

Electronic Supplementary Information (ESI) for

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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Experimental

Single-crystal X-ray diffraction determination and refinement

X-ray single-crystal diffraction data for all compounds were collected on a Bruker Apex II CCD diffractometer at 293(2) K. In each case, a semi-empirical absorption correction was applied with SADABS and the SAINT program was used for integration of the diffraction profiles. The structure was solved by direct methods with the SHELXS program of SHELXTL package and refined with SHELXL. The final refinement was performed by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-H atoms. As a rule, H atoms of C were located geometrically and allowed to ride during the subsequent refinement. N- and O-bound H atoms were first placed in difference Fourier maps and then treated by using a riding model.

In the structural refinement of complex **1**, the lattice water of O5 was assigned to half occupancy to achieve the appropriate thermal parameter. In the case of **2**, the lattice water was disordered over five sites with isotropic refinement for most of them and thus, the affiliated hydrogen atoms were not located.

Crystal data for Hptt: C₇H₆N₄S (*Mr* = 178.22), monoclinic, *C2/c*, *a* = 26.767(4), *b* = 3.9631(6), *c* = 17.583(3) Å, β = 125.024(2)°, *V* = 1527.5(4) Å³, *Z* = 8, μ = 0.364 mm⁻¹, *S* = 1.035, *R* = 0.0318 and *wR* = 0.0746. *Crystal data* for H₂dptt·2H₂O: C₁₄H₁₄N₈O₂S₂ (*Mr* = 390.45), monoclinic, *P2₁/n*, *a* = 15.643(2), *b* = 7.658(1), *c* = 15.707(2) Å, β = 108.450(2)°, *V* = 1784.8(4) Å³, *Z* = 4, μ = 0.326 mm⁻¹, *S* = 1.040, *R* = 0.0463 and *wR* = 0.1103. *Crystal data* for H₂dptt·2CH₃CN (*Mr* = 436.52): monoclinic, *C2/c*, *a* = 7.713(3), *b* = 16.871(7), *c* = 16.121(7) Å, β = 91.764(7)°, *V* = 2097(2) Å³, *Z* = 4, μ = 0.282 mm⁻¹, *S* = 1.009, *R* = 0.0361 and *wR* = 0.0825.

Crystallization of Hptt, H₂dptt·2H₂O and H₂dptt·2CH₃CN

Hptt: A CH₃OH (10 ml) solution of Hptt (8.9 mg, 0.05 mmol) was carefully layered onto a water solution (10 ml) of AgNO₃ (8.5 mg, 0.05 mmol) in a straight glass tube. Strip colorless crystals of Hptt were collected after one week.

H₂dptt·2H₂O: A solution of Co(ClO₄)₂·6H₂O (18.2 mg, 0.05 mmol) in CH₃CN (5 ml) was added to an aqueous solution (5 ml) of Hptt (8.9 mg, 0.05 mmol), and the mixture was further stirred at *ca.* 70 °C for 2 h. The orange solution was left to stand at room temperature, giving colorless block crystals of H₂dptt·2H₂O after several days.

H₂dptt·2CH₃CN: Hptt (3.6 mg, 0.02 mmol) and Co(ClO₄)₂·6H₂O (7.2 mg, 0.02 mmol) were mixed in CH₃CN (10 ml) with stir and then left to stand. Colorless block crystals of H₂dptt·2CH₃CN were obtained after one week. IR (cm⁻¹): 3033m, 2964w, 2804m, 2318w, 1586vs, 1548m, 1519s, 1454s, 1415m, 1231vs, 1127w, 1077w, 1005m, 976m, 875m, 832vs, 738w, 699s, 667w, 546m.

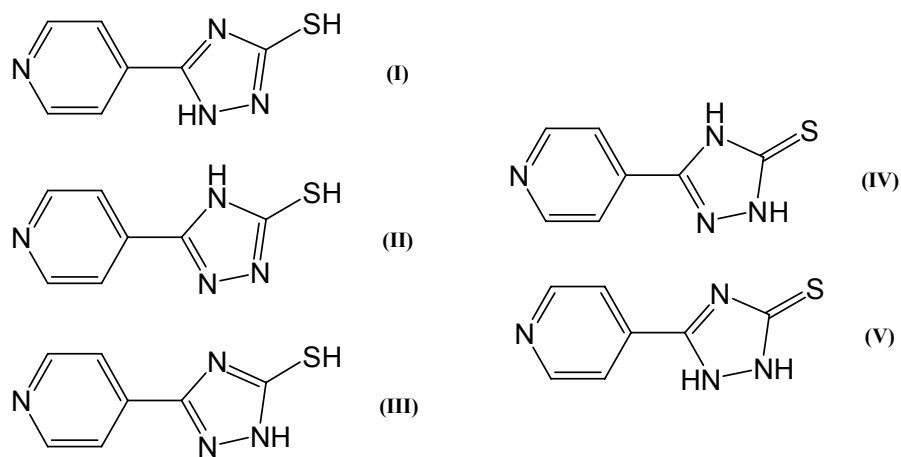
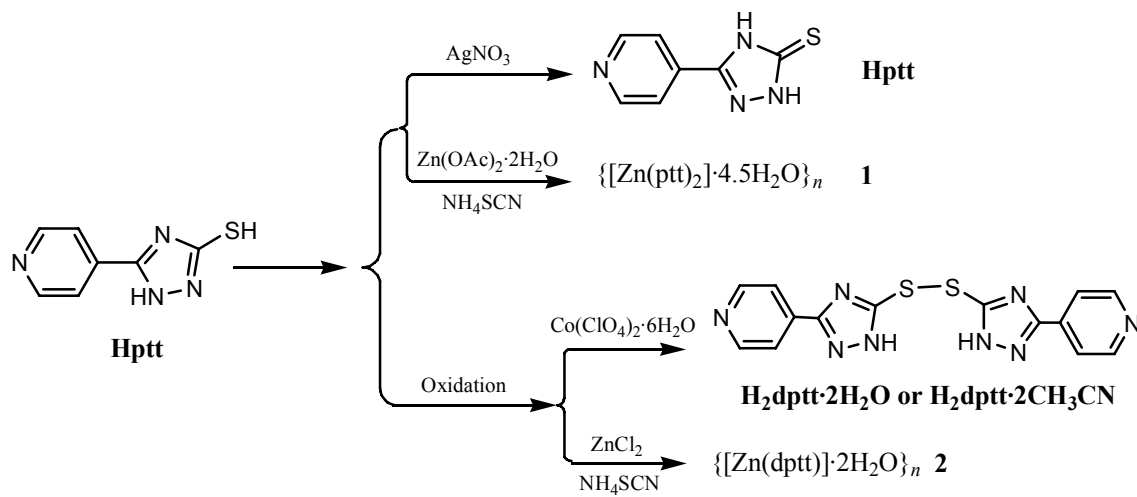


Chart S1 Potential tautomers of Hptt



Scheme S1

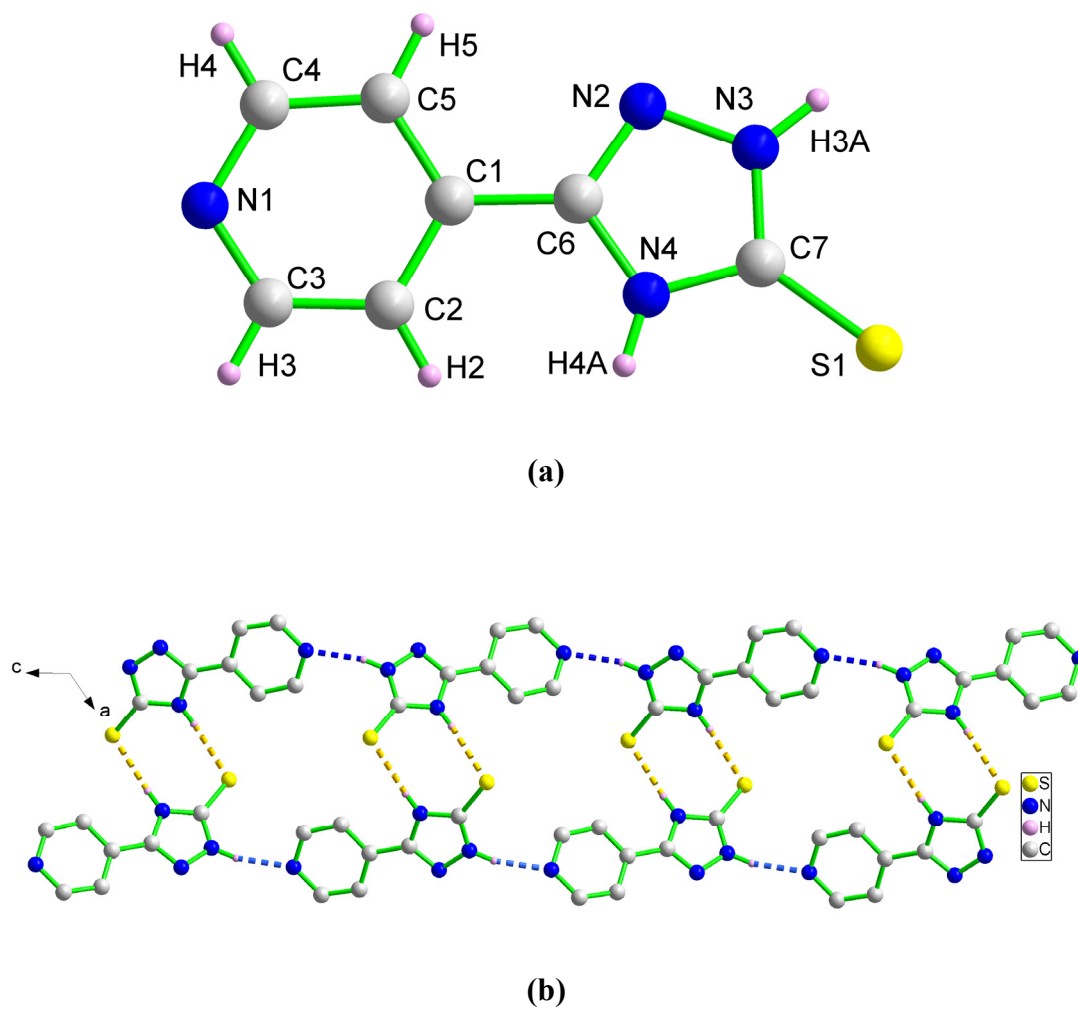
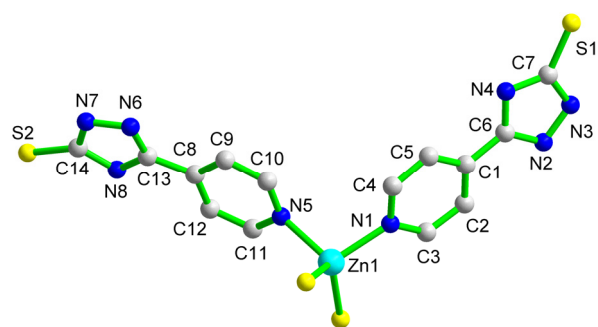
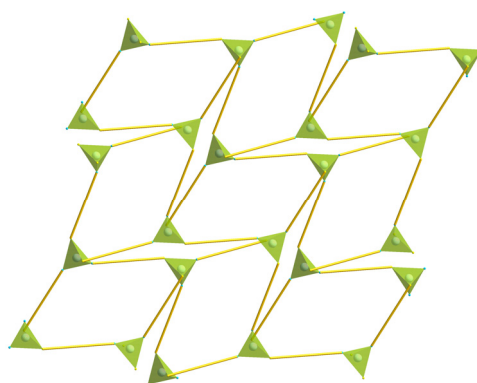


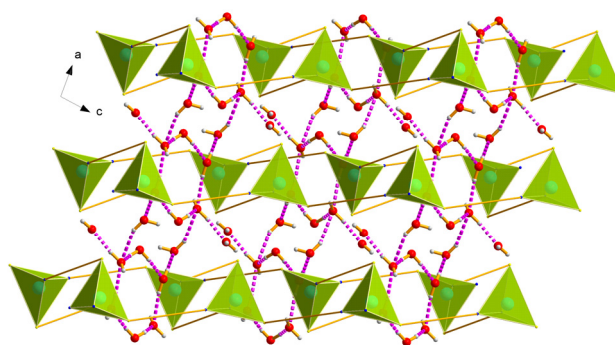
Fig. S1 (a) Molecular structure of the free ligand Hptt that exists in thione form. (b) 1-D hydrogen-bonding tape in the structure of Hptt.



(a)



(b)



(c)

Fig. S2 (a) A portion view of **1** with atom labeling of the asymmetric unit. (b) A schematic representation of the (4,4) network in **1**, in which the tetrahedral Zn^{II} nodes (green polyhedra) are bridged by ptt ligands (yellow rods). (c) 3-D pseudo-polyrotaxane supramolecular architecture of **1** viewed along the [010] direction.

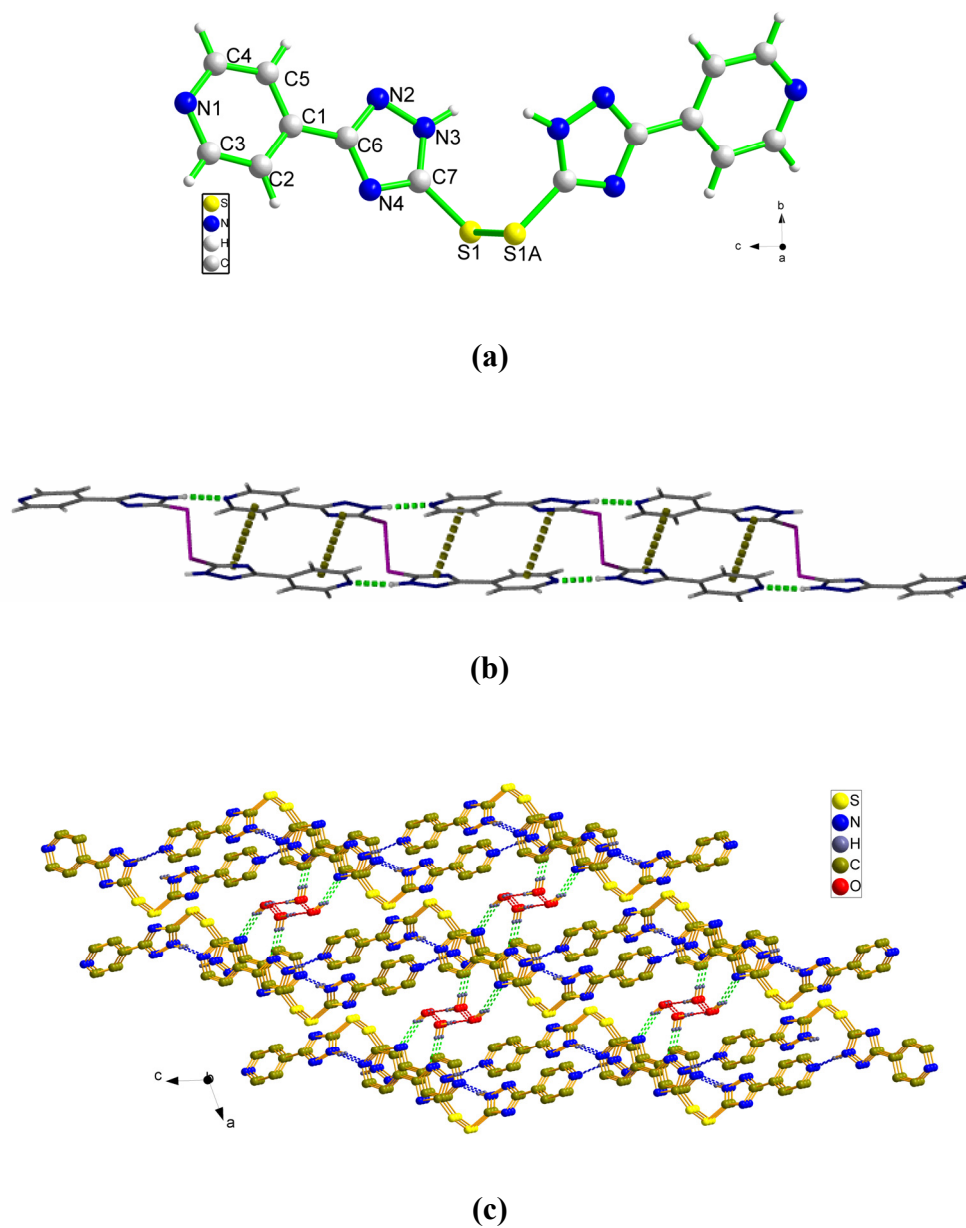
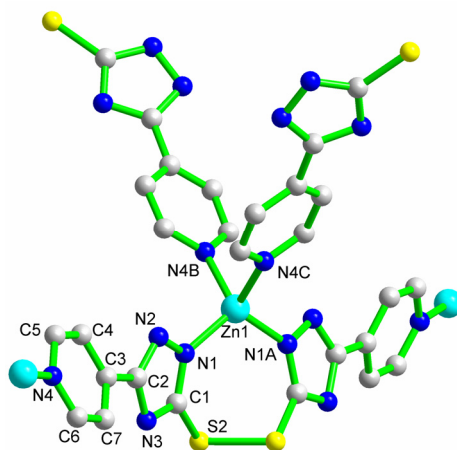
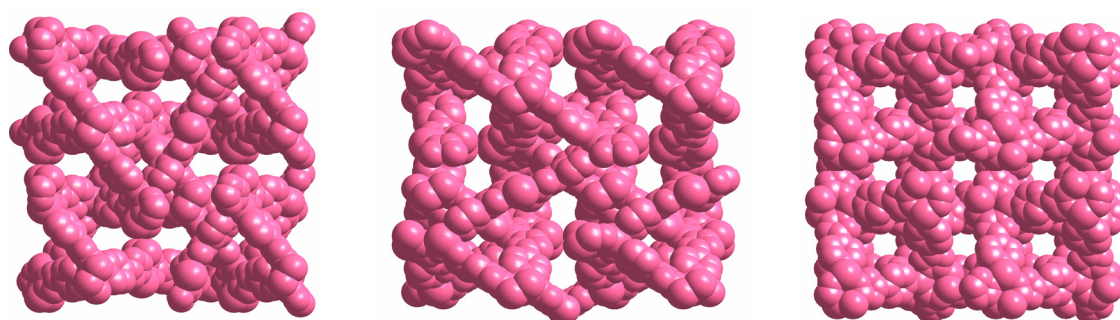


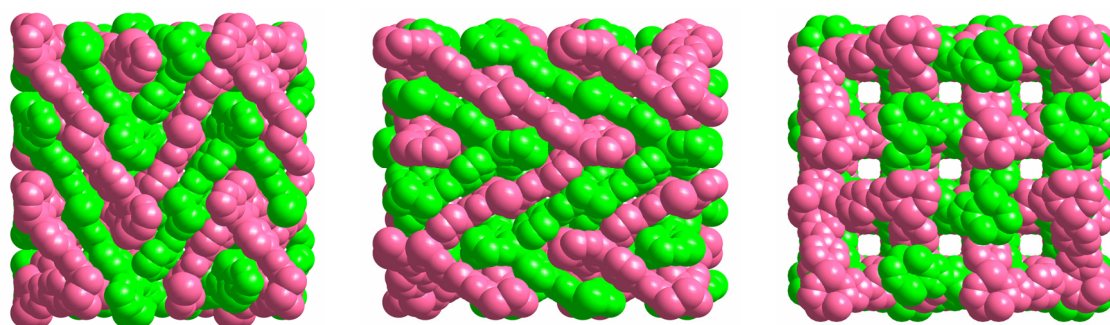
Fig. S3 (a) Molecular structure of H₂dptt in H₂dptt·2CH₃CN. Symmetry code for A: $-x, y, -z + 1/2$. (b) 1-D supramolecular array in both *pseudo*-polymorphs of H₂dptt, in which the N–H···N and π – π stacking interactions are shown as green and brown broken lines. (c) A perspective view of the 3-D hydrogen-bonding network in H₂dptt·2H₂O.



(a)



(b)



(c)

Fig. S4 (a) A portion view of **2** with atom labeling, showing the coordination sphere of Zn^{II} and the binding fashion of dptt. Symmetry codes for A: $-x + 1/2, y, -z$; B: $y - 1/4, x - 1/4, z - 1/4$; C: $-y + 3/4, x - 1/4, -z + 1/4$. (b) Packing diagram of a single **lig** net in **2**, showing channels along *a*, *b*, and *c* axes. (c) Packing diagram of **2** (2-fold interpenetration) along *a*, *b*, and *c* directions, in which the water guests are omitted for clarity.

Table S1 Possible hydrogen-bonding geometries (Å, °)

Compound	D–H...A	D...A	H...A	D–H...A
Hptt	N3–H3A...N1 ^a	2.888(3)	2.01	164
	N4–H4A...S1 ^b	3.253(2)	2.38	175
1	O2–H2A...O5 ^c	2.529(7)	1.94	126
	O2–H2B...O2 ^d	2.914(5)	2.43	117
	O3–H3B...O2 ^e	2.744(5)	1.89	179
	O4–H4A...O3 ^f	3.124(6)	2.35	152
	O5–H5A...O3 ^d	2.880(9)	2.04	170
	O5–H5B...O4 ^g	2.757(8)	1.91	176
	O3–H3A...O1 ^e	2.613(5)	1.90	141
	O1–H1A...N8 ^h	2.838(4)	1.99	177
	O1–H1B...S1 ^g	3.380(4)	2.58	156
	N3–H3'...O2 ^c	2.768(4)	1.93	164
	O4–H4B...N2 ^g	2.979(5)	2.25	144
	N7–H7...N4 ⁱ	2.962(4)	2.13	163
H₂dptt·2H₂O	N2–H2...N8 ^j	2.782(4)	1.93	172
	N6–H6'...N4 ^k	2.723(4)	1.86	178
	O1–H1A...N7 ^l	2.944(4)	2.13	162
	O1–H1B...O2	2.654(7)	1.90	147
	O2–H2A...O1 ^m	2.678(6)	1.83	178
	O2–H2B...N5 ^k	2.914(5)	2.06	176
H₂dptt·2CH₃CN	N3–H3A...N1 ⁿ	2.802(3)	1.89	173

^a $x, -y + 1, z - 1/2$. ^b $-x, y, -z + 1/2$. ^c $x - 1/2, -y + 3/2, z + 1/2$. ^d $-x + 1, -y + 1, -z + 1$. ^e $x + 1/2, -y + 1/2, z + 1/2$. ^f $-x + 3/2, y + 1/2, -z + 3/2$. ^g $x + 1/2, -y + 3/2, z - 1/2$. ^h $x + 1/2, -y + 1/2, z - 1/2$. ⁱ $-x, -y + 1, -z + 1$. ^j $-x + 1, -y + 3, -z + 2$. ^k $-x + 1, -y + 2, -z + 1$. ^l $x, y, z - 1$. ^m $-x + 3/2, y - 1/2, -z + 1/2$. ⁿ $x - 1/2, -y + 3/2, z - 1/2$.

Symmetry codes in Fig. 1c: A: $-x + 1, -y + 1, -z + 1$; B: $-x + 3/2, y + 1/2, -z + 3/2$; C: $x - 1/2, -y + 3/2, z + 1/2$; D: $-x + 1/2, y + 1/2, -z + 3/2$; E: $-x, -y + 1, -z + 1$; F: $-x + 1/2, y - 1/2, -z + 1/2$; G: $x - 1/2, -y + 1/2, z - 1/2$; H: $-x + 3/2, y - 1/2, -z + 1/2$.