Two novel POM-pillared metal-organic frameworks

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Table S1. Crystal Data and Refinement Results for Compounds **1** and **2**

Identification code	**1**	**2**
Empirical formula	$C_{36}H_{40}Cu_5N_{30}O_{48}SiW_{12}$	$C_{72}H_{62}Cu_9Mo_{24}N_{60}O_{87}P_2$
Formula weight	4212.97	6096.18
Crystal system	Triclinic	Triclinic
space group	*P*-1	*P*-1
a (Å)	12.195(10)	13.4510(17)
b (Å)	13.489(11)	14.8499(19)
c (Å)	14.276(12)	21.992(2)
α (º)	104.904(8)	99.752(5)
β (º)	111.632(6)	92.350(2)
γ (º)	105.607(2)	116.253(4)
Volume (Å^3)	1929(3)	3849.2(8)
Z	1	1
Calculated density (Mg/m^3)	3.627	2.630
Absorption coefficient (mm^{-1})	19.287	3.229
F(000)	1897	2909
Crystal size	0.20 × 0.20 × 0.20 mm	0.20 × 0.15 × 0.15 mm
θ range for data collection (º)	2.46 to 27.44	2.00 to 27.48
Limiting indices	-12<=*h*<=15 -17<=*k*<=15 -18<=*l*<=18	-17<=*h*<=17 -19<=*k*<=14 -26<=*l*<=28
Reflections collected / unique	14945 / 8720	30390 / 17348
Data / restraints / parameters	8720 / 120 / 634	17348 / 48 / 1198
Goodness-of-fit on F^2	1.248	1.085
Final *R* indices [I >2*σ*(I)]	R_1 = 0.0940 wR_2 = 0.1730	R_1 = 0.0680 wR_2 = 0.1774
R indices (all data)	R_1 = 0.1111 wR_2 = 0.1804	R_1 = 0.0913 wR_2 = 0.2050

Table S2. Selected Bond Distances for Compound **1**

Bond	Distant (Å)	Bond	Distant (Å)	Bond	Distant (Å)	Bond	Distant (Å)
Si(1)-O(1)	1.59(3)	W(2)-O(11A)	2.00(3)	W(4)-O(17)	1.95(2)	W(6)-O(4)	2.33(3)
Si(1)-O(3)	1.61(3)	W(2)-O(4)#1	2.33(3)	W(4)-O(2)#1	2.28(3)	W(6)-O(3)#1	2.46(3)
Si(1)-O(2)	1.70(3)	W(2)-O(1)	2.48(3)	W(4)-O(1)	2.42(3)	Cu(1)-N(2)	1.97(2)
Si(1)-O(4)	1.71(3)	W(3)-O(13)	1.66(2)	W(5)-O(18)	1.70(2)	Cu(1)-N(25)#2	1.98(2)
W(1)-O(7)	1.70(2)	W(3)-O(11B)#1	1.73(3)	W(5)-O(5)	1.85(2)	Cu(1)-N(29)	1.99(2)
W(1)-O(12)#1	1.84(2)	W(3)-O(15B)	1.84(4)	W(5)-O(17)	1.87(2)	Cu(1)-N(26)	2.02(2)
W(1)-O(6)	1.86(2)	W(3)-O(14)	1.91(2)	W(5)-O(19)	1.89(2)	Cu(1)-O(7)	2.44(2)
W(1)-O(8)	1.87(2)	W(3)-O(12)	1.93(2)	W(5)-O(6)	1.91(2)	Cu(2)-N(13)#3	1.97(2)
W(1)-O(9)	1.89(2)	W(3)-O(11A)#1	2.07(4)	W(5)-O(3)#1	2.33(3)	Cu(2)-OW1	1.98(2)
W(1)-O(2)	2.37(3)	W(3)-O(15A)	2.11(3)	W(5)-O(1)	2.38(3)	Cu(2)-N(12)	1.99(2)
W(1)-O(3)#1	2.44(3)	W(3)-O(4)	2.39(3)	W(6)-O(20)	1.70(2)	Cu(2)-N(22)	2.02(2)
W(2)-O(21)	1.66(2)	W(3)-O(2)#1	2.45(3)	W(6)-O(15B)	1.88(4)	Cu(2)-N(23)	2.27(2)
W(2)-O(22)	1.87(2)	W(4)-O(16)	1.66(2)	W(6)-O(10)#1	1.89(2)	Cu(3)-N(7)	2.01(2)
W(2)-O(10)	1.87(2)	W(4)-O(14)	1.89(2)	W(6)-O(9)	1.91(2)	Cu(3)-N(7)#4	2.01(2)
W(2)-O(11B)	1.90(3)	W(4)-O(8)#1	1.90(2)	W(6)-O(19)	1.92(2)	Cu(3)-N(4)	2.01(2)

Symmetry transformations used to generate equivalent atoms:

#1 -*x*-1,-*y*,-*z*-1; #2 -*x*,-*y*,-*z*; #3 -*x*,-*y*+1,-*z*; #4 -*x*-1,-*y*-1,-*z*

Table S3. Selected Bond Distances for Compound **2**

Bond	Distant (Å)	Bond	Distant (Å)	Bond	Distant (Å)	Bond	Distant (Å)
P(1)-O(4)	1.43(1)	Mo(3)-O(2)#1	2.48(1)	Mo(7)-O(25)	2.46(1)	Mo(11)-O(24)	2.51(1)
P(1)-O(2)	1.54(1)	Mo(4)-O(19)	1.66(1)	Mo(8)-O(35)	1.65(1)	Mo(12)-O(44)	1.66(1)
P(1)-O(1)	1.57(1)	Mo(4)-O(18)	1.83(1)	Mo(8)-O(32)	1.83(1)	Mo(12)-O(39)	1.84(1)
P(1)-O(3)	1.58(1)	Mo(4)-O(20)	1.86(1)	Mo(8)-O(34)	1.86(1)	Mo(12)-O(36)	1.87(1)
P(2)-O(26)	1.50(1)	Mo(4)-O(7B)	1.81(2)	Mo(8)-O(33)	1.99(1)	Mo(12)-O(42)	1.93(1)
P(2)-O(25)	1.51(1)	Mo(4)-O(17)	1.95(1)	Mo(8)-O(31)	1.99(1)	Mo(12)-O(29)	2.00(1)
P(2)-O(24)	1.56(1)	Mo(4)-O(7A)	2.18(2)	Mo(8)-O(24)#2	2.42(1)	Mo(12)-O(23)#2	2.40(1)
P(2)-O(23)	1.59(1)	Mo(4)-O(1)#1	2.48(1)	Mo(8)-O(26)	2.52(1)	Cu(1)-N(48)	1.93(1)
Mo(1)-O(5)	1.66(1)	Mo(4)-O(3)	2.49(1)	Mo(9)-O(38)	1.66(1)	Cu(1)-N(51)	2.08(1)
Mo(1)-O(7B)	1.87(2)	Mo(5)-O(21)	1.65(1)	Mo(9)-O(30)	1.81(1)	Cu(2)-N(57)#4	1.98(1)
Mo(1)-O(8)	1.81(1)	Mo(5)-O(6)	1.82(1)	Mo(9)-O(37)	1.85(1)	Cu(2)-N(36)	1.98(1)
Mo(1)-O(9)	1.92(1)	Mo(5)-O(16)	1.83(1)	Mo(9)-O(36)	1.94(1)	Cu(2)-N(56)	1.98(1)
Mo(1)-O(7A)	1.90(1)	Mo(5)-O(18)	1.99(1)	Mo(9)-O(32)	2.03(1)	Cu(2)-N(62)	2.02(1)
Mo(1)-O(6)	2.01(1)	Mo(5)-O(12)	2.00(1)	Mo(9)-O(24)#2	2.47(1)	Cu(2)-OW1	2.37(1)
Mo(1)-O(1)#1	2.40(1)	Mo(5)-O(1)#1	2.49(1)	Mo(9)-O(25)	2.48(1)	Cu(3)-N(13)#5	1.97(1)
Mo(2)-O(10)	1.66(1)	Mo(6)-O(22)	1.65(1)	Mo(10)-O(41)	1.63(1)	Cu(3)-N(12)	2.01(1)
Mo(2)-O(12)	1.81(1)	Mo(6)-O(14)	1.84(1)	Mo(10)-O(27)	1.82(1)	Cu(3)-N(18)	2.01(1)
Mo(2)-O(13)	1.84(1)	Mo(6)-O(9)#1	1.87(1)	Mo(10)-O(40)	1.84(1)	Cu(3)-OW2	2.02(1)
Mo(2)-O(11)#1	1.97(1)	Mo(6)-O(20)	1.96(1)	Mo(10)-O(34)	1.96(1)	Cu(3)-N(1)	2.24(1)
Mo(2)-O(8)#1	2.02(1)	Mo(6)-O(13)	1.98(1)	Mo(10)-O(39)	1.98(1)	Cu(4)-N(34)	2.03(1)
Mo(2)-O(2)	2.42(1)	Mo(6)-O(3)	2.37(1)	Mo(10)-O(23)#2	2.44(1)	Cu(4)-N(26)	2.03(1)
Mo(3)-O(15)	1.66(1)	Mo(7)-O(28)	1.65(1)	Mo(11)-O(43)	1.64(1)	Cu(4)-N(29)	2.04(1)
Mo(3)-O(11)	1.83(1)	Mo(7)-O(31)#2	1.82(1)	Mo(11)-O(33)#2	1.83(1)	Cu(4)-N(40)	2.06(1)
Mo(3)-O(17)	1.85(1)	Mo(7)-O(29)	1.82(1)	Mo(11)-O(42)	1.86(1)	Cu(4)-N(46)	2.21(1)
Mo(3)-O(16)#1	1.97(1)	Mo(7)-O(27)#2	1.96(1)	Mo(11)-O(37)#2	1.95(1)	Cu(5)-N(4)#6	1.99(1)
Mo(3)-O(14)	1.98(1)	Mo(7)-O(30)	2.01(1)	Mo(11)-O(40)	1.96(1)	Cu(5)-N(24)	1.99(1)
Mo(3)-O(3)	2.47(1)	Mo(7)-O(26)#2	2.46(1)	Mo(11)-O(23)#2	2.48(1)	Cu(5)-N(3)	1.99(1)
Cu(5)-N(7)#6	2.05(1)						

Symmetry transformations used to generate equivalent atoms:

#1 -*x*,-*y*+1,-*z* #2 -*x*+2,-*y*,-*z*+1 #3 -*x*+1,-*y*,-*z*

#4 -*x*,-*y*,-*z* #5 -*x*+1,-*y*+1,-*z*+1 #6 -*x*+2,-*y*+1,-*z*+1

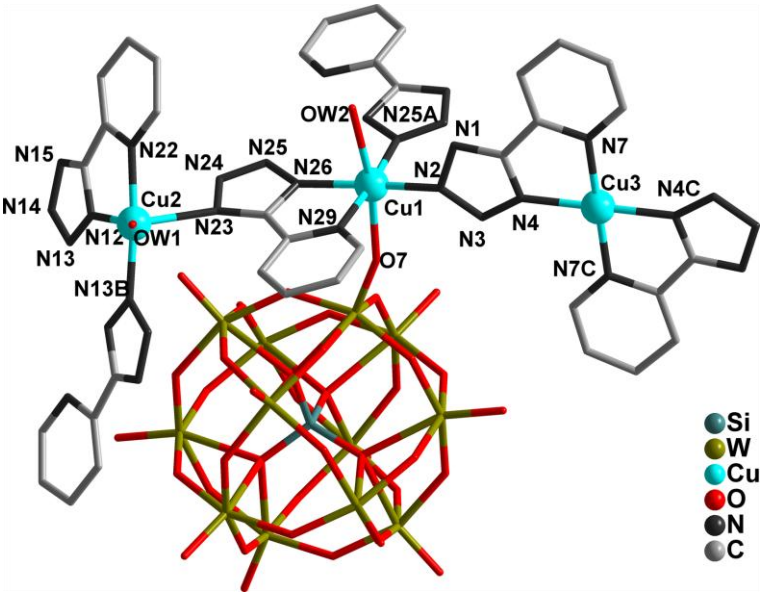

Fig. S1 The coordination environment of copper atoms in compound **1**.

The hydrogen atoms and lattice water molecules are omitted for clarity. (A: -x, -y, -z; B: 1-x, 1-y, -z; C: -1-x, -1-y, -z)

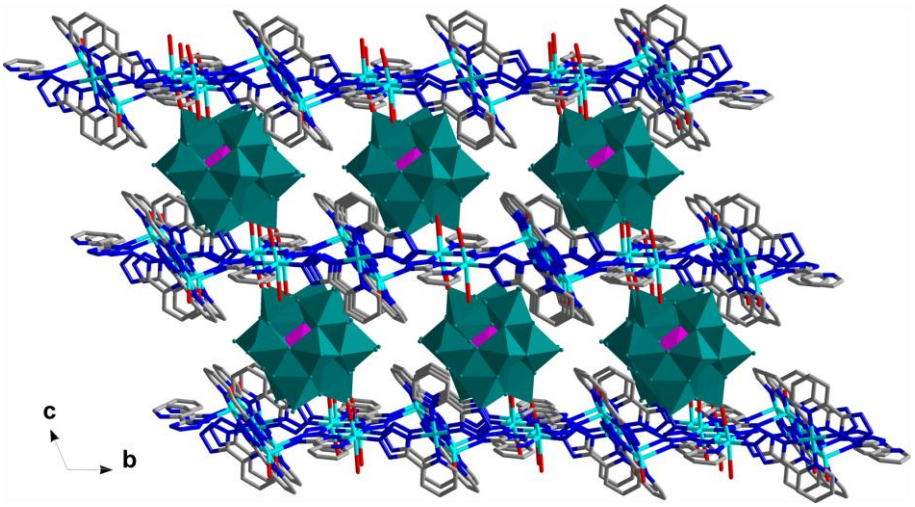

Fig. S2 The 3D framework of compound **1**.

The hydrogen atoms and lattice water molecules are omitted for clarity.

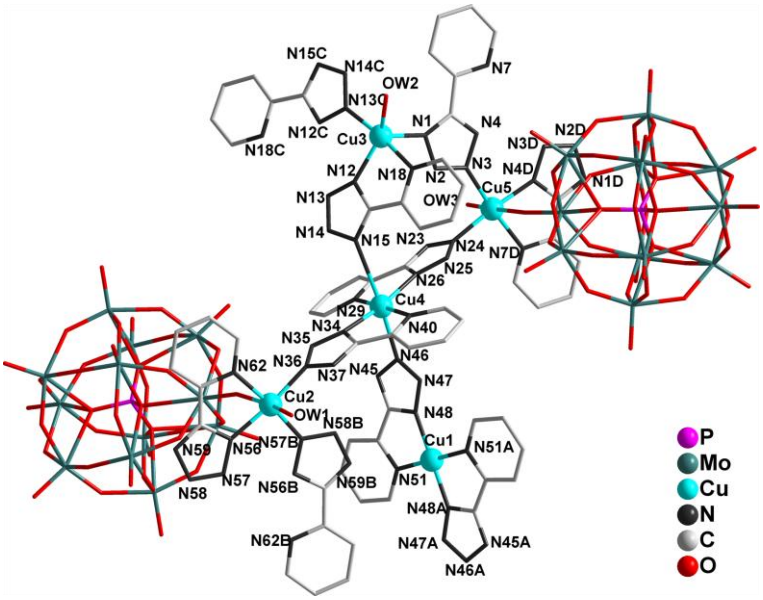

Fig. 3 The coordination environment of copper atoms in compound **2**.

The hydrogen atoms are omitted for clarity. (A: 1-x, 2-y, 1-z; B: 2-x, 2-y, 1-z; C: -x, 1-y, -z; D: 1-x, 1-y, -z)

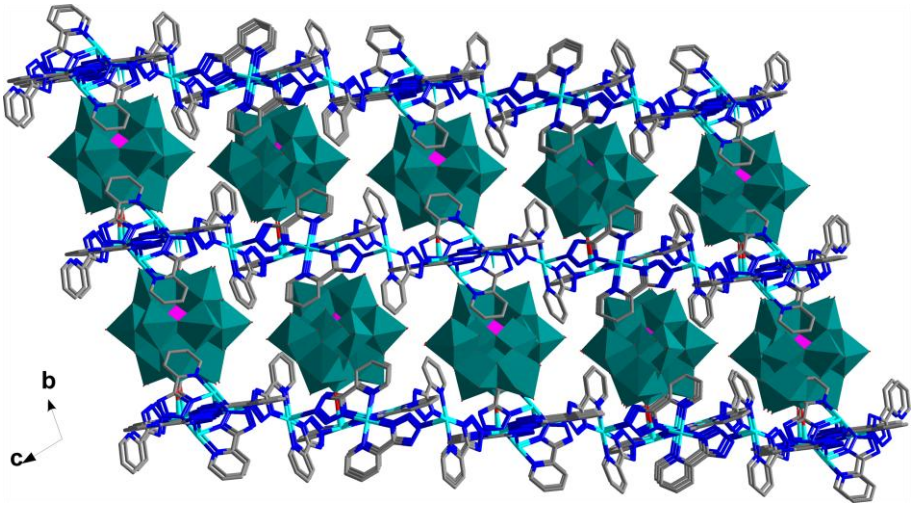

Fig. S4 The 3D framework of compound **2**.

The hydrogen atoms and lattice water molecules are omitted for clarity.

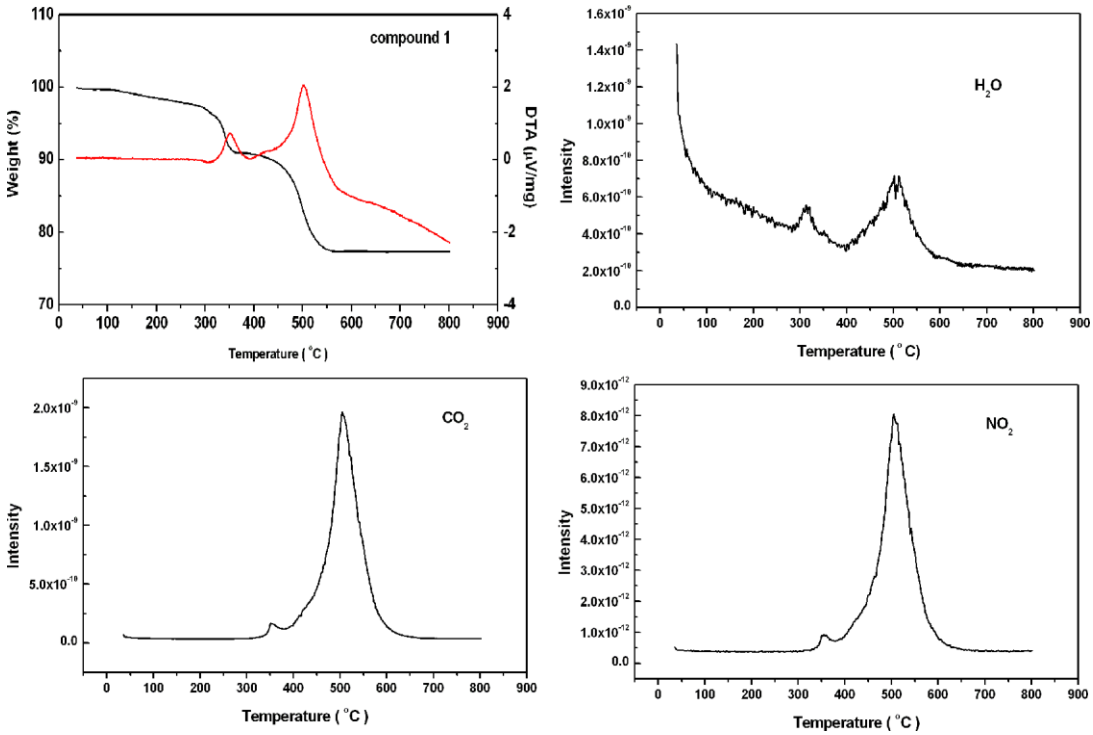

Fig. S5 TGA curves of **1** and MS curves of the decomposed products for **1**.

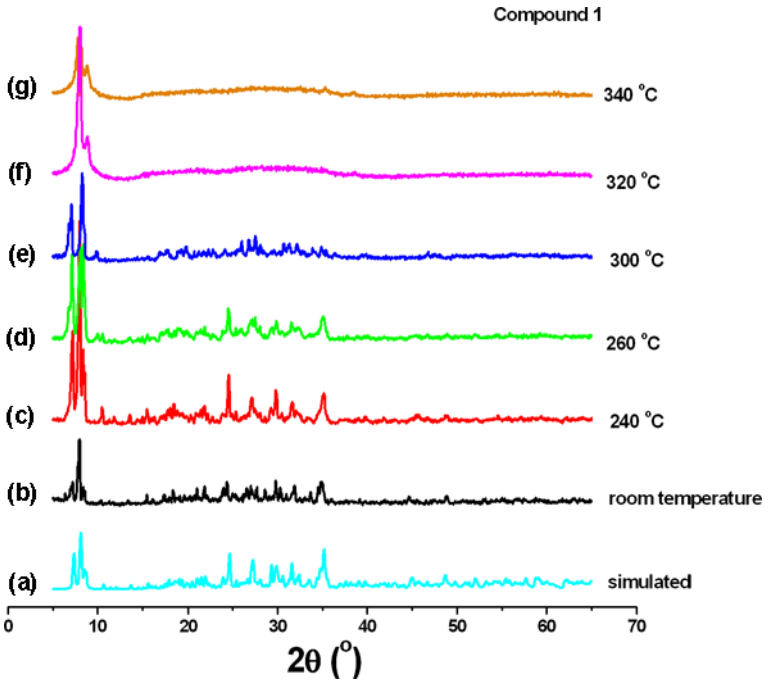

Fig. S6 XRD patterns for **1** (a) calculated on the basis of the structure determined by single-crystal XRD, (b) taken at room temperature, (c) taken after heating at 240 ºC for one hour, (d) taken after heating at 260 ºC for one hour, (e) taken after heating at 300 ºC for one hour, (f) taken after heating at 320 ºC for one hour, (g) taken after heating at 340 ºC for one hour.

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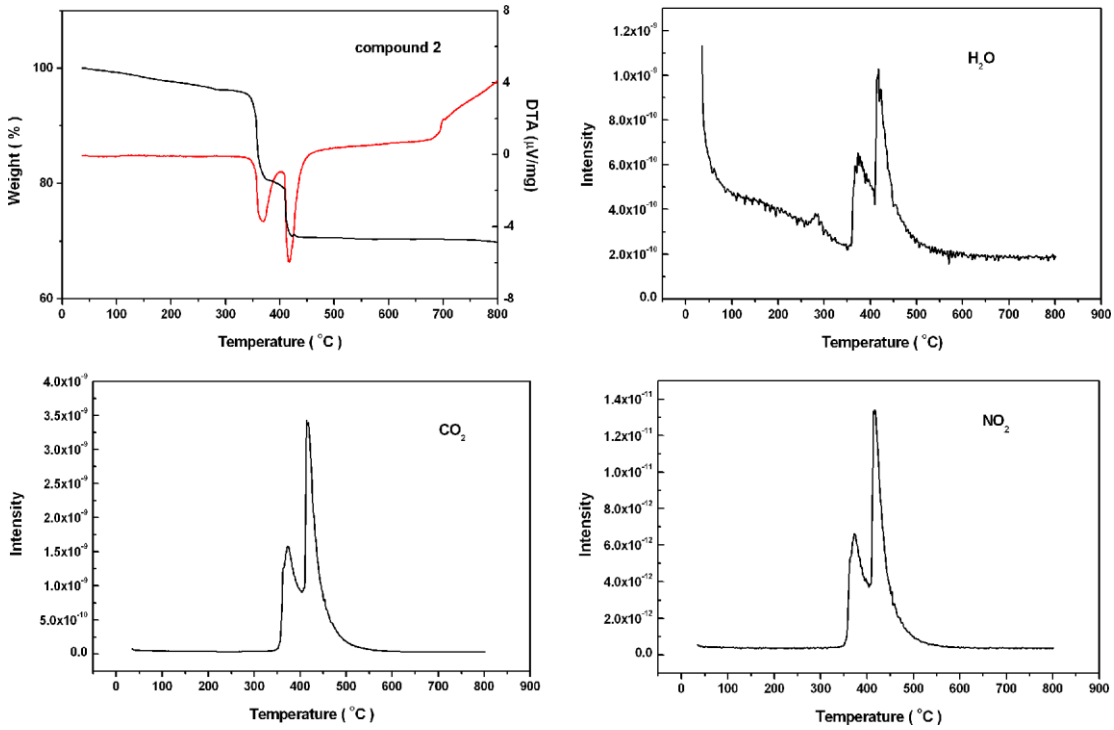

Fig. S7 TGA curves of **2** and MS curves of the decomposed products for **2**.

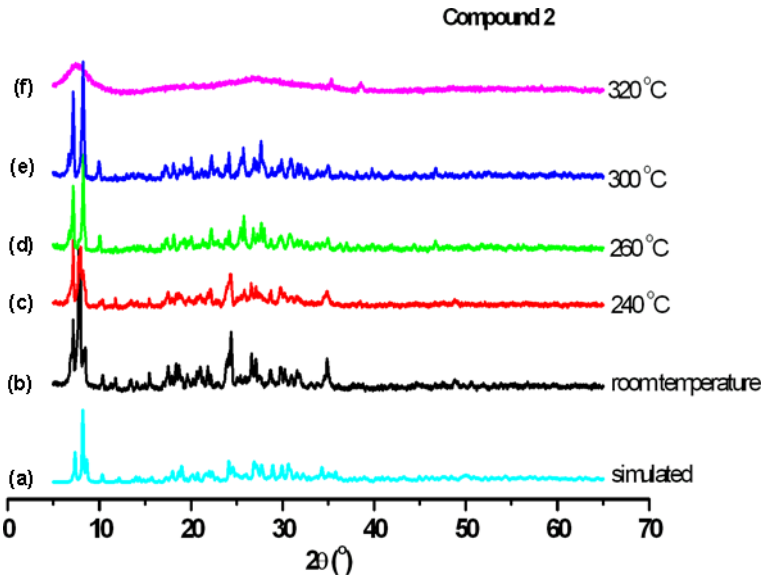

Fig. S8 XRD patterns for **2** (a) calculated on the basis of the structure determined by single-crystal XRD, (b) taken at room temperature, (c) taken after heating at 240 ºC for one hour, (d) taken after heating at 260 ºC for one hour, (e) taken after heating at 300 ºC for one hour, (f) taken after heating at 320 ºC for one hour.

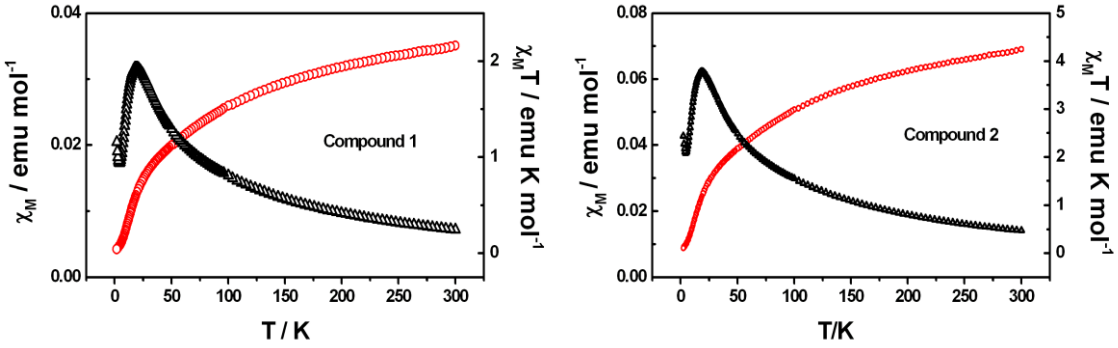

Fig. S9 Plots of the product $\chi_M T$ vs T (○) and χ_M vs T (Δ) for compound **1** and **2**.