Electronic supplementary information (ESI)

Inorganic−organic hybrid compounds based on octamolybdates and metal-organic fragments with flexible multidentate ligand: syntheses, structures and characterization

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Table S1. Selected bond lengths [Å] and angles [°] for **1**-**6**[a]

		Compound **1**	
Cu(1)-N(1)	1.945(6)	Cu(1)-N(1)#3	1.945(6)
Cu(1)-O(1W)	2.013(7)	Cu(1)-O(1W)#3	2.013(7)
Cu(2)-N(8)#4	1.986(6)	Cu(2)-N(8)#5	1.986(6)
Cu(2)-N(6)#6	1.988(6)	Cu(2)-O(5)	2.675(6)
Cu(2)-O(5)#6	2.675(6)	Cu(2)-O(6)	1.988(6)
N(1)#3-Cu(1)-N(1)	180	N(1)#3-Cu(1)-O(1W)	87.7(3)
N(1)-Cu(1)-O(1W)	92.3(3)	N(1)#3-Cu(1)-O(1W)#3	92.3(3)
N(1)-Cu(1)-O(1W)#3	87.7(3)	O(1W)-Cu(1)-O(1W)#3	180
N(8)#4-Cu(2)-N(8)#5	180	N(8)#4-Cu(2)-N(6)	90.5(2)
N(8)#5-Cu(2)-N(6)	89.5(2)	N(8)#4-Cu(2)-N(6)#6	89.5(2)
N(8)#5-Cu(2)-N(6)#6	90.5(2)	N(6)-Cu(2)-N(6)#6	180
O(5)-Cu(2)-O(5)#6	180	N(6)-Cu(2)-O(5)	86.88(5)
O(5)-Cu(2)-N(8)#5	98.99(5)	O(5)-Cu(2)-N(8)#4	81.01(5)
		Compound **2**	
Cu(1)-N(6)#4	1.911(7)	Cu(1)-O(1)	2.344(5)
Cu(1)-O(10)	2.359(6)	Cu(1)-N(1)	1.918(6)
Cu(2)-O(1W)	1.7623(13)	Cu(2)-N(2)	1.935(7)
Cu(2)-N(9)#5	1.914(6)		
N(6)#4-Cu(1)-N(1)	165.7(3)	N(6)#4-Cu(1)-O(1)	103.2(2)
N(1)-Cu(1)-O(1)	88.9(2)	N(6)#4-Cu(1)-O(10)	88.8(3)
N(1)-Cu(1)-O(10)	100.4(2)	O(1)-Cu(1)-O(10)	82.87(19)
O(1W)-Cu(2)-N(9)#5	69.1(2)	O(1W)-Cu(2)-N(2)	112.8(2)
N(9)#5-Cu(2)-N(2)	169.4(3)		
		Compound **3**	
Cu(1)-N(9)	1.878(10)	Cu(1)-N(3)#2	1.92(2)
Cu(2)-N(6)	1.893(8)	Cu(2)-N(12)	1.872(9)
Cu(3)-N(15)	1.882(8)	Cu(3)-N(21)	1.880(8)
Cu(3)-O(1)	2.527(8)	Cu(4)-N(18)	1.872(8)
Cu(4)-N(24)#3	1.900(8)		
N(9)-Cu(1)-N(3)#2	174.9(9)	N(12)-Cu(2)-N(6)	176.8(4)
N(21)-Cu(3)-N(15)	173.1(4)	N(18)-Cu(4)-N(24)#3	165.1(4)
O(1)-Cu(3)-N(21)	90.71(4)	O(1)-Cu(3)-N(15)	94.31(4)
		Compound **4**	
Ni(1)-N(9)#4	2.067(4)	Ni(1)-N(6)#1	2.075(5)
Ni(1)-N(1)	2.074(5)	Ni(1)-O(2W)	2.071(4)
Ni(1)-O(3W)	2.086(4)	Ni(1)-O(1W)	2.099(4)
N(1)-Ni(1)-N(9)#4	92.77(18)	N(1)-Ni(1)-N(6)#1	174.12(18)
N(9)#4-Ni(1)-N(6)#1	93.01(18)	N(1)-Ni(1)-O(2W)	91.00(18)
N(9)#4-Ni(1)-O(2W)	92.54(15)	N(6)#1-Ni(1)-O(2W)	87.68(16)
N(1)-Ni(1)-O(3W)	88.69(19)	N(9)#4-Ni(1)-O(3W)	177.70(19)

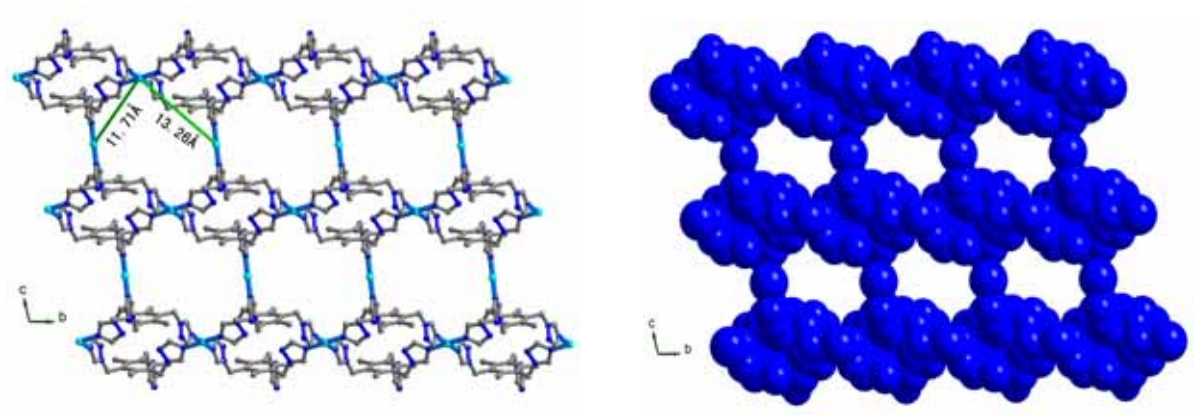
N(6)#1-Ni(1)-O(3W)	85.50(18)	O(2W)-Ni(1)-O(3W)	85.66(16)
N(1)-Ni(1)-O(1W)	89.75(19)	N(9)#4-Ni(1)-O(1W)	90.44(16)
N(6)#1-Ni(1)-O(1W)	91.27(17)	O(2W)-Ni(1)-O(1W)	176.89(16)
O(3W)-Ni(1)-O(1W)	91.34(17)		
		Compound **5**	
Zn(1)-N(8)#4	1.968(3)	N(1)-Zn(1)	1.958(3)
Zn(1)-O(1W)	2.050(4)	Zn(1)-N(6)#1	2.091(4)
Zn(1)-O(5)	2.773(4)		
N(1)-Zn(1)-N(8)#4	146.10(15)	N(1)-Zn(1)-O(1W)	109.90(15)
N(8)#4-Zn(1)-O(1W)	95.88(14)	N(1)-Zn(1)-N(6)#1	97.94(13)
N(8)#4-Zn(1)-N(6)#1	103.66(14)	O(1W)-Zn(1)-N(6)#1	90.45(15)
O(5)-Zn(1)-N(1)	78.29(2)	O(5)-Zn(1)-O(1W)	75.27(2)
O(5)-Zn(1)-N(6)#1	162.68(2)	O(5)-Zn(1)-N(8)#4	87.78(2)
		Compound **6**	
Ag(1)-N(9)#2	2.107(9)	Ag(1)-N(3)	2.137(9)
Ag(1)-O(10)#2	2.671(9)	Ag(2)-N(6)#1	2.184(9)
Ag(2)-O(3)	2.670(9)	Ag(2)-N(2)	2.270(8)
Ag(2)-N(8)	2.577(10)		
N(9)#2-Ag(1)-N(3)	171.9(4)	N(6)#1-Ag(2)-N(2)	155.9(4)
N(6)#1-Ag(2)-N(8)	90.0(4)	N(2)-Ag(2)-N(8)	109.4(4)
N(9)#2-Ag(1)-O(10)#2	91.51(4)	N(3)-Ag(1)-O(10)#2	92.70(4)
N(8)-Ag(2)-O(3)	85.98(4)	N(6)#1-Ag(2)-O(3)	79.55(4)
N(2)-Ag(2)-O(3)	87.57(4)		

Symmetry codes For **1:** #3 -x-2,-y+1,-z-1; #4 -x,-y+1,-z; #5 x,y-1,z; #6 -x,-y,-z; For **2**: #4 x+1,y-1,z; #5 x,y,z+1. For **3**: #2 x-1,y,z; #3 x,y,z-1. For **4**: #1 -x+1,-y,-z+2; #4 x+1/2,-y+1/2,z-1/2. For **5**: #1 -x+2,-y,-z+1; #4 x-1/2,-y+1/2,z+1/2. For **6**: #1 -x+1,-y,-z; #2 -x,-y,-z+1.

Table S2. Hydrogen-bond geometries for compound **4**(Å, ^{o})

D-H···A	D-H [Å]	H···A [Å]	D···A [Å]	<D-H···A [˚]
O(3W)-H(5A)...O(13)#1	0.85(6)	1.90(7)	2.676(6)	150(6)
O(2W)-H(2B)...O(7)	0.85(3)	1.93(2)	2.759(5)	167.5(18)
O(1W)-H(1A)...O(4W)	0.85(5)	2.14(6)	2.681(9)	121(6)

Symmetry codes for **4**: #1 -x+1,-y,-z+2.



(a) **(b)**

Fig. S1 (a) View of the 2D sheet in **1**. (b) 1D tubular channels along the a-axis of **1**

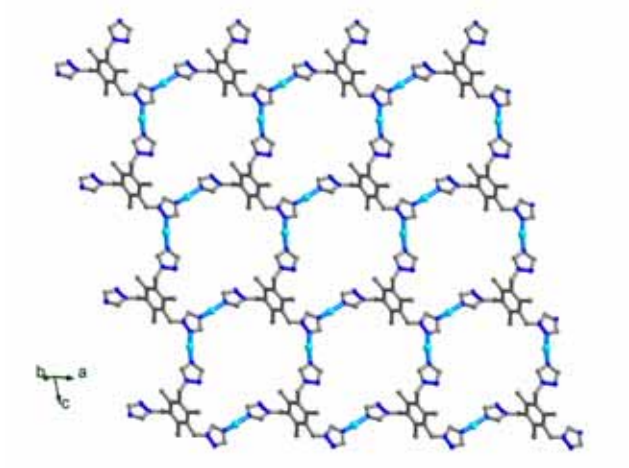
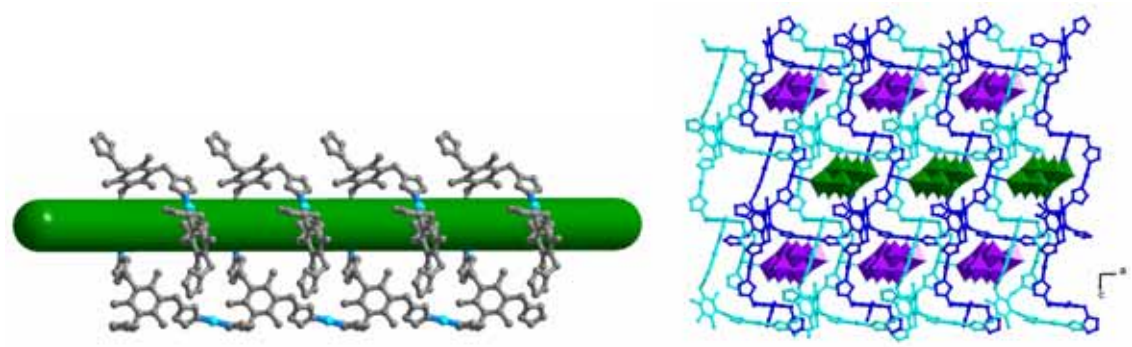


Fig. S2 View of the 2D single sheet in **2**.



(a) (b)

Fig. S3 (a) View of a 1D tubular chain in **3**. (b) Perspective view of the 2-fold interpenetrating net of **2**.

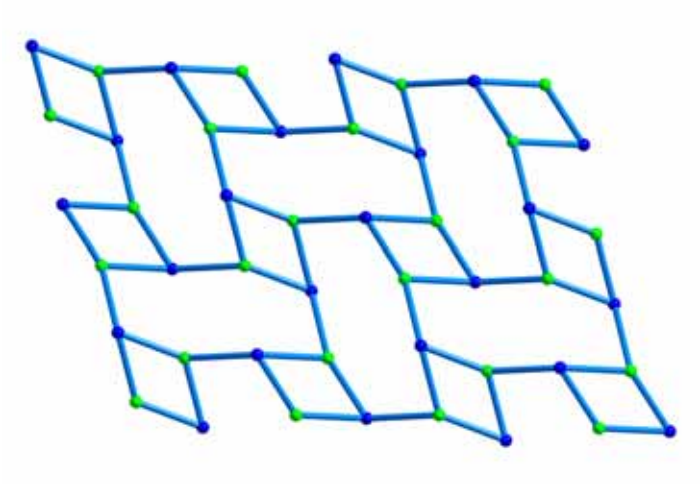


Fig. S4 Schematic view of the $(4^1 \cdot 8^2)_2$ topology of **4**

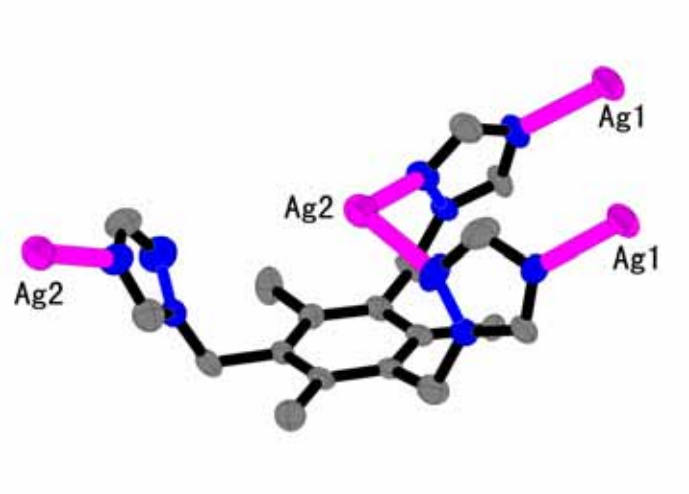


Fig. S5 Coordination fashion of the ttb ligand in **6**.

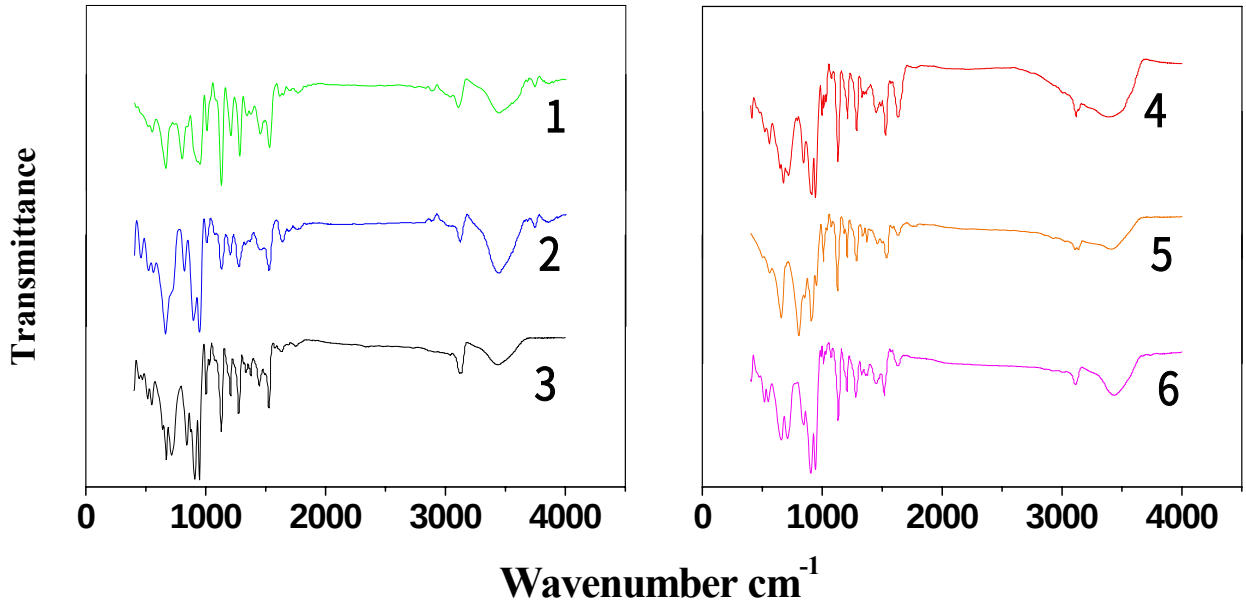


Fig. S6 The IR spectra of compounds **1–6**

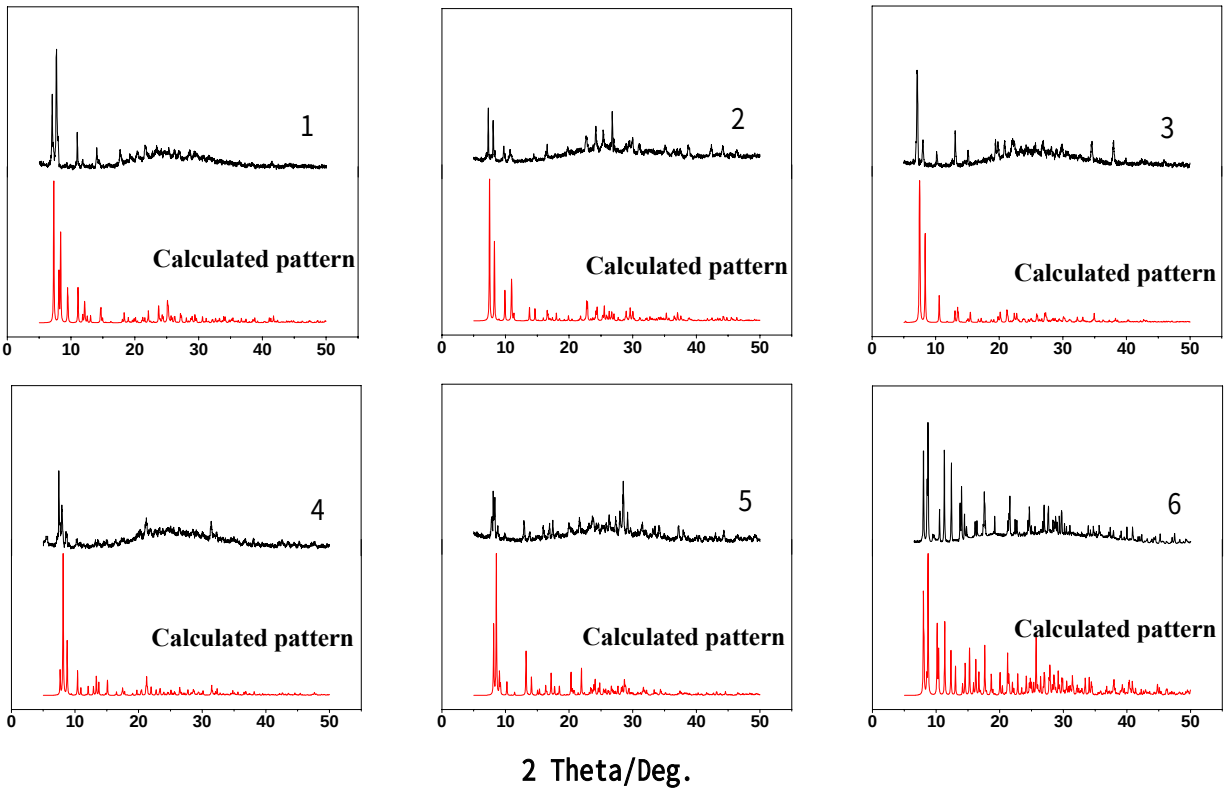


Fig. S7 The calculated and experimental PXRD patterns of compounds **1–6**.

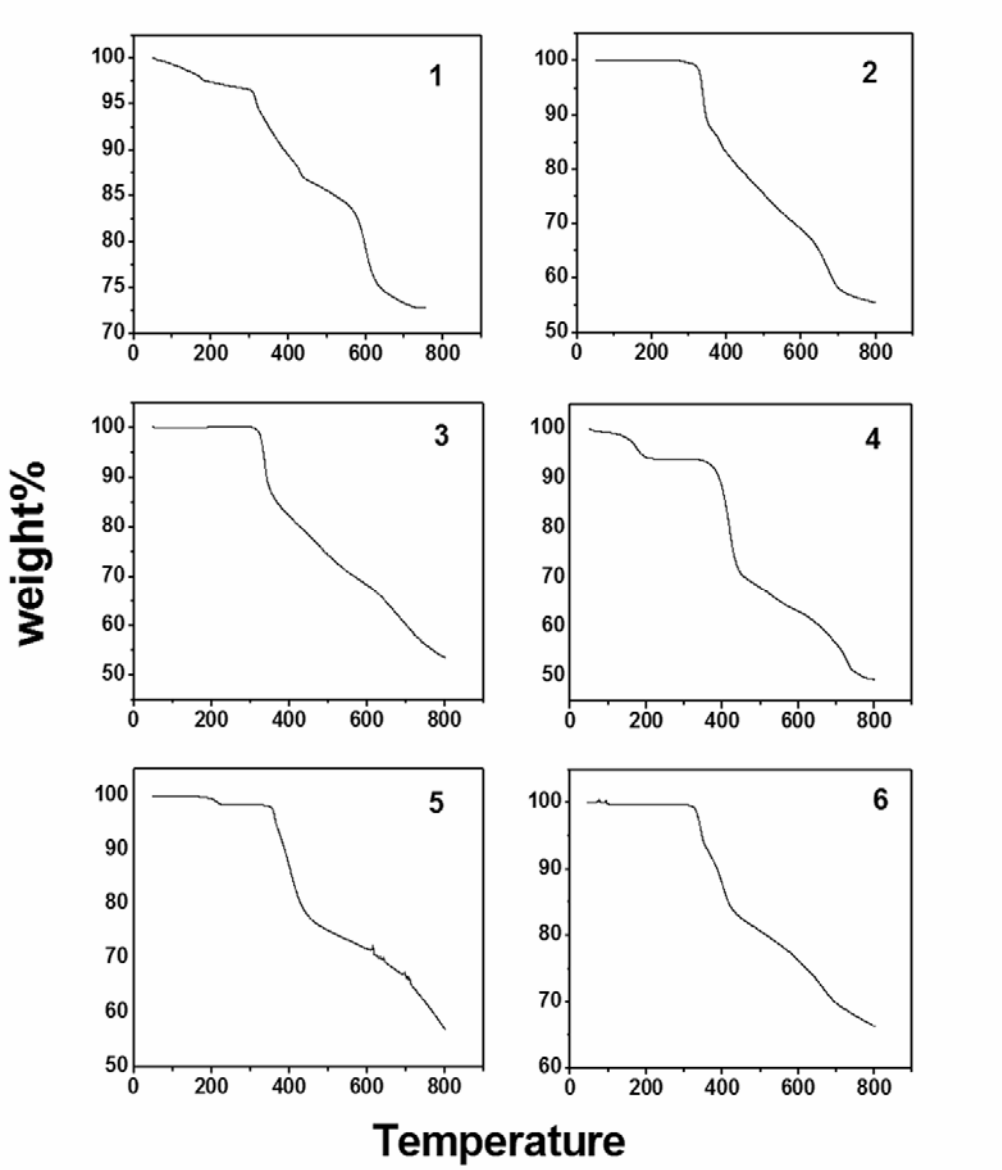


Fig. S8 TGA spectra for **1-6**

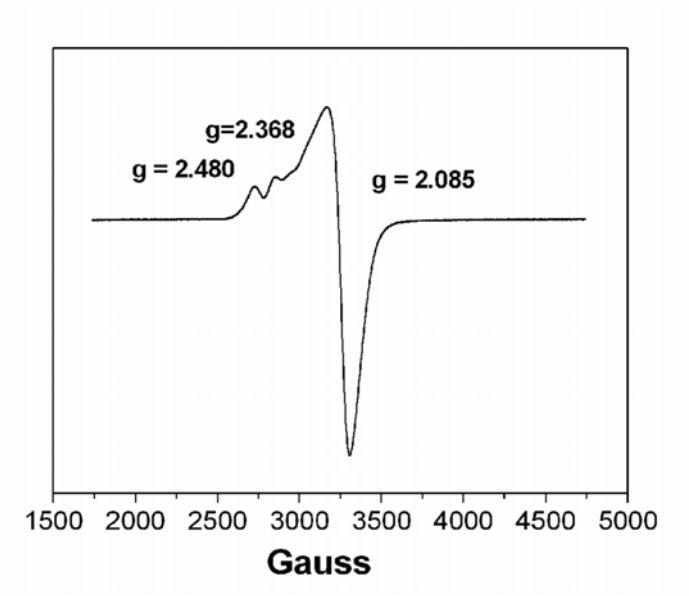


Fig. S9. EPR spectrum of **1**