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ARTICLE TYPE

A Serials of Interdigitated Cd(II) Coordination Polymers based on 4,6-dibenzoylisophthalic acid and Flexible triazole ligands

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A serials of Cd(II) coordination polymers have been attained through hydrothermal self-assembly. During the self-assembly, the flexibility and the scale in length of the ligands play an important role in the construction of interdigitated molecular structures, which supports an alternative approach for designing such networks under the guidance of spacers.

The design and synthesis of novel coordination polymers (CPs) have attracted more and more attentions for their potential applications in fluorescence, nonlinear optics, magnetism and catalysis. [1] As an important class of materials in this field, entangled CPs especially attracted great interest for their intriguing structures and special properties. [2] Up to now, some reviews about entangled systems have been written by Robson, Batten, Ma, Ciani and Leigh. [3] Robson and his co-workers firstly described the interdigitation, where the side arms as a special theme are necessary for the construction of the entangled system. [3a] Moreover, some other terminologies, such as polycatenation, polythreading, polyknotting and polymeric chains, have also been defined. [3c] In principle, the entanglement could be driven by carefully selecting the coordination geometry of the metal centers and the organic ligands with flexible coordination modes. [4] In decades, many efforts have been devoted to the design and synthesis of novel entangled networks. [5] However, it still remains a challenge to clarify which factor controls the construction of the entangled system.

According to the literature, [6] multi-carboxylate aromatic ligands have been widely used due to their flexible coordination modes. In this regard, 4,6-dibenzoylisophthalic acid (H_2L) [7] should be a good candidate for the construction of entangled CPs. To begin with, the two carboxylate groups of H_2L can bridge metal ions to form various frameworks through its versatile coordination modes. Then, bulky benzoyl on the benzene ring can rotate around the C-C bond to generate varieties of geometric conformations. The last but not the least, flexible non-covalent interactions can be expected, i.e. hydrogen bonds, π…π stacking and X–H…π(X = C, N, O) interactions, due to its carbonyl groups and the middle benzene ring, which is expected to play an important role in the guidance of the entangled self-assembly. On the other hand, flexible N-donor ligands with excellent coordination abilities have also been proved to be suitable to the construction of entangled networks. [8]

Herein, we try to utilize the H_2L and flexible *N*-donor ligands, 1,6-di(1H-1,2,4-triazol-1-yl)hexane (L_1), 1,4-bis(pyridin-4-ylmethyl)piperazine (L_2) and 1,3-bis((1H-1,2,4-triazol-1-yl)methyl)benzene (L_3) (Scheme S1), to assemble entangled coordination polymers with Cd(II) ions under hydrothermal conditions. Three new coordination polymers, namely, [Cd(L)(L_1)] (**1**), [Cd(L)(L_2)] (**2**) and [Cd(L)(L_3)] (**3**)[1], have been successfully synthesized and characterized, [9] where both **1** and **2** features a 2D→3D interdigitated network with 4^4-**sql** topology proved by Single-crystal X-ray diffraction analyses (Table S2), whilst **3** exhibits a 3^6-**hxl** topological network without any interdigitation. Additionally, the fluorescence properties of **1**-**3** were also studied in detail.

Complex **1** crystallizes in the triclinic space group *P*-1. The asymmetric unit of **1** comprises one crystallographically independent Cd(II) ion, one L^{2-} anions and one L_1 ligand. As shown in Figure 1a, Cd1 ion is coordinated by four O atoms (O1, O2#1, O3, O4) from three L ligands (Cd–O 2.220(2)-2.493(2) Å) and two N atoms (N1, N4) from two L_1 ligands (Cd–N 2.285(4)-2.295(5) Å), forming a distorted CdN_2O_4 octahedral geometry. Viewing along the *a*-axis, the Cd ions of **1** are connected by the μ_3-η^1:η^1:η^1:η^1-bridging L^{2-} linkers to generate a 1D {CdL} chain with the adjacent Cd···Cd distance of 4.439 and 7.329 Å, respectively (Figure 1b and S3). And then L_1 ligands link the neighboring chains into a 2D layered structure with 4^4-**sql** topology (Figure 1c). [10] Interestingly, the bulky benzoyl groups of L^{2-} anions act as lateral arms projecting both sides of the layers. And, thanks to these bulky benzoyl groups, the adjacent 2D sheets of **1** interdigitated to generate a 2D→3D interdigitation network (Figure 1d). Moreover, the weak C20–H20···O6 hydrogen-bonding interactions should be helpful to guide the self-assembly, and stablize the 3D supramolecular architecture of **1**.

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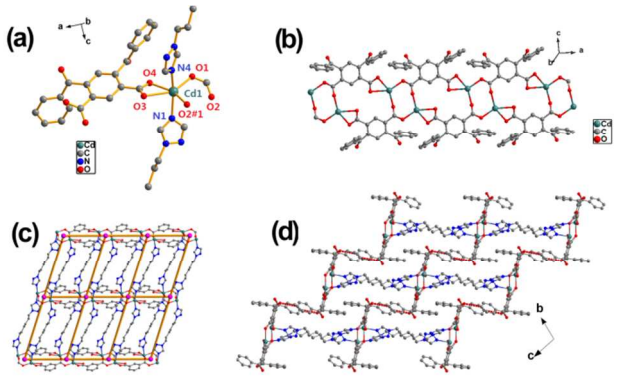

Fig. 1 (a) Coordination environment of Cd ion of **1**. Symmetry codes: #1, 1−x, 1−y, 1−z. (b) View of 1D $\{Cd(L)\}_n$ chain of **1**. (c) Schematic description of 4^4-**sql** layer of **1**. (d) The 3D supramolecular structure of **1** contains a feature of 2D→3D interdigitation. The C20–H20···O6 hydrogen-bonding interactions are showing in dashed red lines

With regards to compound **2**, due to the more rigid L_2, a different framework was attained for comparison. **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **2** contains one crystallographically independent Cd(II) ion, one L^{2-} anion and two half-L_2 molecules. Similar to compound **1**, Cd1 ion is six-coordinated by four O atoms (O1, O2, O3#1, O4#2) from three L ligands (Cd–O 2.227(3)-2.408(3) Å) and two N atoms (N1, N4) from two L_2 ligands (Cd–N 2.311(4)-2.330(4) Å), forming a distorted CdN_2O_4 octahedral geometry (Figure S1a). The Cd ions of **2** are also connected by the L^{2-} linkers to form a 1D $\{CdL\}_n$ chains, which are further linked by L_2 ligands to generate a 2D layered structure with 4^4-**sql** topology (Figure S1b and S1c). [10] However, different from **1**, the layers of **2** are alternately arranged in an ABA fashion (Figure S1d). As the bulky benzoyl groups lateral arms projecting both sides of the layers, the 2D layers of **2** interdigitated with each other to generate a 2D→3D interdigitation (Figure S1d). Meanwhile, the weak C31–H31a···O6 hydrogen bonds should also be helpful to guide and stablize the 3D supramolecular architecture of **2**.

With regards to L_3, it is shorter and more rigid than both L_1 and L_2, which may be not helpful to guide the interdigitation of compound **3**. In the crystal structure of **3**, the asymmetric unit contains one crystallographically independent Cd(II) ion, two half-L^{2-} anions and two half-L_3 molecules. Cd ions are six-coordinated by four O atoms (O1, O2, O3, O4#1) and two N atoms (N1, N4) to generate a distorted CdN_2O_4 octahedral geometry and are then connected by the L^{2-} linkers to form 1D $\{CdL\}_n$ chains (Figure S2a and S2b). It is worth noting that although similar coordination environments of Cd ions and 1D $\{CdL\}_n$ chains with those of compounds **1** and **2** can be found in **3** (Figure S3), the significant different framework was formed after self-assembly. In **3**, 1D $\{CdL\}_n$ chains are connected by L_3 molecules to form a 2D layered structure with 3^6-**hxl** topology (Figure 2a). [10] Otherwise, as the flexibility was reduced gradually from L_1 to L_3, the tilt angles of L^{2-} anions (oppose to the plane of 2D layer) decreased steadily from **1** to **3** (Figure 3). Thus, no interdigitation of the 2D sheets can be found in compound **3** (Figure 2b). Such result indicates that the entanglement of the framework can be efficiently adjusted by intentional designing the flexibility of the bridging ligands.

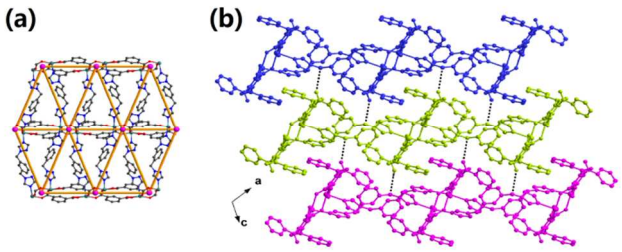

Fig. 2 (a) Schematic description of 3^6-**hxl** layer of **3**. (b) View of the 3D supramolecular structure of **1** based on C25–H25a···O6 hydrogen-bonding interactions (dashed black lines)

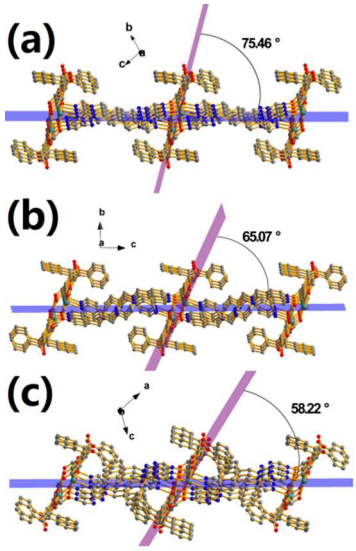

Fig. 3 View of the tilt angles of H_2L molecules in **1** (a), **2** (b) and **3** (c), respectively.

The purity of the title compounds has been characterized by powder X-ray diffraction (PXRD) (Figure S4-S6). The experimental PXRD patterns corresponded well with the results simulated from the single crystal data, indicating the high purity of the synthesized samples. Thermogravimetric analysis was carried out for compounds **1-3** in order to investigate their thermal stability (Figure S7). The experiments were performed on the samples under N_2 atmosphere with a heating rate of 10 °C min^{-1}. All of the three samples exhibit a similar thermal decomposition process with only one decompose step, and the organic groups start to decompose gradually from 287 °C for **1**, 284 °C for **2** and 265 °C for **3**, respectively.

The solid-state fluorescence spectra of **1-3** (Figure 4) and free ligands H_2L, L_1, L_2 and L_3 (Figure S8) have been investigated at room temperature. The main emission bands of the free ligands H_2L, L_1, L_2 and L_3 are at 454 (λ_{ex} = 373 nm), 445 (λ_{ex} = 327 nm), 461(λ_{ex} = 327 nm), and 458 nm (λ_{ex} = 372nm), respectively. These emissions can be assigned to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions as previously reported. The emission spectra of compounds **1**−**3** exhibit the emission maxima at 500 nm (λ_{ex} = 350 nm), 522 nm (λ_{ex} = 350 nm) and 508 nm (λ_{ex} = 380 nm), respectively. The emission bands of compounds **1-3** are similar to those of the free ligands. Since the Zn(II) and Cd(II) ions are difficult to oxidize or to reduce due to their d^{10} configuration, the emissions of compounds **1**−**3** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature.

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[11] Thus, the emission may be assigned to the transitions of both H_2L and N-donor ligands. Compared with the emission spectrum of H_2L and N-donor ligands, red shifts of emission bands for **1**–**3** have been observed, probably due to the deprotonated effect and the coordination interactions of H_2L and N-donor ligands to Cd(II) ions. [11-12]

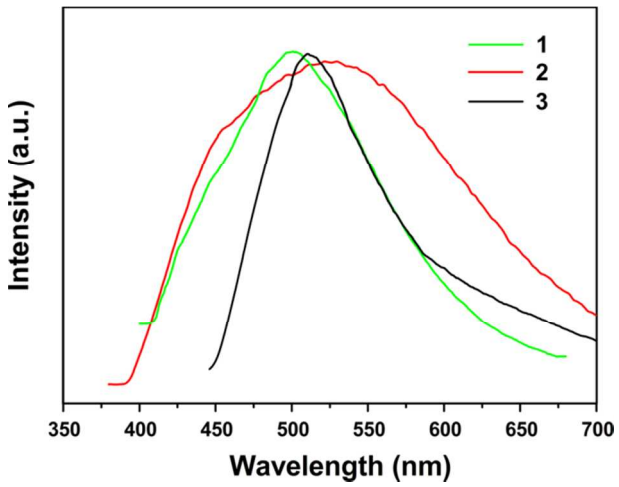

Fig. 4 Emission spectra of **1-3** in the solid state at room temperature

Conclusions

In summary, three Cd(II) coordination polymers have been synthesized under hydrothermal conditions at the presence of H_2L and flexible N-donor ligands. Both **1** and **2** features a 2D→3D interdigitated network with 4^4-**sql** topology under the guidance of the flexible L_1 and L_2. In comparison, compound **3** shows a 3^6-**hxl** topological framework without any interdigitation owing to the lower flexibility of L_3. It can be deduced that the scale in length and the flexibility of the ligands could significantly influence the interdigitation level of the crystal structure. In other words, more flexibility and larger in length the ligands exhibit, more opportunities it will have to attain the interdigitated structures. The observation opens an alternative approach to the systematically assembly of the interdigitated structure for coordination polymers.

Acknowledgment. This work was supported by the NNSFC (No. 20871023), the Jilin Provincial Science Research Foundation of China (No. 20101549), and XiaoNei Foundation of Changchun University of Technology. The 12th Five-Year Plan for Science & Technology Research sponsored by Department of Education of Jilin Province (No. 130 and 146, 2013).

Notes and references

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† Electronic Supplementary Information (ESI) available: [Materials and general methods, Single-crystal X-ray crystallography, Figure S1-S8, Table S1-S6]. See DOI: 10.1039/b000000x/

‡ *CCDC 975867 (**1**), 890982 (**2**) and 975868 (**3**) contain the supplementary X-ray crystallographic files in CIF format can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html.*

1 (a) N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.* 2005, **38**, 176; (b) Y. Cui, Y. Yue, G. Qian and B. *Chen, Chem. Rev.* 2011, **112**, 1126; (c) C. Wang, T. Zhang and W. Lin, *Chem. Rev.* 2011, **112** , 1084; (d) M. Kurmoo, *Chem. Soc. Rev.* 2009, **38**, 1353; (e) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.* 2011, **112**, 1196.
2 (a) X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa and S. R. Batten, *Angew. Chem., Int. Ed.* 2004, **43**, 192; (b) M. H. Zeng, W. X. Zhang, X. Z. Sun and X. M. Chen, *Angew. Chem., Int. Ed.* 2005, **44** , 3079; (c) H. Wu, H. Y. Liu, Y. Y. Liu, J. Yang, B. Liu and J. F. Ma, *Chem. Commun.* 2011, **47** , 1818; (d) J. Yang, J. F. Ma, S. R. Batten and Z. M. Su, *Chem. Commun.* 2008,**44**, 2233; (e) D. Sun, L. L. Han, S. Yuan, Y. K. Deng, M. Z. Xu and D. F. Sun, *Cryst. Growth Des.* 2013, **13** , 377.
3 (a) S. R. Batten, B. F. Hoskins and R. Robson, *Chem. Eur. J.* 2000, **6** , 156; (b) J. Yang, J. F. Ma and S. R. Batten, *Chem. Commun.* 2012, **48**, 7899; (c) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.* 2003, **246**, 247; (d) L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm,* 2003, **5**, 269; (e) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.* 2011, **50** , 9260.
4 (a) Y. L. Gai, F. L. Jiang, L. Chen, Y. Bu, M. Y. Wu, K. Zhou, J. Pan and M. C. Hong, *Dalton Trans*. 2013, **42**, 9954; (b) Y. H. Luo, F. X. Yue, X. Y. Yu, L. L. Gu, H. Zhang and X. Chen, *CrystEngComm,* 2013, **15**, 8116; (c) J. Yang, J. Liu, X. Wang, X. Chi, J. Zhang, H. Zhang, D. Xiao and Q. Luo, *CrystEngComm* 2013, **15**, 10435; (d) X. He, X. P. Lu, Y. Y. Tian, M. X. Li, S. Zhu, F. Xing and R. E. Morris, *CrystEngComm* 2013, **15**, 9437.
5 (a) B. Xu, Z. Lin, L. Han and R. Cao, *CrystEngComm* 2011, **13**, 440; (b) B. Xu, J. Lü and R. Cao, *Cryst. Growth Des.* 2009, **9**, 3003; (c) J. K. Sun, Q. X. Yao, Y. Y. Tian, L. Wu, G. S. Zhu, R. P. Chen and J. Zhang, *Chem. Eur. J.* 2012, **18**, 1924; (d) X. L. Wang, C. Qin, E. B. Wang, Y. G. Li, Z. M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed.* 2005, **44**, 5824.
6 (a) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.* 2000, **100**, 853; b) D. Yuan, D. Zhao, D. Sun and H. C. Zhou, *Angew. Chem., Int. Ed.* 2010, **49**, 5357; (c) D. Zhao, D. Yuan, D. Sun and Zhou, H. C. *J. Am. Chem. Soc.* 2009, **131**, 9186; (d) G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour and I. Margiolaki, *Angew. Chem.* 2004, **116**, 6456; (e) S. C. Manna, S. Mistri and A. D. Jana, *CrystEngComm* 2012, **14**, 7415.
7 (a) D. Du, Z. Jiang, C. Liu, A.M. Sakho, D. Zhu and L. Xu, *J. Organomet. Chem.* 2011, **696**, 2549; (b) Y. H. Luo, F. X. Yue, X. Y. Yu, X. Chen and H. Zhang, *CrystEngComm* 2013, **15,** 6340; (c) Y. Pang, D. Tian, X.-F. Zhu, Y.-H. Luo, X. Zheng and H. Zhang, *CrystEngComm* 2011, **13,** 5142.
8 (a) J. K. Sun, Q. X. Yao, Z. F. Ju and J. Zhang, *CrystEngComm* 2010, **12**, 1709; (b) Y. Q. Lan, S. L. Li, J. S. Qin, D. Y. Du, X. L. Wang, Z. M. Su and Q. Fu, *Inorg. Chem.* 2008, **47**, 10600; (c) B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.* 1997, **119**, 2952; (d) D. Sun, Z. H. Yan, Y. K. Deng, S. Yuan, L. Wang and D. F. Sun, *CrystEngComm* 2012, **14**,7856.
9 A typical synthesis method: A mixture of $CdCl_2{\cdot}2.5H_2O$ (22.8 mg, 0.1 mmol), H_2L (37.4 mg, 0.1 mmol), N-donor ligands (22.3 mg for L_1, 26.8mg for L_2 and 24.3 mg for L_3, 0.1mmol) and H_2O (10 mL) was stirred for 30 min, and the pH of the mixture was adjusted to 5.5 with 0.1 $mol{\cdot}L^{-1}$ NaOH solution. Then it was sealed in a 23 mL Teflon reactor and heated at 160 °C for 72 h. After cooling to room temperature at a rate of 3 $°C{\cdot}h^{-1}$, colorless crystals were isolated by filtration, washed with water, and dried in air. For **1**: about 60% yield based on Cd. Anal. Calcd for $C_{32}H_{28}CdN_6O_6$ (705.01): C, 54.52; H, 4.00; N, 11.92%. Found: C, 54.61; H, 3.93; N, 11.85%. IR (KBr, cm^{-1}): 3061 (w), 2940 (w), 2865(w), 1671 (s), 1600 (s), 1476 (w), 1428 (m), 1382 (s), 1346 (s), 1250 (m), 1136 (w), 1011 (w), 918 (w), 885 (m), 816 (m), 761 (m), 710 (m), 671(w), 621 (w), 524 (w), 482 (w). For **2**: about 42% yield based on Cd. Anal. Calcd for $C_{38}H_{32}CdN_4O_6$ (753.08): C, 60.60; H, 2.96; N, 7.44%. Found: C, 60.68; H, 3.03; N,

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7.35%. IR (KBr, cm^{-1}): 3040 (w), 2941 (w), 2813 (w), 1668 (s), 1617 (s), 1578 (w), 1480 (m), 1402 (s), 1346 (m), 1261 (w), 1135 (w), 1061 (w), 1009 (w), 947 (m), 914 (m), 850 (m), 801 (m), 693 (m), 540(w), 488 (w). For **3**: about 55% yield based on Cd. Anal. Calcd for $C_{34}H_{24}CdN_6O_6$ (725.00): C, 56.33; H, 3.34; N, 11.59%. Found: C, 56.41; H, 3.43; N, 11.65%. IR (KBr, cm−1): 3437 (W), 3110 (w), 1669 (s), 1598 (s), 1521 (s), 1433 (m), 1381 (s), 1261 (m), 1132 (w), 1014 (w), 976 (w), 886 (m), 815 (m), 734 (m), 671 (m), 526 (w).

10 (a) V. A. Baltov, Multipurpose crystallochemical analysis with the program package TOPOS, IUCr CompComm Newsletter, 2006, 4-38; (b) M. O'Keeffe and S. T. Hyde, *Zeolites* 1997, **19**, 370.

11 (a) T. L. Hu, R. Q. Zou, J. R. Li and X. H. Bu, *Dalton Trans.* 2008, **20**, 1302; (b) L. F. Ma, Q. L. Meng, C. P. Li, B. Li, L. Y. Wang, M. Du and F. P. Liang, *Cryst. Growth Des.* 2010, **10**, 3036; (c) L. F. Ma, C. P. Li, L. Y. Wang and M. Du, *Cryst. Growth Des.* 2010, **10,** 2641.

[12] F. F. Li, J. F. Ma, S. Y. Song, J. Yang, Y. Y. Liu and Z. M. Su, *Inorg. Chem.* 2005, **14**, 9374.

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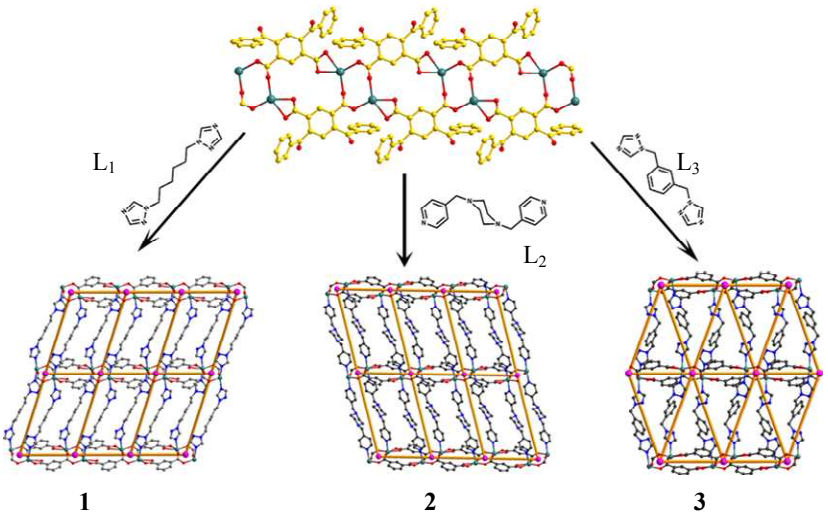

Different bridging ligands with various flexibility and scales in length were utilized to assemble interdigitated coordination polymers with Cd(II) cations. It is of interest to find that the scale in length and the flexibility of the ligands could significantly influence the interdigitation level of the crystal structure, which opens an alternative approach to the systematically assembly of the interdigitated structure for coordination polymers.

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Supporting Information

A Serials of Interdigitated Cd(II) Coordination Polymers based on 4,6-dibenzoylisophthalic acid and Flexible triazole ligands

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Materials and general methods

All reagents and solvents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D_{max} 2000 X-ray diffractometer with graphite monochromatized Cu *K*α radiation (λ = 0.154 nm). The FI-IR spectra were measured in KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analysis (EA) for C, H and N was performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The fluorescent property was measured on a FLS920 Edinburgh Luminescence Spectrometer at room temperature with a light source of Xe lamp.

Single-crystal X-ray crystallography

Colorless block shape single crystal was mounted on a glass fiber for X-ray diffraction analysis. Data was performed at 293(2) K on an Oxford Diffraction Gemini R CCD for **1** and on a Rigaku AFC7R diffractometer for **2** and **3** with graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. [1] All non-hydrogen atoms were refined with anisotropic temperature parameters. All Hydrogen atoms were placed in geometrically idealized position as a riding mode. CCDC 975867 (1), 890982 (2) and 975868 (3) contain the supplementary X-ray crystallographic files in CIF format can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html. The crystallographic data for **1**-**3** is shown in Table S2.

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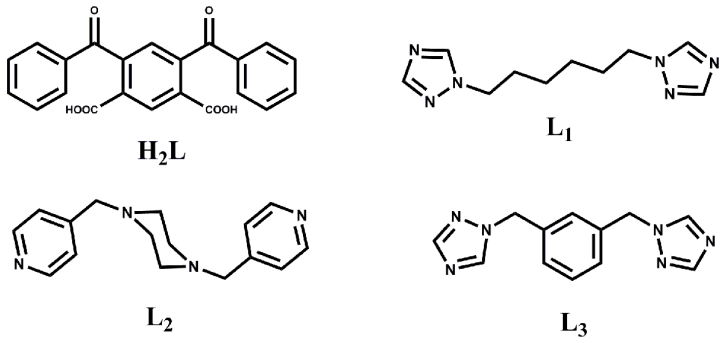

Scheme S1 Schematic representation of ligands used in this work.

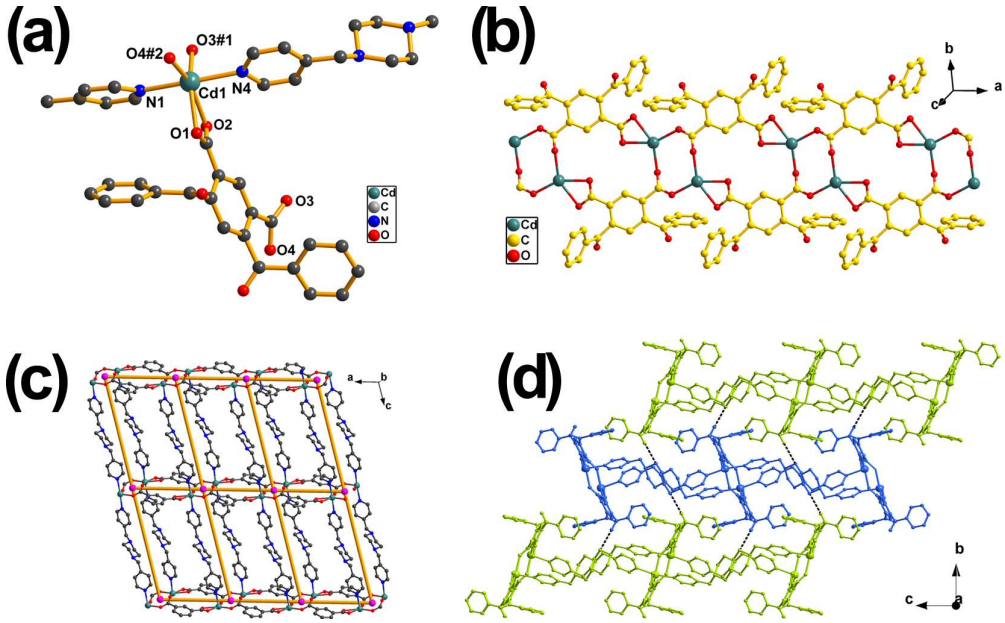

Figure S1 (a) Coordination environment of Cd ion of **2**. Symmetry codes: #1, $x + 1$, y, z; #2, $-x + 1$, $-y + 1$, $-z + 1$. (b) View of 1D $\{Cd(L)\}_n$ chain of **2**. (c) Schematic description of 4^4-**sql** layer of **2**. (d) The 3D supramolecular structure of **2** contains a feature of 2D→3D interdigitation. The C31–H31a···O6 hydrogen-bonding interactions are showing in dashed black lines.

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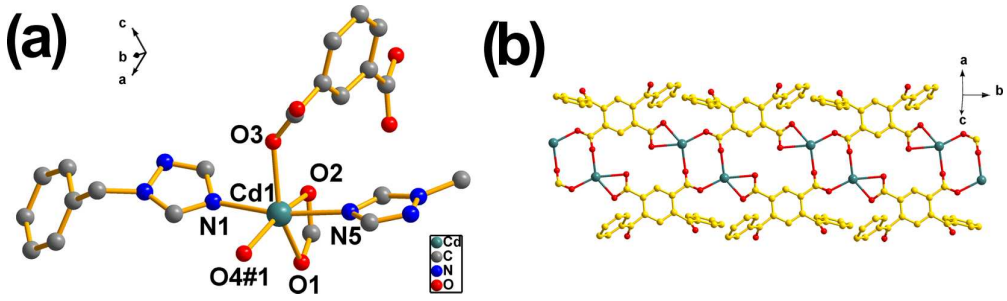

Figure S2 (a) Coordination environment of Cd ion of **3**. Symmetry codes: #1, 1−*x*, 2−*y*, 1−*z*. (b) View of 1D $\{Cd(L)\}_n$ chain of **3**.

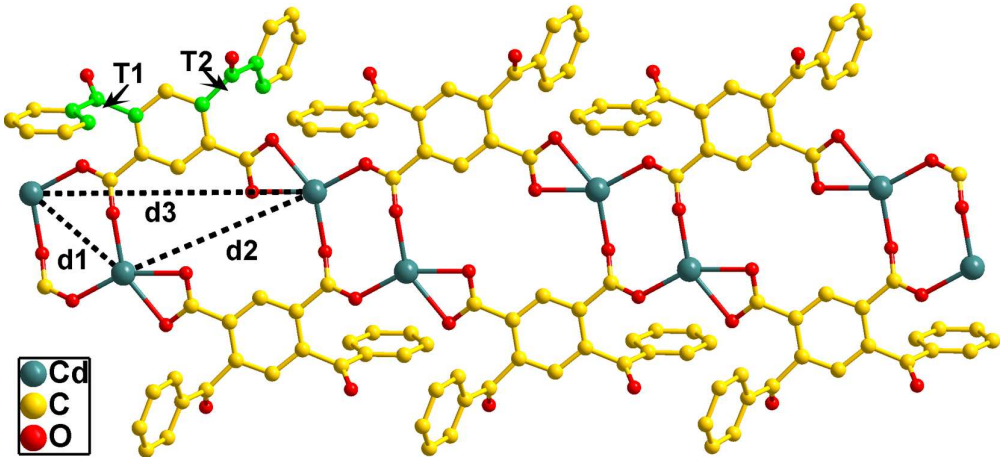

Figure S3 View of the distance and the torsion angels between the selected atoms. As shown in table S1, only slight difference of the 1D $\{Cd(L)\}_n$ chains can be found in the three title compounds. That is, the distances of d_3 gradually increase while the torsion angels of T_1 and T_2 gradually decreases (except for T_2 of compound **2**) as the flexibility of the N-donor ligands reduced from L_1 to L_3.

Table S1 Distances of Cd···Cd and torsion angels of the selected atoms.[a]

	d_1 (Å)	d_2 (Å)	d_3 (Å)	T_1 (°)[b]	T_2 (°)[c]
Compound **1**	4.439	7.329	10.385	26.396(5)	10.654(5)
Compound **2**	4.497	7.563	10.430	25.517(6)	-24.300(7)
Compound **3**	4.454	7.613	10.522	21.013(9)	5.091(9)

[a] d = distance of the selected atoms; T = Torsion angels of the selected atoms.

[b] C3-C8-C9-C14 for **1**, C6-C9-C10-C11 for **2** and C6-C9-C10-C11 for **3**, respectively.

[c] C5-C16-C17-C22 for **1**, C8-C16-C17-C22 for **2** and C8-C16-C17-C18 for **3**, respectively.

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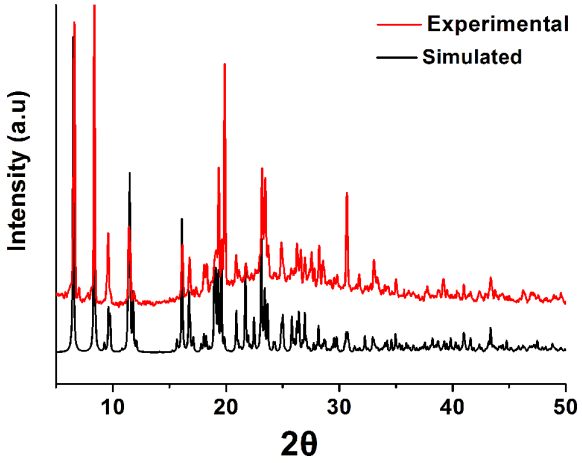

Figure S4 The PXRD patterns of **1**.

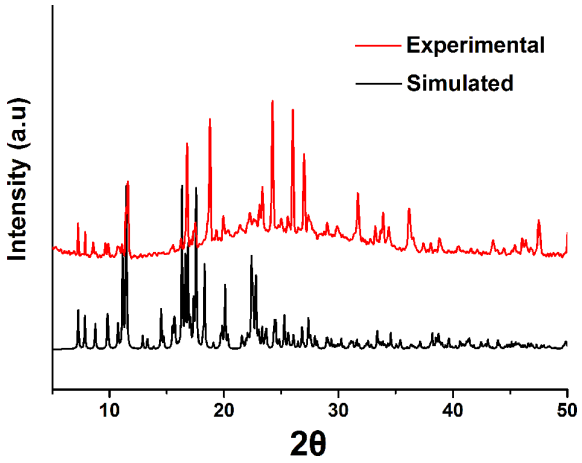

Figure S5 The PXRD patterns of **2**.

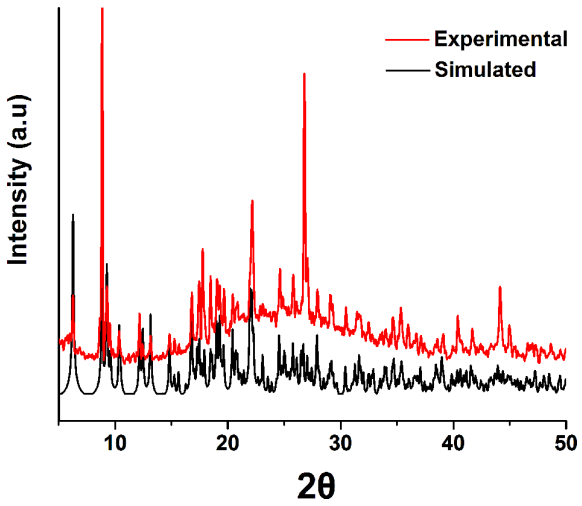

Figure S6 The PXRD patterns of **3**.

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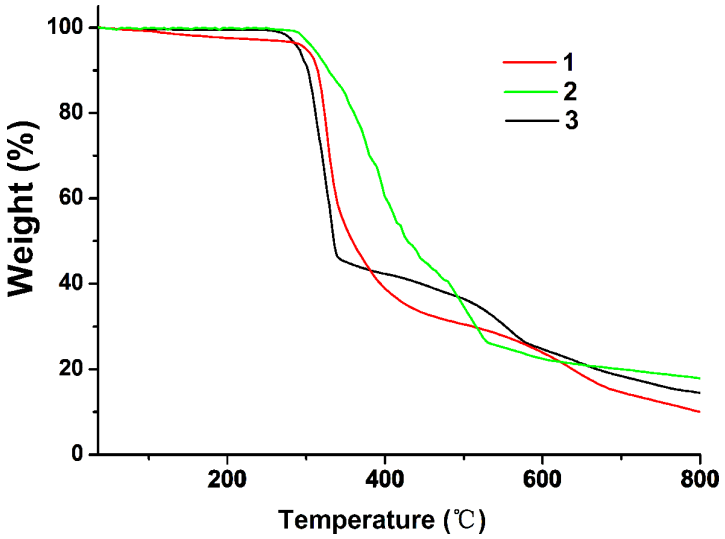

Figure S7 Thermogravimetric analysis curves of **1**-**3**.

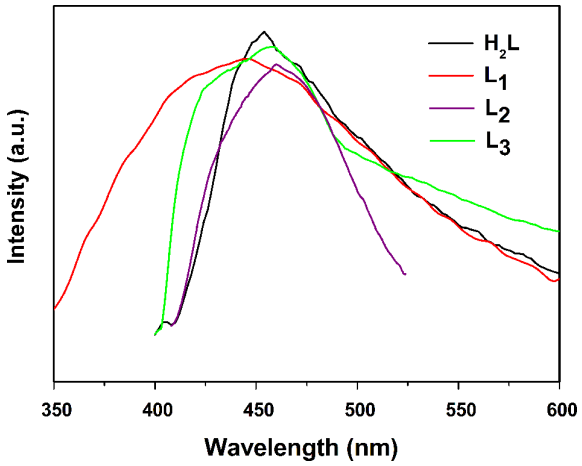

Figure S8 Emission spectra of free ligands.

Table S2 Crystal data and structure refinement parameters for compounds **1**–**3**.

Complex	**1**	**2**	**3**
Formula	$C_{32}H_{28}CdN_6O_6$	$C_{38}H_{32}CdN_4O_6$	$C_{34}H_{24}CdN_6O_6$
Formula weight	705.00	753.08	725.00
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a/Å	10.3849(5)	10.430(5)	15.402(5)
b/Å	11.6302(3)	20.209(8)	10.522(3)
c/Å	13.8223(6)	16.880(7)	20.877(5)
α/°	99.133(3)	90	90.00
β/°	91.357(4)	104.816(7)	114.070(17)
γ/°	112.426(4)	90	90.00

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V/Å^3	1517.11(11)	3440(3)	3089.1(15)
Z	2	4	4
D_c /g cm^{-3}	1.543	1.454	1.559
μ/mm^{-1}	0.775	0.687	0.764
F(000)	716	1536	1464
R_{int}	0.0272	0.0591	0.0678
GOF	1.029	1.183	1.068
R_1, wR_2[a] [$I>2\sigma(I)$]	0.0375, 0.0911	0.0583, 0.1382	0.0596, 0.1498
R_1, wR_2[a] (all data)	0.0439, 0.0954	0.0753, 0.1562	0.0949, 0.1902

[a] $R_1 = \sum||F_0| - |Fc||/\sum|F_0|$. w$R_2 = \sum[w(F_0^2 - Fc^2)^2]/\sum[w(F_0^2)^2]^{1/2}$

Table S3 Selected bond lengths (Å) and Angles (°) of **1-3**. [a]

1			
Cd(1)-O(1)	2.220(2)	Cd(1)-O2#1	2.339(2)
Cd(1)-N(1)	2.285(3)	Cd(1)-O(3)	2.493(2)
Cd(1)-N(4)	2.295(3)	Cd(1)-C(15)	2.727(3)
Cd(1)-O(4)	2.317(2)		
O(1)-Cd(1)-N(1)	109.40(10)	N(4)-Cd(1)-O(2)#1	79.87(10)
O(1)-Cd(1)-N(4)	89.76(10)	O(4)-Cd(1)-O(2)#1	153.07(8)
N(1)-Cd(1)-N(4)	158.79(12)	O(1)-Cd(1)-O(3)	149.57(8)
O(1)-Cd(1)-O(4)	97.72(8)	N(1)-Cd(1)-O(3)	86.03(10)
N(1)-Cd(1)-O(4)	92.18(10)	N(4)-Cd(1)-O(3)	81.32(10)
N(4)-Cd(1)-O(4)	94.20(10)	O(4)-Cd(1)-O(3)	54.46(8)
O(1)-Cd(1)-O(2)#1	108.43(8)	O(2)-Cd(1)-O(3)#1	98.61(8)
N(1)-Cd(1)-O(2)#1	85.31(10)		
2			
Cd(1)-O(4)#1	2.227(3)	Cd(1)-N(1)	2.330(4)
Cd(1)-O(3)#2	2.291(3)	Cd(1)-O(2)	2.400(3)
Cd(1)-N(4)	2.311(4)	Cd(1)-O(1)	2.408(3)
O(3)#2-Cd(1)-O(2)	92.66(11)	N(4)-Cd(1)-O(2)	86.32(13)
O(4)#1-Cd(1)-O(3)#2	112.76(12)	N(1)-Cd(1)-O(2)	87.93(13)
O(4)#1-Cd(1)-N(4)	100.73(13)	O(4)#1-Cd(1)-O(1)	99.38(11)
O(3)#2-Cd(1)-N(4)	87.65(13)	O(3)#2-Cd(1)-O(1)	147.62(12)
O(4)#1-Cd(1)-N(1)	89.10(13)	N(4)-Cd(1)-O(1)	90.21(14)
O(3)#2-Cd(1)-N(1)	81.95(14)	N(1)-Cd(1)-O(1)	95.22(14)
N(4)-Cd(1)-N(1)	167.86(14)	O(2)-Cd(1)-O(1)	54.96(11)
O(4)#1-Cd(1)-O(2)	153.71(11)		
3			
Cd1-O4#1	2.213(4)	Cd1-O3	2.314(4)

View Article Online
DOI: 10.1039/C4RA00246F

Cd1-N1	2.298(5)	Cd1-O1	2.321(4)
Cd1-N5	2.302(5)	Cd1-O2	2.509(4)
O4-Cd1-N1#1	86.47(17)	O3-Cd1-O1	145.91(14)
O4-Cd1-N5#1	105.47(17)	O4-Cd1-O2#1	156.70(13)
N1-Cd1-N5	166.97(19)	N1-Cd1-O2	83.56(16)
O4-Cd1-O3#1	108.26(15)	N5-Cd1-O2	87.08(17)
N1-Cd1-O3	83.19(18)	O3-Cd1-O2	91.42(13)
N5-Cd1-O3	88.02(17)	O1-Cd1-O2	54.55(13)
O4-Cd1-O1#1	105.39(14)	N5-Cd1-O1	88.26(17)
N1-Cd1-O1	93.64(17)		

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1, 1−*x*, 1−*y*, 1−*z*. For **2**: #1, *x* + 1, *y*, *z*; #2, −*x* + 1, −*y* + 1, −*z* + 1. For **3**: #1, 1−*x*, 2−*y*, 1−*z*.

Table S4 Hydrogen-bonding geometry parameters for **1**.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C20–H20···O6	0.93	2.56	3.487(6)	176

Table S5 Hydrogen-bonding geometry parameters for **2**.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C31–H31a···O6	0.97	2.38	3.333(8)	166

Table S6 Hydrogen-bonding geometry parameters for **3**.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C25–H25a···O6	0.97	2.647	3.487(6)	145

References:

[1] (a) G. M. Sheldrick, *SHELXS-97: Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997;
(b) G. M. Sheldrick, *SHELXL-97: Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.