Supporting Materials for

An unprecedented polyoxometalate-based hybrid solid constructed from neutral metal-organic macrocycle and Dawson polyoxotungstate anions

1. Experimental Section:

All the chemical materials were of reagent grade and used without further purification. Inductively coupled plasma (ICP) spectra for W, K, Na and Cu were performed on a Perkin- Elmer Optima 2000 ICP-OES spectrometer. IR spectra were recorded on a Nicolet 170SXFT/IR spectrometer (as KBr pressed pellets). Luminescence measurements were obtained on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

2. IR spectra of compound 1

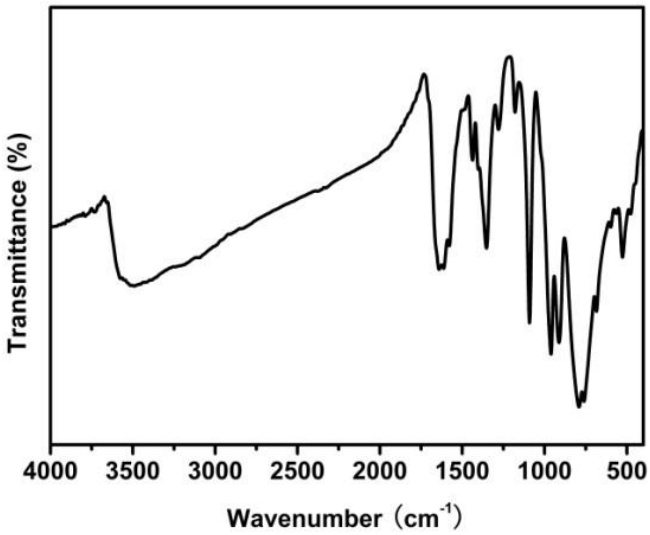


Fig. S1. IR spectra of compound **1**

As shown in Fig. S1, the IR spectra of **1** demonstrate the characteristic bands of the Dawson polyoxotungstate. Four characteristic peaks at 1090, 959, 913, 761 cm^{-1} are attributed to the $\nu_{as}(P–O_a)$, $\nu_{as}(W–O_d)$, $\nu_{as}(W–O_b–W)$ and $\nu_{as}(W–O_c–W)$ stretching vibration, respectively. The broad bands of 3489 cm^{-1} characterize water molecules. The characteristic peaks at 1642, 1579, 1434, 1352, 1279, 1180 cm^{-1} are assigned to features of the H_2pdc molecules.

3. Detail analysis of the statistic of Cu^{2+} and pdc ligand.

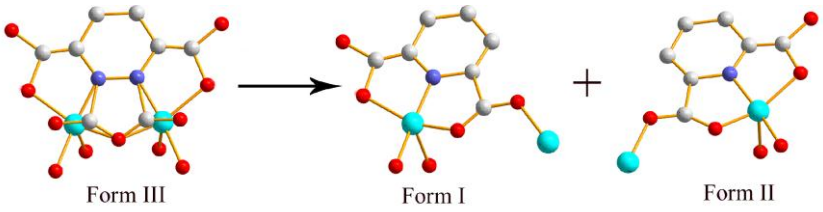
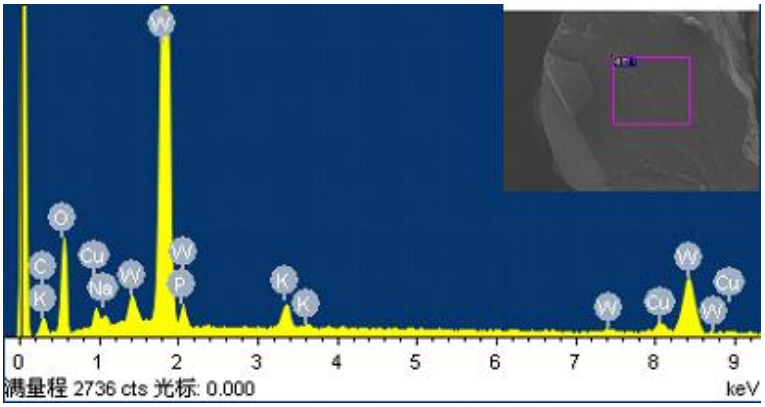


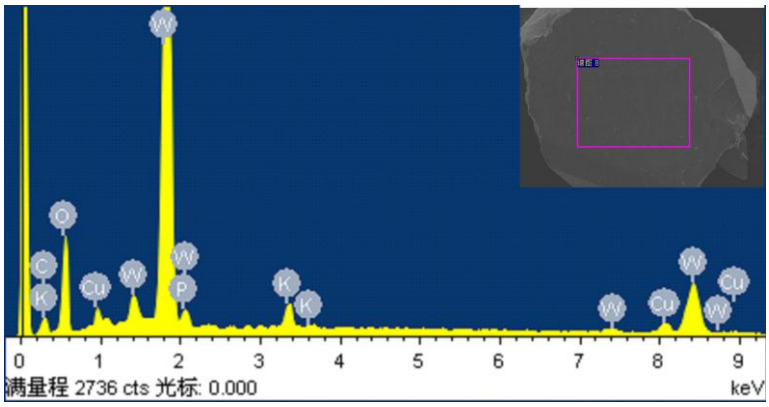
Figure S2. The structural statistic occur in the $Cu_6(pdc)_6$ macrocycle.

When Cu^{2+}presents in the left side, the organic ligand must be the Form I; otherwise, it must be the Form II. Hence the whole crystal data presents a final statistic of Form III for the metallomacrocycle.

4. The EDS spectrum of compounds 1 and 2



(a)



(b)

Figure S3. The EDS spectra of compounds **1** (a) and **2** (b).

5.

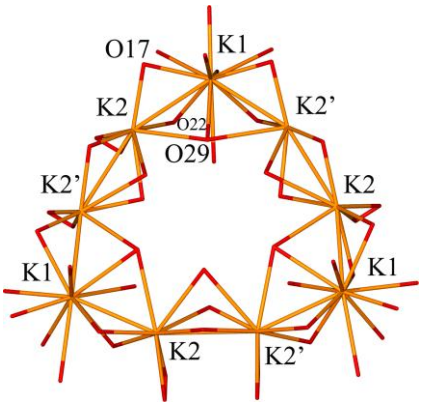


Figure S4. The connectivity of K1 and K2 in compound 1.

6.

The emission spectrum of the ligand H_2pdc in solid state at room temperature are depicted in Fig. S5. It exhibit obvious photoluminescence with abroad emission band at 398nm upon excitation at about 244 nm. The resemblance between compound **1** and H_2pdc implies that the luminescent behavior is ligand-based emission. Compound **1** and the free ligand H_2pdc show absorption bands from 240 to 350 nm with a peak maximum of 241 nm and 244 nm, respectively. Thus, excitation was carried out at about 240 nm in our experiments, and for confirming these results, excitation was also carried out at about 340 nm, which gave similar results in the luminescence intensity and position.

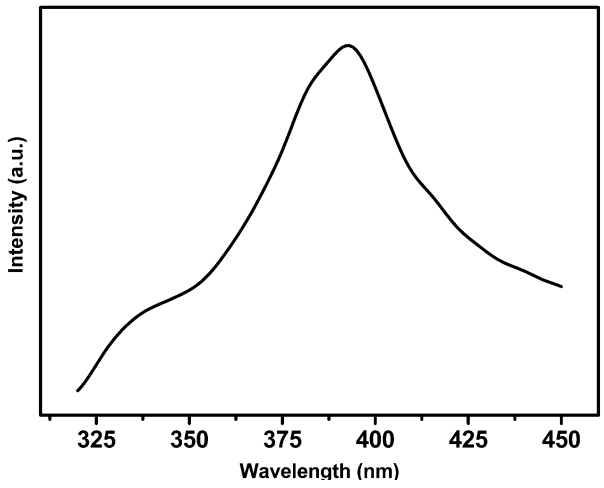


Fig. S5. Emission spectrum of the free ligand H_2pdc in solid state at room temperature.

7.

Atom	*Σs*	Atom	*Σs*	Atom	*Σs*	Atom	*Σs*
W(1)	6.052	O(3)	1.800	O(9)	1.986	O(15)	2.076
W(2)	6.571	O(4)	1.881	O(10)	1.750	O(16)	1.860
W(3)	6.206	O(5)	1.847	O(11)	2.111	O(17)	2.029

W(4)	6.330	O(6)	2.192	O(12)	2.157	O(18)	1.837
O(1)	1.973	O(7)	2.210	O(13)	2.066		
O(2)	1.635	O(8)	2.217	O(14)	1.995		

Table. S1. Bond valence sum calculation for 1.

As shown in Table. S3, according to bond valence sum calculation, all tungsten atoms exhibit +VI oxidation state (average calculated value = 6.324). In additon, all oxygen atoms are not protonated and the average calculated value for O is 2.266, as is agreement with charge balance analysis from the structural data.

8. Selected Bond Distances (Å) and Angles (deg) for Compound 1.

Table S2. Selected Bond Distances (Å) and Angles (º) for Compound **1.**

W(1)-O(2)	1.69(3)	K(2)-O(18)#3	2.72(6)
W(1)-O(8)	1.883(14)	K(2)-O(5)	2.74(4)
W(1)-O(1)	1.922(14)	K(2)-O(2)#4	2.76(4)
W(1)-O(3)	2.32(2)	K(2)-O(19)#3	2.99(7)
W(2)-O(5)	1.70(2)	K(2)-O(26)	3.01(7)
W(2)-O(9)	1.869(18)	K(2)-O(23)	3.09(7)
W(2)-O(7)	1.885(6)	K(2)-O(27)	3.28(5)
W(2)-O(6)	1.887(12)	K(2)-O(25)	3.41(4)
W(2)-O(8)	1.943(14)	P(1)-O(4)	1.54(3)
W(2)-O(4)	2.336(18)	P(1)-O(3)	1.72(4)
W(3)-O(11)	1.709(18)	P(2)-O(10)	1.49(2)
W(3)-O(13)	1.892(6)	P(2)-O(17)	1.69(4)
W(3)-O(9)	1.899(18)	Na(1)-O(30)	2.29(10)
W(3)-O(12)	1.906(11)	O(21)-C(4)	1.22(14)
W(3)-O(14)	1.935(18)	O(21)-C(4)#7	1.22(14)
W(3)-O(10)	2.369(17)	C(1)-C(1)#7	1.35(7)
W(4)-O(16)	1.66(3)	C(1)-C(2)	1.38(5)
W(4)-O(14)	1.882(19)	Cu(1)-N(1)	1.86(3)
W(4)-O(15)	1.925(13)	Cu(1)-O(19)	2.01(6)
W(4)-O(17)	2.32(2)	C(2)-N(1)	1.38(4)
K(1)-O(19)#3	2.59(6)	C(2)-C(3)	1.49(7)
K(1)-O(19)#5	2.59(6)	C(3)-O(19)	1.20(7)
K(1)-O(24)	2.72(6)	C(3)-O(18)	1.28(8)
K(1)-O(16)#6	2.84(3)	C(4)-O(20)	1.28(14)
K(1)-O(18)#5	2.97(6)	C(4)-C(4)#7	1.9(3)
K(1)-O(18)#3	2.97(6)	O(20)-K(1)#14	3.35(8)
K(1)-O(23)	3.06(6)		
K(1)-O(23)#7	3.06(6)		
K(1)-O(21)	3.21(5)		
K(1)-O(25)	3.25(7)		
K(2)-O(26)#3	2.67(7)		
K(2)-O(22)	2.71(5)		

O(2)-W(1)-O(8)	102.3(10)	O(19)#3-K(1)-O(19)#5	139(3)
O(8)-W(1)-O(8)#1	86.4(10)	O(19)#3-K(1)-O(24)	102.4(13)
O(2)-W(1)-O(1)	100.5(11)	O(19)#5-K(1)-O(24)	102.4(13)
O(8)-W(1)-O(1)	88.6(9)	O(19)#3-K(1)-O(16)#6	79.1(14)
O(8)#1-W(1)-O(1)	157.2(9)	O(19)#5-K(1)-O(16)#6	79.1(14)
O(8)#1-W(1)-O(1)#2	88.6(9)	O(24)-K(1)-O(16)#6	69.9(16)
O(1)-W(1)-O(1)#2	87.4(16)	O(19)#3-K(1)-O(18)#5	154.4(18)
O(2)-W(1)-O(3)	169.2(14)	O(19)#5-K(1)-O(18)#5	45.4(16)
O(8)-W(1)-O(3)	85.4(7)	O(24)-K(1)-O(18)#5	59.1(11)
O(1)-W(1)-O(3)	72.0(9)	O(16)#6-K(1)-O(18)#5	77.7(12)
O(5)-W(2)-O(9)	97.9(9)	O(19)#3-K(1)-O(18)#3	45.4(16)
O(5)-W(2)-O(7)	102.8(11)	O(19)#5-K(1)-O(18)#3	154.4(18)
O(9)-W(2)-O(7)	87.6(9)	O(24)-K(1)-O(18)#3	59.1(11)
O(5)-W(2)-O(6)	101.4(10)	O(16)#6-K(1)-O(18)#3	77.7(12)
O(9)-W(2)-O(6)	93.1(10)	O(18)#5-K(1)-O(18)#3	118(2)
O(7)-W(2)-O(6)	155.4(10)	O(19)#3-K(1)-O(23)	53.7(16)
O(5)-W(2)-O(8)	98.1(8)	O(19)#5-K(1)-O(23)	115.0(17)
O(5)-W(2)-O(4)	172.9(9)	O(24)-K(1)-O(23)	141.6(14)
O(9)-W(2)-O(4)	82.4(8)	O(16)#6-K(1)-O(23)	123.6(14)
O(7)-W(2)-O(4)	84.3(9)	O(18)#5-K(1)-O(23)	151.5(16)
O(6)-W(2)-O(4)	71.5(8)	O(18)#3-K(1)-O(23)	87.1(15)
O(8)-W(2)-O(4)	82.2(7)	C(3)#5-K(1)-O(23)	138.1(17)
O(11)-W(3)-O(13)	103.8(11)	C(3)#3-K(1)-O(23)	74.3(16)
O(11)-W(3)-O(9)	97.7(9)	O(19)#3-K(1)-O(23)#7	115.0(17)
O(13)-W(3)-O(9)	86.5(9)	O(19)#5-K(1)-O(23)#7	53.7(16)
O(11)-W(3)-O(14)	98.7(9)	O(24)-K(1)-O(23)#7	141.6(14)
O(13)-W(3)-O(14)	86.5(9)	O(16)#6-K(1)-O(23)#7	123.6(13)
O(9)-W(3)-O(14)	163.3(8)	O(18)#5-K(1)-O(23)#7	87.1(15)
O(12)-W(3)-O(14)	89.3(9)	O(18)#3-K(1)-O(23)#7	151.5(16)
O(11)-W(3)-O(10)	173.0(9)	C(3)#5-K(1)-O(23)#7	74.4(16)
O(13)-W(3)-O(10)	83.2(9)	C(3)#3-K(1)-O(23)#7	138.1(17)
O(16)-W(4)-O(14)	101.3(9)	O(23)-K(1)-O(23)#7	66(2)
O(14)#1-W(4)-O(14)	86.7(11)	O(19)#3-K(1)-O(21)	71.6(13)
O(16)-W(4)-O(15)#2	100.8(10)	O(19)#5-K(1)-O(21)	71.6(13)
O(14)-W(4)-O(15)#2	157.9(9)	O(24)-K(1)-O(21)	154.4(17)
O(16)-W(4)-O(15)	100.8(10)	O(16)#6-K(1)-O(21)	84.5(11)
O(14)-W(4)-O(15)	89.6(10)	O(18)#5-K(1)-O(21)	116.5(12)
O(16)-W(4)-O(17)	170.5(13)	O(18)#3-K(1)-O(21)	116.5(12)
O(14)#1-W(4)-O(17)	85.6(8)	O(23)-K(1)-O(21)	54.8(13)
O(14)-W(4)-O(17)	85.6(8)	O(19)#3-K(1)-O(25)	109.9(14)
O(15)#2-W(4)-O(17)	72.4(9)	O(24)-K(1)-O(25)	67.9(17)
O(23)-K(2)-O(27)	132.1(17)	O(23)-K(1)-O(25)	90.8(15)
O(26)#3-K(2)-O(25)	124.7(17)	O(21)-K(1)-O(25)	137.6(13)

O(22)-K(2)-O(25)	99.9(18)	O(26)#3-K(2)-O(22)	118.9(19)
O(18)#3-K(2)-O(25)	81.8(17)	O(26)#3-K(2)-O(18)#3	124(2)
O(5)-K(2)-O(25)	151.7(15)	O(22)-K(2)-O(18)#3	99.3(17)
O(2)#4-K(2)-O(25)	75.6(14)	O(26)#3-K(2)-O(5)	76.0(14)
O(19)#3-K(2)-O(25)	97.0(18)	O(22)-K(2)-O(5)	82.4(14)
O(26)-K(2)-O(25)	145.9(16)	O(18)#3-K(2)-O(5)	70.0(15)
C(3)#3-K(2)-O(25)	97.2(18)	O(26)#3-K(2)-O(2)#4	74.6(15)
O(23)-K(2)-O(25)	87.5(16)	O(22)-K(2)-O(2)#4	79.8(14)
O(27)-K(2)-O(25)	53.9(13)	O(18)#3-K(2)-O(2)#4	156.9(19)
O(4)-P(1)-O(4)#2	113.3(8)	O(5)-K(2)-O(2)#4	132.1(14)
O(10)-P(2)-O(10)#8	113.6(8)	O(26)#3-K(2)-O(19)#3	81.2(18)
O(4)-P(1)-O(3)	105.3(9)	O(22)-K(2)-O(19)#3	136.6(18)
O(10)-P(2)-O(17)	104.9(10)	O(18)#3-K(2)-O(19)#3	44.4(16)
O(30)#2-Na(1)-O(30)#8	102(3)	O(5)-K(2)-O(19)#3	64.8(14)
O(30)#2-Na(1)-O(30)#9	78(3)	O(2)#4-K(2)-O(19)#3	143.4(16)
O(30)-Na(1)-O(30)#9	179.998(11)	O(26)#3-K(2)-O(26)	21.9(19)
W(1)#8-O(1)-W(1)	122.8(15)	O(22)-K(2)-O(26)	107.7(17)
W(1)-O(2)-K(2)#4	132.2(8)	O(18)#3-K(2)-O(26)	112.2(19)
K(2)#4-O(2)-K(2)#3	94.2(16)	O(5)-K(2)-O(26)	54.4(11)
P(1)-O(3)-W(1)	123.0(8)	O(2)#4-K(2)-O(26)	89.8(15)
W(1)-O(3)-W(1)#8	93.2(11)	O(19)#3-K(2)-O(26)	76.5(17)
P(1)-O(4)-W(2)#12	128.2(7)	O(26)#3-K(2)-O(23)	49.4(16)
W(2)#12-O(4)-W(2)	91.5(9)	O(22)-K(2)-O(23)	168.1(18)
W(2)-O(5)-K(2)	149.7(14)	O(18)#3-K(2)-O(23)	90.9(19)
W(2)-O(6)-W(2)#12	125.0(14)	O(5)-K(2)-O(23)	95.5(16)
W(2)#1-O(7)-W(2)	152.8(15)	O(2)#4-K(2)-O(23)	93.2(15)
W(1)-O(8)-W(2)	150.7(8)	O(19)#3-K(2)-O(23)	50.3(16)
W(2)-O(9)-W(3)	165.0(12)	O(26)-K(2)-O(23)	62.3(15)
P(2)-O(10)-W(3)	129.6(7)	C(3)#3-K(2)-O(23)	72.8(18)
P(2)-O(10)-W(3)#12	129.6(7)	O(26)#3-K(2)-O(27)	127.9(18)
W(3)-O(10)-W(3)#12	90.0(8)	O(22)-K(2)-O(27)	50.1(14)
W(3)#12-O(12)-W(3)	123.0(12)	O(18)#3-K(2)-O(27)	107.8(16)
W(3)#1-O(13)-W(3)	151.8(15)	O(5)-K(2)-O(27)	132.1(14)
W(4)-O(14)-W(3)	150.6(11)	O(2)#4-K(2)-O(27)	54.0(12)
W(4)#8-O(15)-W(4)	122.1(14)	O(19)#3-K(2)-O(27)	146.1(16)
P(2)-O(17)-W(4)#8	123.1(8)	O(26)-K(2)-O(27)	137.2(16)
W(4)#8-O(17)-W(4)	93.1(11)	K(1)-O(25)-K(2)	68.3(12)
P(2)-O(17)-W(4)#2	123.1(8)	K(2)-O(25)-K(2)#7	129(2)
W(4)#8-O(17)-W(4)#2	93.1(11)	O(26)#3-O(26)-K(2)#3	96(6)
K(2)#1-O(22)-K(2)	97(2)	O(26)#3-O(26)-K(2)	62(6)
K(1)-O(23)-K(2)	75.0(14)	K(2)#3-O(26)-K(2)	157(2)
O(21)-Cu(1)-N(1)	81.7(18)	K(2)-O(27)-K(2)#1	76.1(15)
O(21)-Cu(1)-O(19)	161(2)	C(1)#7-C(1)-C(2)	121(2)

N(1)-Cu(1)-O(19)	81.3(18)	C(3)-O(18)-K(1)#14	79(4)
O(21)-Cu(1)-O(23)	94(2)	C(3)-O(19)-Cu(1)	114(5)
N(1)-Cu(1)-O(23)	105.8(19)	C(3)-O(19)-K(1)#14	98(4)
O(19)-Cu(1)-O(23)	99(2)	Cu(1)-O(19)-K(1)#14	130(3)
N(1)-C(2)-C(1)	116(4)	C(3)-O(19)-K(2)#3	83(4)
N(1)-C(2)-C(3)	109(4)	Cu(1)-O(19)-K(2)#3	134(3)
C(1)-C(2)-C(3)	135(4)	K(1)#14-O(19)-K(2)#3	83.9(18)
C(2)-N(1)-Cu(1)	117(2)	O(21)-C(4)-O(20)	138(10)
O(19)-C(3)-O(18)	123(6)	O(21)-C(4)-C(4)#7	41(6)
O(19)-C(3)-C(2)	118(6)	O(20)-C(4)-C(4)#7	169(7)
O(18)-C(3)-C(2)	119(5)	C(4)-O(20)-K(1)#14	150(7)
C(3)-O(18)-K(2)#3	94(4)		

Symmetry transformations used to generate equivalent atoms:

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

#5 y-1,-x+y,-z+1 #6 x-y+1/3,x+2/3,-z+2/3 #7 -x+y-1,y,z

#8 -x+y,-x+1,z #9 -x+2/3,-y+4/3,-z+1/3 #10 y-1/3,-x+y+1/3,-z+1/3

#11 x-y+2/3,x+1/3,-z+1/3 #12 -y+1,-x+1,z #13 y-2/3,-x+y-1/3,-z+2/3

#14 x-y+1,x+1,-z+1