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Two novel entangled metal–organic networks constructed from 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl and dicarboxylates: From polycatenated 2D + 2D → 3D framework to polyrotaxane-like 2D + 2D → 2D layer†

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Two novel entangled metal–organic networks, namely [Cd(bmimbp)(bdc)]_n (**1**) and [Zn(bmimbp)(tbtpa)]_n (**2**) (bmimbp = 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl, H₂bdc = 1,3-benzenedicarboxylic acid, H₂tbtpa = tetrabromoterephthalic acid), exhibit a polycatenated 2D + 2D → 3D framework and a polyrotaxane-like 2D + 2D → 2D layer, respectively. Moreover, the thermal stabilities and photoluminescent properties are also discussed.

Recently, mixed ligand assembly strategies incorporating pyridine- or imidazole-based ligands and polycarboxylates have been verified as an effective approach for the construction of coordination networks.^{1,2} Among these, entangled networks have attracted particular attention for crystal engineers not only due to their intrinsic aesthetic appeal and potential properties, but also for their intricate molecular architectures and topologies.³ There have been some comprehensive reviews by Robson, Batten, and Ciani's groups about fascinating entangled structures and their classification.⁴ Interpenetration as an important subgroup of entanglement, has been a long-standing fascination for chemists, and a variety of appealing interpenetrated networks have been constructed.⁵ Moreover, the rapid advance of crystal engineering has led to novel and more intricate types of entanglement being discovered, such as polyrotaxane, polycatenane and polyknotting as well as self-threading.⁶ As important members in the realm of entangled networks, polycatenated and polyrotaxane-like networks have special structural features: polycatenated networks have a higher dimensionality than that of the component motifs and polyrotaxane-like networks are characterized by the presence of closed loops

and rods or string elements that can thread through these loops, in which the different motifs cannot be disentangled without breaking links. However, until now, polycatenated and polyrotaxane-like coordination networks have usually been constructed from lower dimensional motifs (0D → 1D or 2D; 1D → 2D or 3D), but 2D coordination networks formed from polycatenated or polyrotaxane-like coordination networks (2D → 2D or 3D) have, by comparison, been rarely reported.⁷ Therefore, further research is necessary to enrich and develop this field.

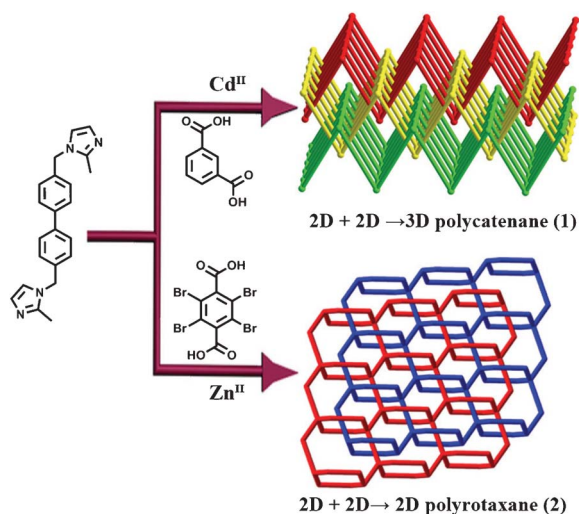
As an ongoing investigation on synthesis of novel entangled networks,⁸ we selected the conformationally flexible ligand 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl (bmimbp) as a main ligand, which has two methylene groups between the biphenyl and imidazole ring which freely rotate around the C–C bonds, giving different possible conformations such as *syn* and *anti*. Thus it may be possible to yield novel entangled coordination networks. On the other hand, as indicated by a CSD (Cambridge Structure Database) survey with the help of ConQuest version 1.3,⁹ only one bmimbp-based coordination network, [Ni₂(bmimbp)₂(dipicolinate)₂(H₂O)₂·4H₂O]_n, has been documented,¹⁰ while other bmimbp-based coordination networks with or without auxiliary ligands have not yet been disclosed. Given the above consideration and our previous work, herein, we synthesized and characterized two novel entangled metal–organic networks, namely [Cd(bmimbp)(bdc)]_n (**1**) and [Zn(bmimbp)(tbtpa)]_n (**2**) (bmimbp = 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl, H₂bdc = 1,3-benzenedicarboxylic acid, H₂tbtpa = tetrabromoterephthalic acid), exhibiting polycatenated 2D + 2D → 3D framework and polyrotaxane-like 2D + 2D → 2D net, respectively (Scheme 1). These entangled fashions in crystal structures, especially the latter, provided new insights into the entangled structures that can be achieved by crystal engineering concepts.

Complexes **1** and **2** were prepared by hydrothermal reaction of Cd(NO₃)₂·4H₂O or Zn(NO₃)₂·6H₂O, bmimbp, H₂bdc or H₂tbtpa, and KOH in methanol–DMF (1 mL, v/v = 1 : 1) (see ESI†). The compositions of **1** and **2** were further deduced from X-ray single crystal diffraction, elemental analysis and IR spectra. The solid-state FT-IR spectra (Fig. S1, ESI†) of complexes **1** and **2** show the characteristic bands for deprotonated carboxyl groups. The powder X-ray diffraction (PXRD) patterns of **1** and **2** are

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Scheme 1 Synthetic procedures of **1** and **2**.

consistent with the simulated pattern derived from the X-ray single crystal data, implying that the bulk sample is the same as the single crystal (Fig. S2, ESI†).

X-ray single-crystal diffraction analysis‡ reveals that **1** is a polycatenated 2D + 2D → 3D framework based on an undulated 4⁴-**sql** single sheet. It crystallizes in the triclinic crystal system with space group of $P\bar{1}$ with an asymmetric unit that contains one Cd(II) ion, two crystallographically unique bmimbp ligands lying on a site of $\bar{1}$ symmetry and a bdc dianion. As depicted in Fig. 1a, the CdI is six-coordinated by four O atoms and two N atoms from two different bdc ligands and two different bmimbp ligands, respectively. The bond angle around the Cd(II) ion vary from 52.43(12) to 136.28(13)°, and the bond lengths from 2.244(3) to 2.584(4) Å. The flexible bmimbp ligand in **1** shows an *anti* conformation and the two phenyl rings are perfectly coplanar as imposed by the inversion center. The dihedral angles between imidazole and phenyl rings are 76.3 and 84.0° for two crystal-

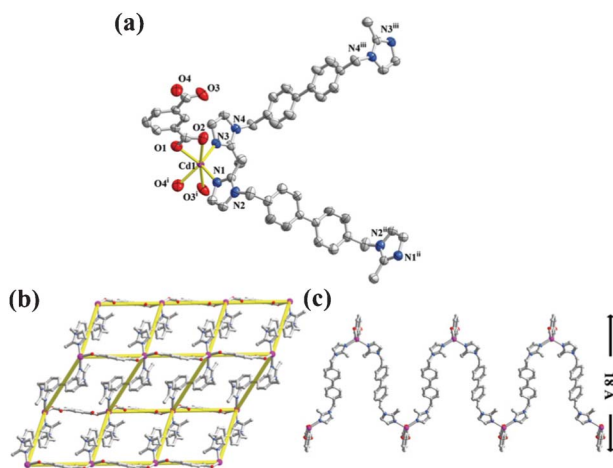


Fig. 1 Crystal structure of **1**. Thermal ellipsoid (50%) plot of **1** showing the coordination environment of the Cd(II) ion (a). Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y - 1, -z + 1$; (iii) $-x + 1, -y, -z + 2$. Ball and stick view of the 2D undulated 4⁴-**sql** sheet along two different orientations (b) and (c). Cd: purple; N: blue; O: red; C: grey.

lographically unique bmimbp ligands, respectively, which are responsible for the formation of highly undulated sheet. The *anti*-bmimbp and μ_2 -bdc in a *syn-syn* mode link Cd(II) ions to generate a 2D undulating sheet (Fig. 1b). From a topological viewpoint, this sheet contains one type of node (CdI ion) and two types of linkers (bmimbp and bdc ligands). In **1**, CdI ions as 4-connected nodes are bridged by 2-connected bmimbp and bdc ligands, so the 2D sheet can be simplified to a 4⁴-**sql** sheet,¹¹ which contains a window of 10.0 × 17.4 Å and exhibits a highly undulated character with a thickness of about 18 Å (Fig. 1c).

A more impressive structural characteristic of complex **1** is that each highly undulated 2D 4⁴-**sql** single sheet is simultaneously penetrated by the two nearest neighbouring ones (one above and the other below), which have parallel but not coincident mean planes (Fig. 2). In contrast to simple 2D → 2D interpenetration,¹² this resulting structure can be described by a 2D → 3D ‘polycatenated network’ because this network results in the overall network with a higher dimensionality than each component of the single motif. The high degree of entanglement is due to: (i) the large enough windows of the net; (ii) the highly undulated nature of the single 4⁴-**sql** sheet. Among the known interpenetrated 4⁴-**sql** networks in coordination networks, most examples show 2D → 2D parallel interpenetration or 2D → 3D inclined polycatenation and only limited 2D → 3D polycatenation structures have been observed in a parallel mode.¹³

When H₂bdc was replaced by H₂tbtpa, we obtained complex **2** as a polyrotaxane-like 2D + 2D → 2D network based on a 6³-**hcb** single sheet. X-ray single-crystal diffraction analysis‡ reveals that the asymmetric unit of **2** contains one Zn(II) ion, one bmimbp ligand and two halves of tbtpa ligands (Fig. 3a). The ZnI is located in a distorted tetrahedral geometry ($\tau_4 = 0.93$),¹⁴ completed by two O atoms from two different tbtpa ligands and two N atoms from two different bmimbp. The bond angles around the Zn(II) center vary from 96.6(3) to 115.0(3)°, and the bond lengths from 1.947(7) to 2.030(8) Å. In **2**, bmimbp shows a *syn*-conformation, different from that in **1**. The dihedral angles between imidazole and phenyl rings are 73.4 and 89.0°, while this parameter for the two central phenyl rings is 28.0°. Two crystallographically unique μ_2 -tbtpa ligands show different coordination conformations, *syn-syn* and *anti-anti* modes, respectively. The two bmimbp ligands link a pair of Zn(II) centers to form Zn₂(bmimbp)₂ loops (8.5 × 16.0 Å, corresponding to the Zn⋯Zn distance and shortest intracycle C–C separation).

The extension of Zn₂(bmimbp)₂ loops into a 2D honeycomb-like sheet (Fig. 3b) is accomplished by μ_2 -tbtpa with an *anti-anti* mode. Each hexagon has four edges represented by the tbtpa

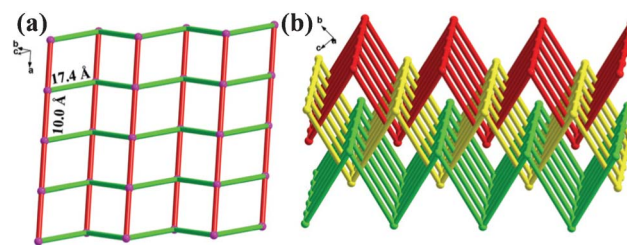


Fig. 2 (a) Simplified single 4⁴-**sql** sheet constructed by Cd(II) centers (purple balls) bmimbp (green rods) and bdc ligands (red rods). (b). Schematic drawing of the 2D + 2D → 3D polycatenated network.

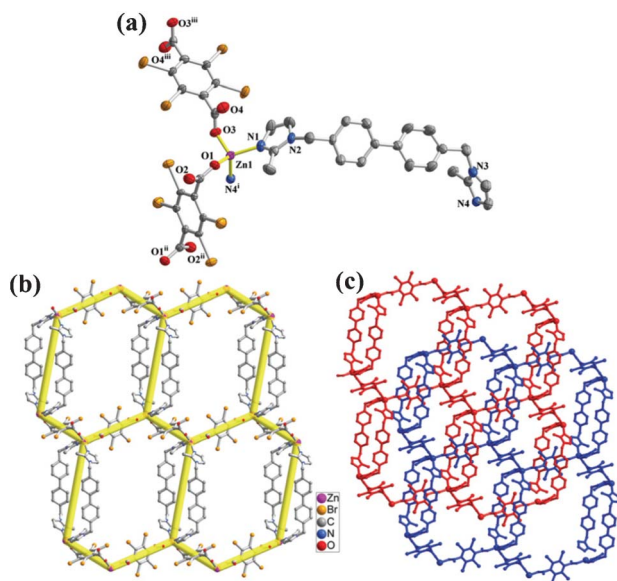


Fig. 3 Crystal structure of **2**. Thermal ellipsoid (50%) plot of **2** showing the coordination environment of the Zn(II) ion (a). Ball and stick view of a 2D 6^3 -hcb single sheet (b). The polyrotaxane-like 2D + 2D \rightarrow 2D network. Symmetry codes: (i) $-x + 1, -y - 1, -z + 2$; (ii) $-x, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$.

ligands and two edges replaced by $\text{Zn}_2(\text{bmimbp})_2$ loops. That is to say, each Zn atom is connected to three others: two *via* single μ_2 -tbtpa bridges and the third one by pairs of bmimbp ligands. In this analysis, this 2D sheet could be simplified to a 3-connected net with 6^3 -hcb topology in which the loops are converted into a 2-connected node, resulting in a network description which cannot properly describe the topology of interpenetration^{4c} as it would require links to pass through the middle of other links. Thus to obtain a network description that can be used to further describe the interpenetration, one must include the 2-membered rings (*i.e.*, the “loops”), resulting in the overall 4-connected ($2 \cdot 6^5$) topology.

The most striking feature of complex **2** is that two identical 2D single 6^3 -hcb sheets are interlocked with each other in a 2D \rightarrow 2D parallel fashion thus directly leading to the formation of a 2D polyrotaxane-like structure containing rotaxane-like motifs (Fig. 3c). As shown in Fig. 4a, the $\text{Zn}_2(\text{bmimbp})_2$ loops of each sheet are threaded by one Zn-tbtpa-Zn rod of the other sheet, and *vice versa*. Although 2D \rightarrow 2D parallel interpenetrated 6^3 -hcb nets, in particular with most typical AgN_3 coordination environments, have appeared in the literature,¹⁵ reports of the polyrotaxane-like network involving a 2D 6^3 -hcb sheet are exceedingly sparse

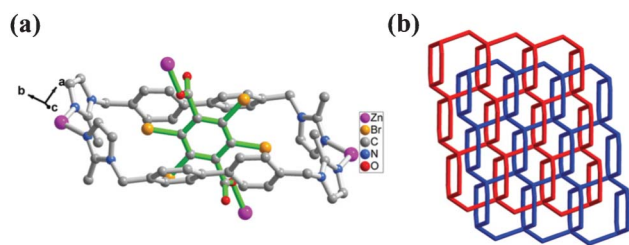


Fig. 4 (a) Stereochemical relationship between a Zn-tbtpa-Zn rod and a $\text{Zn}_2(\text{bmimbp})_2$ loop. (b) Schematic view of the simplified polyrotaxane-like 2D + 2D \rightarrow 2D network in **2**.

because these systems require the presence of loops and rods which can thread the loops. One of the most famous examples similar to **2** is $[\text{Zn}(1,4\text{-bix})_2(\text{NO}_3)_2 \cdot 4.5\text{H}_2\text{O}]_n$ (bix = bis(imidazol-1-ylmethyl)-benzene) reported by Robson and co-workers,¹⁶ in which both the loop and rod elements are flexible bix ligands. Following this, some mixed-ligand polyrotaxane-like networks¹⁷ containing flexible N-donors as loop linker and aromatic dicarboxylate as rods, such as $[\text{Co}_2(1,3\text{-bix})_2(\text{bpea})_2]_n$ (H_2bpea = biphenylene-4,4'-dicarboxylic acid), $[\text{Cd}(\text{tp})(\text{bpp})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$ (H_2tp = terephthalic acid, bpp = 1,3-bis(4-pyridyl)propane), and $[\text{Co}(\text{bimh})(\text{bpd})]_n$ (bimh = 1,6-bis(imidazol-1-yl)-hexane, H_2bpd = biphenyl-4,4'-dicarboxylate), were also reported.

It has been shown that the variation of entangled fashions in complexes **1** and **2** are mainly associated with the conformations of bmimbp ligand and coordination modes of auxiliary dicarboxylates (Table 1). The combination of these two factors are key to influence the final entangled fashions, which depends on the competition and adaptability of the components. In **1** and **2**, the main ligand bmimbp adopts the completely different conformations of *anti* and *syn*, respectively. The former contributes to the formation of a highly undulated sheet and the latter to the loop. The auxiliary dicarboxylates (bdc and tbtpa) adopt the same μ_2 - η^1, η^1 coordination mode but different coordination conformations. The bdc adopts a *syn-syn* mode in **1**, but tbtpa shows both *syn-syn* and *anti-anti* in **2**. Notably, steric hindrance of four Br atoms on tbtpa imposed the plane determined by the carboxyl group being nearly perpendicular to the central phenyl ring, while the carboxyl group is nearly coplanar with central phenyl ring for the bdc ligand. These results show that dicarboxylates and bmimbp can fine-tune themselves to match with the coordination preference of metal centers and lower the energetic arrangement in the self-assembly process.

To investigate the thermal stability of both complexes, thermogravimetric analysis (TGA) experiments were carried out in the temperature range of 30–600 °C under a flow of nitrogen with a heating rate of 10 °C min^{-1} (Fig. 5). They exhibit similar thermal behaviors. There is no obvious weight loss before 360 and 307 °C for **1** and **2**, respectively. Then the frameworks begin to collapse, accompanying the loss of organic ligands.

The photoluminescence spectra of the complexes **1** and **2** are shown in Fig. 6. The ligand bmimbp displays photoluminescence with emission maximum at 323 nm ($\lambda_{\text{ex}} = 300$ nm). It can be

Table 1 Comparison of conformations of bmimbp and dicarboxylates in **1** and **2**^a

	1	2
bmimbp		
Dicarboxylates		

^a Purple: Cd or Zn; yellow: Br; red: O; blue: N; grey: C.

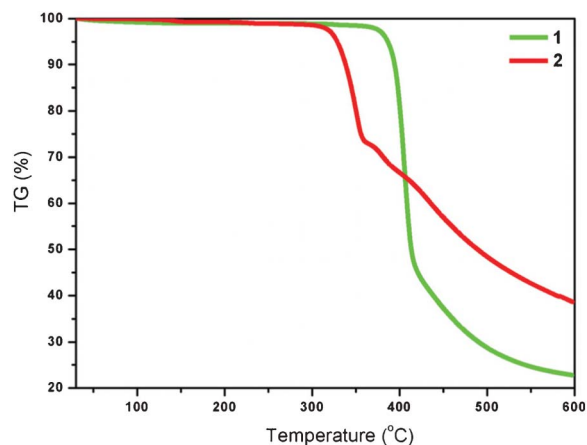


Fig. 5 The TGA curves of **1** and **2**.

presumed that this peak originate from the $\pi^* \rightarrow \pi$ transition. 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 the bmimbp, so the dicarboxylates almost have no contribution to the fluorescent emission of as-synthesized complexes.¹⁸ Upon complexation of these ligands with Cd(II) or Zn(II) ions, red-shifted emissions are observed at 395 nm for **1** and 410 nm for **2**, under 320 nm excitation, respectively. Owing to their d^{10} electronic configuration, Cd(II) and Zn(II) are difficult to oxidize or reduce, so the emissions here are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer. Since the profiles and positions of the emission bands of **1** and **2** are similar to those observed in the free bmimbp ligand, they can be assigned mainly to the intraligand transition of bmimbp which is modified by metal coordination.¹⁹ The emissions in the blue region suggests that both two complexes may be potential blue-light-emitting materials.

In summary, we have presented two novel entangled mixed-ligand metal-organic networks, which vary from polycatenated $2D + 2D \rightarrow 3D$ framework to polyrotaxane-like $2D + 2D \rightarrow 2D$ layer. The structural comparison suggests that the conformations of bmimbp ligand and coordination modes of auxiliary dicarbox-

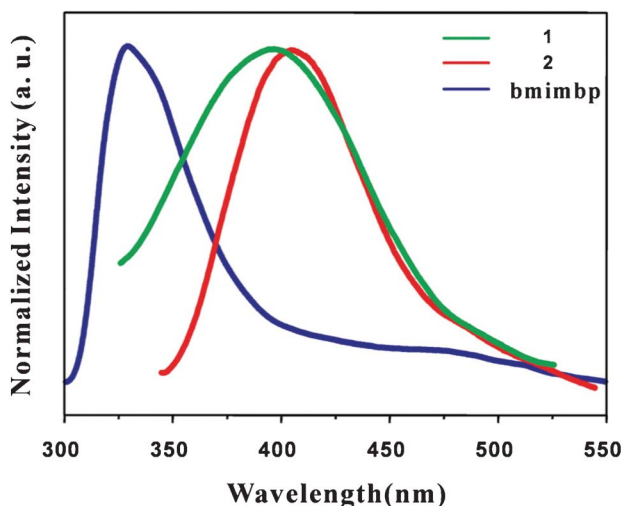


Fig. 6 The photoluminescence spectra of **1**, **2** and bmimbp ligand.

ylates are key points to influence the final entangled fashions. Moreover, their thermal stabilities and emissive behaviors were also discussed.

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‡ Crystal data for **1**: $C_{30}H_{26}N_4O_4Cd$, $M = 618.95$, triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $T = 298(2)$ K, $a = 9.995(2)$ Å, $b = 11.410(3)$ Å, $c = 11.572(3)$ Å, $\alpha = 87.877(4)^\circ$, $\beta = 88.749(4)^\circ$, $\gamma = 83.876(3)^\circ$, $V = 1311.1(6)$ Å³, $\mu(\text{Mo-K}\alpha) = 0.877$, 6456 reflections measured, 4534 unique ($R_{\text{int}} = 0.0174$) which were used in all calculations. The final wR_2 was 0.1043 (all data) and R_1 was 0.0382 ($>2\sigma(I)$). Crystal data for **2**: $C_{30}H_{22}Br_4N_4O_4Zn$, $M = 887.53$, triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $T = 298(2)$ K, $a = 10.237(12)$ Å, $b = 11.827(14)$ Å, $c = 14.256(16)$ Å, $\alpha = 91.67(2)^\circ$, $\beta = 109.35(2)^\circ$, $\gamma = 103.26(2)^\circ$, $V = 1575(3)$ Å³, $\mu(\text{Mo-K}\alpha) = 5.897$, 7596 reflections measured, 5390 unique ($R_{\text{int}} = 0.0501$) which were used in all calculations. The final wR_2 was 0.1523 (all data) and R_1 was 0.0532 ($>2\sigma(I)$).

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