Supplementary Information

Metal-organic frameworks constructed from $[MS_4Cu_x]^{x-2}$ (M = W, Mo) unit: isomerization of the cluster unit induced by temperature

Mei-Mei Meng,[a] Ji-Ming Xi,[a] Li-Fei Wang,[a] Rui Zhu,[a] Rui Zhang,*[a] Zhen-Zhong Lu,*[a,b] He-Gen Zheng,*[b] Wei Huang[a,c]

a. Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211800, China.

b. State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China.

c. Institute of Flexible Electronics (IFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China

Table 1. Crystal and Structure Refinement Data for compound **1, 2** and **3.**

	1	**2**	**3**
Empirical formula	$C_{72}H_{48}Cu_4I_2WN_6S_4$	$C_{132}H_{88}Cu_{12}I_8N_{11}S_8W_2$	$C_{72}H_{48}Cu_4I_2MoN_6S_4$
Formula weight	1817.21	4230.08	1729.30
Temperature (K)	290	190	290
Diffrn. wavelength (Å)	0.71073	1.34138	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C* 2/c	*P* -1	*C* 2/c
a (Å)	41.445(2)	20.178(1)	41.487(1)
b (Å)	7.934(1)	20.200(1)	7.937(1)
c (Å)	30.992(1)	26.662(1)	30.998(1)
a (°)	90	109.032(2)	90
β (°)	129.393(1)	103.717(2)	129.454(1)
γ (°)	90	100.951(2)	90
V, Å^3	7876.2(8)	9548.7(8)	7882.1(6)
Z	4	2	4
ρ_{calc} Mg/m^3	1.532	1.471	1.457
μ, mm^{-1}	3.448	16.262	2.146
F(000)	3528	4010.0	3400
Refl. collected	28741	138028	29193
Independent refl.	6475	25235	6676
Final R indices(R_1)	0.0364	0.0412	0.0310
(all data) wR_2	0.1221	0.1210	0.1232
GOOF	1.036	1.066	1.051

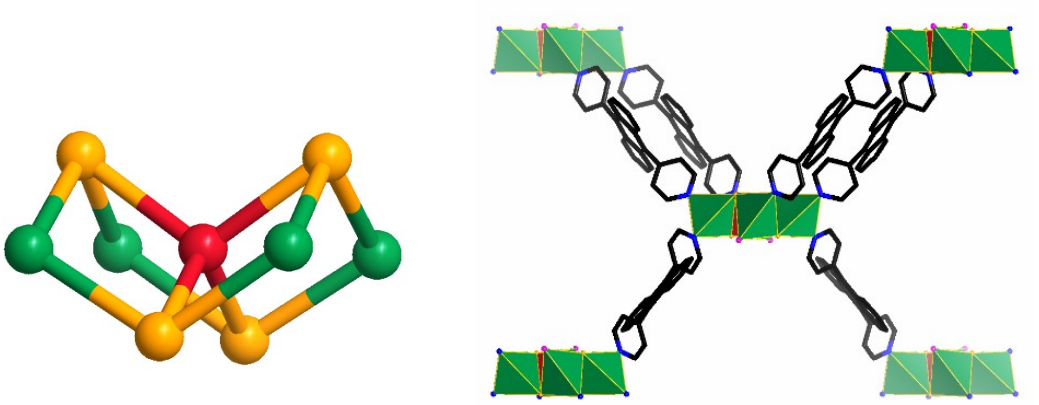

Figure S1. (Left) The penta-nuclear $[WS_4Cu_4]^{2+}$ unit in **1**. (Right) A diagram showing the tetrahedral connectivity of the $[WS_4Cu_4]^{2+}$ unit in **1**. (C, dark grey; N, blue; S, golden; I, pink; W, dark red; Cu, green, H atoms are omitted for clarity)

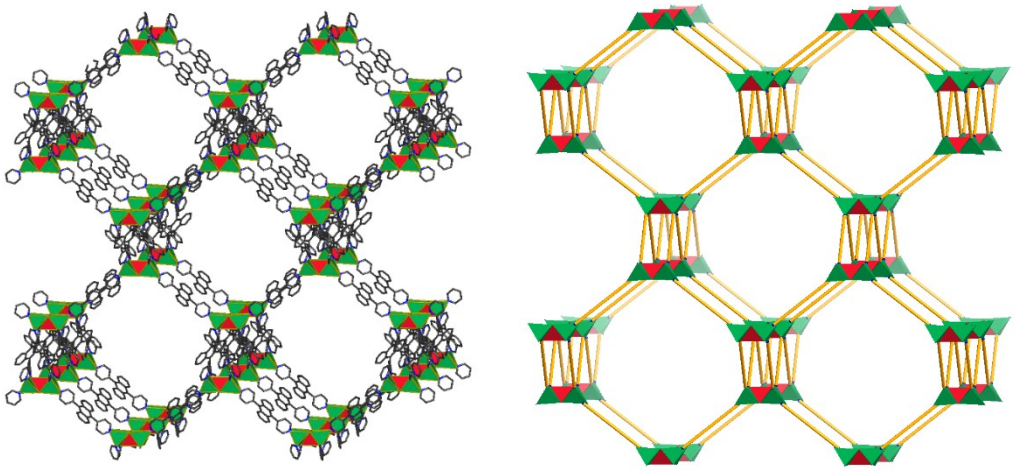

Figure S2. (Left) One of the diamondoid networks in **1**. (Right) A schematic view showing the diamondoid topology in **1**. (C, dark grey; N, blue; S, golden; W, dark red polyhedron; Cu, green polyhedron, H atoms are omitted for clarity)

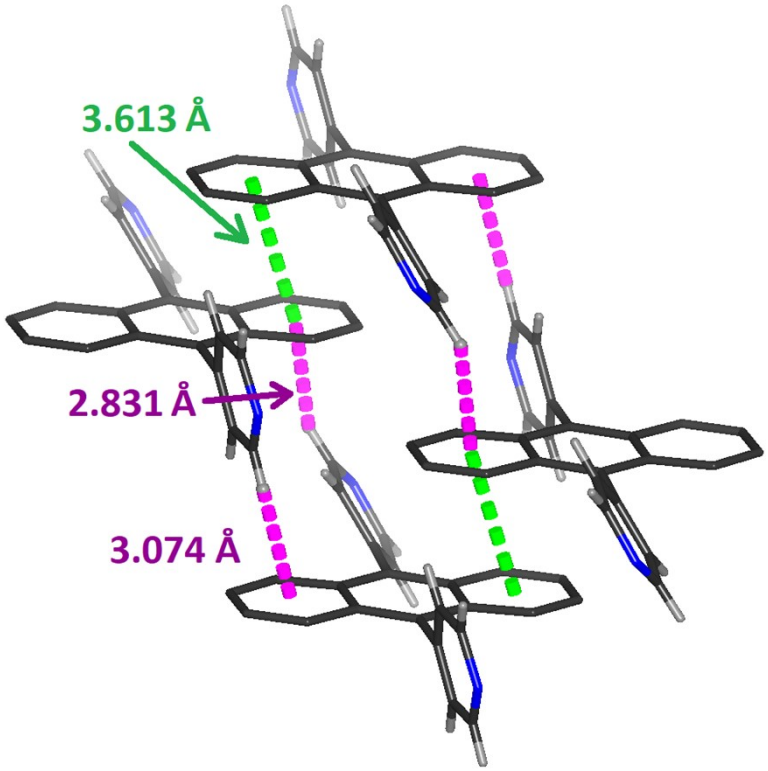

Figure S3. A diagram showing the π-π interactions (green dashed lines) and C-H···π interactions (pink dashed lines) in **1** (The π-π interactions are formed between the anthracene groups of the *dpa* ligands (3.613 Å), the C-H···π interactions are formed between the pyridine group and the anthracene groups of the *dpa* ligands from adjacent interpenetrated networks).

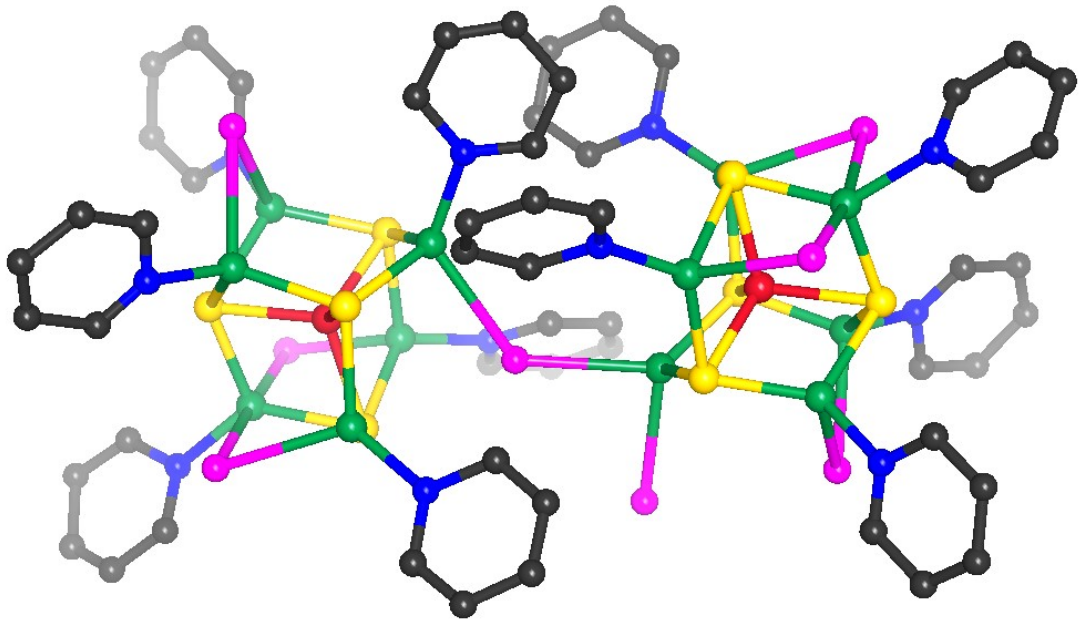

Figure S4. The coordination environment of the $[WS_4Cu_6]^{4+} \cdot I^- \cdot [WS_4Cu_6]^{4+}$ cluster unit in **2** (C, black; N, blue; S, golden; I, pink; W, dark red; Cu, green, H atoms are omitted for clarity).

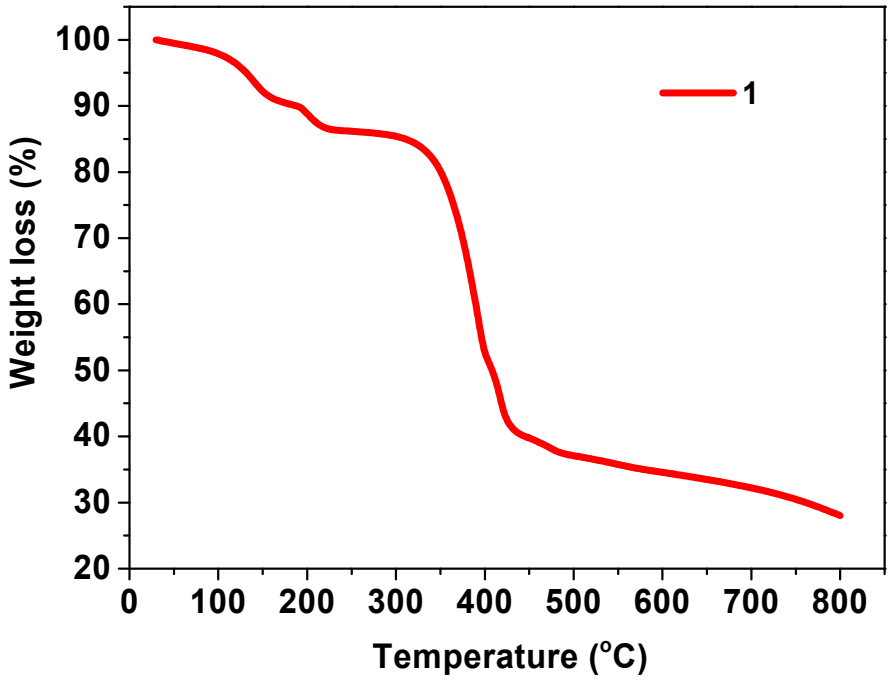

Figure S5 TGA result of **1**.

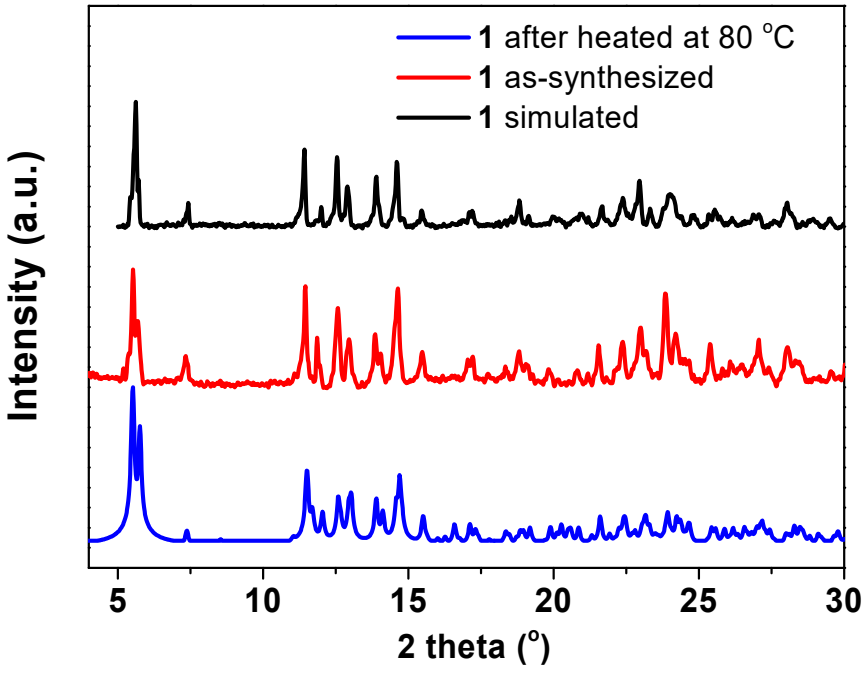

Figure S6. Powder XRD result of **1**.

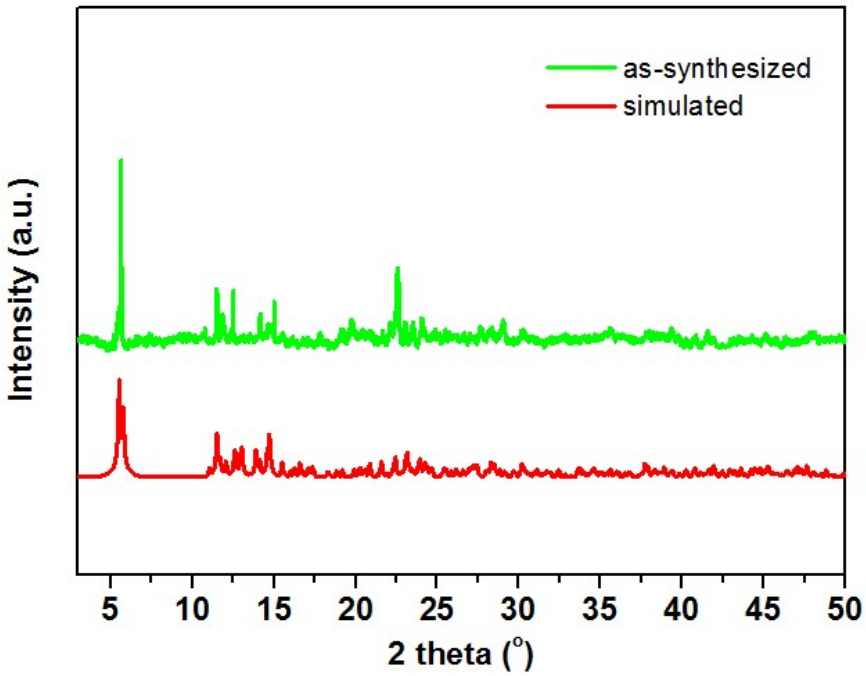

Figure S7. Powder XRD result of **3**.