Supporting Information

Synthesis and photo-/electro-catalytic properties of 3D POMOF material based on interpenetrated copper coordination polymer linked by in-situ dual-ligands and Dawson-type phosphotungstate

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1. Structural figure

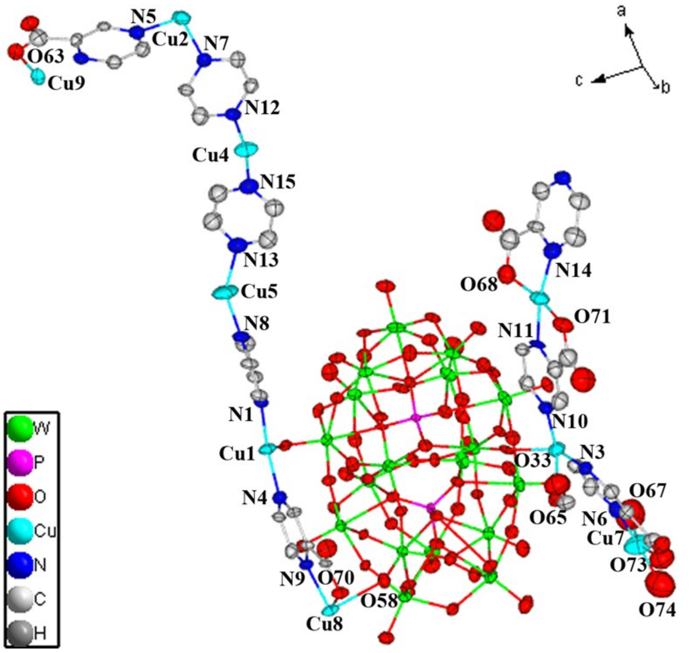

Fig. S1 Stick-ellipsoid representation of molecule structure of compound **1**

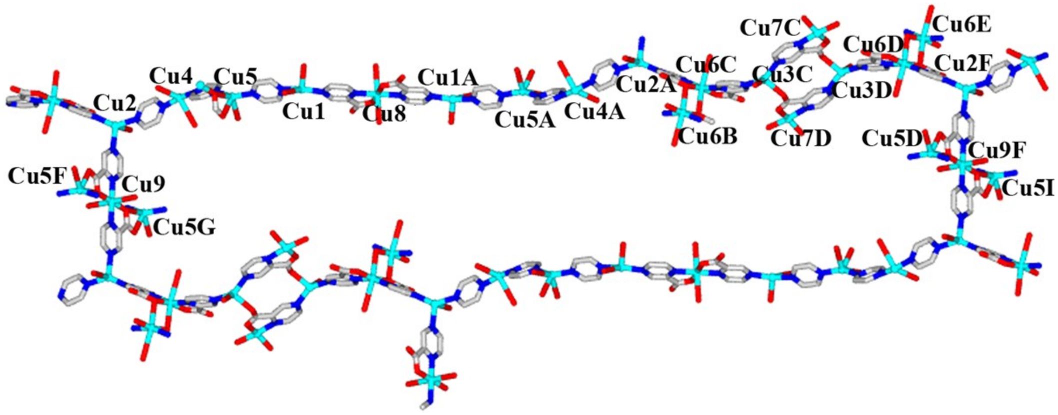

Fig. S2 The coordination environment of Cu/pz/pzc big ring. Symmetry code: A: –1–x, 2–y, 2–z; B: –2–x, 3–y, 2–z; C: –2+x, 2+y, 1+z; D: –3–x, 4–y, 2–z; E: –3+x, 3+y, 1+z; F: –4+x, 4+y, 1+z; G: x, –1+y, z; I: –4+x, 3+y, 1+z.

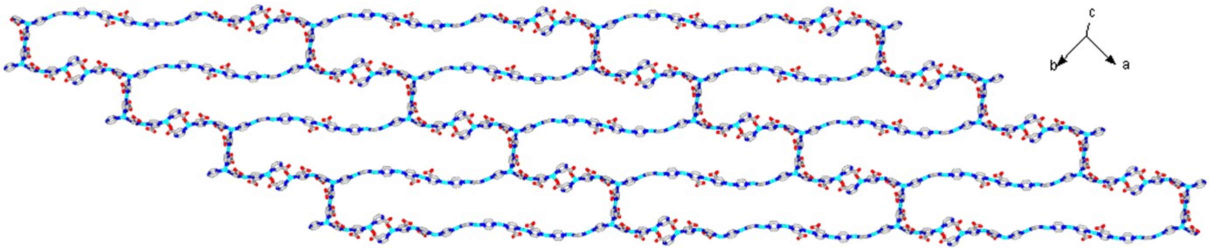

Fig. S3 The 6-connected 2-D Cu/pz/pzc metal organic layer.

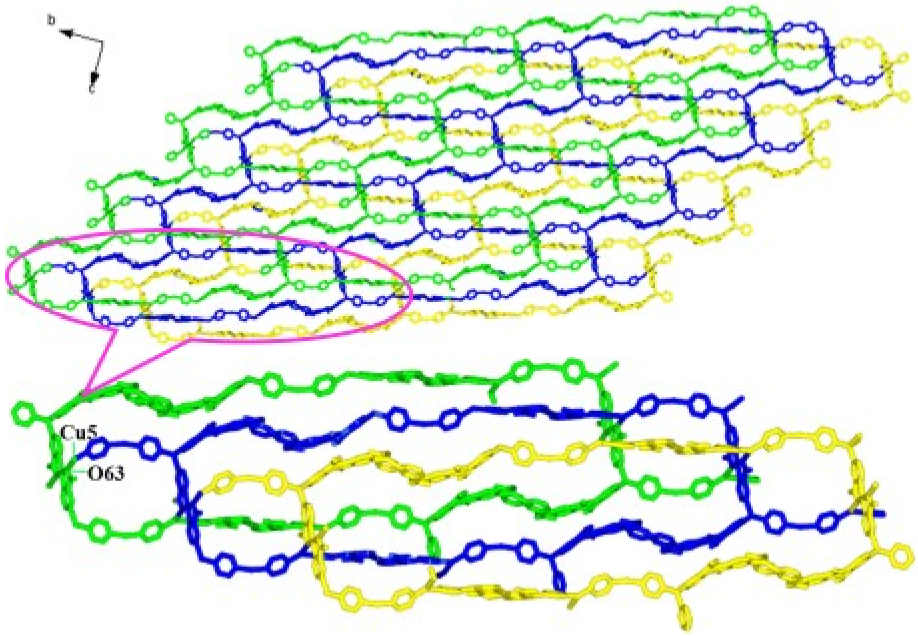

Fig. S4 The 2-D layer structure is extented by Cu_5-O_{63} along bc plane to form interpenetrated structure.

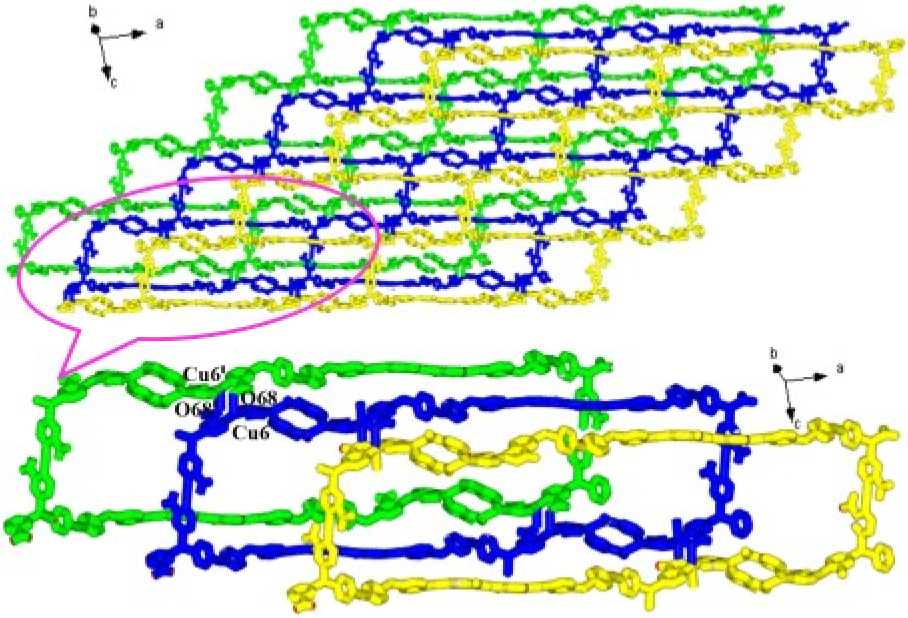

Fig. S5 The 2-D layer structure is extented by Cu_6-O_{68} along ac plane to form interpenetrated structure.

2. Structural data

Table S1 Selected bond lengths (Å) and bond angles (º) of compound **1**

W(1)-O(10)	1.691(10)	W(1)-O(5)	1.898(10)	W(1)-O(2)	1.900(10)
W(1)-O(3)	1.907(10)	W(1)-O(9)	1.919(10)	W(1)-O(18)	2.346(10)
W(2)-O(58)	1.697(11)	W(2)-O(1)	1.879(10)	W(2)-O(2)	1.888(10)
W(2)-O(35)	1.910(10)	W(2)-O(4)	1.947(10)	W(2)-O(62)	2.370(10)
W(3)-O(28)	1.712(10)	W(3)-O(41)	1.876(10)	W(3)-O(8)	1.895(10)
W(3)-O(9)	1.908(10)	W(3)-O(24)	1.946(11)	W(3)-O(18)	2.355(10)
W(4)-O(53)	1.702(10)	W(4)-O(25)	1.896(10)	W(4)-O(7)	1.901(11)
W(4)-O(43)	1.904(10)	W(4)-O(1)	1.924(10)	W(4)-O(50)	2.396(10)
W(5)-O(20)	1.692(10)	W(5)-O(3)	1.894(10)	W(5)-O(25)	1.900(10)
W(5)-O(26)	1.920(10)	W(5)-O(6)	1.947(10)	W(5)-O(19)	2.335(10)
W(6)-O(57)	1.704(11)	W(6)-O(26)	1.898(10)	W(6)-O(56)	1.898(10)
W(6)-O(11)	1.918(10)	W(6)-O(8)	1.917(11)	W(6)-O(19)	2.377(10)
W(7)-O(15)	1.722(11)	W(7)-O(22)	1.886(11)	W(7)-O(4)	1.902(9)
W(7)-O(12)	1.922(10)	W(7)-O(5)	1.929(10)	W(7)-O(29)	2.396(11)
W(8)-O(51)	1.712(10)	W(8)-O(32)	1.895(11)	W(8)-O(14)	1.897(10)
W(8)-O(30)	1.906(10)	W(8)-O(37)	1.957(11)	W(8)-O(45)	2.390(10)
W(9)-O(61)	1.712(10)	W(9)-O(6)	1.874(10)	W(9)-O(7)	1.919(11)
W(9)-O(42)	1.918(11)	W(9)-O(14)	1.955(10)	W(9)-O(45)	2.382(10)
W(10)-O(23)	1.698(12)	W(10)-O(39)	1.871(10)	W(10)-O(11)	1.906(10)
W(10)-O(37)	1.915(11)	W(10)-O(42)	1.944(10)	W(10)-O(45)	2.387(11)
W(11)-O(34)	1.700(11)	W(11)-O(40)	1.887(11)	W(11)-O(47)	1.904(10)
W(11)-O(16)	1.917(10)	W(11)-O(35)	1.924(10)	W(11)-O(62)	2.365(10)
W(12)-O(59)	1.702(12)	W(12)-O(56)	1.899(11)	W(12)-O(46)	1.903(11)
W(12)-O(52)	1.917(11)	W(12)-O(39)	1.973(11)	W(12)-O(31)	2.369(10)
W(13)-O(33)	1.704(10)	W(13)-O(55)	1.873(10)	W(13)-O(16)	1.880(10)
W(13)-O(43)	1.902(10)	W(13)-O(32)	1.936(11)	W(13)-O(50)	2.338(10)
W(14)-O(60)	1.699(11)	W(14)-O(52)	1.878(11)	W(14)-O(41)	1.898(11)
W(14)-O(36)	1.910(11)	W(14)-O(49)	1.916(11)	W(14)-O(48)	2.361(10)
W(15)-O(38)	1.701(12)	W(15)-O(21)	1.878(11)	W(15)-O(40)	1.908(10)
W(15)-O(17)	1.930(11)	W(15)-O(36)	1.939(10)	W(15)-O(48)	2.364(11)
W(16)-O(54)	1.706(10)	W(16)-O(24)	1.898(11)	W(16)-O(49)	1.908(11)
W(16)-O(29)	2.378(9)	W(16)-O(12)	1.914(11)	W(16)-O(13)	1.926(11)
W(17)-O(13)	1.903(10)	W(17)-O(44)	1.712(12)	W(17)-O(17)	1.902(11)
W(17)-O(47)	1.914(10)	W(17)-O(22)	1.940(11)	W(17)-O(29)	2.410(11)
W(18)-O(27)	1.712(11)	W(18)-O(46)	1.913(10)	W(18)-O(30)	1.920(11)
W(18)-O(55)	1.938(10)	W(18)-O(31)	2.385(10)	W(18)-O(21)	1.913(11)
P(1)-O(48)	1.531(11)	P(1)-O(62)	1.527(10)	P(1)-O(18)	1.543(11)
P(1)-O(29)	1.563(11)	P(2)-O(31)	1.519(10)	P(2)-O(19)	1.537(10)
P(2)-O(50)	1.540(11)	P(2)-O(45)	1.572(11)	Cu(1)-O(20)	2.284(10)
Cu(1)-O(9)	2.688	Cu(1)-N(4)	1.908(14)	Cu(1)-N(1)	1.924(13)
Cu(2)-N(16)#1	1.960(15)	Cu(2)-N(7)	1.981(14)	Cu(2)-N(5)	2.055(14)
Cu(3)-O(65)	2.191(14)	Cu(3)-O(33)	2.230(11)	Cu(3)-N(10)	1.951(14)
Cu(3)-N(3)	1.967(13)	Cu(4)-O(35)	2.521	Cu(4)-O(57)	2.713
Cu(4)-N(12)	1.912(13)	Cu(4)-N(15)	1.920(15)	Cu(5)-O(64)#3	2.378(13)
Cu(5)-O(28)	2.687	Cu(5)-O(63)	2.738	Cu(5)-N(8)	1.923(14)
Cu(5)-N(13)	1.944(17)	Cu(6)-O(71)	1.875(16)	Cu(6)-O(68)	1.925(16)
Cu(6)-O(36)	2.771	Cu(6)-N(14)	1.941(16)	Cu(6)-N(11)	1.991(14)
Cu(7)-O(73)	2.00(2)	Cu(7)-O(74)#2	2.028(17)	Cu(7)-O(67)	2.08(2)
Cu(7)-N(6)	1.951(15)	Cu(8)-O(70)	1.947(10)	Cu(8)-O(70)#4	1.947(10)
Cu(8)-O(58)	2.539	Cu(8)-O(58)#4	2.539	Cu(8)-N(9)	1.966(13)
Cu(8)-N(9)#4	1.966(13)	Cu(9)-O(63)#5	1.967(12)	Cu(9)-O(63)	1.967(12)

Cu(9)-O(15)#5	2.626	Cu(9)-O(15)	2.626	Cu(9)-N(2)#5	1.940(13)
Cu(9)-N(2)	1.940(13)				
O(10)-W(1)-O(5)	97.0(5)	O(58)-W(2)-O(1)	98.8(5)	O(28)-W(3)-O(41)	104.4(5)
O(10)-W(1)-O(2)	100.6(5)	O(58)-W(2)-O(2)	103.2(5)	O(28)-W(3)-O(8)	100.0(5)
O(10)-W(1)-O(3)	98.5(5)	O(58)-W(2)-O(35)	98.9(5)	O(28)-W(3)-O(9)	98.3(5)
O(10)-W(1)-O(9)	101.2(5)	O(58)-W(2)-O(4)	96.1(5)	O(28)-W(3)-O(24)	95.7(5)
O(10)-W(1)-O(18)	173.7(4)	O(58)-W(2)-O(62)	171.4(5)	O(28)-W(3)-O(18)	170.4(4)
O(53)-W(4)-O(25)	104.0(5)	O(20)-W(5)-O(3)	98.3(5)	O(57)-W(6)-O(26)	99.5(5)
O(53)-W(4)-O(7)	96.7(5)	O(20)-W(5)-O(25)	100.3(4)	O(57)-W(6)-O(56)	102.4(5)
O(53)-W(4)-O(43)	100.5(5)	O(20)-W(5)-O(26)	101.0(5)	O(57)-W(6)-O(11)	97.9(5)
O(53)-W(4)-O(1)	99.2(5)	O(20)-W(5)-O(6)	96.0(4)	O(57)-W(6)-O(8)	98.6(5)
O(53)-W(4)-O(50)	172.2(4)	O(20)-W(5)-O(19)	173.8(4)	O(57)-W(6)-O(19)	172.2(4)
O(15)-W(7)-O(22)	99.7(5)	O(51)-W(8)-O(32)	102.0(5)	O(61)-W(9)-O(6)	103.9(5)
O(15)-W(7)-O(4)	102.9(5)	O(51)-W(8)-O(14)	100.1(5)	O(61)-W(9)-O(7)	102.5(5)
O(15)-W(7)-O(12)	100.2(5)	O(51)-W(8)-O(30)	103.4(5)	O(61)-W(9)-O(42)	100.6(5)
O(15)-W(7)-O(5)	104.1(5)	O(51)-W(8)-O(37)	100.6(5)	O(61)-W(9)-O(14)	100.2(5)
O(15)-W(7)-O(29)	170.0(4)	O(51)-W(8)-O(45)	170.8(5)	O(61)-W(9)-O(45)	170.4(5)
O(23)-W(10)-O(39)	101.5(5)	O(34)-W(11)-O(40)	103.2(5)	O(59)-W(12)-O(56)	102.2(5)
O(23)-W(10)-O(11)	102.9(5)	O(34)-W(11)-O(47)	99.9(5)	O(59)-W(12)-O(46)	100.1(5)
O(23)-W(10)-O(37)	99.6(5)	O(34)-W(11)-O(16)	96.4(5)	O(59)-W(12)-O(52)	99.3(5)
O(23)-W(10)-O(42)	99.4(5)	O(34)-W(11)-O(35)	99.6(5)	O(59)-W(12)-O(39)	97.0(5)
O(23)-W(10)-O(45)	169.9(4)	O(34)-W(11)-O(62)	172.2(4)	O(59)-W(12)-O(31)	173.8(5)
O(33)-W(13)-O(55)	101.3(5)	O(60)-W(14)-O(52)	99.3(5)	O(38)-W(15)-O(21)	97.3(5)
O(33)-W(13)-O(16)	99.1(5)	O(60)-W(14)-O(41)	101.6(5)	O(38)-W(15)-O(40)	101.2(5)
O(33)-W(13)-O(43)	99.8(4)	O(60)-W(14)-O(36)	100.4(5)	O(38)-W(15)-O(17)	98.5(5)
O(33)-W(13)-O(32)	95.7(5)	O(60)-W(14)-O(49)	97.1(5)	O(38)-W(15)-O(36)	100.3(5)
O(33)-W(13)-O(50)	172.8(4)	O(60)-W(14)-O(48)	174.5(5)	O(38)-W(15)-O(48)	174.0(5)
O(54)-W(16)-O(24)	103.6(5)	O(44)-W(17)-O(17)	103.0(5)	O(27)-W(18)-O(21)	97.9(5)
O(54)-W(16)-O(49)	102.3(5)	O(44)-W(17)-O(13)	101.6(5)	O(27)-W(18)-O(46)	97.6(5)
O(54)-W(16)-O(12)	101.3(5)	O(44)-W(17)-O(47)	103.0(5)	O(27)-W(18)-O(30)	99.0(5)
O(54)-W(16)-O(13)	99.1(5)	O(44)-W(17)-O(22)	101.8(5)	O(27)-W(18)-O(55)	104.2(5)
O(54)-W(16)-O(29)	170.2(5)	O(44)-W(17)-O(29)	171.5(5)	O(27)-W(18)-O(31)	170.7(4)
O(48)-P(1)-O(62)	112.6(6)	O(48)-P(1)-O(18)	111.3(6)	O(48)-P(1)-O(29)	106.9(6)
O(31)-P(2)-O(19)	110.9(5)	O(31)-P(2)-O(50)	112.6(6)	O(31)-P(2)-O(45)	107.4(6)
N(4)-Cu(1)-N(1)	160.1(5)	N(4)-Cu(1)-O(20)	88.7(5)	N(1)-Cu(1)-O(20)	107.4(5)
N(16)#1-Cu(2)-N(7)	139.1(6)	N(16)#1-Cu(2)-N(5)	110.9(6)	N(7)-Cu(2)-N(5)	109.9(6)
N(10)-Cu(3)-N(3)	145.0(6)	N(10)-Cu(3)-O(65)	113.0(5)	N(3)-Cu(3)-O(65)	94.7(5)
N(10)-Cu(3)-O(33)	97.0(5)	N(3)-Cu(3)-O(33)	95.2(5)	O(65)-Cu(3)-O(33)	106.2(5)
N(12)-Cu(4)-N(15)	168.1(7)	N(8)-Cu(5)-N(13)	147.3(7)	N(8)-Cu(5)-O(64)#3	102.9(5)
N(13)-Cu(5)-O(64)#3	109.8(6)	O(71)-Cu(6)-O(68)	167.8(7)	O(71)-Cu(6)-N(14)	101.5(7)
O(68)-Cu(6)-N(14)	83.0(7)	O(71)-Cu(6)-N(11)	82.9(6)	O(68)-Cu(6)-N(11)	96.3(6)
N(14)-Cu(6)-N(11)	162.1(6)	N(6)-Cu(7)-O(73)	174.0(8)	N(6)-Cu(7)-O(74)#2	81.8(6)
O(73)-Cu(7)-O(74)#2	93.6(9)	N(6)-Cu(7)-O(67)	92.0(8)	O(73)-Cu(7)-O(67)	93.7(9)
O(74)#2-Cu(7)-O(67)	156.4(8)	O(70)-Cu(8)-O(70)#4	180.0(6)	O(70)-Cu(8)-N(9)	84.0(5)
O(70)#4-Cu(8)-N(9)	96.0(5)	O(70)-Cu(8)-N(9)#4	96.0(5)	O(70)#4-Cu(8)-N(9)#4	84.0(5)
N(9)-Cu(8)-N(9)#4	179.999(3)	N(2)-Cu(9)-N(2)#5	179.999(2)	N(2)-Cu(9)-O(63)	83.5(5)
N(2)#5-Cu(9)-O(63)	96.5(5)	N(2)-Cu(9)-O(63)#5	96.5(5)	N(2)#5-Cu(9)-O(63)#5	83.5(5)
O(63)-Cu(9)-O(63)#5	180.000(2)				

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z；#2 -x+1/2,-y+1/2,-z

2. Physical characterization

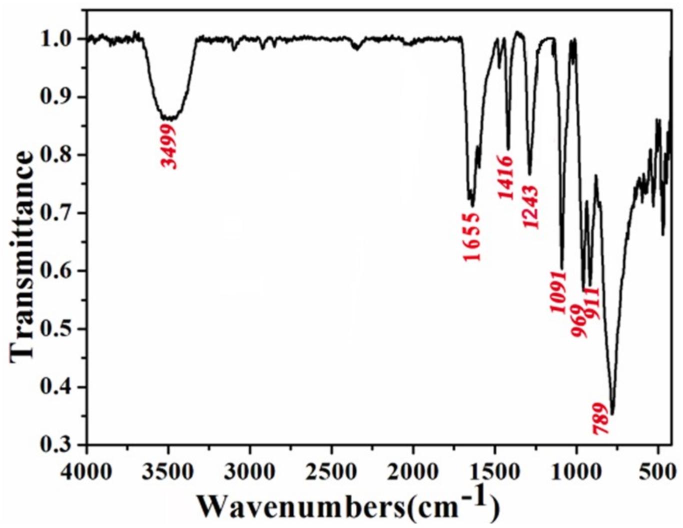

Fig. S6 IR spectra of compound **1**

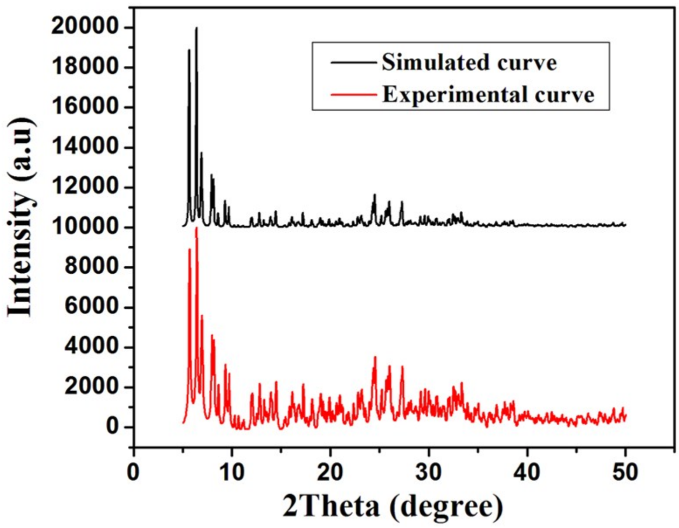

Fig. S7. The PXRD contrast curves of compound **1**

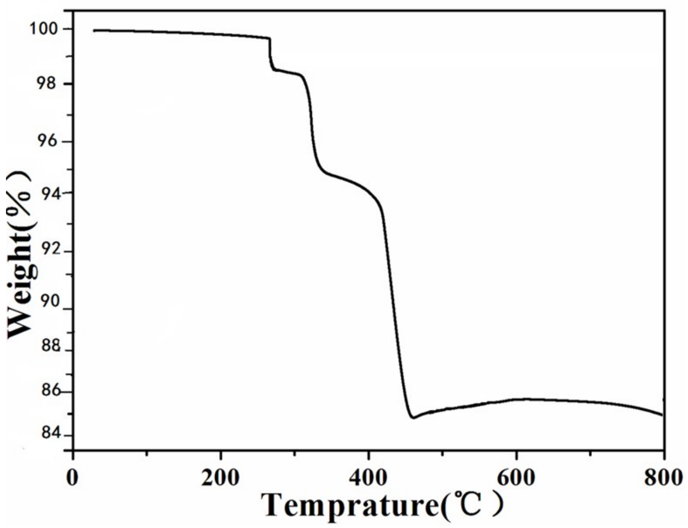

Fig. S8 TG curve of compound **1**

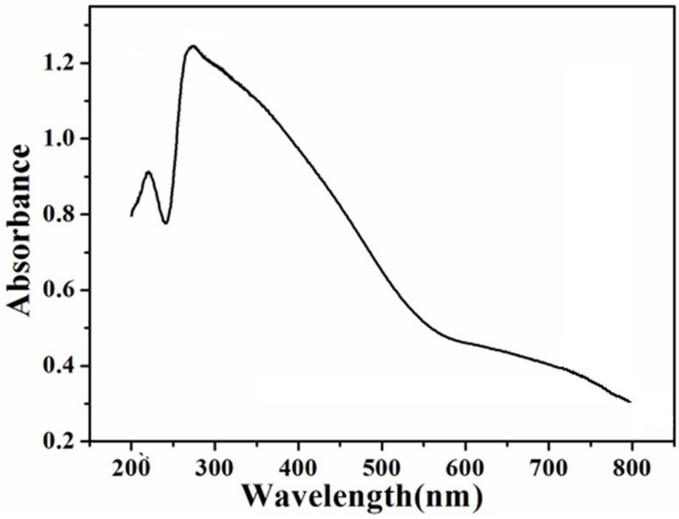

Fig. S9 The UV-vis spectra of compound **1** in solid state at room temperature**.**

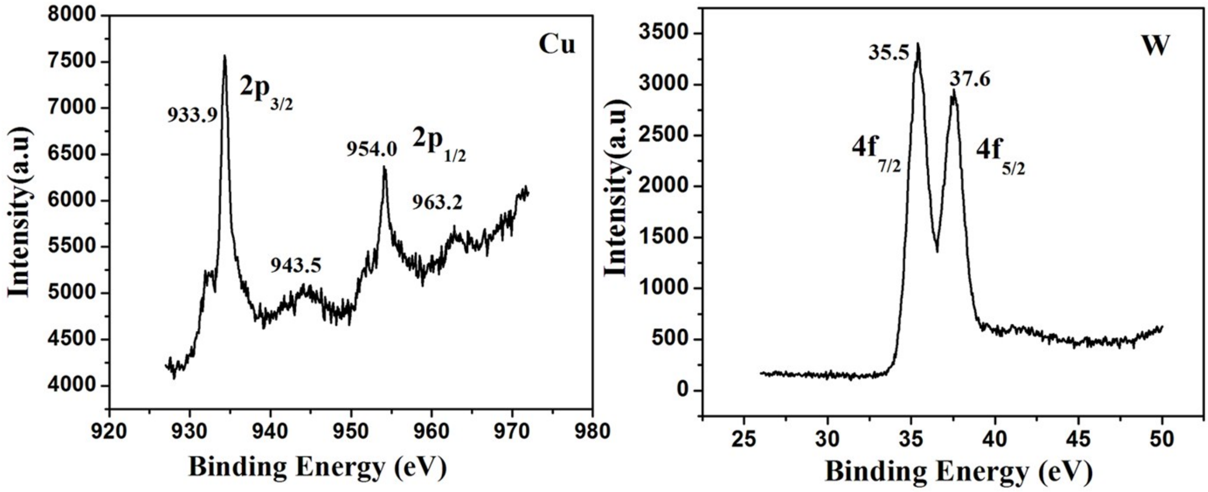

Fig. S10 The XPS spectrum of compound **1.**

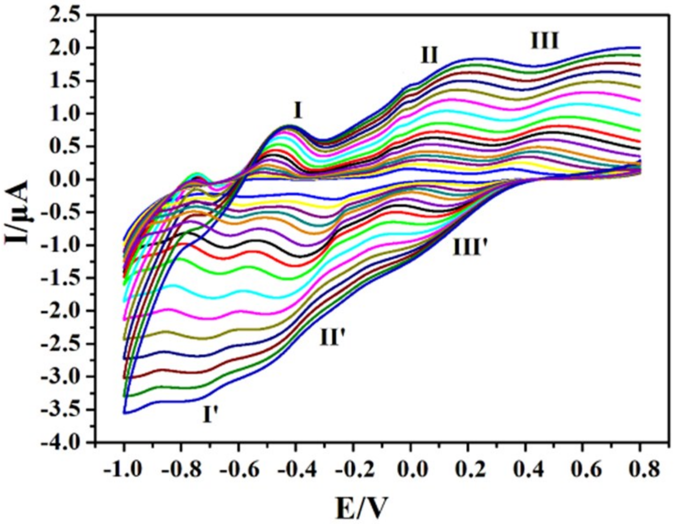

Fig. S11 Cyclic voltammograms of **1-CPE** (scan rates from inner to outer: 20,30, 40, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}). Potentials vs. SCE.

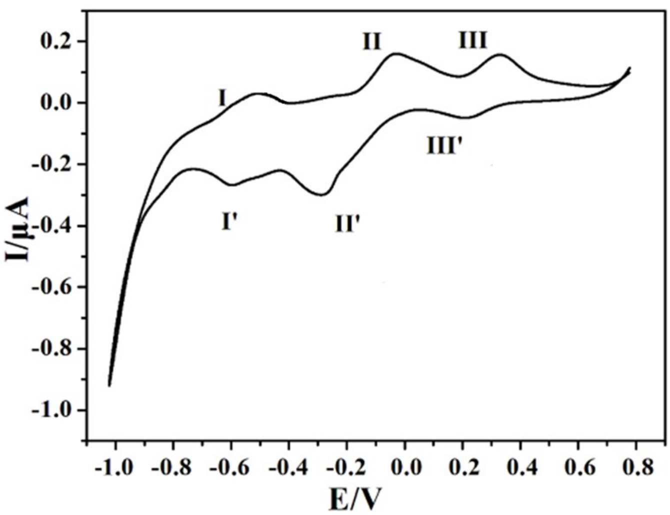

Fig. S12 Cyclic voltammograms of **1-CPE** in the 1.0 M H_2SO_4 solution at scan rate of 20 mVs^{-1}. Potentials vs. SCE.