Electronic Supplementary Material (ESI) for CrystEngComm.

Crystal engineering towards the luminescent property trimming of hybrid coordination polymer

(Supplementary data)

Table S1 Selected Bond lengths (Å) and angles (°) for compounds **1**-**4**.

Compound 1			
Cu(1)-S(1)	2.5185(13)	Cu(1)-N(3)#2	2.014(3)
Cu(1)-N(4)#1	1.972(3)	Cu(1)-N(2)#3	2.033(3)
N(4)#1-Cu(1)-S(1)	102.16(8)	N(3)#2-Cu(1)-S(1)	100.40(8)
N(4)#1-Cu(1)-N(3)#2	121.35(11)	N(3)#2-Cu(1)-N(2)#3	109.65(11)
N(4)#1-Cu(1)-N(2)#3	120.29(11)	N(2)#3-Cu(1)-S(1)	96.77(9)
Compound 2			
Cu(1)-Cl(1)	2.3459(5)	Cu(2)-Cl(1)#1	2.4062(6)
Cu(1)-S(1)	2.3264(6)	Cu(2)-Cl	2.4438(5)
Cu(1)-N(1)	2.0019(15)	Cu(2)-N(3)	2.0291(15)
Cu(1)-N(2)	2.0409(15)	Cu(2)-N(4)#2	2.0175(15)
S(1)-Cu(1)-Cl(1)	113.481(19)	Cl(1)#1-Cu(2)-Cl(1)	98.693(17)
N(1)-Cu(1)-Cl(1)	122.18(5)	N(3)-Cu(2)-Cl(1)	99.08(5)
N(1)-Cu(1)-S(1)	105.07(5)	N(3)-Cu(2)-Cl(1)#1	119.47(5)
N(1)-Cu(1)-N(2)	108.37(6)	N(4)#2-Cu(2)-Cl(1)	126.80(5)
N(2)-Cu(1)-Cl(1)	99.59(5)	N(4)#2-Cu(2)-Cl(1)#1	104.06(5)
N(2)-Cu(1)-S(1)	107.19(5)	N(4)#2-Cu(2)-N(3)	109.77(6)
Compound 3			
Cu(1)-S(1)	2.4790(7)	Cu(1)-N(2)#2	2.0102(18)
Cu(1)-N(1)#1	1.9752(18)	Cu(1)-N(3)#3	2.0331(17)
N(1)#1-Cu(1)-S(1)	102.64(5)	N(2)#2-Cu(1)-S(1)	100.11(5)
N(1)#1-Cu(1)-N(2)#2	120.78(7)	N(2)#2-Cu(1)-N(3)#3	110.94(7)
N(1)#1-Cu(1)-N(3)#3	119.45(7)	N(3)#3-Cu(1)-S(1)	96.82(5)
Compound 4			
Cu(1)-Cl(1)	2.3268(10)	Cu(2)-Cl(1)	2.4221(11)
Cu(1)-S(1)	2.3171(11)	Cu(2)-Cl(1)#1	2.4459(11)
Cu(1)-N(1)	2.025(3)	Cu(2)-N(3)	2.040(3)
Cu(1)-N(2)	2.073(3)	Cu(2)-N(4)#2	2.007(3)
S(1)-Cu(1)-Cl(1)	112.28(4)	Cl(1)-Cu(2)-Cl(1)#1	93.39(4)
N(1)-Cu(1)-Cl(1)	124.63(9)	N(3)-Cu(2)-Cl(1)#1	119.25(10)
N(1)-Cu(1)-S(1)	105.89(10)	N(3)-Cu(2)-Cl(1)	99.75(9)
N(1)-Cu(1)-N(2)	102.03(12)	N(4)#2-Cu(2)-Cl(1)	130.06(10)
N(2)-Cu(1)-Cl(1)	101.17(9)	N(4)#2-Cu(2)-Cl(1)#1	106.69(9)

N(2)-Cu(1)-S(1)	109.61(10)	N(4)#2-Cu(2)-N(3)	108.46(12)

Symmetry code: for **1**: #1 1-X, -1/2+Y, 1/2-Z; #2 +X, -1+Y, +Z; #3 1-X, 1-Y, 1-Z; for **2**: #1 1/2-X, 1/2-Y, 1-Z; #2 -X, -Y, 1-Z; for **3** #1 1-X, 1/2+Y, 1/2-Z; #2 +X, 1+Y, +Z; #3 1-X, -Y, 1-Z; for **4**: #1 1/2-X, 1/2-Y, 1-Z; #2 -X, 1-Y, 1-Z.

Table S2 The bond valance sum calculations for compounds **1**-**4**.

Compound	**1**	**2**		**3**	**4**	
Cu site	Cu1	Cu1	Cu2	Cu1	Cu1	Cu2
BVS	1.199	1.204	1.078	1.218	1.178	1.068
Assigned O.S.	+1	+1	+1	+1	+1	+1

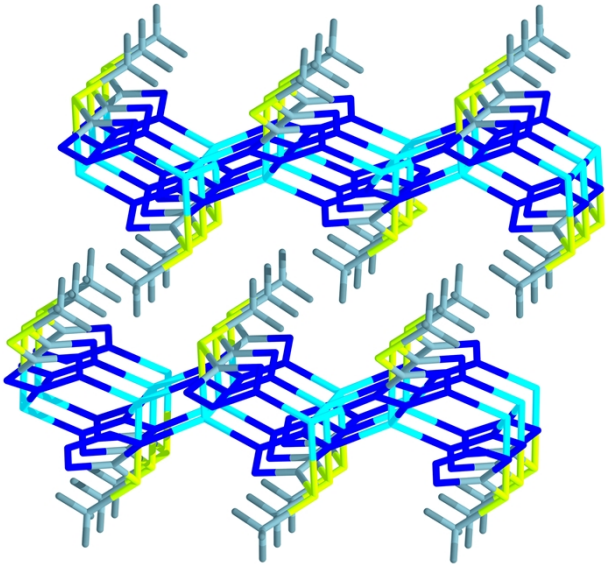


Fig. S1 3D supramolecular arrangement of compound **1**.

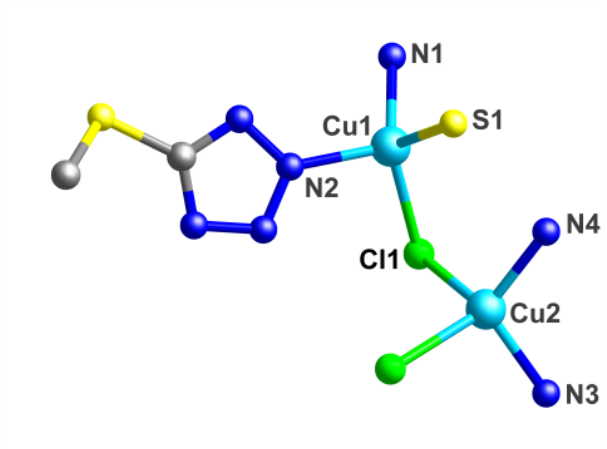


Fig. S2 The asymmetric unit of **2**. Hydrogen atoms are omitted for clarity.

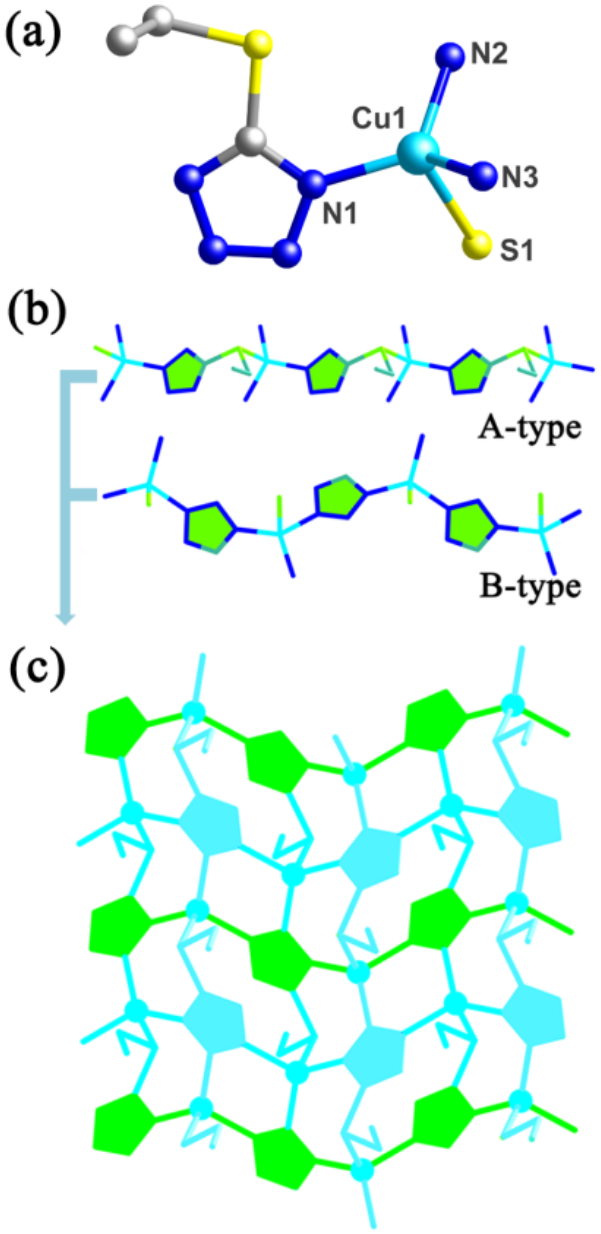


Fig. S3 (a) The asymmetric unit of **3**. Hydrogen atoms are omitted for clarity. (b) Two types of 1D chains. (c) The 2D layer connected by A- and B-type chains.

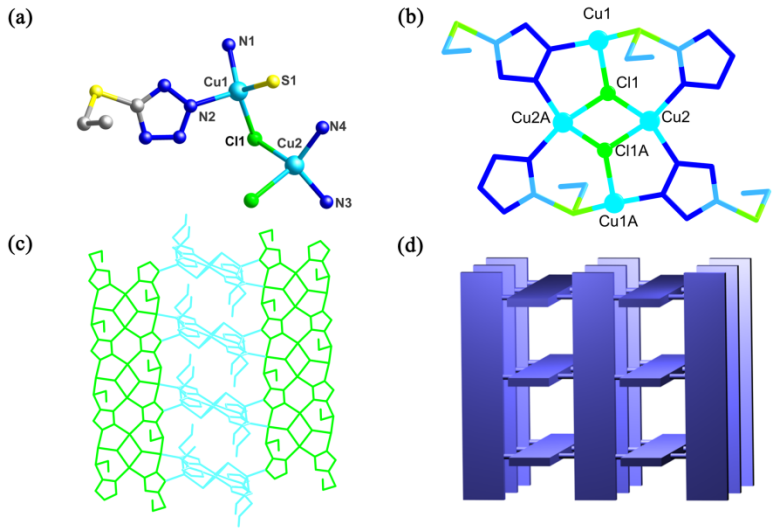


Fig. S4 (a) The asymmetric unit of **4**. Hydrogen atoms are omitted for clarity. (b) Perspective views showing the $[Cu_4Cl_2(ettz)_4]^{2-}$ tetranuclear unit of **4**. (c) The 2D layer connected by strip-like chains. (c) Schematic representation of 3D structure.

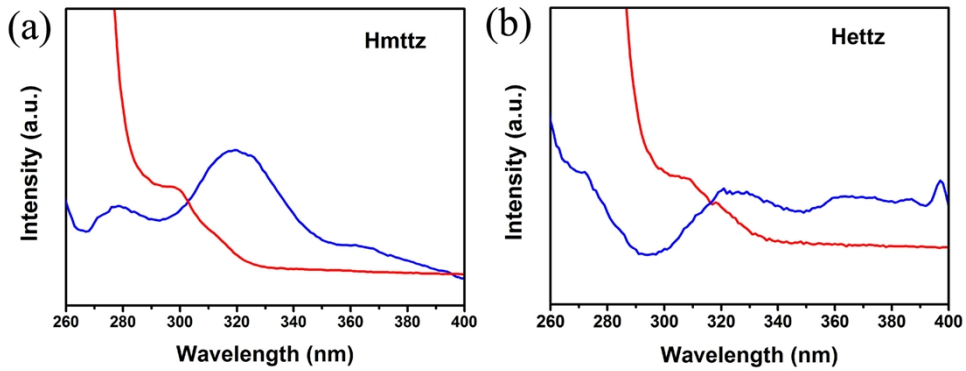


Fig. S5 Solid-state excitation spectra (blue curves) and UV-Vis absorbance spectra (red curves) of (a) free Hmttz and (b) Hettz ligands in aqueous solution at room temperature. Excitation spectra are monitored at 460 and 462 nm for Hmttz and Hettz.

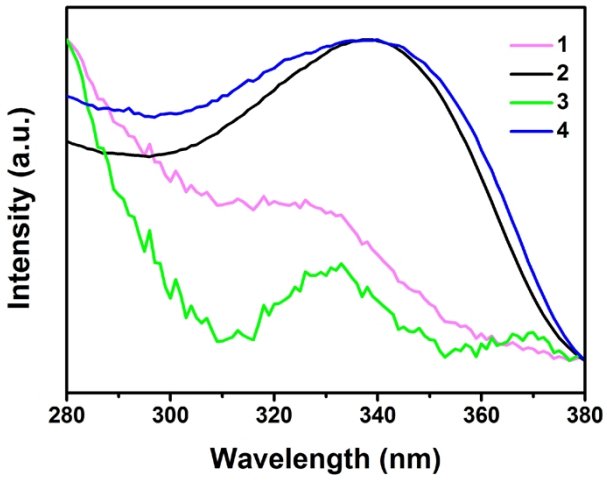
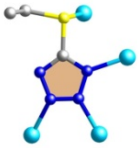
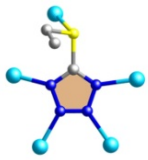
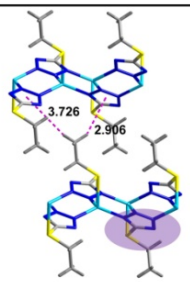
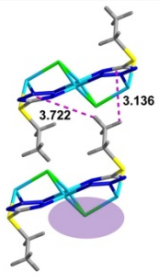
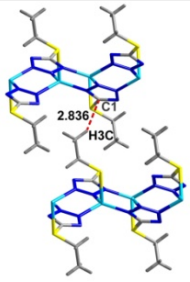
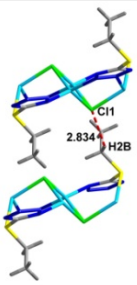


Fig. S6 Excitation spectra of compounds **1-4** in the solid state at room temperature monitored at 454, 475, 460 and 456 nm for **1**, **2**, **3** and **4**, respectively.

Table S3 A summary of detailed structural information within compounds **3** and **4**. Pink dashed lines show the distance between the nearest ettz molecules from ethyl group to tetrazole rings. Pseudo-replacement of Cl atom and ettz molecular at the corresponding position is highlighted by pink ellipsoid. Red dashed lines show the hydrogen bonding interactions.

	3	4
Rigidity	 μ_4-η^1:η^1:η^1:η_s^1	 μ_5-η^1:η^1:η^1:η^1:η_s^1
Distance and Arrangement		
Hydrogen Bonds		

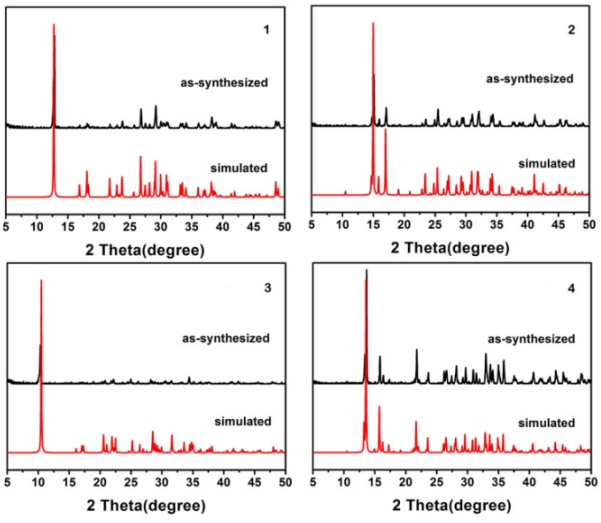


Fig. S7 Experimental and simulated XRPD patterns of compounds **1**-**4**. The diffraction peaks of both simulated and experimental patterns match in the key positions, indicating the phase purities of the four compounds.

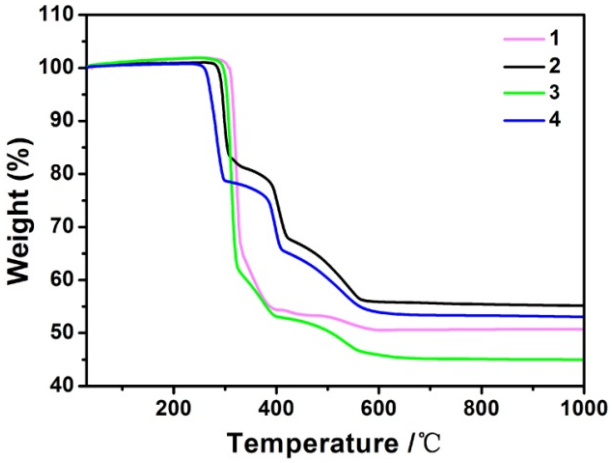


Fig. S8 The TG curves of **1**-**4**. To study the thermal stability, TG analyses were performed in N_2 atmosphere at a heating rate of 10°C/min from 30 to 1000°C. The TGA curves show that compounds **1** and **3** are similar and consist of three main steps of the weight losses accompanied by the endothermal or exothermal peaks. For **1**, the overall framework begins to decompose from 305 to 572°C, corresponding to the decomposition of organic groups (remaining 50.83%). For **2**, decomposition starts at 286°C, and continued till 576°C. The remaining weight of 45.89% corresponds to the organic matter pieces with copper. The TGA curves of **2** and **4** are similar and also exhibit three main steps of weight loss. For **2**, the TGA curve shows a weight loss of 56.09% in the temperature range 285 to 573°C, which is attributed to the decomposition of the framework of **2**, during which the organic groups are burned to unidentified products (remaining 43.91%). For **4**, the decomposition occurs from 254 to 597°C. The residue (46.16%) is organic matter pieces with copper.

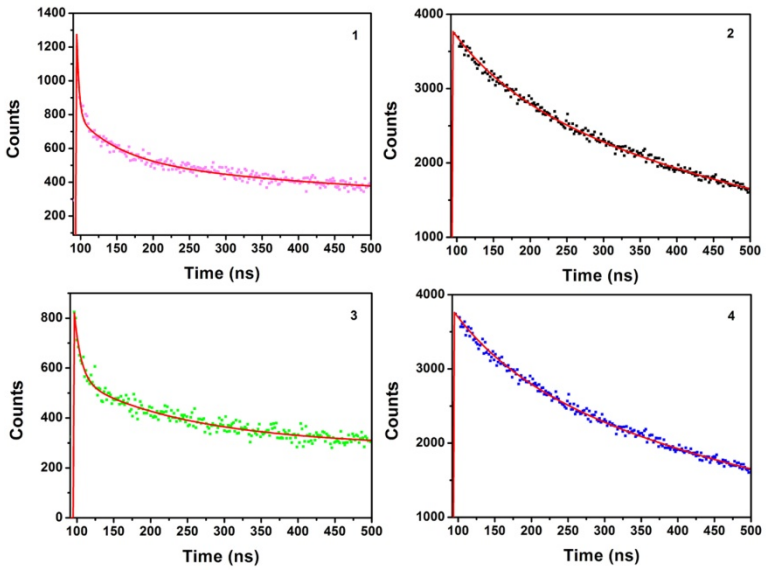


Fig. S9 Fluorescence decay curves of compounds **1-4** in solid state measured at room temperature.

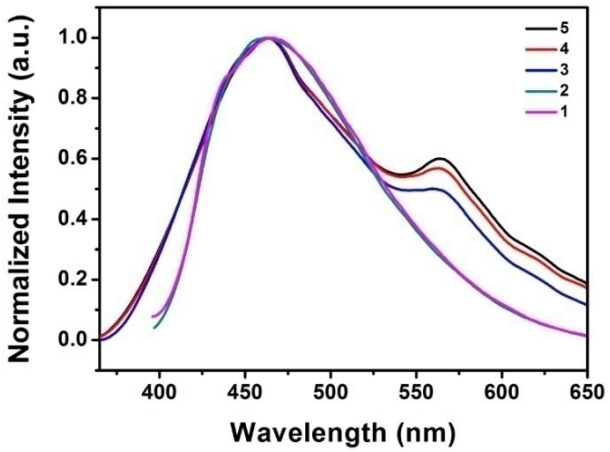


Fig. S10 The luminescent spectra of free Hettz ligand measured at room temperature upon excitation at 320 nm. Curves 1 and 2 are spectra of ligand Hettz in aqueous solution. The concentrations of 1 and 2 are 0.008 and 0.014 g/mL. Curves 3-5 are spectra of Hettz in solid-liquid heterogeneous system. Ratio of Hettz power and distilled water are 1:50, 1:25, 1:10 (g:mL) for 3, 4 and 5, respectively.

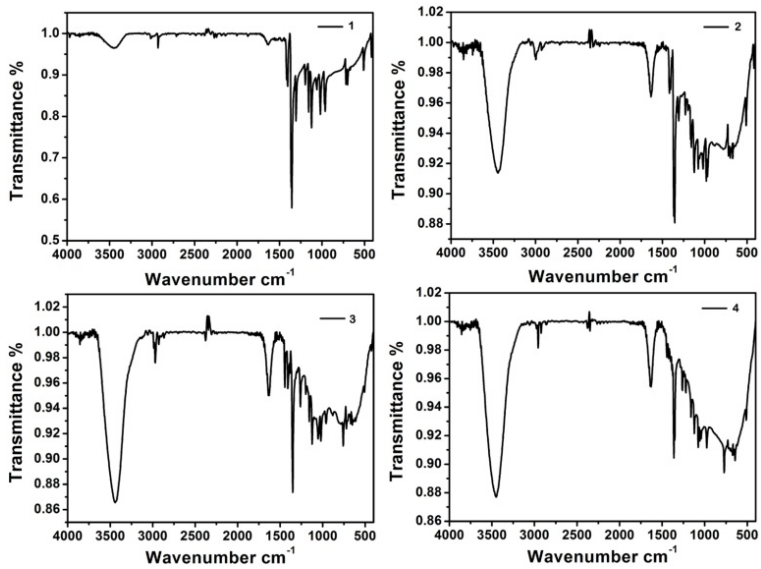


Fig. S11 IR spectra of compounds **1**-**4**. The observed bands in the region of 600-1640 cm^{-1} are assigned to the vibrations of the flexible ligands, respectively.