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**COMMUNICATION**

# Ligand-concentration-dependent self-organization of Hoffman- and PtS-type frameworks from one-pot crystallization†

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**Hoffman- and PtS-type frameworks were isolated from one-pot crystallization and characterized structurally. A ligand-concentration effect was proposed in such a self-organized system.**

The design and self-organization of metal–organic frameworks have been of great interest owing to their intriguing variety of architectures and topologies, as well as their potential applications.[1] A variety of assemblies with mineral structures, such as quartz, perovskite, sodalite, rutile, diamond, and cooperite, have been artificially produced by utilizing the well-defined "building block" approach.[2] Recently, Hoffman-type networks that are usually assembled by the copolymerization of transition-metal ions, tetracyanometallates $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) and pillar ligands, have been synthesized and exhibited interesting properties.[3–5] Unfortunately, a successful synthetic strategy for preparing Hoffman-like porous frameworks is still a tremendous challenge.

As part of our ongoing efforts in the design and synthesis of new structural types of functional crystalline materials,[6–8] we chose pillared bidentate ligands to react with transition-metal ions and tetracyanometallates, in order to construct three-dimensional (3D) functional Hoffman networks. Herein, we report the self-organization of a longer pillared bidentate ligand *N*-(4-pyridyl)isonicotinamide) (L), zinc(II) ions, and the $[Ni(CN)_4]^{2-}$ precusor by slow diffusion method.‡ Unexpectedly, two new 3D frameworks, Hoffman-type $[ZnL][Ni(CN)_4]\cdot 3H_2O$ (**1**), and PtS-type $ZnNi(CN)_4$ (**2**), were formed in the one-pot reaction. In addition, a distorted guest-involved PtS-type net $ZnNi(CN)_4\cdot 2CH_3CN$ (**3**) was isolated with the absence of L. In particular, the spontaneous self-adjustment of the ligand-concentration offers a strong driving force determining the self-assembled frameworks.

To identify the driving forces and controlling factors involved in such self-organization process in detail, a series of experiments on the dynamic adjustment of the $Zn^{II}/L/Ni^{II}$ ratio to modify the equilibrium conditions were performed. Different amounts of ligand were added into the system, while holding the $Zn^{II}/Ni^{II}$ ratio fixed (1 : 1).

Although reaction temperature-, time-, pH-, solvent-, and anion-dependent polymorphisms have been observed,[9–12] tuning the ligand-concentration in this case results in a controllable structural self-adaptation in the frameworks. **1** or **2** can be obtained simultaneously as the major product by varying the concentration of ligand. Under the condition of higher ligand concentration, colorless columns of **1** were mainly obtained with colorless blocks of **2** as the minor product. As the amounts of added ligand decreased, the self-organization direction autonomously changed in favor of the generation of **2** and the probability of producing **1** was weaker, thus indicating that **2** is kinetically favored compared to **1**. Then, **2** was the major product upon decreasing the ligand concentration further. It should be noted that, a distorted guest-involved PtS-type network (**3**) was formed exclusively in the extreme case of the absence of ligand, indicating that **3** was the most kinetically favored product.

Single-crystal X-ray structural analysis revealed that **1** crystallizes in monoclinic space group $P2_1/m$ with an asymmetric unit containing one $[ZnL]^{2+}$ cation, one $[Ni(CN)_4]^{2-}$ moiety and three guest water molecules (Fig. 1a).§ The Ni1 atom lies on an inversion center, and the Zn1 atom and the L ligand lie on a mirror plane. The $[Ni(CN)_4]$ unit has a square planar geometry with four cyanide-nitrogen atoms, while the coordination sphere of Zn center is six-coordinated with a slightly distorted octahedral geometry. Four $[Ni(CN)_4]^{2-}$ units saturate the equatorial positions of $[ZnN_6]$ octahedron, generating an infinite 2D $\{Zn[Ni(CN)_4]\}_n$ layers, while the remaining axial positions are occupied by two ligands, which act as bridges connecting the Zn centers of two adjacent layers, resulting in an extented 3D open Hoffman-type framework (Fig. 1b, Fig. 1c, Fig. S1†). The pillar ligand separates consecutive $\{Zn[Ni(CN)_4]\}_n$ layers by *ca.* 13.6 Å, and the total accessible solvent void space without the guest molecules is *ca.* 572 Å$^3$ (44%) according to a calculation performed with PLATON,[13] which is the largest accessible volume found for Hoffman clathrates reported up to now.

The powder X-ray diffraction (XRD) pattern of the as-synthesized product of **1** corresponded well with that simulated from the single-crystal XRD data (Fig. S2†). TG result showed that the well-pronounced weight loss of 11.0% from 20 to 130 °C, corresponded to the release of three crystallized water molecules (11.2%, Fig. S3†). No further weight loss was observed between 130 and 210 °C, above which the framework collapsed. Sorption studies (Fig. S4†) of evacuated samples indicated that **1** was nonporous to gases. The lack

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† Electronic supplementary information (ESI) available: Packing diagrams of **1**–**3**, TG curve and sorption isotherms of **1**. CCDC reference numbers 823867 (**1**), 823868 (**2**), and 823869 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05699a

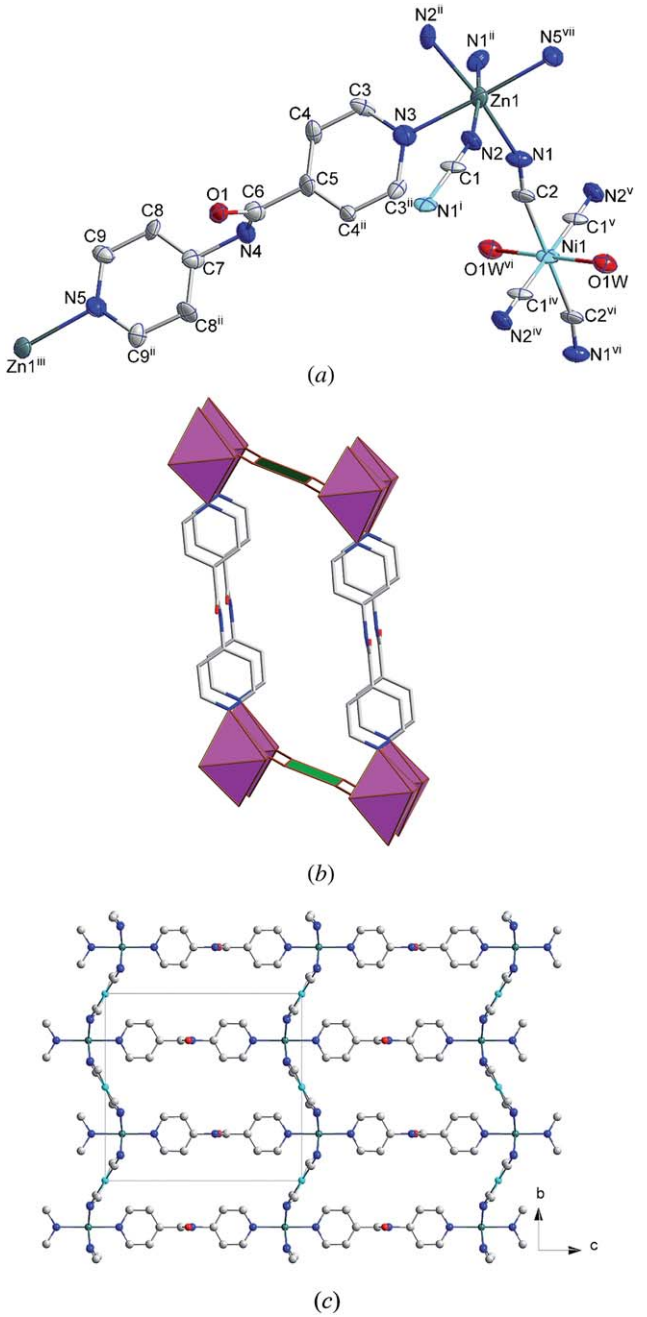


**Fig. 1** (a) ORTEP diagram of **1**, showing the 30% probability thermal motion ellipsoid. Hydrogen atoms and crystallized water molecules have been omitted for clarity. Symmetry codes: (i) $x-1, y, z$; (ii) $x, -y+3/2, z$; (iii) $x, y, z+1$; (iv) $-x+1, -y+2, -z$; (v) $x+1, y, z$; (vi) $-x+2, -y+2, -z$; (vii) $x, y, z-1$; (b) Hoffman-like structure of **1**, in which octahedral Zn and square-planar Ni centers are shown as pink and green, respectively; (c) The 3D open framework of **1** veiwed along the *a* axis.

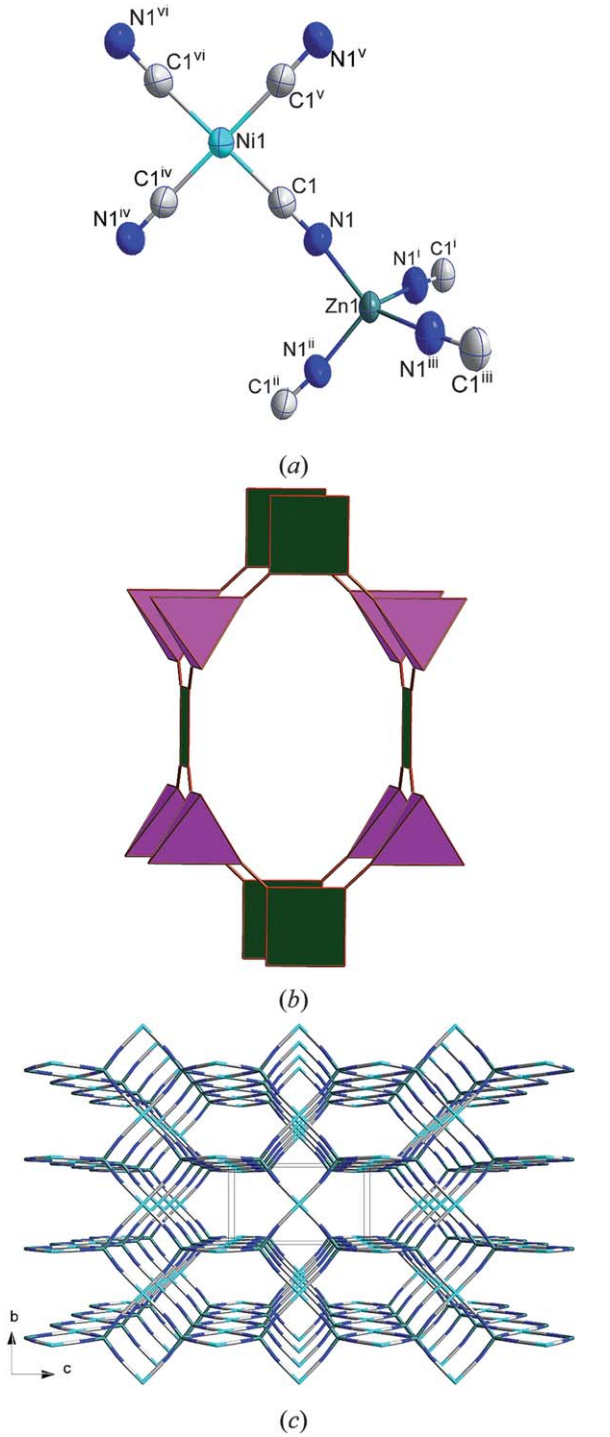


**Fig. 2** (a) ORTEP diagram of **2**, showing the 30% probability thermal motion ellipsoid. Symmetry codes: (i) $-y, x, -z+1/2$; (ii) $-x, -y, z$; (iii) $y, -x, -z+1/2$; (iv) $x, y, -z$; (v) $-x+1, -y, z$; (vi) $-x+1, -y, -z$; (b) tetrahedral (pink) and square-planar (green) building units to form a PtS net of **2**; (c) The 3D open framework of **2** viewed along the *a* axis.

of permanent porosity can be attributed to the protrusion of oxygen atoms from ligands into the pore and the framework instability caused by loss of the water molecules.

X-ray diffraction of **2** indicated that it crystallizes in tetragonal $P4_2/mmc$ space group.§ The asymmetric unit contains one Zn atom and one $[Ni(CN)_4]^{2-}$ unit (Fig. 2a). The Zn1 and Ni1 atoms lie at sites with $-42m$ and $mmm$ symmetries, respectively, and the N1 and C1 atoms lie at a site with $m$ symmetry. Each Zn center displays a tetrahedral geometry with four nitrogen atoms from four bridging cyanide groups, while each $[Ni(CN)_4]^{2-}$ anion acts as a square-planar $\mu_4$-linker and bridges two adjacent Zn sites. As a result, Zn and Ni centers are linked alternatively through linear rods, generating a 3D

open framework, which can be described as a 4-connected PtS net with the Schläfli symbol $4^2 8^4$ (Fig. 2b, Fig. 2c, Fig. S5†). The structure exhibits non-interpenetrated, although the 3D pore system accounts for approximately 60% of the crystal volume of **2**. This is not consistent with the tendency to form interpenetrated compounds if the cavity created is more than 50% of the crystal by volume.[14] To the best of our knowledge, PtS-type cyanide-based frameworks have scarcely been highlighted, expect for the two-fold interpenetrated $ZnM(CN)_4$ (M = Ni, Pd, Pt) and ionic $[NMe_4][CuPt(CN)_4]$ reported previously.[15,16]

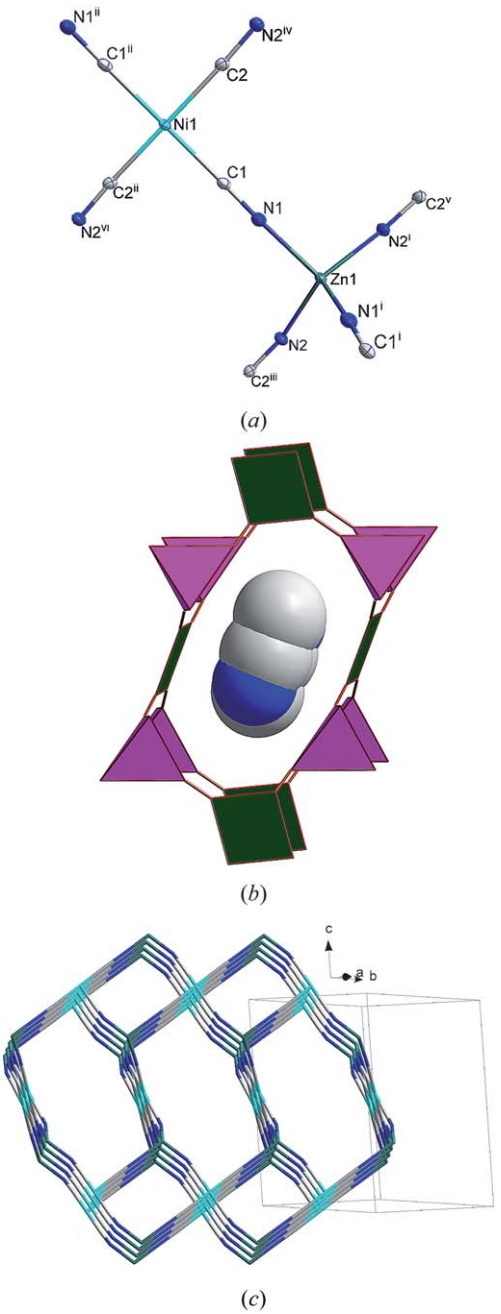


**Fig. 3** (a) ORTEP diagram of **3**, showing the 30% probability thermal motion ellipsoid. The $CH_3CN$ molecules have been omitted for clarity. Symmetry codes: (i) $-x, y, -z + 1/2$; (ii) $-x - 1/2, -y - 1/2, -z$; (iii) $x + 1/2, y + 1/2, z$; (iv) $x - 1/2, y - 1/2, z$; (v): $-1/2 - x, 1/2 + y, 1/2 - z$; (vi) $-x, -y, -z$; (b) tetrahedral (pink) and square-planar (green) building units to form a distorted PtS net of **3**, in which the guest $CH_3CN$ molecules (space-filling spheres) are filled; (c) The 3D open framework of **3**.

**3** crystallized in monoclinic space group *C*2/*c*, compared to the tetragonal $P4_2/mmc$ of **2**. The structure of **3** is composed of a tetrahedral site occupied by Zn atom, a square-planar site defined by the anion $[Ni(CN)_4]^{2-}$, and two guest $CH_3CN$ molecules (Fig. 3a). The Ni1 atom lies on an inversion center and the Zn1 atom lies on a twofold axis. **3** also displays a 3D PtS-type network with $4^2 8^4$ topology (Fig. 3b, Fig. 3c). The difference is that the resulting network is distorted significantly, compared to the ideal PtS net and the structure of **2**. As a result, the void occupies 50% of the unit cell volume, which is lower than the 60% of **2**.

In summary, Hoffman- and PtS-type frameworks were isolated from one-pot reaction and characterized by X-ray crystallography. A ligand-concentration effect was proposed in such a self-organized system. Our results provide a better understanding of a few unique and ambiguous phenomenon in cyanide systems. Further research is ongoing in our lab to prepare novel 3D open frameworks and to explore their valuable properties, using tetracyanometallates as building blocks.

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## Notes and references

‡ *Syntheses* of $[ZnL][Ni(CN)_4]\cdot 3H_2O$ (**1**) and $ZnNi(CN)_4$ (**2**): Single crystals of **1** and **2** were prepared at room temperature by slow diffusion of a $CH_3CN$–$H_2O$ (1 : 1) solution (2 mL) containing $Zn(NO_3)_2\cdot 6H_2O$ (0.05 mmol) and *N*-(4-pyridyl)isonicotinamide) (0.05 mmol) into a $CH_3CN$–$H_2O$ (1 : 1) solution (20 mL) of $K_2Ni(CN)_4$ (0.05 mmol). After two weeks, colorless columns (**1**) and colorless blocks (**2**) were obtained simultaneously. The crystals were seperated by hand picking, washed with $CH_3CN$–$H_2O$ (1 : 1) solvent, and air-dried. IR (KBr, $cm^{-1}$) for **1**: $\nu_{C\equiv N} = 2146, 2192$. *Synthesis* of $ZnNi(CN)_4$ (**3**): Single crystals of **3** were prepared at room temperature by slow diffusion of a $CH_3CN$–$H_2O$ (1 : 1) solution (2 mL) containing $Zn(NO_3)_2\cdot 6H_2O$ (0.05 mmol) into a $CH_3CN$–$H_2O$ (1 : 1) solution (20 mL) of $K_2Ni(CN)_4$ (0.05 mmol). After two weeks, colorless blocks were obtained. *Note*: the crystals of **1** were found to be stable, while those of **2** and **3** were fragile and degraded upon removal from the mother liquor. We have taken the following method when the single-crystal X-ray diffraction experiments of **2** and **3** were performed: as soon as one single crystal was removed from mother liquid, it was immediately introduced into a glass capillary having an open end and fixed. Then the capillary was soon filled with the mother liquor, and sealed for single-crystal X-ray structure determination at 291(2) K. EDS results (Fig. S6†) of all materials revealed the existence of Ni and Zn atoms, although crystals of **2** and **3** were fragile and easily degraded.

§ *Crystal data* for **1**: $C_{15}H_{16}N_7NiO_5Zn$, $M_r = 498.43$, monoclinic, space group $P2_1/m$, $a = 7.3620(18)$, $b = 12.946(2)$, $c = 13.6280(13)$ Å, $V = 1298.5(4)$ Å$^3$, $Z = 2$, $D_c = 1.275$ g cm$^{-3}$, $R_1$ ($wR_2$) = 0.0597 (0.1178) and $S = 1.024$ for 2662 reflections with $I > 2\sigma(I)$. *Crystal data* for **2**: $C_4N_4NiZn$, $M_r = 228.16$, tetragonal, space group $P4_2/mmc$, $a = b = 7.4474(12)$, $c = 13.050(4)$ Å, $V = 723.8(3)$ Å$^3$, $Z = 2$, $D_c = 1.047$ g cm$^{-3}$, $R_1$ ($wR_2$) = 0.0216 (0.0581) and $S = 1.157$ for 436 reflections with $I > 2\sigma(I)$. *Crystal data* for **3**: $C_8H_6N_6NiZn$, $M_r = 310.27$, monoclinic, space group $C2/c$, $a = 12.6429(19)$, $b = 7.9421(12)$, $c = 12.4142(19)$ Å, $V = 1228.4(3)$, Å$^3$, $Z = 4$, $D_c = 1.678$ g cm$^{-3}$, $R_1$ ($wR_2$) = 0.0232 (0.0533) and $S = 1.041$ for 1208 reflections with $I > 2\sigma(I)$.

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