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Eight Zn(II) coordination networks based on flexible 1,4-di(1*H*-imidazol-1-yl)butane and different dicarboxylates: crystal structures, water clusters, and topologies†

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Eight new Zn(II) coordination polymers based on flexible 1,4-di(1*H*-imidazol-1-yl)butane and different dicarboxylates, [Zn(dimb)(suc)·2DMF]_n (**1**), [Zn(dimb)(mbda)·3H₂O]_n (**2**), [Zn(dimb)(adip)·DMF·2H₂O]_n (**3**), [Zn(dimb)(pma)·2.5H₂O]_n (**4**), [Zn₂(dimb)(tha)₂(H₂O)]_n (**5**), [Zn(dimb)(chda)·2H₂O]_n (**6**), [Zn(dimb)(obda)·DMF]_n (**7**), [Zn(dimb)(tdga)·CH₃OH]_n (**8**) (dimb = 1,4-di(1*H*-imidazol-1-yl)butane, H₂suc = succinic acid, H₂mbda = *m*-benzenediacetic acid, H₂adip = adipic acid, H₂pma = pimelic acid, H₂tha = thiophene-2,5-dicarboxylic acid, H₂chda = 1,4-cyclohexanedicarboxylic acid, H₂obda = *o*-benzenediacetic acid, H₂tdga = thiodiglycolic acid; DMF = *N,N'*-dimethylformamide), have been synthesized and structurally characterized by single-crystal X-ray diffraction analyses, and further characterized by infrared spectra (IR), elemental analyses, powder X-ray diffractions (PXRD) and thermogravimetric analyses (TGA). Single-crystal X-ray diffraction analysis reveals that **1**, **2**, **4**, **7** and **8** are 2D wavy 4⁴-sqI networks with different dimensions of quadrilateral window units, depending on the conformation and length of dimb and dicarboxylates. Complex **3** is a 2D a 6³-hcb network incorporating a [Zn₂(dimb)₂] cyclic subunit. In complex **5**, Zn(II) centers as 3-connected node are linked by dimb and tha to form a 3D 8-fold interpenetrating ThSi₂ network. Complex **6** is a 4-connected noninterpenetrating cds network. Interestingly, an infinite T4(2)6 (2) water tape and a D_{2h} cyclic water tetramer are also found in complexes **2** and **3**, respectively. In **1–8**, all Zn(II) centers are located in a four-coordinated environment, and dimb and dicarboxylates are 2-connected linkers, but networks with diverse topologies are built, which indicates the linkage of central metal ion, the conformation of dimb and dicarboxylate have important influences on the resulting structures. Furthermore, the solid-state photoluminescence properties of the **1–8** were investigated at 298 and 77 K.

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Introduction

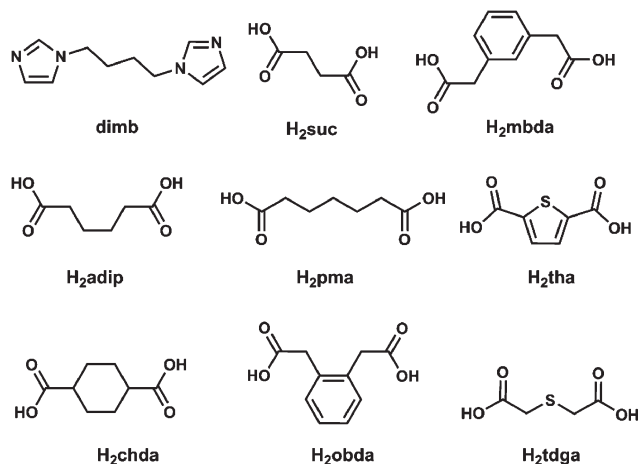
Recently, coordination polymers (CPs) have attracted considerable attention because of their aesthetic appeal of molecular connectivities and topologies as well as potential applications as functional materials in luminescence, magnetism, sensors, gas adsorption, ion exchange and catalysis.^{1,2} Despite the impressive progress, it is still difficult to design and predict a

new CP structure, especially that based on flexible ligands, with a specific net topology.³ In general, the assembly of CPs depends on several factors, such as coordination geometry of the central metal and the nature of organic ligand, solvent, temperature, concentration and ratio of reactants, reaction time, and pH, and so on.⁴ In contrast to the widely studied rigid and aromatic ligands, flexible ligands have not been well investigated. To achieve the flexibility, ligands built from multiple functional groups linked by aliphatic chains have been widely investigated. For example, the flexible ligand 1,3-bis(4-pyridyl)propane⁵ can adopt different conformations such as *anti-anti*, *gauche-anti*, and two kinds of *gauche-gauche* forms, which may thus result in diverse fascinating networks with novel topologies or entanglements.

In terms of crystal engineering, an effective route for the synthesis of novel CPs with attractive topological structures is employment of mixed ligands.⁶ Mixed N- and O-donor ligands

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†Electronic supplementary information (ESI) available: Powder X-ray diffraction (PXRD) patterns for **1–8**, solid-state photoluminescent spectra for **1–8**, structural graphics for **2**, **4**, **7** and **8**, additional tables. CCDC reference numbers 932564–932571. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51114f



Scheme 1 Structures of dimb and dicarboxylate ligands used in this work.

have been selected as the best combination in the crystal engineering field.⁷ Inspired by this strategy, a great number of CPs have been reported by the utilization of pyridyl or imidazolyl based bridging ligands and aliphatic or aromatic polycarboxylic acids.⁸ Among the flexible N-donor bridging ligands, the 1,4-di(1*H*-imidazol-1-yl)butane (dimb) ligand with a long alkyl (–CH₂)₄ spacer allows it to bend and rotate freely so as to satisfy the demand of coordination environments of metal ions in the assembly process to produce favored arrangements with beautiful architectures and useful functional properties.⁹

Taking inspiration from the aforementioned points and our previous work,¹⁰ we successfully applied a mixed ligand strategy (Scheme 1) and obtained eight new CPs, namely, [Zn(dimb)(suc)·2DMF]_{*n*} (**1**), [Zn(dimb)(mbda)·3H₂O]_{*n*} (**2**), [Zn(dimb)(adip)·DMF·2H₂O]_{*n*} (**3**), [Zn(dimb)(pma)·2.5H₂O]_{*n*} (**4**), [Zn₂(dimb)(tha)₂(H₂O)]_{*n*} (**5**), [Zn(dimb)(chda)·2H₂O]_{*n*} (**6**), [Zn(dimb)(obda)·DMF]_{*n*} (**7**), [Zn(dimb)(tdga)·CH₃OH]_{*n*} (**8**) (dimb = 1,4-di(1*H*-imidazol-1-yl)butane, H₂suc = succinic acid, H₂mbda = *m*-benzenediacetic acid, H₂adip = adipic acid, H₂pma = pimelic acid, H₂tha = thiophene-2,5-dicarboxylic acid, H₂chda = 1,4-cyclohexanedicarboxylic acid, H₂obda = *o*-benzenediacetic acid, H₂tdga = thiodiglycolic acid; DMF = *N,N'*-dimethylformamide). These CPs vary their structures from 2D 4⁴-sqf and 6³-hcb networks to 3D 8-fold interpenetrating ThSi₂ network and non-interpenetrating cds network. Their syntheses, crystal structures, topologies, thermal stabilities and photoluminescent properties are reported in this paper.

Experimental section

Materials and general methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. C, N and H analyses were performed on an EA1110 CHNS-O CE 65 elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence

Spectrophotometer equipped with a Dewar flask with a Suprasil quartz cold finger. Powder-XRD measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-Kα radiation. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{−1}.

Preparation of complexes 1–8

[Zn(dimb)(suc)·2DMF]_{*n*} (**1**). A mixture of Zn(NO₃)₂·6H₂O (29.7 mg, 0.10 mmol), dimb (19.0 mg, 0.10 mmol) and H₂suc (11.8 mg, 0.10 mmol) in DMF–CH₃OH–H₂O (6.0 mL, v : v : v = 2 : 1 : 1) was treated by ultrasound (160 W, 40 kHz, 50 °C). The resultant solution was allowed to evaporate slowly at room temperature for several days to afford the product as crystals of **1**. The pale-yellow crystals were collected and washed with EtOH and dried in the air (yield: 62%). Elemental analysis: calc. (%) for **1** (C₁₀H₁₆N₃O₃Zn_{0.5}): C 46.38, H 6.23, N 16.23; found: C 46.18, H 6.36, N 16.45. Selected IR peaks (cm^{−1}): 3438 (s), 1612 (s), 1561 (s), 1492 (s), 1396 (m), 1350 (m), 765 (m), 633 (m).

[Zn(dimb)(mbda)·3H₂O]_{*n*} (**2**). The synthesis of **2** was similar to that of **1**, but using H₂mbda (19.4 mg, 0.10 mmol) instead of H₂suc. Ammonia (25%, 15 drops) was added to dissolve the mixture. The yellow crystals were collected and washed with EtOH and dried in the air (yield: 69%). Elemental analysis: calc. (%) for **2** (C₂₀H₂₈N₄O₇Zn): C 47.87, H 5.62, N 11.16; found: C 47.21, H 5.85, N 11.45. Selected IR peaks (cm^{−1}): 3441 (s), 1632 (s), 1566 (s), 1500 (s), 1387 (m), 1357 (m), 766 (m), 639 (m).

[Zn(dimb)(adip)·DMF·2H₂O]_{*n*} (**3**). The synthesis of complex **3** was similar to that of **1** but using H₂adip (14.6 mg, 0.10 mmol) instead of H₂suc. Pale-yellow crystals of **3** were collected and washed with EtOH and dried in the air (yield: 61%). Elemental analysis: calc. (%) for **3** (C₁₉H₃₃N₃O₇Zn): C 44.84, H 6.54, N 13.72; found: C 44.99, H 6.64, N 13.41. Selected IR peaks (cm^{−1}): 3399 (s), 1621 (s), 1588 (s), 1502 (s), 1392 (m), 1357 (m), 806 (m), 680 (m).

[Zn(dimb)(pma)·2.5H₂O]_{*n*} (**4**). The synthesis of complex **4** was similar to that of **1** but using H₂pma (16.0 mg, 0.10 mmol) instead of H₂suc. Ammonia (25%, 15 drops) was added to dissolve the mixture. Pale-yellow crystals of **4** were collected and washed with EtOH and dried in the air (yield: 55%). Elemental analysis: calc. (%) for **4** (C₁₇H₂₉N₄O_{6.5}Zn): C 44.50, H 6.37, N 12.21; found: C 44.25, H 6.23, N 12.17. Selected IR peaks (cm^{−1}): 3455 (s), 1630 (s), 1545 (s), 1501 (s), 1381 (m), 1355 (m), 780 (m), 662 (m).

[Zn₂(dimb)(tha)₂(H₂O)]_{*n*} (**5**). A mixture of Zn(NO₃)₂·6H₂O (29.7 mg, 0.10 mmol), dimb (9.5 mg, 0.05 mmol), H₂tha (8.6 mg, 0.05 mmol) and 1.0 mL DMF–CH₃OH–H₂O (v : v : v = 2 : 1 : 1) was sealed in a glass tube and heated to 130 °C for 10 h, kept 130 °C for 50 h then slowly cooled to 30 °C for 15 h. Yellow crystals of **5** were collected and washed with EtOH and dried in the air (yield: 75%). Elemental analysis: calc. (%) for **5** (C₄₄H₄₄N₈O₂₀S₄Zn₄): C 37.89, H 3.18, N 8.03; found: C 37.64,

H 3.25, N 8.47. Selected IR peaks (cm^{-1}): 3405 (s), 1655 (s), 1582 (s), 1487 (s), 1388 (m), 1354 (m), 761 (m), 655 (m).

[Zn(dimb)(chda)·2H₂O]_n (6). Synthesis of complex **6** was similar to that of **5** but using H₂chda (8.6 mg, 0.050 mmol) instead of H₂tha. Pale-yellow crystals of **6** were collected and washed with EtOH and dried in the air (yield: 74%). Elemental analysis: calc. (%) for **6** (C₃₆H₅₆N₈O₁₂Zn₂): C 46.81, H 6.11, N 12.13; found: C 46.92, H 6.68, N 12.59. Selected IR peaks (cm^{-1}): 3456 (s), 1622 (s), 1588 (s), 1499 (s), 1385 (m), 1353 (m), 762 (m), 652 (m).

[Zn(dimb)(obda)·DMF]_n (7). The synthesis of complex **7** was similar to that of **1** but using H₂obda (19.4 mg, 0.10 mmol) instead of H₂suc. Ammonia (25%, 23 drops) was added to dissolve the mixture. Yellow crystals of **7** were collected and washed with EtOH and dried in the air (yield: 53%). Elemental analysis: calc. (%) for **7** (C₂₃H₂₉N₅O₅Zn): C 53.03, H 5.61, N 13.44; found: C 53.23, H 5.66, N 13.82. Selected IR peaks (cm^{-1}): 3440 (s), 1617 (s), 1565 (s), 1491 (s), 1389 (m), 1355 (m), 746 (m), 652 (m).

[Zn(dimb)(tdga)·CH₃OH]_n (8). Synthesis of complex **8** was similar to that of **1** but using H₂tdga (15.0 mg, 0.10 mmol) instead of H₂suc. Ammonia (25%, 6 drops) was added to dissolve the mixture. The yellow crystals were collected and washed with EtOH and dried in the air (yield: 64%). Elemental analysis: calc. (%) for **8** (C₁₅H₂₂N₄O₅SZn): C 41.34, H 5.09, N 12.86; found: C 41.79, H 5.21, N 12.58. Selected IR peaks (cm^{-1}): 3440 (s), 1615 (s), 1573 (s), 1499 (s), 1393 (m), 1351 (m), 762 (m), 657 (m).

X-Ray crystallography

Single crystals of the complexes **1–8** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with a graphite-monochromated Mo-K α radiation source ($\lambda = 0.71073$ Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. For **1–8**, data were measured using ω scans of 0.5° per frame for 5 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.¹¹ Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.¹¹ In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97¹² and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.¹³ Atoms were located from iterative examination of difference F -maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON¹⁴ to assure that

no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table 1. Selected bond lengths and angles are collated in Table S1, ESI.† Topological analysis of coordination networks in all complexes was performed with the program package TOPOS.¹⁵

Results and discussion

Structure descriptions. [Zn(dimb)(suc)·2DMF]_n (**1**), [Zn(dimb)(mbda)·3H₂O]_n (**2**), [Zn(dimb)(pma)·2.5H₂O]_n (**4**), [Zn(dimb)(obda)·DMF]_n (**7**) and [Zn(dimb)(tdga)·CH₃OH]_n (**8**)

Complexes **1**, **2**, **4**, **7** and **8** have similar 2D wavy nets. In them, all Zn(II) atoms are located in tetrahedral four-coordinated environments, and both dimb and different dicarboxylates are uniformly 2-connected linkers, so that 4⁴-sql nets were obtained. Herein, we only describe the structure of **1** and the interesting infinite T4(2)6(2) water tape in **2** in detail. The structural graphics for the other four structures are shown in ESI.†

X-Ray single-crystal diffraction analysis reveals that **1** is a 2D 4⁴-sql net. It crystallizes in the monoclinic crystal system with space group of $C2/c$. The asymmetric unit contains one Zn(II) ion passed by one C_2 axis, half of one dimb ligand, half of one suc dianion and one lattice DMF molecule. A C_2 axis also passes the midpoint of C5–C5 of a dimb ligand, whereas the suc dianion is disordered, imposed by a crystallographic inversion center. As shown in Fig. 1a, the Zn1 atom is in a ZnN₂O₂ tetrahedral geometry (Zn1–N1 = 2.0012(17) and Zn1–O2A = 1.849(9) Å). The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser¹⁶ to describe the geometry of a four-coordinate metal system, which is 0.87 for Zn1 (for an ideal tetrahedron $\tau_4 = 1$). Both Zn–N and Zn–O bond lengths are well-matched to those observed in similar complexes.¹⁷ The dimb ligand adopts an *anti-gauche-anti* conformation¹⁸ with torsion angles along the C chain of 175.2(2), –87.4(3) and 175.2(2)°. The suc shows a perfect *anti* conformation due to the torsion angle of 180°, imposed by an inversion center. The dimb and suc ligands adopt a bidentate bridging mode to extend the Zn(II) atoms to the resulting 2D 4⁴-sql network (Fig. 1b), in which the quadrilateral window has a dimension of 9.15 × 13.45 Å. Although this 2D sheet has large windows and also exhibits an undulating character with a thickness of about 3.94 Å, interpenetration between adjacent sheets is not observed, which may be due to the occupancy of a pair of opposite arranged DMF molecules in each window. The adjacent 2D sheets are packed into the resulting 3D supramolecular framework by non-classical C–H...O hydrogen bonds ranging from 3.074(8) to 3.325(8) Å.

For **2**, the solvent accessible voids are occupied by free water molecules, which are associated by O–H...O hydrogen bonds, leading to a 1D infinite staircase-like water tape (Fig. 2). This water tape can be seen as the combination of chair-like cyclic hexamer (O1W...O2W...O3W...O1Wⁱⁱⁱ...O2Wⁱⁱⁱ...O3Wⁱⁱⁱ) and *uudd* tetramer (O1W...O3Wⁱⁱⁱ...O1W^v...O3Wⁱⁱ)

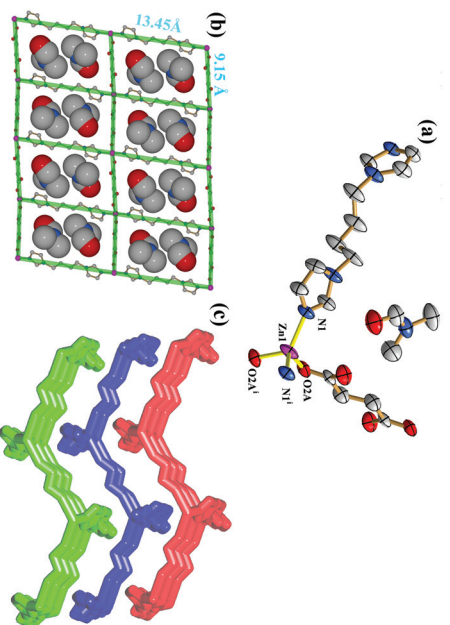


Fig. 1 (a) The coordination environment of Zn(II) ion in **1** with thermal ellipsoids at 50% probability level (symmetry code: (i) $-x + 1, y, -z + 3/2$). (b) Ball-and-stick view of the 2D 4⁴-sqi net (purple; Zn: blue; N: red; O: gray; C: gray). (c) The packing of 2D nets in the crystal (networks individually colored).

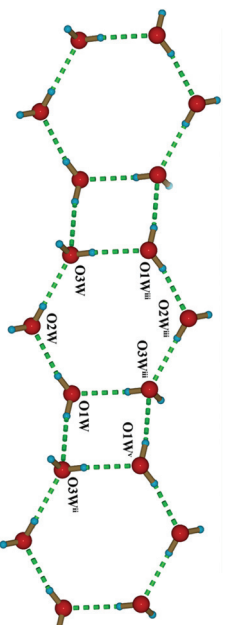


Fig. 2 The 1D T4(2)6(2) water tape in the void of **2** (symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $x - 1, y + 1, z$).

Table 2 Hydrogen bond geometries for **2** and **3**

D-H...A	D-H	H...A	D...A	D-H...A
Complex 2				
O1W-H1WA...O2W	0.85	2.00	2.837 (4)	166.9
O1W-H1WB...O3W ⁱⁱ	0.85	2.14	2.980 (4)	169.1
O2W-H2WA...O3W	0.85	2.00	2.807 (4)	157.1
O2W-H2WB...O2	0.85	2.28	3.001 (3)	143.4
O3W-H3WA...O1W ⁱⁱⁱ	0.85	2.00	2.826 (4)	165.3
O3W-H3WB...O3 ^{iv}	0.85	1.91	2.735 (3)	164.4
Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 1, -y + 1, -z$; (iv) $x - 1, y + 1, z$.				
Complex 3				
O1W-H1WA...O2	0.85	2.00	2.803 (3)	157.9
O1W-H1WB...O4 ⁱⁱ	0.85	1.91	2.747 (4)	166.0
O2W-H2WA...O1W	0.85	2.06	2.902 (4)	169.9
O2W-H2WB...O1W ⁱⁱⁱ	0.85	2.10	2.928 (4)	164.1
Symmetry codes: (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$.				

Table 1 Crystal data for **1–10**

Complex	1	2	3	4	5	6	7	8
Empirical formula	C ₁₀ H ₁₆ N ₃ O ₃ Zn _{0.5}	C ₂₀ H ₂₈ N ₄ O ₇ Zn	C ₁₉ H ₃₃ N ₅ O ₇ Zn	C ₁₇ H ₂₉ N ₄ O _{6.5} Zn	C ₁₁ H ₁₁ N ₂ O ₅ SZn	C ₁₈ H ₂₈ N ₄ O ₆ Zn	C ₂₀ H ₂₂ N ₄ O ₄ Zn	C ₁₄ H ₁₈ N ₄ O ₄ SZn
<i>M</i> _r	258.94	501.83	508.87	458.81	348.68	461.81	447.79	403.75
<i>T</i> /K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> /Å	13.453(2)	7.3767(12)	9.1919(12)	8.2532(11)	11.664(5)	9.8348(10)	7.984(2)	35.840(3)
<i>b</i> /Å	11.1544(17)	9.6740(16)	11.4363(14)	9.6073(12)	11.683(5)	15.2564(17)	8.729(2)	9.0465(8)
<i>c</i> /Å	16.508(3)	16.395(3)	13.0821(16)	14.1941(19)	19.847(8)	13.8403(15)	16.898(4)	12.2671(11)
α /°	90.00	86.541(3)	66.308(2)	96.513(2)	90.00	90.00	93.577(4)	90.00
β /°	99.666(3)	84.230(3)	78.744(2)	96.661(2)	90.00	95.714(2)	95.508(5)	90.468(2)
γ /°	90.00	83.400(3)	80.613(2)	104.406(2)	90.00	90.00	103.030(4)	90.00
<i>V</i> /Å ³	2442.1(7)	1154.9(3)	1229.6(3)	1070.8(2)	2704.7(19)	2066.3(4)	1137.7(5)	3977.2(6)
<i>Z</i>	8	2	2	2	8	4	2	8
<i>D</i> _c /mg mm ^{−3}	1.409	1.443	1.374	1.423	1.712	1.484	1.307	1.349
μ /mm ^{−1}	1.052	1.111	1.045	1.188	1.990	1.231	1.110	1.362
Reflections collected	5901	5771	6026	5363	10 054	9921	5658	9304
Independent reflections	2140 [<i>R</i> (int) = 0.0225]	4034 [<i>R</i> (int) = 0.0202]	4255 [<i>R</i> (int) = 0.0275]	3724 [<i>R</i> (int) = 0.0219]	2373 [<i>R</i> (int) = 0.0440]	3630 [<i>R</i> (int) = 0.0609]	3972 [<i>R</i> (int) = 0.0332]	3496 [<i>R</i> (int) = 0.1032]
Goodness-of-fit on <i>F</i> ²	1.026	1.043	1.029	1.039	1.039	1.026	0.946	1.158
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0797	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0847	<i>R</i> ₁ = 0.0424, <i>wR</i> ₂ = 0.0972	<i>R</i> ₁ = 0.0433, <i>wR</i> ₂ = 0.0961	<i>R</i> ₁ = 0.0368, <i>wR</i> ₂ = 0.1083	<i>R</i> ₁ = 0.0599, <i>wR</i> ₂ = 0.1608	<i>R</i> ₁ = 0.0468, <i>wR</i> ₂ = 0.1047	<i>R</i> ₁ = 0.0776, <i>wR</i> ₂ = 0.2323
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0407, <i>wR</i> ₂ = 0.0865	<i>R</i> ₁ = 0.0381, <i>wR</i> ₂ = 0.0879	<i>R</i> ₁ = 0.0561, <i>wR</i> ₂ = 0.1048	<i>R</i> ₁ = 0.0602, <i>wR</i> ₂ = 0.1055	<i>R</i> ₁ = 0.0500, <i>wR</i> ₂ = 0.1196	<i>R</i> ₁ = 0.0933, <i>wR</i> ₂ = 0.1840	<i>R</i> ₁ = 0.0659, <i>wR</i> ₂ = 0.1113	<i>R</i> ₁ = 0.1018, <i>wR</i> ₂ = 0.2452

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

by sharing two water molecules (O1W and O3Wⁱⁱⁱ), which can be defined as a T4(2)6(2) water tape.¹⁹ The geometric parameters of the water tape are summarized in Table 2. The O_{water}...O_{water} distances range from 2.826(4) to 2.980(4) Å, and

the average distance is 2.863(4) Å, which are all close to the distance of O...O in ice I_c (2.75 Å) and I_h (2.759 Å) determined at -130 and -90 °C.²⁰ Within the water tape, O1W acts as a double hydrogen bond donor and single hydrogen bond acceptor, O2W acts as single hydrogen bond donor and single hydrogen bond acceptor, while O3W act as acts as a single hydrogen bond donor and double hydrogen bond acceptor. The water tape connects with the host framework with hydrogen-bond interactions of O2W...O2, and O3W...O3^{iv}, and penetrates the windows of 2D network (Fig. S1, ESI†). Up to now, only limited T4(2)6(2) motifs have been reported in the literature,²¹ and Mascari *et al.* also enumerated some occurrence of T4(2)6(2) water tapes according to the search in Cambridge Structural Database (CSD).^{19c}

The coordination networks of complexes 2, 4, 7 and 8 are depicted in Fig. S2–S5, ESI†. They possess similar 4⁴-sqI nets but with different window size and fold amplitude depending on the conformation and linkage orientation of dimb and different dicarboxylate ligands.

[Zn(dimb)(adip)·DMF·2H₂O]_n (3)

Complex 3 is a 2D 6³-hcb network incorporating [Zn₂(dimb)₂] cyclic subunits. The asymmetric unit of 3 consists of one Zn(II) ion, one dimb, two adip dianions lying on the inversion center, one DMF and two water molecules. As depicted in Fig. 3a, Zn1 is four-coordinated by two nitrogen atoms from two dimb ligands and two oxygen atoms from two adip anions in a distorted tetrahedral coordination environment ($\tau_4 = 0.86$). Three torsion angles for dimb are 175.7(3), 169.5(3) and 61.4(4)°, which defines an *anti-anti-gauche* conformation, while the conformation of adip is *anti-anti-anti* (175.4(3), 180, 175.4(3)°). A pair of centrosymmetric dimb ligands bind two Zn(II) ions to form a 22-membered ring, which is extended by the adip ligand to generate a 2D honeycomb-like sheet with a dimension of 24.75 × 21.94 Å (Fig. 3b). Each hexagon has four edges represented by the adip ligands and two edges replaced by Zn₂(dimb)₂ loops. That is to say, each Zn atom is connected to three others by two single μ_2 -adip bridges and one pair of dimb ligands. In this analysis, this 2D sheet could be

simplified to a 3-connected net with 6³-hcb topology in which the loops become 2-connected linkers.

In the hydrophilic pores of the 2D network in 3, a rare D_{2h} water tetramer is observed. Each water molecule in the D_{2h} water tetramer is in a tetrahedral environment and it is involved in the formation of four hydrogen bonds, two are O2W...O1W and O2W...O1Wⁱⁱⁱ and the other two are O1W...O2 and O1W...O4ⁱⁱ (Fig. 3c). Geometrical parameters of the water cluster are listed in Table 2. The average hydrogen bond distance within the water tetramer in this case is 2.915(4) Å. O1W and O2W act as double hydrogen bond acceptor and donor, respectively, as a result, the hydrogen bond motif for this tetramer is $R_4^2(8)$, according to graphset analysis nomenclature.²² The hydrogen atoms of O1W are 0.72(2) and 0.69(2) Å above and below the ring, respectively. Such an arrangement results in a D_{2h} symmetry.²³ As a simple two-structure model for liquid water,²⁴ the cyclic water tetramer is of particular interest. Although theoretical studies on the basis of *ab initio* electronic structure calculations have predicted several configurations of cyclic water tetramers, such as *udud*, *uudd*, *uuud*, C_4 and C_s ,²⁵ and some of them have been characterized by far-infrared vibration-rotation tunneling spectroscopy²⁶ or found in different crystal hosts,²⁷ crystallographic observation and analysis of a D_{2h} cyclic water tetramer is very sparse. The formation of the less stable D_{2h} water tetramer in 3 indicates that the cooperative association of the water clusters and crystal host plays an important role in stabilizing the water cluster (symmetry codes: (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$).

[Zn₂(dimb)(tha)₂(H₂O)]_n (5)

The single-crystal diffraction analysis indicates that complex 5 crystallized in an orthorhombic manner with space group *Pbcn*. There is one Zn(II) ion, one dimb ligand, one tha dianion, and one coordination water molecule in an asymmetric unit of 5. The coordination environment around the Zn(II) atom is shown in Fig. 4a. The Zn1 is four-coordinated by two N atoms from two different dimb, and two O atoms from one tha and one water molecule, respectively. The τ_4 parameter is 0.83 for

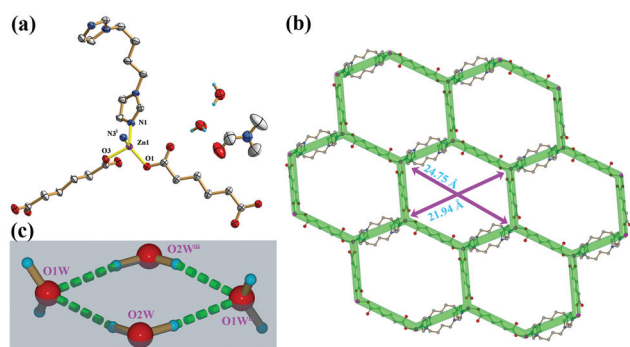


Fig. 3 (a) The coordination environment of Zn(II) ion in 3 with thermal ellipsoids at 50% probability level (symmetry code: (i) $-x + 2, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$). (b) Ball-and-stick view of the 2D 6³-hcb net (purple: Zn; blue: N; red: O; gray: C). (c) The D_{2h} water tetramer in 3.

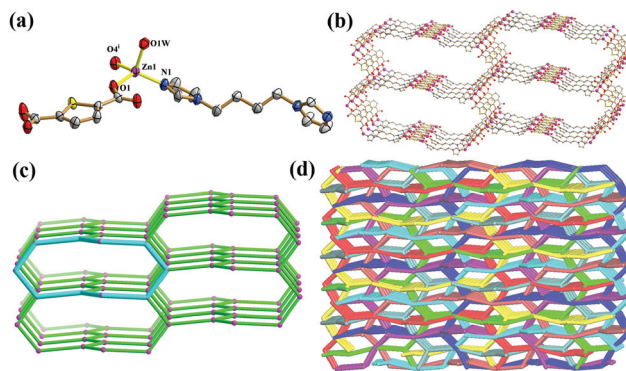


Fig. 4 (a) The coordination environment of Zn(II) ion in 5 with thermal ellipsoids at 50% probability level (symmetry code: (i) $x - 1, y - 1, z$). (b) Ball-and-stick view of single 3D network (purple: Zn; blue: N; red: O; gray: C). (c) Simplified single ThSi₂ network. (d) View of simplified 8-fold interpenetrated ThSi₂ network (networks individually colored).

Zn1. The dimb and tha adopt *anti-anti-anti* and planar conformations, respectively, to extend Zn(II) atom into a complicated 3D network (Fig. 4b).

Better insight of the complicated 3D architecture can be achieved by topology analysis. Due to the coordination of the water molecule, the four-coordinated Zn(II) atom just acts as a 3-connected node and both ligands are 2-connected linkers, then, each node has three angles and each of the angles forms part of a 10-membered shortest circuit and hence the 3D network has the Wells point symbol/Schläfli symbol of 10^3 .²⁸ So this 3D net could be simplified to a 3-connected uninodal net of **ThSi₂** topology (Fig. 4c) with the vertex symbol of $\{10_2 \cdot 10_4 \cdot 10_4\}$. To explain the vertex symbol further, in the **ThSi₂** network, one angle is associated with two 10-membered fundamental rings and the other two angles are associated with four 10-membered fundamental rings. The single 3D network consists of large rectangular windows, which are filled *via* mutual interpenetration of eight independent equivalent networks, generating a 8-fold interpenetrated 3D network (Fig. 4d). According to the interpenetration classification,²⁹ complex 5 belongs to rare Class IIIa interpenetration, that is, the overall interpenetration is generated both by pure translations and by space group symmetry elements. In detail, the translationally related four **ThSi₂** nets are observed showing the only one translational interpenetrating vector of [001] (the crystallographic *c* axis), then, the presence of a non-translational interpenetrating symmetry element (inversion center) generates the overall 8-fold interpenetration. As we know, the 2-, 3-, 4-, 6- and highest 9-fold interpenetrated **ThSi₂** nets have been documented in the literature,³⁰ however, 8-fold interpenetrated **ThSi₂** nets, especially the Class IIIa interpenetrated **ThSi₂** net, has rarely been observed.

[Zn(dimb)(chda)·2H₂O]_n (6)

Complex 6 is a 4-connected non-interpenetrating **cds** 3D network. Structural analysis indicates that complex 6 crystallizes in the monoclinic crystal system with space group of *P*₂₁/*n*. The asymmetric unit of 6 consists of one crystallographically independent Zn(II) atom, two half dimb ligands lying on an inversion center, one chda dianion and two lattice water molecules. The coordination environment around the Zn(II) atom is shown in Fig. 5a. Zn1 is in a slightly ZnN₂O₂ tetrahedral geometry with τ_4 of 0.91. Two crystallographically unique dimb adopt similar *gauche-anti-gauche* conformations with two sets of three torsion angles of 59.3(8), 180, 59.3(8) and 62.3(8), 180, 62.3(8)°, respectively, whereas chda shows a *e,a-cis* conformation.³¹ The dimb and chda extend the Zn(II) atom into a 3D network (Fig. 5b).

From the view of topology, by treating the Zn(II) atom as a single node and connecting the nodes according to the connectivity defined by dimb and chda ligands, a $\{6^5 \cdot 8\}$ 3D network supported by 4-coordinated nodes is then obtained as illustrated in Fig. 5c. Although there is only one type of node in this net, there are two types of linkers identified by three different node...node distances (8.894, 12.356 and 12.431 Å). The two different linkers and the flexibility of ligands make

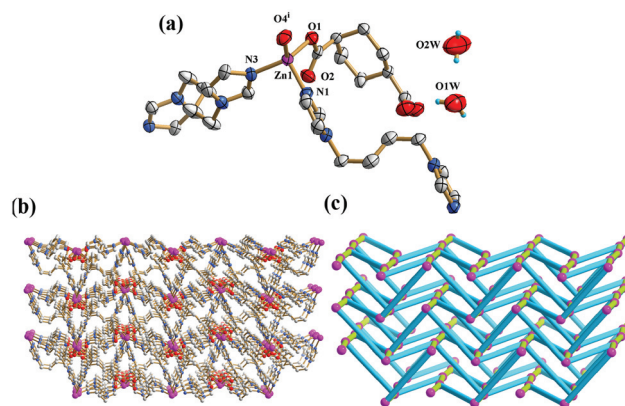
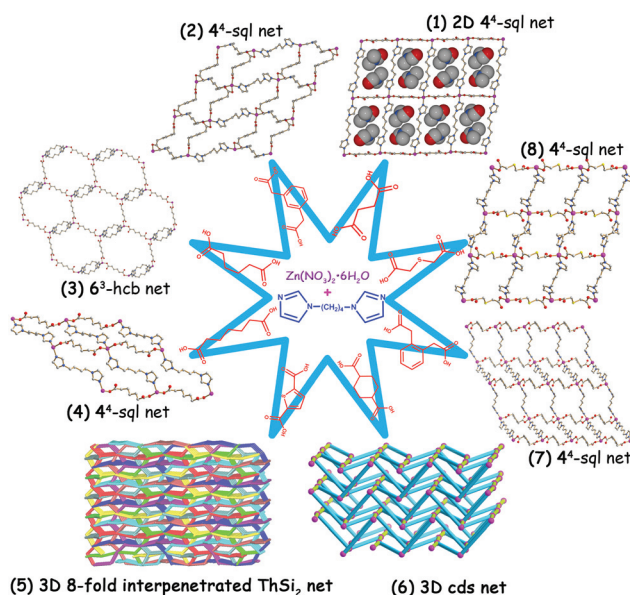


Fig. 5 (a) The coordination environment of Zn(II) ion in 6 with the thermal ellipsoids at 50% probability level (symmetry code: (i) $x + 1/2$, $-y + 1/2$, $z - 1/2$). (b) Ball-and-stick view of 3D network (purple: Zn; blue: N; red: O; gray: C). (c) Topological representation of **cds** network (purple ball: Zn; cyan stick: dimb; green stick: chda).

the 4-coordinated node distorted from square-planarity, causing a distorted **cds** network.³²

Comparison of CPs 1–8 and the factors influencing the network

In CPs 1–8, flexible dimb has been used as the main ligand, eight different dicarboxylates were used as the auxiliary ligands and Zn(II) was the central ion, aiming at exploring the influence of dicarboxylate on the assembly and structure of target CPs (Scheme 2). From the structure description above, we can see that all Zn(II) atoms in 1–8 are located in a tetrahedral four-coordinated environment, and both dimb and different dicarboxylates are uniformly 2-connected linkers, so the resulting CPs intuitively should be 4-connected networks based on a topological viewpoint. However, two exceptions



Scheme 2 Synthesis procedure for 1–8.

(3 and 5) occurred in this series of CPs. Although Zn(II) atoms are four-coordinated in 3 and 5, they are 3-connected nodes because of the existence of $\text{Zn}_2(\text{dimb})_2$ loops and terminal co-ordinated water molecule; as a result, 3-connected 2D 6^3-hcb and 3D 8-fold interpenetrated 10^3-ThSi_2 networks were obtained for 3 and 5, respectively. Excluding 3 and 5, what is interesting is that the basic coordination environment of the Zn(II) atoms, basically two coordinating imidazoles and two carboxylates, yields 2D 4^4-sql and 3D noninterpenetrating **cds** networks that are dependent on the conformation and linkage orientation of dimb and different dicarboxylate ligands. Due to the different conformations of dimb and dicarboxylate ligands, the dimensions of windows defined by the length of them in the 4^4-sql networks of 1, 2, 4, 7 and 8 are dramatically different (Table S2, ESI[†]). Differently, the tetrahedral Zn(II) atoms are extended by dimb and chda to form a 4-connected 3D **cds** network of 6, which suggests that the linkage of central metal ion, the conformation and linkage orientation of organic ligands have significant effects on the resultant topology of the networks as well as their dimensions.

PXRD results and thermal analysis

To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments were carried out for 1–8. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in Fig. S6, ESI[†]. They show that the synthesized bulk materials and the measured single crystals are the same.

The TG analysis was performed in N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ on polycrystalline samples of CPs 1–8, and the TG curves are shown in Fig. 6. The TGA curves for 1–8 suggested that their host networks were stable up to 277, 310, 267, 259, 271, 282, 200 and $310\text{ }^\circ\text{C}$, respectively, then they start to gradually lose their ligands as a result of thermal decomposition. The removal of solvent molecules was observed for 1–8 with weight losses of 28.5% (calc. 28.2%), 11.2% (calc. 10.8%), 20.8% (calc. 21.4%) and 8.9% (calc.

9.8%), 6.1% (calc. 5.2%), 7.2% (calc. 7.8%), 17.0% (calc. 16.3%) and 7.1% (calc. 7.9%), respectively.

Photoluminescence properties

The emission spectra of 1–8 were examined in the solid state at 298 and 77 K, shown in Fig. S7 (ESI[†]). The free ligand dimb displays photoluminescence with emission maxima at 398 nm, assigned to $\pi^*\rightarrow\pi$ or $\pi^*\rightarrow n$ transition.³³ To the best of our knowledge, the emission of dicarboxylate belongs to $\pi^*\rightarrow n$ transitions which is very weak compared to that of the $\pi^*\rightarrow\pi$ transition of dimb, so the polycarboxylates almost have no contribution to the fluorescent emission of as-synthesized CPs.³⁴ At 298 K, the emission spectra exhibit maximum emission peaks at 450 nm for 1, 438 nm for 2, 458 nm for 3, 448 nm for 4, 446 nm for 5, 456 nm for 6, 439 nm for 7, and 437 nm for 8, respectively, under excitation at 365 nm. According to the literature, the Zn(II) ion is difficult to oxidize or reduce because of the d^{10} configuration. As a result, the emissions of these CPs are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature.³⁵ Thus, they may be assigned to a mixture characteristic of intraligand and ligand-to-ligand charge transition (LLCT), as reported for other Zn(II) CPs constructed from mixed N-donor and O-donor ligands.³⁶ The difference of the emission behaviors for 1–8 probably derive from the differences in the rigidity of solid-state crystal packing. In exploration of luminescence thermochromic complexes,³⁷ the photoluminescent properties of as-synthesized CPs were also investigated at 77 K. Upon cooling by liquid nitrogen, the emission spectra exhibit maximum emission peaks at 447 nm for 1, 448 nm for 2, 454 nm for 3, 449 nm for 4, 441 nm for 5, 458 nm for 6, 439 nm for 7, and 460 nm for 8, respectively, under excitation at 365 nm. The emission intensities of 1, 2, 5, 7 and 8 were enhanced, whereas the others were diminished at 77 K. Photoluminescence intensity differences among the same samples at different temperature are reliable, because the same powder sample was used for all measurements. The slightly different emission behaviours of 1–8 at different temperatures may arise from the temperature-induced variation of solid-state crystal packing.³⁸

Conclusions

In conclusion, eight new Zn(II) CPs constructed from a bidentate imidazole-based ligand and different dicarboxylates have been successfully obtained by ultrasonic treatment or solvothermal method. Based on four-coordinated metal centers and two-connected linkers, a series of networks ranging from 3-connected 2D 6^3-hcb (3) and 3D 8-fold interpenetrating **ThSi**₂ networks (5) to 2D 4^4-sql (1, 2, 4, 7 and 8) and non-interpenetrating **cds** networks (6), were constructed. Interestingly, an infinite T4(2)6(2) water tape and a D_{2h} cyclic water tetramer are also unmasked in complexes 2 and 3, respectively. The structural analysis indicates that the linkage of metal centers, and conformation of organic ligands have important

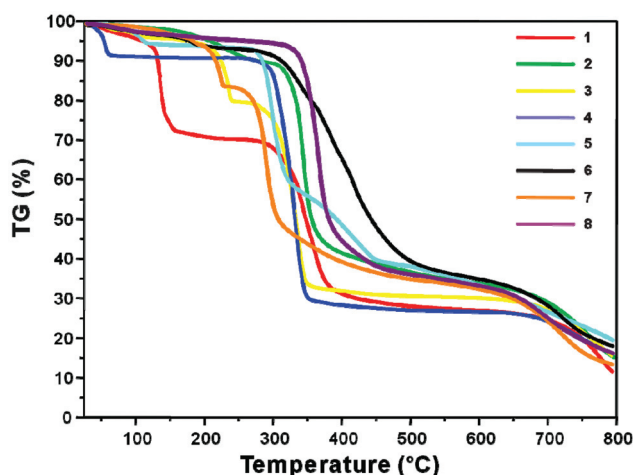


Fig. 6 TGA curves for CPs 1–8.

influences on the resulting network topology. Furthermore, the solid-state photoluminescence properties of the CPs at 298 and 77 K were investigated.

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