Electronic Supplementary Material (ESI) for *CrystEngComm*

Supporting Information for

Unusual three-dimensional coordination networks with $[WS_4Cu_6]$ clusters nodes and α-C_3N_4 topology

Zhao-Rui Pan, Xiao-Qiang Yao, He-Gen Zheng,* Yi-Zhi Li,* Zi-Jian Guo and Stuart R. Batten*

Table S1 Selected Bond Distances (Å) and Angles (deg) for compounds 1 and 2

Compound 1			
Br1 – Cu1	2.4443(10)	Cu1 – N1	2.039(6)
Cu1 – S1	2.3237(16)	Cu1 – S1a	2.3389(18)
Cu1 – W1	2.7441(7)	Cu2 – N3	1.988(5)
Cu2 – S1	2.2794(16)	Cu2 – W1	2.6627(10)
S1 – W1	2.2132(14)		
N1 – Cu1– S1a	121.71(16)	N1– Cu1– S1	110.74(18)
S1a – Cu1– S1	101.57(7)	N1– Cu1 –Br1	99.16(17)
S1a – Cu1– Br1	112.69(5)	S1– Cu1 – Br1	111.21(5)
N1– Cu1– W1	129.87(17)	S1a– Cu1– W1	50.86(4)
S1– Cu1– W1	50.97(4)	Br1– Cu1– W1	130.50(3)
N3 – Cu2 – N3b	93.7(3)	N3 – Cu2 – S1b	110.01(16)
N3 – Cu2 – S1	119.35(14)	S1b – Cu2 –S1	105.03(8)
N3 – Cu2 – W1	133.15(15)	S1– Cu2 – W1	52.51(4)
W1– S1– Cu2	72.68(5)	W1 – S1– Cu1c	74.39(5)
Cu2 – S1 – Cu1c	117.39(7)	W1– S1– Cu1	74.09(5)
Cu2 – S1– Cu1	106.93(6)	Cu1c – S1 – Cu1	112.96(6)
S1a – W1– S1	109.40(4)	S1 – W1 – S1b	109.62(8)
S1a – W1 –Cu2	125.19(4)	S1– W1 – Cu2	54.81(4)
Cu2c – W1 – Cu2	180.0	S1a – W1 – Cu1	54.64(4)

S1– W1– Cu1	55.05(4)	S1b – W1– Cu1	120.39(5)
Cu2 – W1 – Cu1	86.670(17)	Cu1 – W1 – Cu1b	173.34(4)
S1 – W1– Cu1a	130.21(4)	Cu2 – W1 – Cu1a	93.330(18)
Cu1– W1– Cu1a	90.193(2)		
Compound 2			
Br1– Cu1	2.4221(15)	Cu1– N1	2.010(9)
Cu1 – S1	2.302(3)	Cu1– W1	2.7163(11)
Cu2 – N4	2.071(8)	Cu2– S1a	2.325(2)
Cu2 – W1	2.6699(16)	S1– W1	2.265(2)
S1a– Cu1	2.332(3)		
N1 – Cu1 – S1	119.3(3)	N1– Cu1– S1b	103.9(3)
S1– Cu1– S1	105.24(11)	N1– Cu1– Br1	103.7(3)
S1– Cu1– Br1	114.02(8)	S1b– Cu1– Br1	110.22(7)
N1– Cu1– W1	122.2(3)	S1– Cu1 – W1	52.89(6)
S1b– Cu1– W1	52.65(6)	Br1– Cu1 – W1	133.06(5)
N4c– Cu2– N4	99.0(4)	N4– Cu2– S1a	112.2(2)
N4– Cu2 – S1b	113.3(2)	S1 a–Cu2 –S1b	106.80(12)
N4 – Cu2 – W1	130.5(2)	S1a– Cu2 – W1	53.40(6)
W1– S1– Cu1	72.99(7)	W1– S1 – Cu2b	71.13(7)
Cu1– S1– Cu2b	115.77(10)	W1– S1 – Cu1a	72.41(7)
Cu1 – S1–Cu1a	112.28(9)	Cu2b – S1 – Cu1a	105.05(9)
S1 – W1 – S1c	110.95(11)	S1– W1– S1a	108.74(5)
S1 – W1 – Cu2	124.52(5)	S1a– W1 – Cu2	55.48(5)
Cu2 –W1 –Cu2b	180.0	S1 – W1 – Cu1a	54.94(6)
S1b – W1– Cu1a	130.71(6)	Cu2 – W1– Cu1a	93.35(3)
S1– W1– Cu1	54.12(6)	S1c– W1 – Cu1	130.71(6)
S1a – W1 – Cu1	120.55(6)	Cu2 – W1 – Cu1	86.65(3)
Cu1a – W1 – Cu1	90.195(3)	Cu1– W1– Cu1c	173.30(5)

Symmetry transformations used to generate equivalent atoms:

a = -*x* + 1/4, -*z* + 7/4, *y* - 1/4; b = *x*, -*y* + 2, -*z* + 3/2; c = -*x* + 1/4, *z* + 1/4, -*y* + 7/4.

(compound **1**).

a = -*x* +1/4, -*z* +7/4, *y* -1/4; b = -*x* +1/4, *z* +1/4, -*y* +7/4; c = *x*, -*y* + 2, -*z* + 3/2.

(compound **2**).

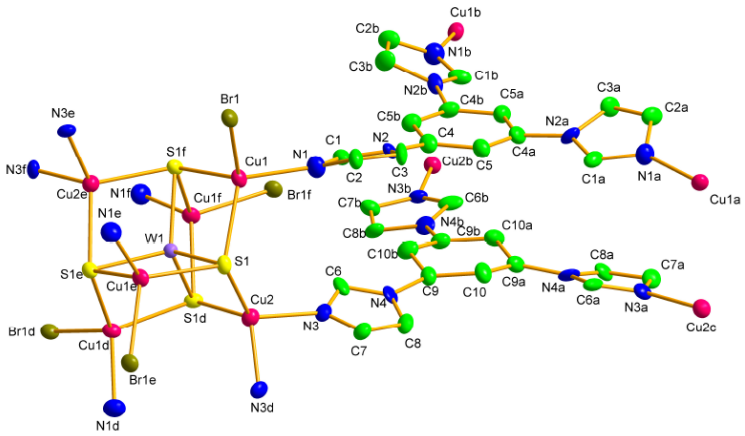

Fig. S1 Structural unit of $[(WS_4Cu_6Br_4)(timp)_{8/3}(H_2O)_{40/3}]_n$ (**1**) with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms and water molecules have been omitted for clarity. Symmetry Code: a = 0.5 – *z*, 1 – *x*, -0.5 + *y*; b = 1 – *y*, 0.5 + *z*, 0.5 – *x*; c = -1 + *z*, 1 – *x*, 1.5 – *y*; d = *x*, 2 – *y*, 1.5 – *z*; e = 0.25 – *x*, 0.25 + *z*, 1.75 – *y*; f = 0.25 – *x*, 1.75 – *z*, -0.25 + *y*.

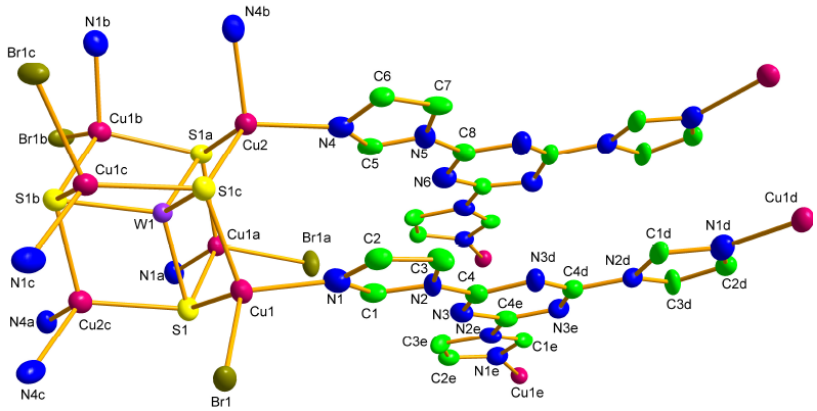

Fig. S2 Structural unit of $[(WS_4Cu_6Br_4)(timtz)_{8/3}(H_2O)_{40/3}]_n$ (**2**) with atom numbering, showing 30% thermal ellipsoids. Hydrogen atoms and water molecules have been omitted for clarity. Symmetry Code: a = 0.25 – *x*, 1.75 – *z*, -0.25 + *y*; b = *x*, 2 – *y*, 1.5 – *z*; c = 0.25 – *x*, 0.25 + *z*, 1.75 – *y*; d = -0.5 + *y*, 1.5 – *z*, 1 – *x*; e = 1 – *z*, 0.5 + *x*, 1.5 – *y*.

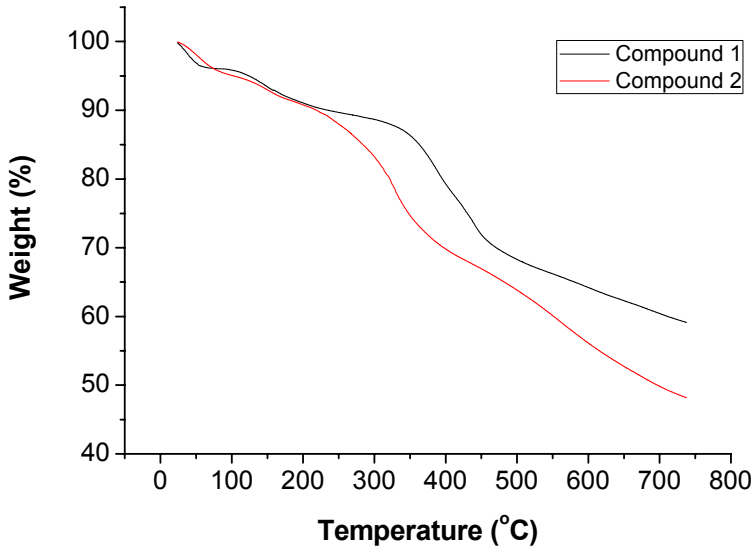

Fig. S3 TG plot of compounds **1** and **2.**

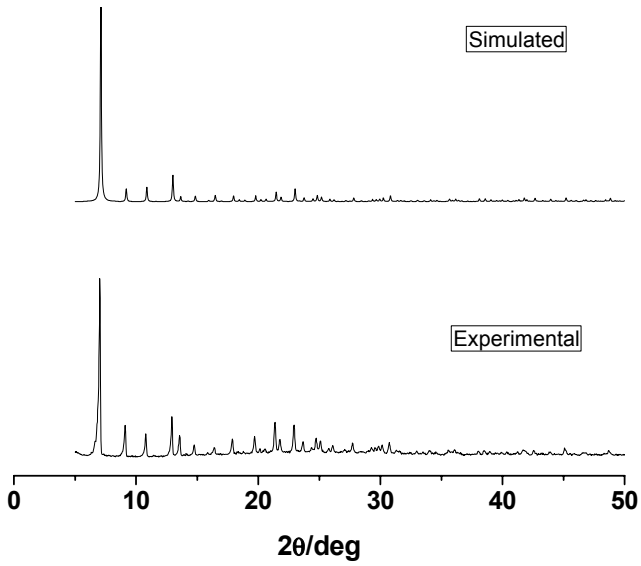

Fig. S4 Simulated and experimental PXRD pattern of compound **1.**

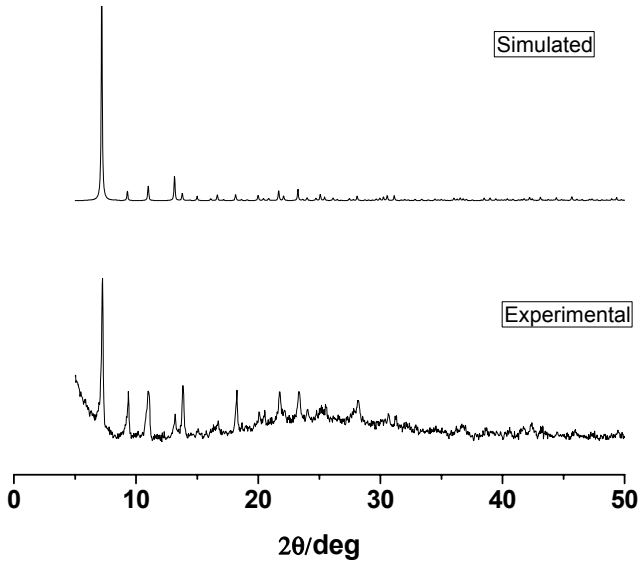

Fig. S5 Simulated and experimental PXRD pattern of compound **2**.

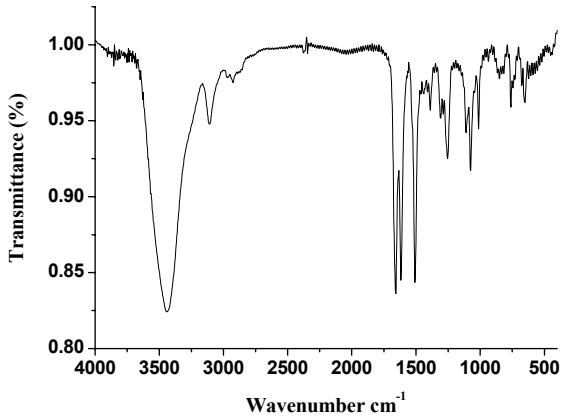

Fig. S6 IR spectrum of compound **1.**

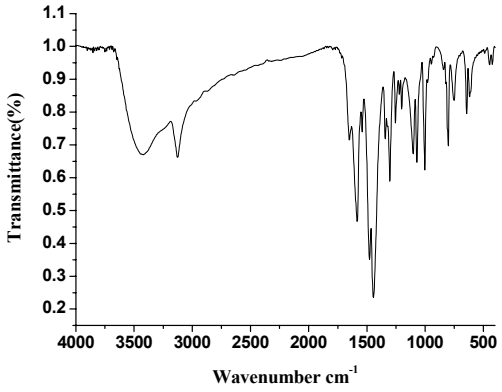

Fig. S7 IR spectrum of compound **2.**

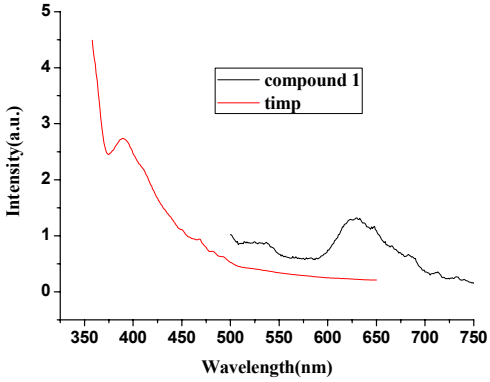

Fig. S8 Solid-state photoluminescent spectra of compound **1** and timp ligand at room temperature.

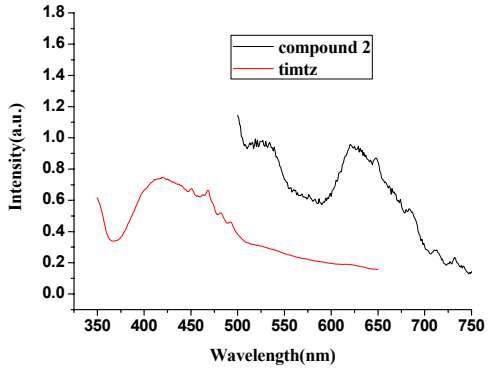

Fig. S9 Solid-state photoluminescent spectra of compound **2** and timtz ligand at room temperature.