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Short communication

# Solvent directed assembly of two zinc(II)-2-(4-pyridyl)-4,5-imidazoledicarboxylate frameworks

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ABSTRACT

Two zinc(II)-2-(4-pyridyl)-4,5-imidazoledicarboxylate frameworks, formulated as $\{[Zn_3(HPIDC)_3(DMF)_2](DMF)_2(H_2O)_2\}_n$ (1) and $\{[Zn_4(HPIDC)_4(DMF)_4](DMF)_2(FMA)_2(H_2O)\}_n$ (2) ($H_3PIDC$ = 2-(4-pyridyl)-1H-4,5-imidazoledicarboxylic acid, DMF = *N*,*N*′-dimethylformamide, FMA = formamide) have been solvothermally synthesized depending on whatever solvents are used. In both structures, the $HPIDC^{2-}$ anions act as tripodal connectors to chelating with three zinc(II) cations while the zinc(II) cations coordinate with three $HPIDC^{2-}$ anions, to form the T-shape molecular building blocks $[Zn_n(HPIDC)_n]$, which further connect in interdigitating or alternating fashion to result in the assembly of two different 3,3-connected networks. The luminescence behaviors and solvent effect were also discussed.



Metal-organic framework (MOF) is an active research area attracted more and more research groups around the world. The vigorous development in this field can be attributed to the following reasons: (a) structural variety is continuously being sought [1]; (b) functionality becomes urgent important [2]; (c) and more specifically, potential applications in fields such as ion exchange [3], catalysis [4], gas storage and separation [5], drug delivery [6], luminescence [7], biomedical materials [8], etc. are investigated.

Numerous MOFs have been well-documented for the selection of varied organic ligands and metal ions; however, the targeted synthesis of MOFs is still an intellectual challenge because the final structure can be affected by many factors, not only the organic ligand or metal ion but also the external physical and chemical conditions including reaction solvent, temperature and pH value, etc. Solvent is an important role during the crystallization process of MOFs for that can affect reaction rate, and even change reaction process and mechanism to get different products [9]. Prior to the reaction process, by appropriately choosing solvent with pre-defined polarity and shapes, much novel frameworks can be obtained to meet people's expectations.

In our previous work on MOFs of the tripodal ligand 2-(4-pyridyl)-1H-4,5-imidazoledicarboxylic acid ($H_3PIDC$) and different metal ions, we prepared a series of new frameworks such as **ant** network based on lanthanide ions, two chiral frameworks with **bmn** and **lcy-a** networks based on copper ions [10]. Considering with other reported structures of $H_3PIDC$ [11], more recently, we focus our attention on the solvent direct effect to structure variety during the crystallization process. By incorporating variety of solvents to the reaction system of zinc and $H_3PIDC$, two zinc(II)-2-(4-pyridyl)-4,5-imidazoledicarboxylate frameworks, formulated as $\{[Zn_3(HPIDC)_3(DMF)_2](DMF)_2(H_2O)_2\}_n$ (1) and $\{[Zn_4(HPIDC)_4(DMF)_4](DMF)_2(FMA)_2(H_2O)\}_n$ (2) with different 3,3-connected networks have been synthesized. In this contribution, we report the synthesis, crystal structures, solvent direct effect and luminescent property of above compounds.

Two compounds were prepared from the reaction of $Zn(NO_3)_2{\cdot}4H_2O$, $H_3PIDC$, $HNO_3$, DMF/$H_2O$ or DMF/FMA under solvothermal conditions [12]. The phase purity is further confirmed by the evident similar between the simulated and as-synthesized PXRD patterns (Fig. S1 and Fig. S2)·Crystal data as well as details of the data collection and refinements [13] are summarized in Table 1.

Crystal Structure of $\{[Zn_3(HPIDC)_3(DMF)_2](DMF)_2(H_2O)_2\}_n$ (1). Single-crystal analysis reveals that **1** is composed of a 3D neutral framework $[Zn_3(HPIDC)_3(DMF)_2]$, four guest molecular including two DMF and two water. There are two unique Zn(II) cations in the asymmetric unit whereas the Zn(1) presents a pentahedral geometry $ZnO_2N_3$ as seen in Fig. S3 and Fig. 1a, three nitrogen atoms come from two imidazole ring and one pyridine ring while two oxygen atoms come from carboxylate group of two separate $HPIDC^{2-}$ ligands. The Zn(2) cation assumes octahedral geometry $ZnN_3O_3$ whereas three nitrogen atoms and two of the oxygen atoms come from three $HPIDC^{2-}$ ligands while the other oxygen atom is from the DMF molecular (Fig. S3 and Fig. 1b). The distance of Zn–O ranges from 2.073(6) to 2.240(6)Å and the Zn–N ranges from 2.032(6) to 2.207(6)Å (Table S1), respectively. Two independent divalent $HPIDC^{2-}$ anions both act as T-shape connectors with three nitrogen atoms and two carboxylic oxygen atoms bridging three Zn(II) ions. There are three types of basic multi-member ring in the structure: a transformative 14-member ring (14-MR) in which three Zn(1), four Zn(2) atoms are connected with seven $HPIDC^{2-}$

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**Table 1**
Crystal data and structure refinements for two compounds.

| | 1[a] | 2[b] |
|---|---|---|
| Empirical formula | $C_{42}H_{47}N_{13}O_{18}Zn_3$ | $C_{60}H_{66}N_{20}O_{25}Zn_4$ |
| Formula weight | 1218.12 | 1728.81 |
| Temperature (K) | 100(2) | 100(2) |
| Crystal system, space group | Monoclinic, *C2/c* | Orthorhombic, *Pccn* |
| a (Å) | 18.206(5) | 18.087(6) |
| b (Å) | 18.320(5) | 24.867(11) |
| c (Å) | 14.765(4) | 17.611(8) |
| β (deg) | 92.161(5) | 90 |
| Volume ($Å^3$) | 4921(2) | 7921(6) |
| Z, $D_{calc}$ ($Mg/m^3$) | 4, 1.599 | 4, 1.584 |
| Absorption coefficient ($mm^{-1}$) | 1.537 | 1.293 |
| F (000) | 2364 | 3856 |
| θ range (deg) | 1.58 to 25.13 | 1.64 to 25.13 |
| Index range (deg) | −21 ≤ h ≤ 20, −21 ≤ k ≤ 17, −17 ≤ l ≤ 17 | −12 ≤ h ≤ 14, −29 ≤ k ≤ 29, −21 ≤ l ≤ 3 |
| Reflections collected/ unique (Rint) | 11490/4352 [R(int) = 0.1069] | 18326/5842 [R(int) = 0.0905] |
| Crystal size ($mm^3$) | 0.16 × 0.18 × 0.20 | 0.16 × 0.16 × 0.18 |
| Data / restraints / parameters | 4352/0/345 | 5842/0/552 |
| Goodness-of-fit on $F^2$ | 1.011 | 1.069 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0712, 0.1717 | 0.0871, 0.1958 |
| $R_1$, $wR_2$ (all data)) | 0.1246, 0.2074 | 0.1257, 0.2165 |
| Largest difference in peak and hole (e $Å^{-3}$) | 1.076, −0.708 | 0.989, −0.590 |

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

anions alternately (Fig. 1c); a 12-MR in which two Zn(1), four Zn(2) atoms are connected with six $HPIDC^{2-}$ anions alternately (Fig. 1d); and a parallelogram 4-MR in which two Zn(2) linked to two $HPIDC^{2-}$ anions (Fig. 1e). The 14-MR, 12-MR and 4-MR connect with each other to give rise to the 3D open framework as seen in Fig. 1f. The inner space of the 3D framework approximates 5 × 12 Å in diameter along the [001] direction (Fig. 1f), which is occupied by free DMF and water molecular. Topologically, the Zn(II) cation and $HPIDC^{2-}$ anion both can be simplified to be 3-connected nodes, therefore, a 2-nodal 3,3-connected network with Schlafli symbol of {4.8.10}2{$8^2$.12} has been emerged by TOPOS4.0 [15] (Fig. 1g and Table S2). And the coordination sequence (1 − 10) for two nodes is 3.5.9.16.24.34.49.67.81.93 and 3.6.10.14.24.40.51.58.77.104, respectively.

Crystal Structure of $\{[Zn_4(HPIDC)_4(DMF)_4](DMF)_2(FMA)_2(H_2O)\}_n$ (2). Compound **2** is composed of a 3D neutral framework $[Zn_4(HPIDC)_4(DMF)_4]$, five guest molecular including two DMF, two FMA and one water. Two unique Zn(II) cations are present in the asymmetric unit which assume the same coordination mode as the Zn(2) cations in structure **1** and two independent $HPIDC^{2-}$ anions both act as T-shape connectors as well (Fig. S4 and Fig. 2a). The distance of Zn–O ranges from 2.041(7) to 2.308(6) and the Zn–N ranges from 2.094(7) to 2.153(7) (Table S1), respectively. Two types of basic multi-member rings are present in **2**: a transformative 16-MR in which four Zn(1), four Zn(2) atoms are connected with eight $HPIDC^{2-}$ anions (Fig. 2b); and a parallelogram 4-MR as well as in **1** (Fig. 2c). They link with each other to result in the 3D open framework as seen

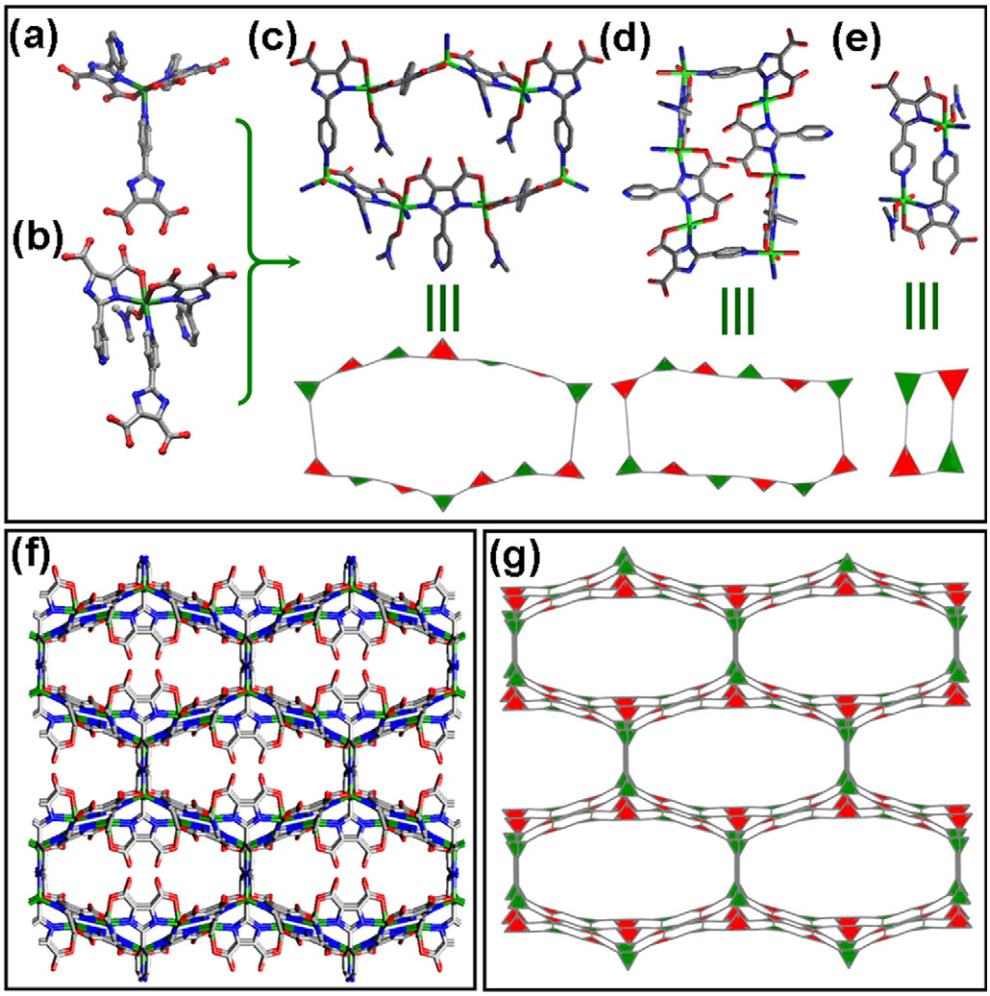


**Fig. 1.** Description of **1**: (a), (b) the coordination mode of Zn(1) and Zn(2) cations; (c)-(e) the 14-MR, 12-MR and 4-MR of Zn(II) and $HPIDC^{2-}$ ligand; (f) the framework along the [001] direction; (g) polyhedral view of the 3,3-connected network. Color scheme: carbon = gray, nitrogen = blue, oxygen = red, zinc = green.