

Cite this: *RSC Advances*, 2011, 1, 1682–1686

www.rsc.org/advances

Two novel isomeric organic anion-water aggregations: 1D tape and 3D 2-fold interpenetrated diamond network^{†‡}

Tuoping Hu,^{*a} Xiaoliang Zhao,^b Xiaoqin Hu,^a Yumin Xu,^a Di Sun^{*b} and Daofeng Sun^{*b}

Received 8th September 2011, Accepted 23rd September 2011

DOI: 10.1039/c1ra00695a

Two novel hydrogen-bonded isomeric water-imdn aggregations were observed in two Co(II) coordination compounds, formulated as $\{[\text{Co}(2,2'\text{-bpy})_3][(\text{imdn})_2(\text{H}_2\text{O})_4]\}_n$ (**1**) and $\{[\text{Co}(4,4'\text{-bpy})_2][(\text{imdn})_2(\text{H}_2\text{O})_4]\}_n$ (**2**) (bpy = bipyridine, Himdn = 2*H*-imidazole-4,5-dicarbonitrile). The water-imdn aggregation in **1** is a 1D hydrogen-bonded tape based on an octamer water cluster. For **2**, two imdn and four water molecules are hydrogen bonded to an unprecedented bag-like binary supramolecular cluster which acts as a tetrahedral node to be hydrogen-bonded to its four neighbors, giving a 3D network with a diamond topology. Two translationally equivalent diamond networks mutually interpenetrate each other to form the resulting 2-fold diamond network. The different host structural motifs are responsible to the dissimilarity of two isomeric water-imdn aggregations.

Accompanying the recent upsurge of interest in metal–organic frameworks (MOFs), hydrogen bond in supramolecular network has attracted considerable attention due to their directionality and robustness.¹ Compared to the widely reported interpenetrated MOFs, there are few instances involving entangled hydrogen-bonded network,² which is still a major challenge in the crystal engineering of molecular solids due to elusive linking mode between the supramolecular synthons. One of the most famous hydrogen-bonded interpenetrated network was an elongated 5-fold diamond structure based on tetrahedral adamantane-1,3,5,7-tetracarboxylic acid.³ On the other hand, water has captured more interest because of its fundamental importance in many biological and chemical processes.⁴ Small water clusters are the subject of considerable theoretical and

experimental interest as they are the first step toward understanding the behavior of bulk water as well as its anomalous behavior.⁵ Diverse water aggregations such as discrete tetramers,⁶ hexamers,⁷ heptamers,⁸ octamers,⁹ nonamers,¹⁰ decamers,¹¹ dodecamers,¹² tetradecamers,¹³ hexadecamers,¹⁴ octadecamers,¹⁵ icosadecamers¹⁶ and infinite 1D chains,¹⁷ 1D tapes,¹⁸ 2D layers¹⁹, 3D water structures²⁰ have been characterized in the cavities of MOFs or metal-free organic hosts by X-ray crystallography. As a branch of water chemistry, anion-water aggregations are important in understanding the behaviour of anions in water-based biological systems.²¹ As we know, only limited examples related to inorganic anion-water aggregations such as $[(\text{NO}_3)_4(\text{H}_2\text{O})_6]^{4-}$, $[\text{Cl}(\text{H}_2\text{O})_4]^-$, $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$, and $[\text{Br}_2(\text{H}_2\text{O})_6]^{2-}$ have been reported so far,²² and what is less recognised, however, is organic anion-water aggregations.²³ Two different well-resolved 2D dicarboxylate-water aggregations, $\{[(\text{bdc})_2(\text{H}_2\text{O})_{12}]^{4-}\}_n$ ^{24a} and $\{[(\text{bdc})(\text{H}_2\text{O})_8]^{2-}\}_n$ ^{24b} (H₂bdc = 1,3-benzenedicarboxylic acid) have been observed in a silver(I) and a copper(II) supramolecular frameworks, respectively.

As we know, 2*H*-imidazole-4,5-dicarbonitrile (Himdn) is a potential versatile ligand in the construction of MOFs due to (i) up to four N coordination sites with different orientations, (ii) various deprotonated forms; (iii) vulnerable CN group which can form a carboxylate or tetrazole group through *in situ* ligand reaction. We previously reported two open Zn(II) MOFs based on 2*H*-imidazole-4,5-dicarboxylic acid and 4,5-di(1*H*-tetrazol-5-yl)-2*H*-imidazole, which are *in situ* generated from hydrolysis of Himdn and cycloaddition of Himdn with azide, respectively.²⁵ Nevertheless, because of its strong coordination ability and vulnerable nature, the imdn inclusion compounds, especially hydrated imdn species are very scarce.²⁶

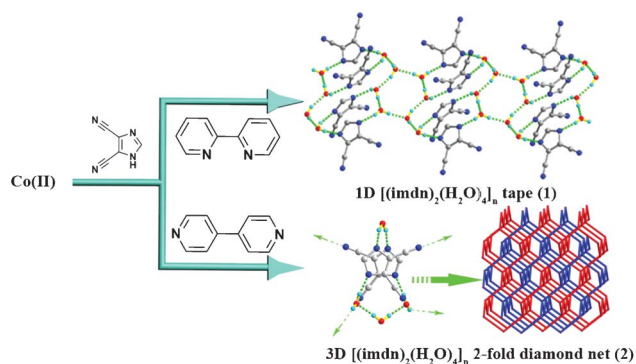
Considering the points mentioned above and our previous work, we selected chelating 2,2'-bipyridine (2,2'-bpy) and bridging 4,4'-bipyridine (4,4'-bpy) as ligands incorporating 2*H*-imidazole-4,5-dicarbonitrile as auxiliary ligand to construct Co(II) MOFs, and surprisingly obtained two supramolecular compounds, formulated as $\{[\text{Co}(2,2'\text{-bpy})_3][(\text{imdn})_2(\text{H}_2\text{O})_4]\}_n$ (**1**) and $\{[\text{Co}(4,4'\text{-bpy})_2][(\text{imdn})_2(\text{H}_2\text{O})_4]\}_n$ (**2**) (Himdn = 2*H*-imidazole-4,5-dicarbonitrile) featuring two novel isomeric water-imdn aggregations with the same composition of $[(\text{imdn})_2(\text{H}_2\text{O})_4]_n$ (Scheme 1). The water-imdn aggregation in **1** is a 1D hydrogen-bonded tape based on an octamer water cluster, while water-imdn aggregation in **2** becomes a 3D 2-fold interpenetrated diamond network based on an unprecedented $[(\text{imdn})_2(\text{H}_2\text{O})_4]$ binary supramolecular cluster.

^aDepartment of Chemistry, North University of China, Taiyuan, Shanxi, 030051, P. R. China. E-mail: hutuopingsx@yahoo.com.cn

^bSchool of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China. E-mail: dsun@sdu.edu.cn; dfsun@sdu.edu.cn

[†] Electronic Supplementary Information (ESI) available: The synthesis of complexes **1–2**, selected bond lengths and angles, TGA curve and X-ray crystallographic data. CCDC 838340–838341. See DOI:10.1039/c1ra00695a.

[‡] Crystal data for **1**: C₄₀H₃₄CoN₁₄O₄, fw = 833.74 g mol⁻¹, monoclinic, space group *P*2₁/*c*, *Z* = 4, *T* = 173(2)K, *a* = 9.8648(9), *b* = 29.440(2), *c* = 13.9210(13) Å, β = 94.890(2), *V* = 4028.6(2) Å³, *D*_c = 1.375 g cm⁻³, *R*₁ = 0.0423, *wR*₂ = 0.0918, μ = 0.486 mm⁻¹, *S* = 1.013. Crystal data for **2**: C₃₀H₂₆CoN₁₂O₄, fw = 677.56 g mol⁻¹, tetragonal, space group *I*4₁/cd, *Z* = 8, *T* = 173(2)K, *a* = *b* = 16.2028(3), *c* = 24.4818(9) Å, *V* = 6427.2(3) Å³, *D*_c = 1.400 g cm⁻³, *R*₁ = 0.0372, *wR*₂ = 0.0743, μ = 0.590 mm⁻¹, *S* = 0.988. For crystallographic data in CIF or other electronic format see DOI:10.1039/c1ra00695a.



Scheme 1 The isomeric water-imdn aggregations in **1** and **2**.

Complexes **1** and **2** were obtained by adding aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Himdn and tetrabutyl ammonium bromide to bpy in the cuvette (see ESI†). The mixtures were capped and allowed to stand at room temperature until crystals formed within ten days. The thermal stabilities of **1** and **2** were explored by thermogravimetric analysis (TGA, Fig. S1). The TGA curve of **1** shows the weight loss of 37.8% in the temperature range of 30–300 °C, corresponding to the exclusion of four lattice water molecules and two imdn (calcd: 36.7%), then the residual component collapses. Complex **2** shows the weight loss of 43.8% from 30 to 350 °C (calcd: 45.2%), corresponding to the losses the guest components and two coordinated water molecules, then the guest-free framework starts to decompose. The +2 oxidation states of Co atoms in **1** and **2** are determined on the basis of charge balance consideration and bond valence sum (BVS) calculations.²⁷

The crystal structure of **1** was determined by single-crystal X-ray diffraction analysis (see ESI†). Complex **1** crystallizes in monoclinic space group of $P2_1/c$ with an asymmetric unit that contains one Co(II) ion, three 2,2'-bpy ligand, two imdn anions and four water

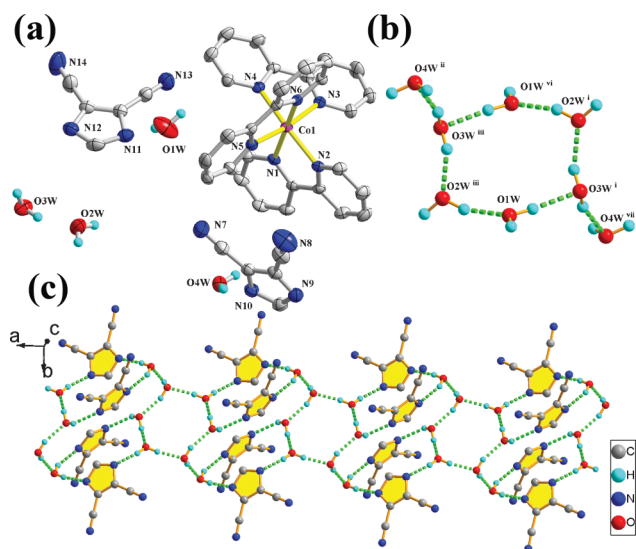


Fig. 1 (a) ORTEP representation of **1** showing the local coordination environment around Co(II) center with 50% thermal ellipsoid probability. Hydrogen atoms on C atoms have been omitted for clarity. (b) Octamer water cluster based on a chair-like hexamer (Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (vi) $-x, -y + 1, -z$; (vii) $x - 1, y, z - 1$). (c) 1D hydrogen-bonded water-imdn aggregation in **1**.

molecules. As shown in Fig. 1a, the Co1 is coordinated by six N atoms from three 2,2'-bpy ligand, displaying an octahedral geometry. The Co–N bond lengths range from 2.109(2) to 2.154(2) Å, which are comparable to the related Co(II) compounds.²⁸ The N–Co–N angles range from 76.63(8)–171.71(8)°. The $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$ complex cation and imdn anion are connected by non-classic C–H \cdots N_{CN} hydrogen bonding interactions. Although the supramolecular systems based on $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$ unit and various anionic counterparts (such as polyoxovanadate and octamolybdate) were widely observed,²⁹ marriage of imdn anions and this common cationic unit is unprecedented.

The most noteworthy feature of **1** is a 1D hydrogen-bonded imdn-water aggregation based on an octamer water cluster. As shown in Fig. 1b, the centrosymmetric octamer water cluster consists of four water molecules (O1W–O4W) and their centrosymmetric equivalents. The short contacts and the angles between them indicate the existence of hydrogen bonds, which drive the formation of a hydrophilic octamer water cluster. The water octamer can be seen as a chair-like hexamer in the core which links two additional water molecules dangling at two diagonally opposite ends of the chair with a distance of 8.573(3) Å, which is structurally analogous to the simple hydrocarbon (1*r*,4*r*)-1,4-dimethylcyclohexane. In the cyclic hexamer, each water molecules act as single hydrogen bond donor and single hydrogen bond acceptor, as a result, the hydrogen bonding motif is $R_6^6(12)$, according to the graphset analysis nomenclature.³⁰ The O3W derives from the plane determined by O1W, O2Wⁱⁱⁱ, O1W^{vi} and O2Wⁱ of 0.73 Å. As listed in Table 1, the O \cdots O distances in the octamer water cluster fall in the range of 2.678(3)–2.774(3) Å with an average value of 2.729(3) Å, compared to 2.76 Å (–90 °C) in hexagonal (I_h) ice,³¹ 2.74 Å in cubic (I_c) ice³² or 2.85 Å in liquid water.³³ The O \cdots O \cdots O angles vary from 93.91(9) to 117.63(10)° with an average value of 111.9° which slightly deviates from the angle of 109.3° in hexagonal ice. The deprotonated Himdn used the heterocyclic N atoms as double hydrogen bond acceptors to bridge the octamer water clusters into 1D tape along the *a* axis (Fig. 1c). The O \cdots N contacts span the range of 2.831(3)–2.875(3) Å with an average value of 2.858(3) Å, which is ~0.1 Å longer than that of O \cdots O distances. In the 1D tape, two imdn anions and three water molecules (O1Wⁱⁱⁱ, O2W and O4Wⁱⁱ) are hydrogen-bonded to a

Table 1 The hydrogen bond geometries (Å and °) for **1–2**

| Compound 1 ^a | | | | |
|--------------------------------------|------|--------------|--------------|----------------|
| D–H \cdots A | D–H | H \cdots A | D \cdots A | D–H \cdots A |
| O1W–H1WA \cdots O3W ⁱ | 0.85 | 1.88 | 2.717(3) | 170.1 |
| O1W–H1WB \cdots N11 | 0.85 | 2.01 | 2.855(3) | 170.3 |
| O2W–H2WA \cdots N9 ⁱⁱ | 0.85 | 2.13 | 2.831(3) | 140.0 |
| O2W–H2WB \cdots O1W ⁱⁱⁱ | 0.85 | 1.88 | 2.678(3) | 156.2 |
| O3W–H3WA \cdots O4W ^{iv} | 0.85 | 1.95 | 2.774(3) | 162.9 |
| O3W–H3WB \cdots O2W | 0.85 | 1.93 | 2.746(3) | 161.9 |
| O4W–H4WA \cdots N12 ^v | 0.85 | 2.03 | 2.870(3) | 171.6 |
| O4W–H4WB \cdots N10 | 0.85 | 2.09 | 2.875(3) | 154.3 |

^a Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $x, y, z - 1$; (v) $x, y, z + 1$.

| Compound 2 ^b | | | | |
|------------------------------------|------|--------------|--------------|----------------|
| D–H \cdots A | D–H | H \cdots A | D \cdots A | D–H \cdots A |
| O1W–H1WA \cdots N3 ^{iv} | 0.85 | 1.90 | 2.718(5) | 161.0 |
| O2W–H2WA \cdots O3W | 0.85 | 1.87 | 2.713(4) | 174.8 |
| O3W–H3WA \cdots N4 ^v | 0.85 | 1.94 | 2.778(5) | 168.4 |
| O3W–H3WB \cdots N5 | 0.85 | 2.09 | 2.938(5) | 175.2 |

^b Symmetry codes: (iv) $y + 1, x - 1/2, z - 1/4$; (v) $-y, x - 1/2, z + 1/4$.

$R_5^5(14)$ motif which is further bound together with its inversion-related equivalent by O3W and O3Wⁱⁱⁱ (Fig. S2†). (Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (vi) $-x, -y + 1, -z$).

When using the bidentate bridging ligand in the replacement of bidentate chelating ligand, we obtained compound **2** as a 2D sheet with (4,4)-**sql** topology. Compound **2** crystallizes in tetragonal crystal system of $I4_1cd$ space group. The asymmetric unit of **2** contains one Co(II) ions with half occupancy, one 4,4'-bpy, one imdn anion, and three water molecules, two of which are half occupancy. One crystallographic 2-fold axis passes through the Co1, O1W and O2W. As shown in Fig. 2a, the Co(II) ion also locates in an octahedral coordination environment, completed by four N atom from four different 4,4'-bpy and two O atoms of water molecules. The rigid bridging 4,4'-bpy ligands link the Co(II) centers to form a 2D sheet along the ab plane with the window size of $11.46 \times 11.46 \text{ \AA}$, which is suitable to accommodate of a pair of imdn anions. The pairs of imdn anions in each grid are packed together through weak $\pi \cdots \pi$ interaction with an inter-centroid distance of $3.764(2) \text{ \AA}$ (Fig. 2b). A similar 2D (4,4)-**sql** net has been observed in a $[\text{Zn}(4,4'\text{-bpy})_2(\text{NO}_3)_2]_n$ coordination polymer where pairs of *o*-dichlorobenzene (*o*-DCB) molecules were located within the square grids and pyrene molecules were intercalated between the 2D nets. The inclined

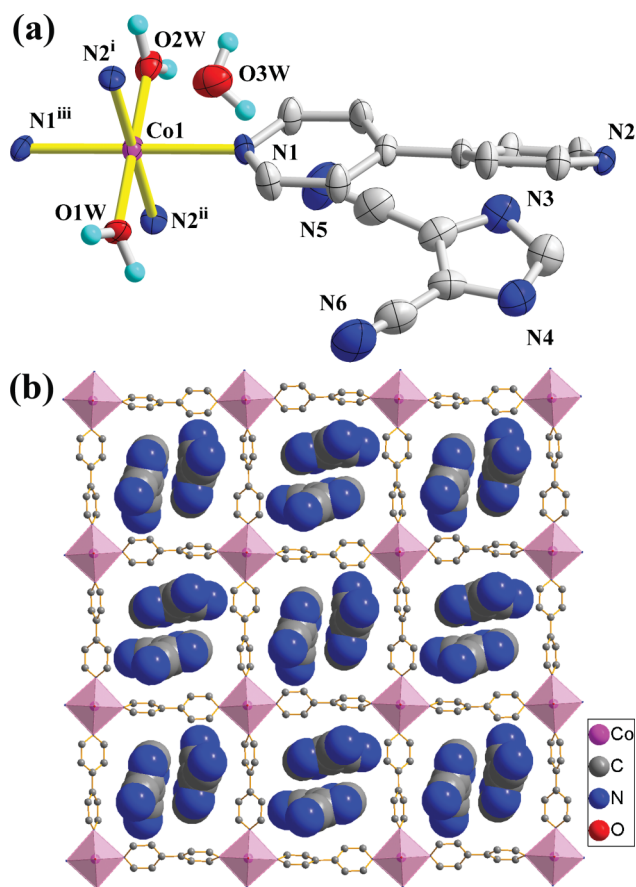


Fig. 2 (a) ORTEP representation of **2** showing the local coordination environment around Co(II) center with 50% thermal ellipsoid probability. Hydrogen atoms on C atoms have been omitted for clarity. (Symmetry codes: (i) $-x + 1/2, y + 1/2, z$; (ii) $x + 1/2, -y - 1/2, z$; (iii) $-x + 1, -y, z$). (b) Ball-and-Stick representation of the 2D (4,4)-**sql** net with encapsulated imdn anions in the grids represented with space-filling mode.

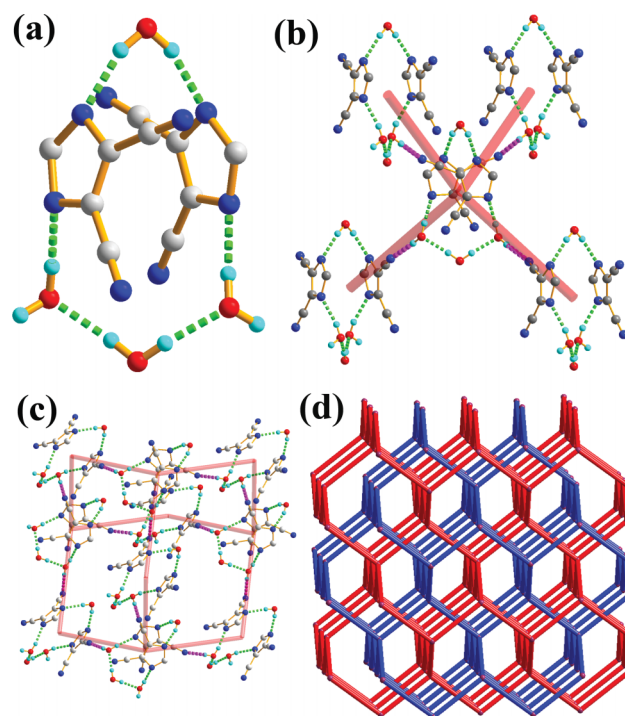


Fig. 3 Ball-and-stick representation of $[(\text{imdn})_2(\text{H}_2\text{O})_4]$ supramolecular cluster. (b) Tetrahedral linking mode of the supramolecular cluster. (c) Formation of superadamantane framework in **2**. (d) Two-fold interpenetrated diamond networks.

interpenetration was also found between the $[(o\text{-DCB})_2(\text{pyrene})]_n$ noncovalent sheets and the (4,4)-**sql** nets.³⁴

The most striking feature of **2** was disclosed by close inspection of the supramolecular networks formed between hydrogen-bonded water molecules and imdn anions. As shown in Fig. 3a, two imdn anions and four water molecules are hydrogen-bonded ($2.713(4)$ – $2.778(5) \text{ \AA}$) to an unprecedented bag-like $[(\text{imdn})_2(\text{H}_2\text{O})_4]$ supramolecular cluster which is further tetrahedrally linked by its four neighbors through the $\text{O3W} \cdots \text{N5}$ hydrogen bond ($2.938(5) \text{ \AA}$) to form the resulting 3D network. From the topology point, the $[(\text{imdn})_2(\text{H}_2\text{O})_4]$ supramolecular cluster can be seen as a four-connected node (Fig. 3b), as a result, the whole 3D hydrogen-bonded network is topologically similar to diamond, in which $[(\text{imdn})_2(\text{H}_2\text{O})_4]$ replaces adamantyl nucleus as super-C atom. The smallest subunit of this diamond network looks like a superadamantane which has a top-to-bottom length of $24.4818(9) \text{ \AA}$, equivalent to crystallographic c -axis length, and consists of 60 molecules (20 imdn and 40 water) linked together by 72 hydrogen bonds (20 $\text{O}-\text{H} \cdots \text{O}$ and 52 $\text{N}-\text{H} \cdots \text{O}$) (Fig. 3c). This large superadamantane gives the single diamond network huge void, which is filled by another identical net leading to 2-fold interpenetration (Fig. 3d). The distance between adjacent four-connected nodes belonging to two distinct diamond networks is $\sim 11.46 \text{ \AA}$ (Fig. S3†). Notably, hydrogen bonds occur only within a particular diamond network but not between different networks. To the best of our knowledge, the diamond networks can be obtained by connecting tetrahedral centers such as T_d -symmetry metallic or organic compounds. Particularly, self-complementary multiple hydrogen bonds have realized the construction of diamond networks based on tetrahedral carboxylic acid, pyridone, and diaminotriazine derivatives.³⁵ However, most known

hydrogen-bonded diamond networks obtained so far are homomolecular species^{2h} and using binary supramolecular cluster to construct the multi-component organic diamond networks is still rare.³⁶ A related example is a 1 : 2 adduct of tetrahedral tetrakis[4-(3-hydroxyphenyl)methane] and linear benzoquinone which are hydrogen-bonded to an elongated diamond network showing the largest known superadamantane unit and highest recorded 11-fold interpenetration.³⁷

It is worth stressing that water-imdn aggregations in **1** and **2** have the identical chemical composition with the same molecular formula of [(imdn)₂(H₂O)₄]_n, but they have different hydrogen-bonded networks, 1D tape and 3D 2-fold interpenetrated diamond network, belonging to a pair of isomers. The different water-imdn aggregations are strongly relevant to the environment of void created by the hosts. In **1**, three bidentate chelating 2,2'-bpy ligands ligated one Co(II) to form mononuclear [Co(2,2'-bpy)₃] units, which were packed in the crystal lattice to form 1D channel where accommodates the 1D [(imdn)₂(H₂O)₄]_n tape. In **2**, bidentate bridging 4,4'-bpy ligands connected Co(II) to form a 2D (4,4)-sqI net possesses nano-sized windows which are traversed by 2-fold interpenetrated hydrogen-bonded diamond networks (Fig. S4). These results demonstrate that the water-imdn aggregations form not only by a simple void-filling but also by somewhat templating effect, that is to say, the shape and size of the void somewhat determines the morphologies of the water-imdn aggregation. To the best of our knowledge, most supramolecular isomers refer to the coordination frameworks with or without consideration of the guest species,³⁸ however, supramolecular isomeric hydrogen-bonded guests still received less attention.³⁹

In summary, we observed two novel isomeric water-imdn aggregations in two different hosts. The water-imdn aggregation in **1** is a 1D tape containing an octamer water cluster, while a 3D 2-fold interpenetrated diamond network based on a supramolecular cluster was observed in **2**. The results unambiguously unearth that different host structural motifs are responsible to the dissimilarity of two isomeric water-imdn aggregations.

Acknowledgements

This work was supported by the NSFC (Grant No. 90922014), the Shandong Natural Science Fund for Distinguished Young Scholars (2010JQE27021), the NSF of Shandong Province (BS2009L007, Y2008B01), and Independent Innovation Foundation of Shandong University (2010JQ011), the International Scientific and Technological Cooperation Projects of Shanxi Province (No: 2011081022).

References

- (a) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48; (b) T. Steiner and G. R. Desiraju, *Chem. Commun.*, 1998, 891; (c) M. J. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283; (d) K. V. Domasevitch, I. Boldog, J. C. Daran, A. N. Chernega, E. B. Rusanov and H. Krautscheid, *Cryst. Growth Des.*, 2009, **9**, 2895; (e) K. V. Domasevitch, I. Boldog, E. B. Rusanov, A. N. Chernega and J. Sieler, *Angew. Chem., Int. Ed.*, 2001, **40**, 3435; (f) I. Boldog, E. B. Rusanov, J. Sieler and K. V. Domasevitch, *New J. Chem.*, 2004, **28**, 756; (g) I. A. Baburina and V. A. Blatov, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2007, **B63**, 791; (h) B. Li, R.-J. Wei, J. Tao, R.-B. Huang, L.-S. Zheng and Z. J. Zheng, *J. Am. Chem. Soc.*, 2010, **132**, 1558.
- (a) B. R. Bhogala, P. Vishweshwar and A. Nangia, *Cryst. Growth Des.*, 2002, **2**, 325; (b) B. Olenik, T. Smolka, R. Boese and R. Sustmann, *Cryst. Growth Des.*, 2003, **3**, 183; (c) B. R. Bhogala and A. Nangia, *Cryst. Growth*

- Des.*, 2003, **3**, 547; (d) C. B. Aakeröy, A. M. Beatty and B. A. Helfrich, *J. Am. Chem. Soc.*, 2002, **124**, 14425; (e) P. Vishweshwar, A. Nangia and V. M. Lynch, *Cryst. Growth Des.*, 2003, **3**, 783; (f) R. D. B. Walsh, M. W. Bradner, S. G. Fleischman, L. A. Morales, B. Moulton, N. Rodríguez-Hornedo and M. J. Zaworotko, *Chem. Commun.*, 2003, 186; (g) K. Biradha and G. Mahata, *Cryst. Growth Des.*, 2005, **5**, 61; (h) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *Cryst. Growth Des.*, 2008, **8**, 519; (i) E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm*, 2011, **13**, 3947; (j) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2008, **10**, 1822.
- O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747.
- P. Ball, *H₂O: A Biography of Water*, Weidenfeld & Nicolson, London, 1999.
- (a) K. Liu, M. G. Brown, C. Carter, R. J. Saykally, J. K. Gregory and D. C. Clary, *Nature*, 1996, **381**, 501; (b) K. Nauta and R. E. Miller, *Science*, 2000, **287**, 293; (c) J. M. Ugalde, I. Alkorta and J. Elguero, *Angew. Chem., Int. Ed.*, 2000, **39**, 717; (d) R. Ludwig, *Angew. Chem., Int. Ed.*, 2001, **40**, 1808; (e) J. Kim, D. Majumdar, H. M. Lee and K. S. Kim, *J. Chem. Phys.*, 1999, **110**, 9128; (f) K. Liu, J. D. Cruzan and R. J. Saykally, *Science*, 1996, **271**, 929; (g) P. Rodríguez-Cuamatzi, G. Vargas-Díaz and H. Höpfl, *Angew. Chem., Int. Ed.*, 2004, **43**, 3041; (h) R. Natarajan, J. P. H. Charmant, A. G. Orpen and A. P. Davis, *Angew. Chem., Int. Ed.*, 2010, **49**, 5125.
- (a) L. S. Long, Y. R. Wu, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2004, **43**, 3798; (b) M. Zuhayra, W. U. Kampen, E. Henze, Z. Soti, L. Zsolnai, G. Huttner and F. A. Oberdorfer, *J. Am. Chem. Soc.*, 2006, **128**, 424.
- (a) S. K. Ghosh and P. K. Bharadwaj, *Inorg. Chem.*, 2003, **42**, 8250; (b) D. Sun, Z. H. Wei, C. F. Yang, D. F. Wang, N. Zhang, R. B. Huang and L. S. Zheng, *CrystEngComm*, 2011, **13**, 1591; (c) R. Custelcean, C. Afloreaei, M. Vlassa and M. Polverejan, *Angew. Chem., Int. Ed.*, 2000, **39**, 3094; (d) R. Luna-García, B. M. Damián-Murillo, V. Barba, H. Höpfl, H. I. Beltrán and L. S. Zamudio-Rivera, *Chem. Commun.*, 2005, 5527; (e) S. Kohmoto, S. Okuyama, N. Yokota, M. Takahashi, K. Kishikawa, H. Masu and I. Azumaya, *Cryst. Growth Des.*, 2011, **11**, 3698.
- (a) M. H. Mir and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2007, **46**, 5925; (b) M. H. Mir and J. J. Vittal, *Cryst. Growth Des.*, 2008, **8**, 1478; (c) D. Sun, H.-R. Xu, C.-F. Yang, Z.-H. Wei, N. Zhang, R.-B. Huang and L.-S. Zheng, *Cryst. Growth Des.*, 2010, **10**, 4642.
- (a) D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 746; (b) S. Khatua, J. Kang, J. O. Huh, C. S. Hong and D. G. Churchill, *Cryst. Growth Des.*, 2010, **10**, 327; (c) C. Maxim, L. Sorace, P. Khuntia, A. M. Madalan, V. Kravtsov, A. Lascialfari, A. Caneschi, Y. Journaux and M. Andruh, *Dalton Trans.*, 2010, **39**, 4838; (d) W. B. Blanton, S. Gordon-Wylie, G. R. Clark, K. D. Jordan, T. J. Wood, U. Geiser and T. J. Collins, *J. Am. Chem. Soc.*, 1999, **121**, 3551; (e) R. J. Doedens, E. Yohannesb and M. I. Khanb, *Chem. Commun.*, 2002, 62; (f) J. L. Atwood, L. J. Barbour, T. J. Ness, C. J. Raston and P. L. Raston, *J. Am. Chem. Soc.*, 2001, **123**, 7192; (g) B. Q. Ma, H. L. Sun and S. Gao, *Chem. Commun.*, 2005, 2336; (h) S. K. Ghosh and P. K. Bharadwaj, *Eur. J. Inorg. Chem.*, 2005, 4886.
- (a) D. Sun, D.-F. Wang, N. Zhang, R.-B. Huang and L.-S. Zheng, *Cryst. Growth Des.*, 2010, **10**, 5031; (b) S. K. Ghosh and P. K. Bharadwaj, *Inorg. Chem.*, 2005, **44**, 5553.
- (a) L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 2000, 859; (b) M. Yoshizawa, T. Kusukawa, M. Kawano, T. Ohhara, I. Tanaka, K. Kurihara, N. Niimura and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127**, 2798.
- (a) B.-Q. Ma, H.-L. Sun and S. Gao, *Angew. Chem., Int. Ed.*, 2004, **43**, 1374; (b) S. K. Ghosh and P. K. Bharadwaj, *Angew. Chem., Int. Ed.*, 2004, **43**, 3577; (c) X. Wang, H. Lin, B. Mu, A. Tian and G. Liu, *Dalton Trans.*, 2010, **39**, 6187; (d) S. Neogi, G. Savitha and P. K. Bharadwaj, *Inorg. Chem.*, 2004, **43**, 3771; (e) H. H. Song and B. Q. Ma, *CrystEngComm*, 2007, **9**, 625; (f) F. Dai, H. He and D. Sun, *J. Am. Chem. Soc.*, 2008, **130**, 14064.
- S. K. Ghosh, J. Ribas, M. S. E. Fallah and P. K. Bharadwaj, *Inorg. Chem.*, 2005, **44**, 3856.
- (a) S. K. Ghosh and P. K. Bharadwaj, *Inorg. Chem.*, 2004, **43**, 6887; (b) Y. Bi, W. Liao, H. Zhang and D. Li, *CrystEngComm*, 2009, **11**, 1213.
- (a) K. Raghuraman, K. K. Katti, L. J. Barbour, N. Pillarsetty, C. L. Barnes and K. V. Katti, *J. Am. Chem. Soc.*, 2003, **125**, 6955; (b) X. Luan, Y. Chu, Y. Wang, D. Li, P. Liu and Q. Z. Shi, *Cryst. Growth Des.*, 2006, **6**, 812.
- R. L. Sang and L. Xu, *CrystEngComm*, 2010, **12**, 1377.

- 17 (a) A. Mukherjee, M. K. Saha, M. Nethaji and A. R. Chakravarty, *Chem. Commun.*, 2004, 716; (b) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, S. Antonijevic and G. Bodenhausen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5720; (c) B. K. Saha and A. Nangia, *Chem. Commun.*, 2005, 3024; (d) Y. Cui, M. L. Cao, L. F. Yang, Y. L. Niu and B. H. Ye, *CrystEngComm*, 2008, **10**, 1288; (e) R. Natarajan, J. P. H. A. Charmant, G. Orpen and A. P. Davis, *Angew. Chem., Int. Ed.*, 2010, **49**, 5125; (f) D. Sun, D.-F. Wang, N. Zhang, F.-J. Liu, H.-J. Hao, R.-B. Huang and L.-S. Zheng, *Dalton Trans.*, 2011, **40**, 5677.
- 18 (a) X. F. Shi, H. B. Song, L. He and W. Q. Zhang, *CrystEngComm*, 2009, **11**, 542; (b) M. Tadokoro, S. Fukui, T. Kitajima, Y. Nagao, S. Ishimaru, H. Kitagawa, K. Isobe and K. Nakasui, *Chem. Commun.*, 2006, 1274; (c) R. Custelcean, C. Afloroaei, M. Vlassa and M. Polverejan, *Angew. Chem., Int. Ed.*, 2000, **39**, 3094.
- 19 (a) C. Janiak, T. G. Scharamann and S. A. Mason, *J. Am. Chem. Soc.*, 2002, **124**, 14010; (b) N. S. Oxtoby, A. J. Blake, N. R. Champness and C. Wilson, *Chem.–Eur. J.*, 2005, **11**, 4643; (c) Z. F. Fei, T. J. Geldbach, D. B. Zhao, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2005, **44**, 5200; (d) P. Rodríguez-Cuamatzi, G. Vargas-Diaz and H. Höpfl, *Angew. Chem., Int. Ed.*, 2004, **43**, 3041; (e) J. P. Zhang, X. C. Huang, Y. Y. Lin and X. M. Chen, *Inorg. Chem.*, 2005, **44**, 3146; (f) X. J. Luan, Y. C. Chu, Y. Y. Wang, D. S. Li, P. Liu and Q. Z. Shi, *Cryst. Growth Des.*, 2006, **6**, 812; (g) P. S. Lakshminarayanan, E. I. Suresh and P. Ghosh, *J. Am. Chem. Soc.*, 2005, **127**, 13132; (h) A. H. Yang, H. Zhang, H. L. Gao, W. Q. Zhang, L. He and J. Z. Cui, *Cryst. Growth Des.*, 2008, **8**, 3354.
- 20 (a) R. Carballo, B. Covelo, C. Lodeiro and E. M. Vázquez-López, *CrystEngComm*, 2005, **7**, 294; (b) R. Carballo, B. Covelo, N. Fernández-Hermida, E. García-Martínez, A. B. Lago, M. Vázquez and E. M. Vázquez-López, *Cryst. Growth Des.*, 2006, **6**, 629; (c) C. H. Li, K. L. Huang, J. M. Dou, Y. N. Chi, Y. Q. Xu, L. Shen, D. Q. Wang and C. W. Hu, *Cryst. Growth Des.*, 2008, **8**, 3141.
- 21 (a) P. S. Lakshminarayanan, E. Suresh and P. Ghosh, *Angew. Chem., Int. Ed.*, 2006, **45**, 3807; (b) J. R. Butchard, O. J. Curnow, D. J. Garrett and R. G. A. R. MacLagan, *Angew. Chem., Int. Ed.*, 2006, **45**, 7550; (c) X. B. Wang, X. Yang, J. B. Nicholas and L. S. Wang, *Science*, 2001, **294**, 1322; (d) W. H. Robertson, E. G. Diken, E. A. Price, J. W. Shin and M. A. Johnson, *Science*, 2003, **299**, 1367.
- 22 (a) R. Custelcean and M. G. Gorbunova, *J. Am. Chem. Soc.*, 2005, **127**, 16362; (b) C. K. Lam, F. Xue, J. P. Zhang, X. M. Chen and T. C. W. Mak, *J. Am. Chem. Soc.*, 2005, **127**, 11536; (c) M. A. Hossain, P. Morehouse, D. Powell and K. Bowman-James, *Inorg. Chem.*, 2005, **44**, 2143; (d) P. S. Lakshminarayanan, D. K. Kumar and P. Ghosh, *Inorg. Chem.*, 2005, **44**, 7540; (e) S. Bartoli, C. Bazzicalupi, S. Biagini, L. Borsari, A. Bencini, E. Faggi, C. Giorgi, C. Sangregorio and B. Valtancoli, *Dalton Trans.*, 2009, 1223; (f) Y. Li, L. Jiang, X. L. Feng and T. B. Lu, *Cryst. Growth Des.*, 2008, **8**, 3689; (g) A. Bakhoda, H. R. Khavasi and N. Safari, *Cryst. Growth Des.*, 2011, **11**, 933; (h) D. Liu, H.-X. Li, Z.-G. Ren, Y. Chen, Y. Zhang and J.-P. Lang, *Cryst. Growth Des.*, 2009, **9**, 4562.
- 23 X. L. Wang, C. Qin and E. B. Wang, *Cryst. Growth Des.*, 2006, **6**, 439.
- 24 (a) D. Sun, N. Zhang, Q.-J. Xu, G.-G. Luo, R.-B. Huang and L.-S. Zheng, *J. Mol. Struct.*, 2010, **969**, 176; (b) G.-G. Luo, H.-B. Xiong and J.-C. Dai, *Cryst. Growth Des.*, 2011, **11**, 507.
- 25 T. Hu, W. Bi, X. Hu, X. Zhao and D. Sun, *Cryst. Growth Des.*, 2010, **10**, 3324.
- 26 B. L. V. Prasad, H. Sato, T. Enoki, S. Cohen and T. P. Radhakrishnan, *J. Chem. Soc., Dalton Trans.*, 1999, 25.
- 27 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **B47**, 192.
- 28 (a) D. Maspocho, D. Ruiz-Molina, K. Wurst, G. Vaughan, N. Domingo, J. Tejada, C. Rovira and J. Veciana, *CrystEngComm*, 2004, **6**, 573; (b) D. J. Szalda, C. Creutz, D. Mahajan and N. Sutin, *Inorg. Chem.*, 1983, **22**, 2372; (c) R. Sieber, S. Decurtins, H. Stoeckli-Evans, C. Wilson, D. Yufit, J. A. K. Howard, S. C. Capelli and A. Hauser, *Chem.–Eur. J.*, 2000, **6**, 361.
- 29 (a) Y.-G. Li, Y. Lu, G.-Y. Luan, E.-B. Wang, Y.-B. Duan, C.-W. Hu, N.-H. Hu and H.-Q. Jia, *Polyhedron*, 2002, **21**, 2601; (b) C. Sun, E. Wang, D. Xiao, H. An and L. Xu, *J. Mol. Struct.*, 2005, **741**, 149.
- 30 (a) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (b) J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.
- 31 D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press: Oxford, UK, 1969.
- 32 L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671.
- 33 A. H. Narton, W. E. Thiessen and L. Blum, *Science*, 1982, **17**, 1033.
- 34 G. J. McManus, J. J. Perry, M. Perry, B. D. Wagner and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2007, **129**, 9094.
- 35 (a) O. Ermer and A. Eling, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 829; (b) M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696; (c) P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, 1997, **119**, 2737.
- 36 (a) D. S. Reddy, D. C. Craig and G. R. Desiraju, *J. Am. Chem. Soc.*, 1996, **118**, 4090; (b) A. Jayaraman, V. Balasubramaniam and S. Valiyaveetil, *Cryst. Growth Des.*, 2005, **5**, 1575; (c) S. Roy, G. Mahata and K. Biradha, *Cryst. Growth Des.*, 2009, **9**, 5006.
- 37 D. S. Reddy, T. Dewa, K. Endo and Y. Aoyama, *Angew. Chem.*, 2000, **112**, 4436.
- 38 (a) T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (c) S.-S. Chen, M. Chen, S. Takamizawa, P. Wang, G.-C. Lv and W.-Y. Sun, *Chem. Commun.*, 2011, **47**, 4902; (d) D. Sun, S. Ma, J. M. Simmons, J.-R. Li, D. Yuan and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 1329; (e) J.-P. Zhang, X.-L. Qi, C.-T. He, Y. Wang and X.-M. Chen, *Chem. Commun.*, 2011, **47**, 4156; (f) J.-P. Zhang, X.-C. Huang and X.-M. Chen, *Chem. Soc. Rev.*, 2009, **38**, 2385; (g) Z. Zhang, L. Wojtas and M. J. Zaworotko, *Cryst. Growth Des.*, 2011, **11**, 1441.
- 39 (a) A. Nangia, *Acc. Chem. Res.*, 2008, **41**, 595; (b) V. S. S. Kumar, A. Addlagatta, A. Nangia, W. T. Robinson, C. K. Broder, R. Mondal, I. R. Evans, J. A. K. Howard and F. H. Allen, *Angew. Chem., Int. Ed.*, 2002, **41**, 3848.