Controllable preparation of Zn^{II} coordination polymers: unusual solvothermal formation of a LiGe-type framework directed by *in situ* S–S coupling of 5-(4-pyridyl)-1*H*-1,2,4-triazole-3-thiol†

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Controlled assembly of Zn^{II} with a versatile ligand 5-(4-pyridyl)-1*H*-1,2,4-triazole-3-thiol (Hptt) in conventional or solvothermal condition affords two distinct coordination frameworks, in which the former shows a unique 3-D pseudo-polyrotaxane architecture with 1-D water tapes penetrating the 2-D Zn–ptt layers, whereas the later is generated from *in situ* S–S coupling of Hptt and has a very rare 2-fold interpenetrating LiGe (lig) topology.

Crystal engineering of solid-state supramolecular entities such as coordination polymers has provided a nice bit of successful examples for the rational assembly of target materials,[1] which are normally realized by deliberate design of the ligands with adjustable connectivity and/or judicious selection of the metal ions with specific coordination tendency.[2] However, despite the remarkable achievements in this highly active topic, to predict and further accurately control the framework array of a given crystalline product still remains a considerable challenge at this stage due to the relative unpredictability of the subtle assembly process.[3] On the other hand, there has been increasing interest in coordination chemistry of sulfur-involved ligands, especially thiolates, which is primarily ascribed to their existence around the metal centers of some metalloproteins and possible application in chelation therapy.[4] Besides, such efforts have also offered diverse coordination complexes with useful properties such as semiconductivity, fluorescence, and biomimicry.[5]

In this context, our recent studies on coordination chemistry of a versatile organic ligand 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol (Hpyt) have presented distinct Zn^{II} and Cd^{II} coordination polymers dominated by reaction routes,[6] and thus triggered our further activity on this topic. As a matter of fact, a comparable multidentate building block 5-(4-pyridyl)-1*H*-1,2,4-triazole-3-thiol (Hptt), which may show several potential tautomers (Chart S1, ESI)† and different binding features, was used to construct new framework solids. And as well, the influence of synthetic pathways on the final crystalline products was explored as one of our continued focuses on controllable preparation of coordination polymers.[6,7] As a result, we present herein two disparate coordination frameworks produced from Zn^{II} and Hptt under different synthetic conditions, *viz.* $\{[Zn(ptt)_2]\cdot 4.5H_2O\}_n$ (**1**) and $\{[Zn(dptt)]\cdot 2H_2O\}_n$ (**2**). Significantly, unexpected *in situ* S–S coupling of Hptt into a novel anionic ligand bis(5-(4-pyridyl)-1,2,4-triazolate-3-yl)disulfide (dptt) was observed (see Scheme S1, ESI)† in the solvothermal synthesis of **2**, which has a very rare 2-fold interpenetrating LiGe (**lig**) network structure.

Assembly of Zn^{II} with Hptt using a conventional procedure affords crystalline phase $\{[Zn(ptt)_2]\cdot 4.5H_2O_n\}$ (**1**).‡ Notably, it has been confirmed that the existence of NH_4SCN is required in this process, although the mechanism is not clear. Owing to the versatility of Hptt, solid-state structural information of this ligand can provide helpful insights into the possible changes of its molecular configuration during metal-involved assemblies. However, direct attempts to obtain suitable crystals of Hptt by recrystallization were not hit, which were fortunately achieved as a byproduct when trying to prepare its Ag^I complex.[8]

X-Ray structural analysis (ESI)† of Hptt reveals a thione form (**IV** in Chart S1),[9] being similar to that of Hpyt.[10] Each Hptt takes a nearly planar conformation (Fig. S1a), with the dihedral angle of 6.8° between the pyridyl and triazolyl. Intermolecular N–H···N and N–H···S bonds (Table S1, ESI)† connect the Hptt molecules to form a 1-D tape (Fig. S1b, ESI)† along [001].

The asymmetric unit of **1** § comprises one Zn^{II} atom, a pair of anionic ptt ligands and the lattice water molecules. Two N and two S donors from four separate ptt components constitute the tetrahedral sphere of Zn^{II} (Fig. S2a, ESI).† As far as the ligand, both ptt take the thiolate form (**III** in Chart S1),[11] in which the dihedral angles between the pyridyl and triazole rings are 7.6° and 10.0°, respectively. As a consequence, the Zn^{II} centers are linked by the bidentate ptt bridges to afford a 2-D (4,4) layer along $(10\bar{1})$, which is corrugated and consists of two types of parallelogram grids (Fig. 1(a)) due to the tetrahedral configuration of each Zn^{II} node (Fig. S2b, ESI)†. Both grids have the same border lengths [11.300(3) and 9.933(4) Å] but different diagonal separations [20.783(7) and 4.559(1) Å for type **A** and 17.878(8) and 11.536(4) Å for type **B**]. Such 2-D layers stack along [100] in a parallel style without offset, and hence, a 3-D host lattice with 1-D channels (a volume of 559.5 $Å^3$, 27.8% of the unit cell volume as evaluated by *PLATON*[12]) is formed, in which the solvent water molecules are included.

Interestingly, the lattice water molecules are congregated to 1-D tapes, which penetrate the 2-D layers to form a fascinating

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† Electronic supplementary information (ESI) available: A Table for hydrogen-bonding parameters, additional experimental details, and complementary chemical chart/scheme and structural illustrations. See DOI: 10.1039/b716461k

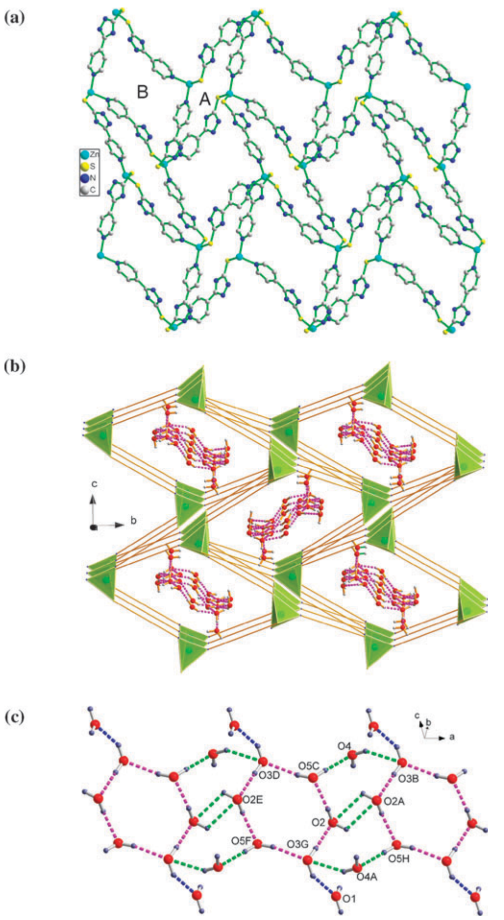

Fig. 1 (a) Layered coordination network in **1**. (b) 3-D pseudo-polyrotaxane architecture of **1**, in which the ptt connectors are simplified as rods for clarity. (c) 1-D water tape in **1**. Symmetry codes are listed in ESI.†

3-D pseudo-polyrotaxane architecture (Fig. 1(b) and Fig. S2c). Each water tape (Fig. 1(c)) is made up of cyclic water hexamers and paired pentamers that are fused alternately along the [100] direction. Notably, unusual double hydrogen-bonded bridges[13] (O2···O2A) are found between the adjacent hexamers, which also joint the paired pentamers. Such a 1-D water pattern has not been reported so far. The hexamer is centrosymmetric and displays a typical chair conformation. The average O···O edge distances (see Table S1 for details, ESI)† of the hexamer and pentamer are 2.718 and 2.814 Å, deviating slightly from those of ice I_h (2.759 Å)[14] and liquid water (2.85 Å).[15] This result may provide new structural information on water congeries. In addition, the water molecules of O1 act as dangling pendants around the 1-D tapes, which also anchor the host layers by O–H···N/O–H···S bonds. This 3-D supramolecular lattice is further reinforced by multiple host–guest O–H···N/N–H···O as well as inter-ligand N–H···N contacts (see Table S1, ESI)†.

Remarkably, solvothermal reaction of Zn^{II} with Hptt in the presence of NH_4SCN produces an unexpected 3-D framework $\{[Zn(dptt)]\cdot 2H_2O\}_n$ (**2**),‡ in which Hptt undergoes *in situ* S–S coupling to give a new elongated ligand dptt. It is known that *in situ* S–S cleavage may occur in solvothermal preparation of a coordination polymer,[16] whereas such a reverse process in this instance is undocumented.[17] Single crystals of two solvates of H_2dptt [*viz*. bis(5-(4-pyridyl)-2*H*-1,2,4-triazol-3-yl)disulfide] were also isolated by accident in preparing the Co^{II} complexes with Hptt.[8] It should be noted that the free H_2dptt ligand is not stable in air and becomes black within several days. Thus, an attempt to prepare its coordination complexes by direct metal–ligand reaction is unfeasible.

X-Ray diffraction (ESI)† of $H_2dptt\cdot 2H_2O$ and $H_2dptt\cdot 2CH_3CN$ indicates a pair of pseudo-polymorphs.[18] The asymmetric unit of $H_2dptt\cdot 2H_2O$ contains one H_2dptt and two lattice water, and the dihedral angles between the adjacent pyridyl and triazolyl rings are 4.1 and 4.9°. For $H_2dptt\cdot 2CH_3CN$, the H_2dptt entity (Fig. S3a) has an imposed C_2 symmetry and crystallizes with one acetonitrile in the local structure, where the pyridyl ring is inclined to the adjacent triazole by 3.5°. In both structures, the C–S–S–C torsion angles for H_2dptt are comparable (82.7 and 88.1°), indicating the similar molecular configurations; the adjacent H_2dptt units are linked *via* N–H···N bonds to afford a 1-D array, which is also sustained by aromatic stacking (Fig. S3b).[19] Notably, in the case of $H_2dptt\cdot 2H_2O$, such 1-D arrays are connected to 1-D helical water chains (*via* O–H···O bonds; along [010]) in virtue of O–H···N contacts (Table S1) to form a 3-D supramolecular architecture (see Fig. S3c).

In the structure of **2**,§ the asymmetric unit consists of a half-occupied Zn^{II} ion that lies on a 2-fold axis passing through the mid-point of the S–S bond of dptt, half of a dptt ligand and a lattice water. The tetrahedral geometry of Zn^{II} is composed of two pyridyl-N atoms from separate dptt ligands and a pair of triazolyl-N atoms from another dppt (see Fig. S4a). As for the deprotonated dptt anion, the pyridyl–triazolyl dihedral angle is 27.9° and the C–S–S–C torsion angle is 95.3°, being significantly larger than those in the free H_2dptt molecules.[20] These structural features reveal a more twisted configuration of dptt in **2**. As a result, each dptt adopts a μ_3-bridging fashion to link the Zn^{II} ions to form a 3-D coordination framework. From the perspective of network topology, both dptt and Zn^{II} represent 3-connecting nodes and are topologically equivalent (vertex symbol $8.8.10_3$), constituting a LiGe-type (**lig**[21]) framework (see Fig. 2(a)).[22,23] Though different 1-D channels are observed along *a*, *b* and *c* directions of a single net (see Fig. S4b, ESI),† interpenetration of two complementary subnets that are related by a center of symmetry (class IIa for interpenetration[24]) is practically found in the structure of **2**, and thus, available 1-D voids are only obtained along [001] (see Fig. 2(b) and Fig. S4c). Such channels have a volume of 1095.7 Å^3 (15.5% of the unit cell volume) and are occupied by disordered lattice water.[25]

In conclusion, controllable synthesis of two Zn^{II} coordination polymers with unusual supramolecular frameworks is achieved from a multifunctional ligand Hptt *via* distinct reaction routes, in which solvothermal *in situ* S–S coupling of Hptt is found to give an elongated anionic module dptt. This work may provide further insights into both synthetic and structural chemistry of such hybrid crystalline materials.

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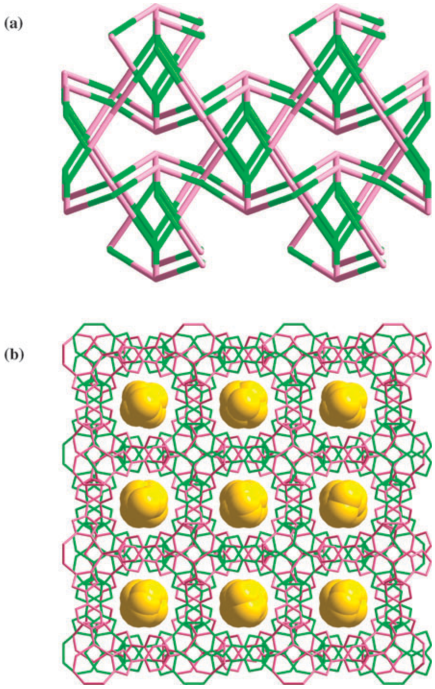

Fig. 2 (a) A schematic view of the **lig** network in **2** (dptt and Zn are shown as pink and green nodes). (b) A perspective view of **2** along [100], showing the 2-fold interpenetrating framework with the inclusion of water guests (yellow balls).

Notes and references

‡ *Preparation* of $\{[Zn(ptt)_2]\cdot 4.5H_2O\}_n$ (**1**). A methanol solution (15 ml) of Hptt (36 mg, 0.2 mmol) was added to a water–methanol solution (15 ml, 1 : 1) containing $Zn(OAc)_2\cdot 2H_2O$ (44 mg, 0.2 mmol) and NH_4SCN (15 mg, 0.2 mmol), and the mixture was stirred at *ca.* 60 °C for 1 h. The resultant clear solution was left to stand at room temperature, and colorless prism crystals of **1** were obtained after three weeks. Yield: 30% (15 mg, based on Hptt). Anal. Calc. for $C_{14}H_{19}N_8O_{4.5}S_2Zn$: C, 33.57; H, 3.82; N, 22.37. Found: C, 33.28; H, 3.69; N, 22.15%. IR (cm^{-1}): 3371br, 3108br, 2972m, 2932m, 1623s, 1512w, 1451m, 1430m, 1390w, 1329m, 1311s, 1243w, 1218w, 1169w, 1112w, 1059w, 1024m, 843w, 722m, 668w.

Preparation of $\{[Zn(dptt)]\cdot 2H_2O\}_n$ (**2**). A mixture of Hptt (36 mg, 0.2 mmol), $ZnCl_2$ (27 mg, 0.2 mmol), and NH_4SCN (15 mg, 0.2 mmol) in water–methanol (14 ml, 1 : 1) was sealed in a Teflon-lined stainless steel vessel (20 ml), which was heated at 140 °C for 5 days and then gradually cooled to room temperature at a rate of -5 °C h^{-1}. Pale-yellow block single crystals of **2** were collected in a yield of 11% (5 mg, based on Hptt). Anal. Calc. for $C_{14}H_{12}N_8O_2S_2Zn$: C, 37.05; H, 2.67; N, 24.69. Found: C, 36.79; H, 2.92; N, 24.55%. IR (cm^{-1}): 3455br, 1657m, 1623s, 1588s, 1550w, 1532w, 1497w, 1481m, 1466m, 1443m, 1407m, 1351w, 1328w, 1285w, 1220w, 1093w, 1060w, 1027w, 852m, 754w, 727m, 668m.

§ *Crystal data* for **1**: $C_{14}H_{19}N_8O_{4.5}S_2Zn$ (M_r = 500.86), monoclinic, $P2_1/n$, a = 7.284(3), b = 18.525(8), c = 15.046(6) Å, β = 97.575(6)°, V = 2012(1) $Å^3$, Z = 4, μ = 1.471 mm^{-1}, S = 1.029, R = 0.0335 and wR = 0.0775. *Crystal data* for **2**: $C_{14}H_{12}N_8O_2S_2Zn$ (M_r = 453.80), tetragonal, $I4_1/acd$, a = b = 17.962(1), c = 21.890(2) Å, V = 7062.7(9) $Å^3$, Z = 16, μ = 1.657 mm^{-1}, S = 1.034, R = 0.0284 and wR = 0.0619.

CCDC 665212–665216. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716461k

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20 The C–S bond distances in these structures are comparable ($\sim$1.75 Å), and the S–S length in **2** (2.044(2) Å) is slightly shorter than those in the solvates of H_2dptt (2.066(1) and 2.065(1) Å).
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25 Thermal gravimetric analyses reveal that **1** undergoes the consecutive weight loss from 45 °C, which does not stop until the heating ends at 600 °C, whereas for **2**, the elimination of lattice water is found in the temperature range of 80–145 °C, and the host framework keeps stable up to 235 °C. The heating treatment of a fresh sample of **2** (*ca.* 160 °C for 2 h) indicates the exclusion of lattice water (7.45 and 7.94% for observed/calculated mass loss of the sample). Notably, the dehydrated solid retains framework integrity of the original crystalline network, as confirmed by X-ray powder diffraction.