 / 394
Final R_1 / wR_2 [$I \geq 2\ \sigma(I)$]^a	0.0315 / 0.0828	0.0364 / 0.0934	0.0244 / 0.0643
R_1 / wR_2 (all data)^a	0.0533 / 0.0985	0.0441 / 0.0981	0.0275 / 0.0657
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.46 / −0.52	0.94 / −0.31	0.32 / −0.32

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP^2+BP)]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0)+2F_c{}^2)/3$ and A and B are constants adjusted by the program.

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