Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary information for

Distinct anion sensing by a 2D self-assembled Cu(I)-based metal-organic polymer with versatile visual colorimetric responses and efficient selective separations *via* anion exchange

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Materials and Methods:

All reagents and solvents used were received from commercial suppliers without further purification. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS Elemental Analyzer and Energy Dispersive X-ray Spectroscopy (EDX) analyses were conducted on a Scanning Electron Microscope of JSM-6700F. The infrared spectra with KBr pellet were recorded in the range of 4000-400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR Spectrometer. Thermal analysis was performed on a NETZSCH STA 449C instrument from room temperature to 800 ℃ with a heating rate of 10 ℃/min^{-1} under nitrogen flow. The UV/Vis spectra were carried out on a PE Lambda 800 UV/Vis/NIR spectrometer equipped with an integrating sphere, and the $BaSO_4$ plate was used as the reference. The EPR spectra were acquired on a Bruker ER-420 spectrometer with a 100 KHz magnetic field in X band and an electronic field of 9655.448 MHz at room temperature. Powder X-ray diffraction (PXRD) data were collected on a DMAX-2500 diffractometer with Cu K_α.

Synthesis:

α,α'-bis(N-glutamyl)-p-xylene (bgxH_4).

L-Glutamic acid (7.36 g, 0.05 mol) and sodium hydroxide (4.0 g, 0.1 mol) were dissolved in the solution of 30 ml methanol and 30 ml water. A solution of terephthalaldehyde (3.35 g, 0.025 mol) in 60mL of methanol was added and the mixed solution was stirred at room temperature for 3 hours. Whilst it was cooled to 0 ℃, the solution of sodium borohydride (2.27 g, 0.06 mol) in 40 ml methanol was slowly added into the mixture, and stirring was continued for one more hour. Then, the solution was adjusted to pH 3.0~4.0 by dropwise addition of concentrated hydrochloric acid. After filtration, the white solid was then washed twice with dry ethanol and ether, recrystallized and dried under vacuum at ambient temperature to give 70% yield. ^{1}H NMR (400MHz, D_2O): δ 1.80 (m, 4H); 2.30 (t, *J*=1.37Hz, 4H); 3.0 (t, *J*=1.37Hz, 2H); 4.52 (d, *J*=1.37Hz, 2H); 4.82 (d, *J*=1.37Hz, 2H); 7.42 ppm (s, 4H); ESI-MS: m/z 395.2 ($[M-1]^+$, calcd 396.4), elemental analysis calcd (%) for $C_{18}H_{24}N_2O_8$: C 54.54, H 6.10, N 7.07; found: C 54.41, H 6.19, N 6.98.

During the solvothermal process, Cu(Π) ions have been transformed to Cu(I) cations, whilst α,α'-bis(N-pyroglutamyl)-p-xylene (bpgxH_2) forms in situ reaction from intramolecular cyclization of bgxH_4.

$[Cu_4(bipy)_4(L\text{-}bgxH_2)](NO_3)_2$ $(H_2O)_4$ (compound **1**)**.** Copper nitrate trihydrate (0.0377 g, 0.2 mmol) and 4,4'-bipyridine (0.0312 g, 0.2 mmol) were added to the solution of bgxH_4 (0.0396 g, 0.1 mmol) in 5 ml DMF/ethanol/water (v:v:v=1:1:1). The reaction suspension was stirred for 10 min and was transferred into a 12 ml vessel. The vessel was sealed and heated at 105 ℃ for 1 day and slowly cooled to the room temperature. After using ultrasonic treatments for 10 minutes and rinsing thoroughly with distilled water and dry ethanol, the red prism crystals of compound **1** were obtained in ca. 58% yield based on bgxH_2. Anal. Calcd for for $Cu_4C_{58}H_{58}N_{12}O_{16}$ (**1**): M=1432.34; elemental analysis: calcd (%) for $Cu_4N_{12}O_{16}C_{58}H_{57}$: C 48.64, H 4.01, N 11.73; found: C 48.55, H 4.14, N 11.58.

Crystallographic Analyses:

The structural determination of single crystal was performed on Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The structures were solved by direct methods and refined by the full-matrix leasts-squares technique on F^2 using the SHELXTL-97 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon atoms were generated geometrically (C-H bond fixed at 0.97 Å). Notably, the water molecules in the two complexes were refined by using the pseudo-isotropic "ISOR" restraint to make the ADP values of the disordered oxygen atoms more reasonable. And the selected bond lengths and angles of the complexes are listed in Table S1-S2.

Tablet S1. Crystal Data and Structure Refinements for compound **1**

Compound	**1**
Formula	$Cu_4C_{58}H_{58}N_{12}O_{16}$
FW	1431.31
Temperature	293K
Cryst syst m	triclinic
Space group	*P* 1
a (Å)	9.1100(3)
b (Å)	10.3806(7)
c (Å)	16.1429(10)
α(deg)	82.065(13)
β(deg)	77.497(9)
γ(deg)	82.299(13)
V ($Å^3$)	1467.53(14)
Z	1
D_c (g cm^{-3})	1.61945
μ(mm^{-1})	1.511
Reflns collcd	16907
Unique reflns (Rint)	12212
GOF	1.032
R1,[a] wR2[b] [I>2σ(I)]	0.0378, 0.0915
R1,[a] wR2[b] (all data)	0.0463, 0.0969
[α]$R1 = \sum(\| F_o \| - \| F_c \|) / \sum \| F_o \|$. [b]$wR2 = \{\sum w [(F^2_o - F^2_c)] / \sum w [(F^2_o)^2]\}^{0.5}$.	

Tablet S2. Selected Bong Lengths [Å] and Angles [°] for compound **1**

Cu1-N3	1.938(3)	Cu1-N5	1.935(4)	Cu1-O1	2.189(3)
Cu2-N7	1.909(3)	Cu2-N9	1.915(3)	Cu2-O1	2.251(3)
Cu3-N4	1.921(3)	Cu3-N6a	1.929(3)	Cu3-O5b	2.330(4)
Cu4-N10a	1.913(4)	Cu4-N8	1.924(3)	Cu4-O4b	2.138(3)
N6-Cu3c	1.929(3)	N10-Cu4c	1.913(4)	O5-Cu3d	2.330(3)
O4-Cu4d	2.138(3)				
N3-Cu1-N5	155.98(14)	N3-Cu1-O1	98.81(13)	N5-Cu1-O1	105.02(13)
N7-Cu2-N9	157.96(14)	N7-Cu2-O1	99.27(12)	N9-Cu2-O1	100.06(12)
N4-Cu3-N6a	156.20(14)	N4-Cu3-O5b	106.17(14)	N6a-Cu3-O5b	97.12(14)
N10a-Cu4-N8	160.29(14)	N10a-Cu4-O4b	98.61(15)	N8-Cu4-O4b	100.54(15)

[a]Symmetry codes: a x-2,y,z+1; b x-1,y-1,z;c x+2,y,z-1;d x+1,y+1,z.

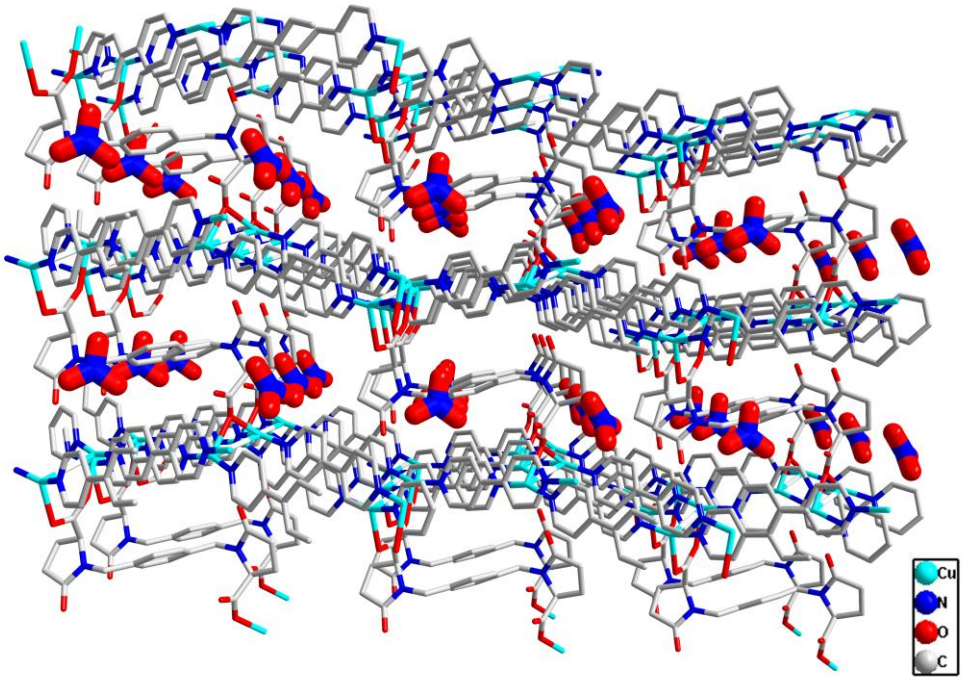


Fig.S1. The voids are occupied by uncoordinated nitrate anions in space filling representation**.**

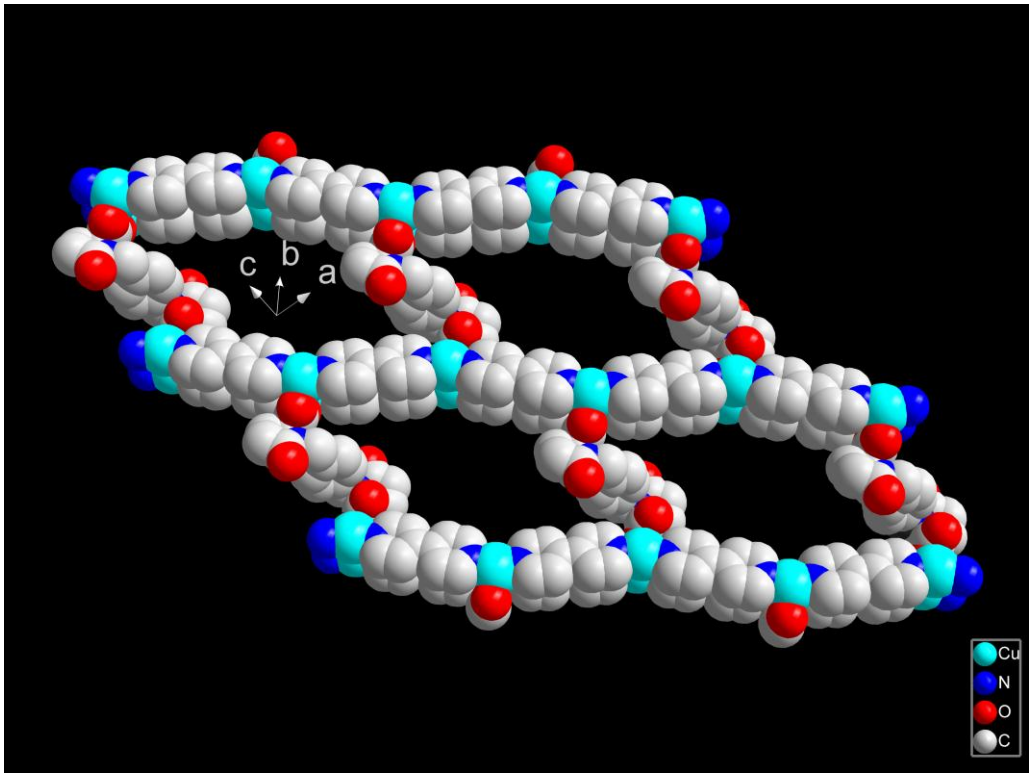


Fig.S2. Space-filling representation of single layer in compound **1** (The uncoordinated nitrate anions and water molecules are omitted.)

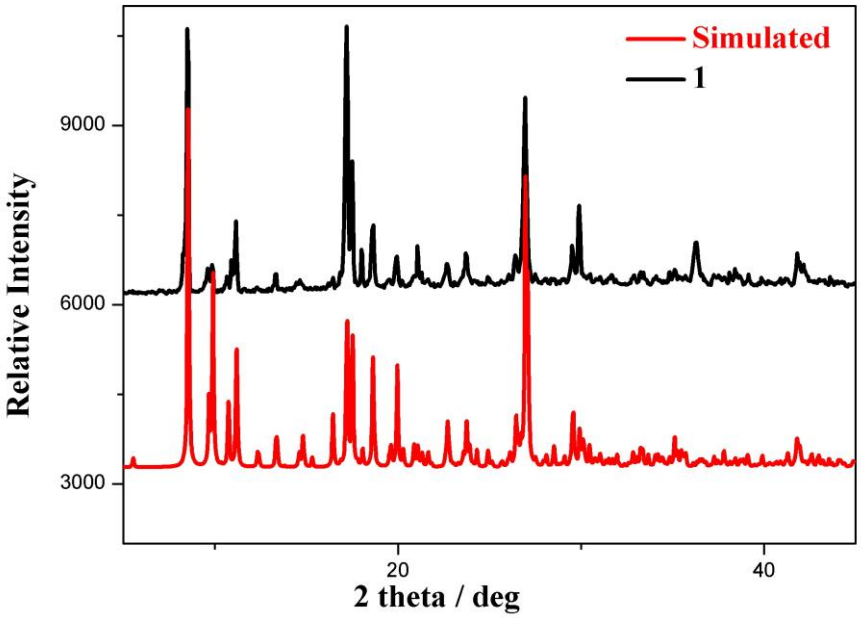


Fig.S3. Powder X-ray diffractions for simulated and experimental compound **1**

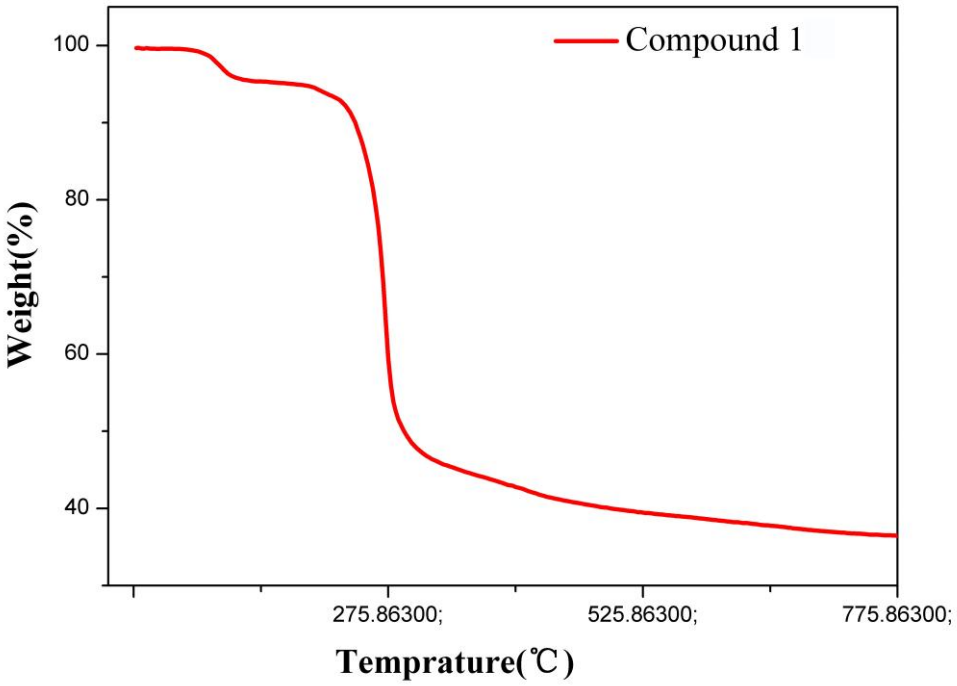


Fig.S4. TGA curve of compound **1.**

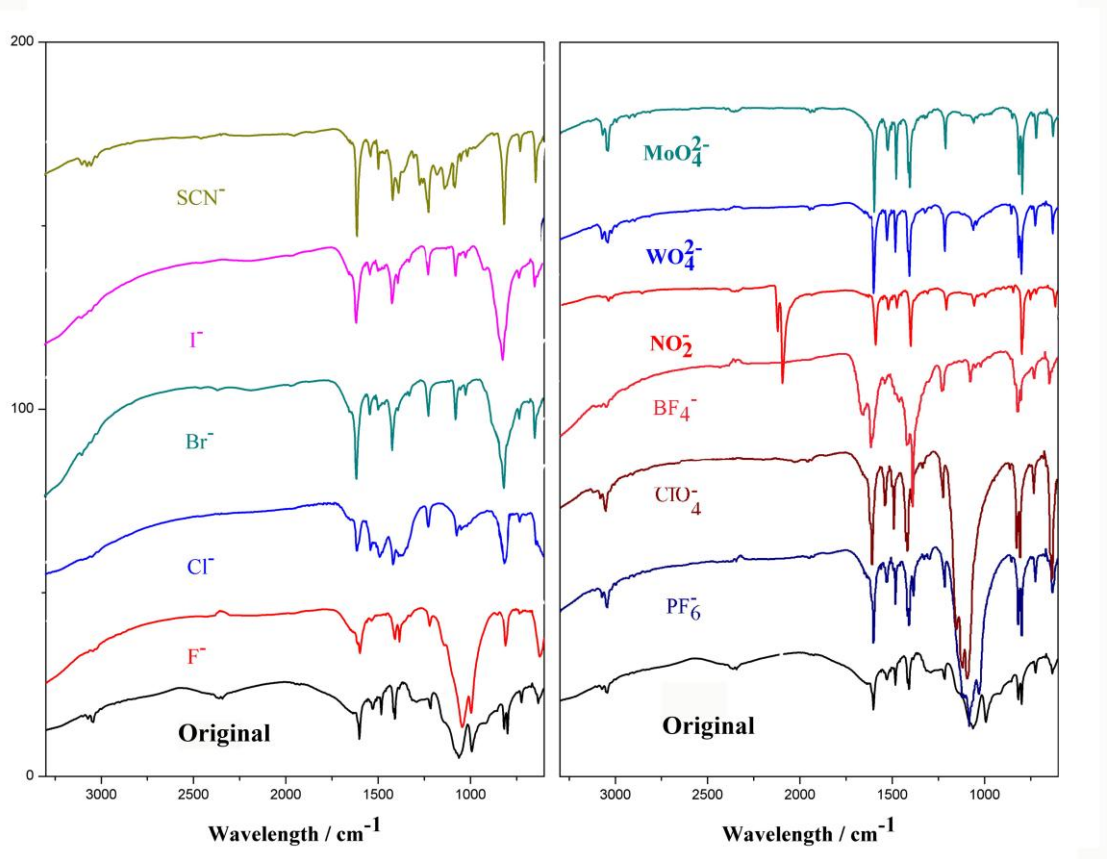
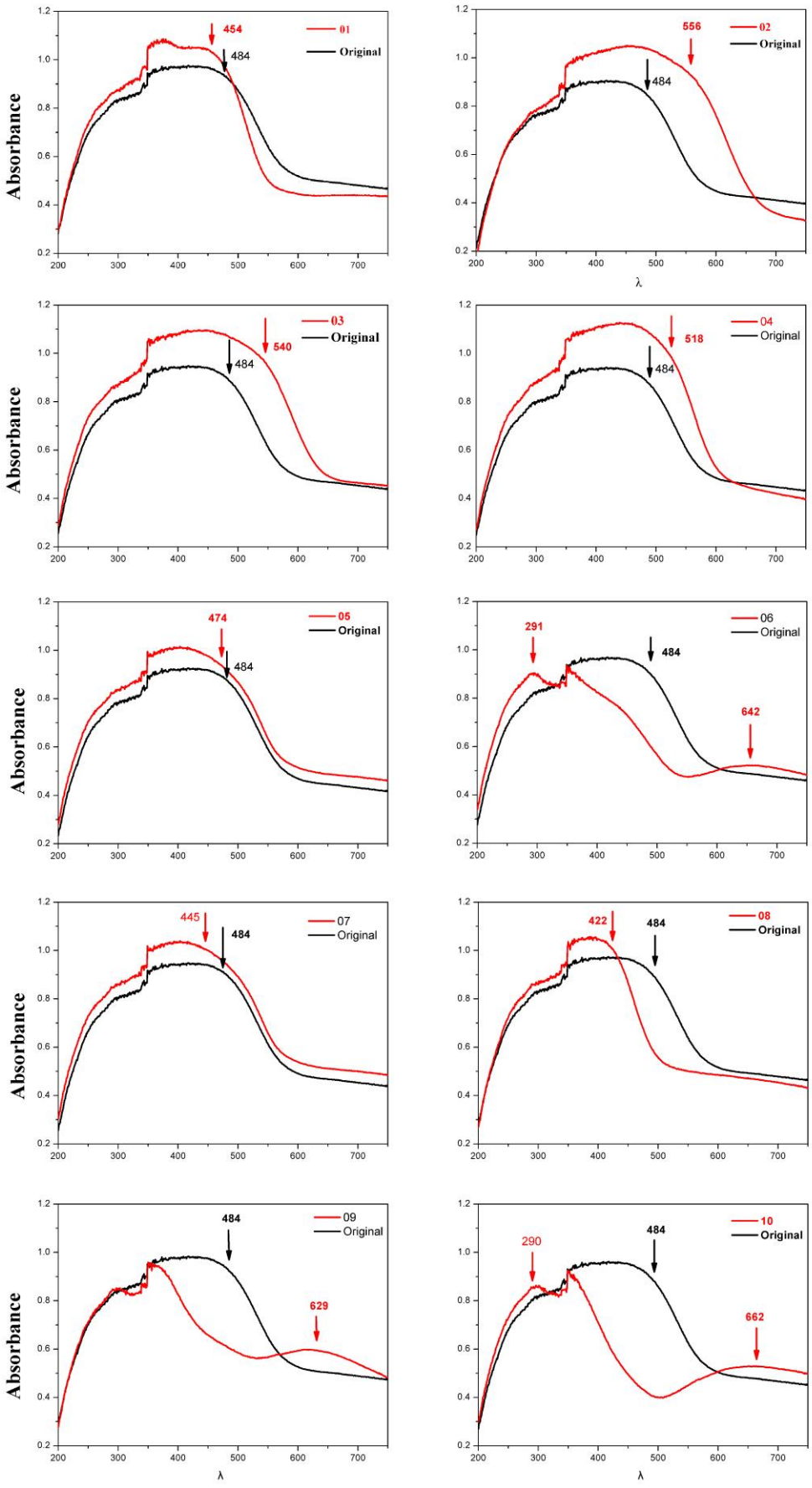


Fig.S5. IR spectra based on anion-exchanged products.



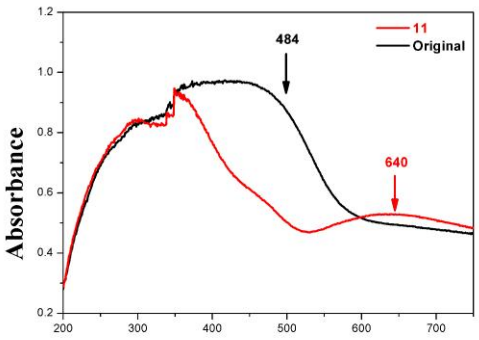
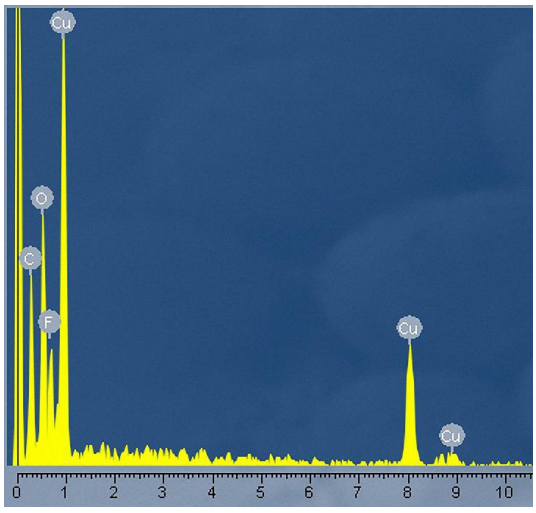
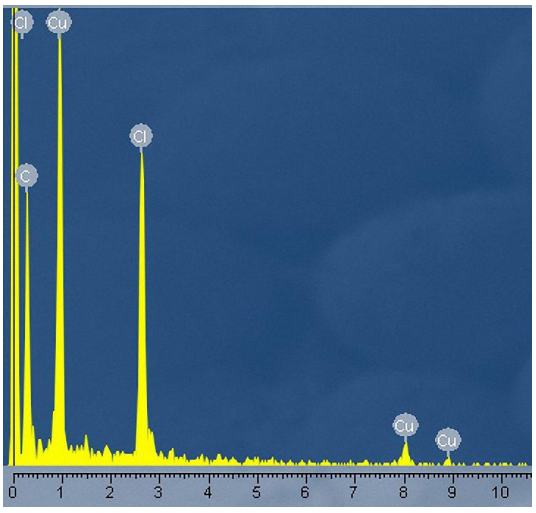


Fig.S6: Solid-state UV/Vis spectra based on anion-exchanged products

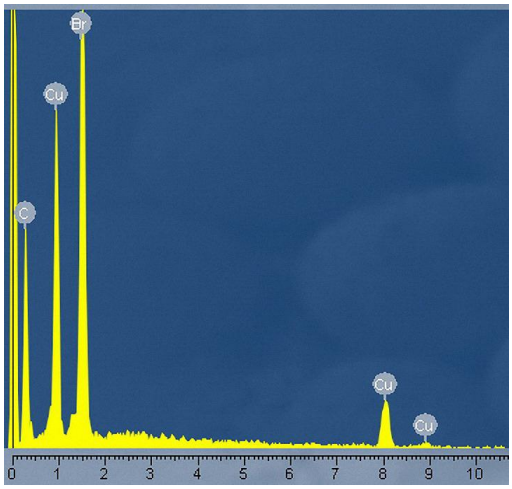
Fig.S7: EDX and Elemental Analyses



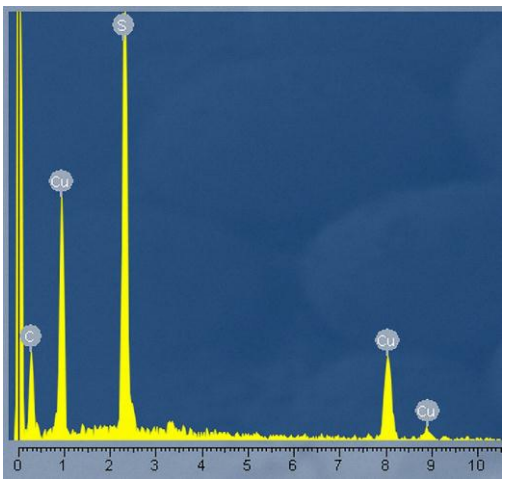


Products of 01		
Element	Calcd (%)	Found (%)
C	49.88	50.42
H	4.19	4.65
N	10.65	10.87

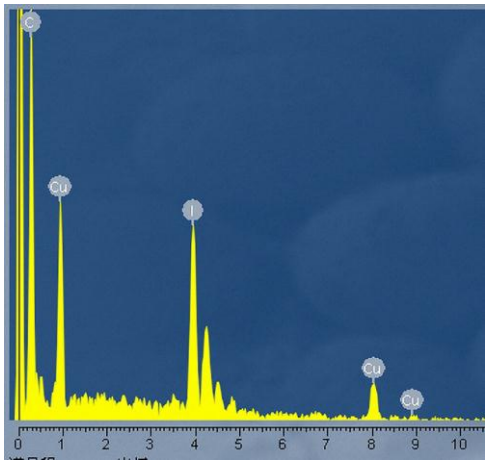
Products of 02		
Element	Calcd (%)	Found (%)
C	50.01	50.58
H	4.20	4.54
N	11.12	11.57



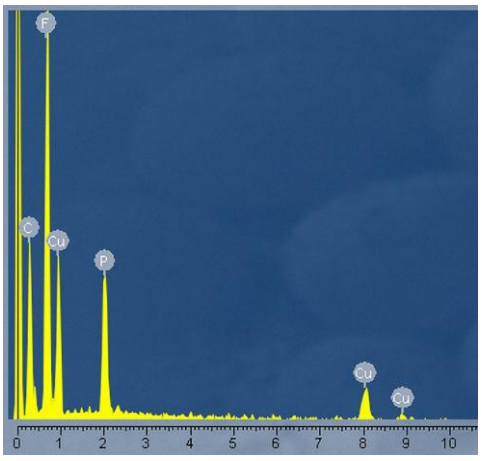
Products of 03		
Element	Calcd (%)	Found (%)
C	47.48	47.98
H	3.98	4.60
N	9.65	9.68



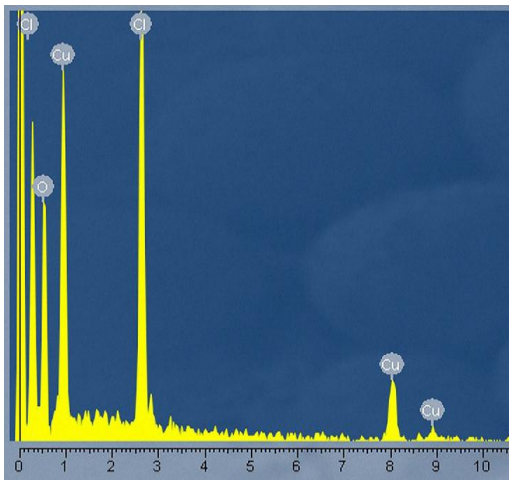
Products of 05		
Element	Calcd (%)	Found (%)
C	49.14	49.25
H	4.08	4.79
N	10.74	10.80



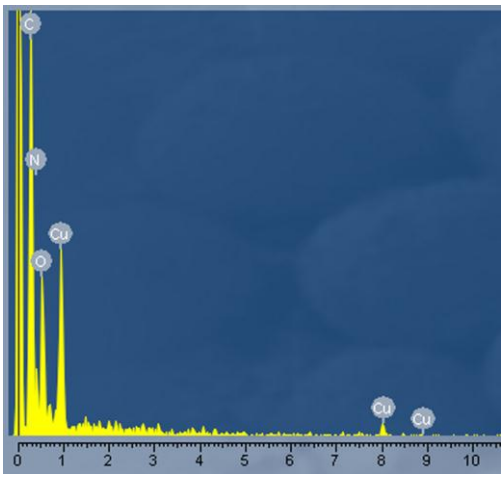
Products of 04		
Element	Calcd (%)	Found (%)
C	47.30	47.83
H	3.97	4.33
N	10.83	10.84



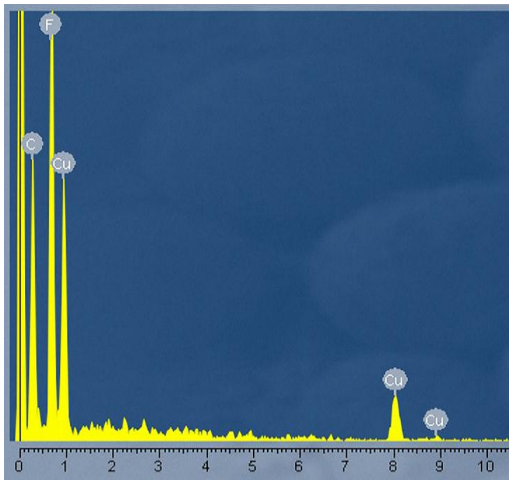
Products of 06		
Element	Calcd (%)	Found (%)
C	46.71	47.32
H	3.92	4.63
N	10.61	11.62



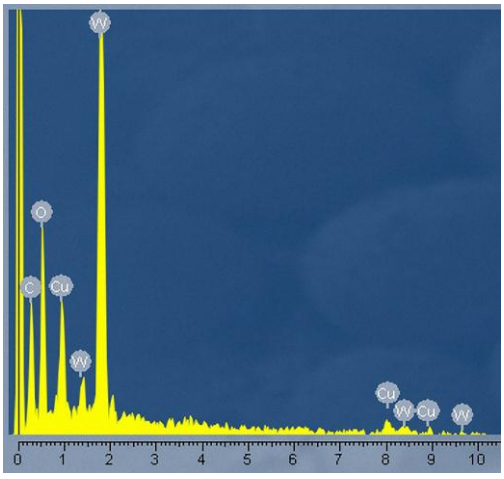
Products of 07		
Element	Calcd (%)	Found (%)
C	47.39	47.54
H	3.98	4.06
N	10.50	10.51



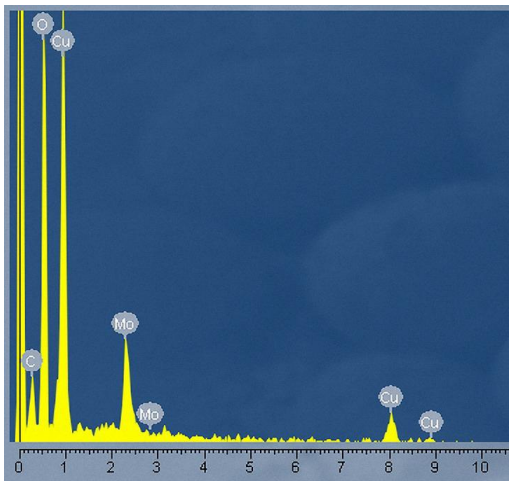
Products of 09		
Element	Calcd (%)	Found (%)
C	48.86	48.48
H	4.10	4.27
N	11.79	12.11



Products of 08		
Element	Calcd (%)	Found (%)
C	47.76	47.75
H	4.00	3.37
N	10.54	10.54

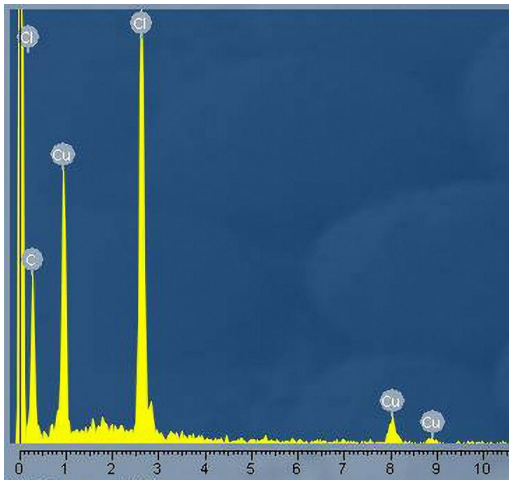


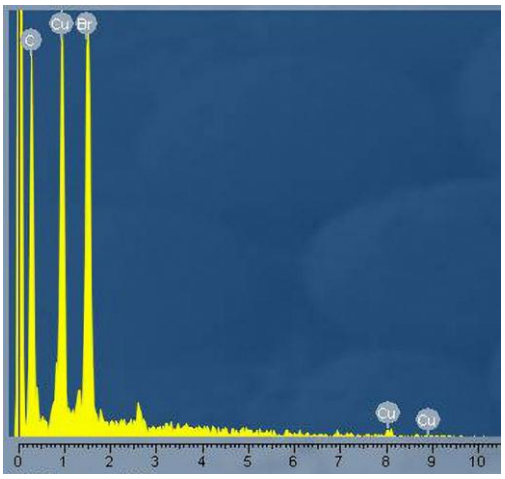
Products of 10		
Element	Calcd (%)	Found (%)
C	46.26	46.57
H	3.88	4.19
N	10.80	10.90



Products of 11		
Element	Calcd (%)	Found (%)
C	47.34	47.07
H	3.97	3.71
N	10.05	10.12

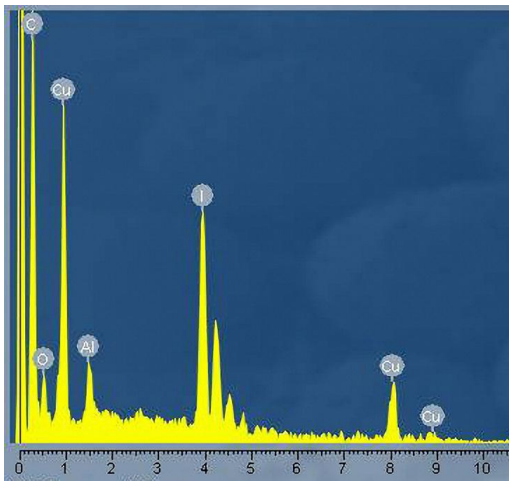
Anion-exchange Selectivity:





Products of 01’		
Element	Calcd (%)	Found (%)
C	49.33	48.84
H	4.09	4.41
N	11.15	10.42

Products of 02’		
Element	Calcd (%)	Found (%)
C	47.97	48.42
H	3.96	4.69
N	10.50	11.35



Products of 03’		
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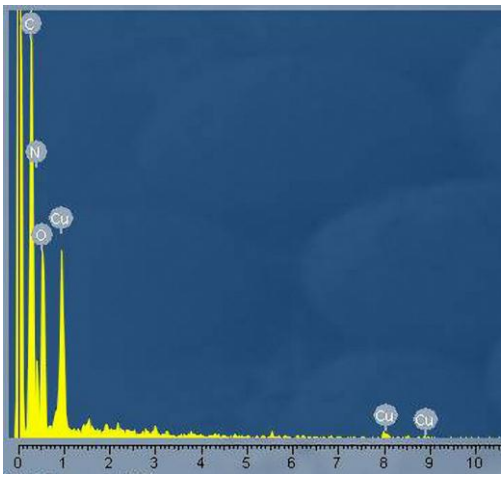
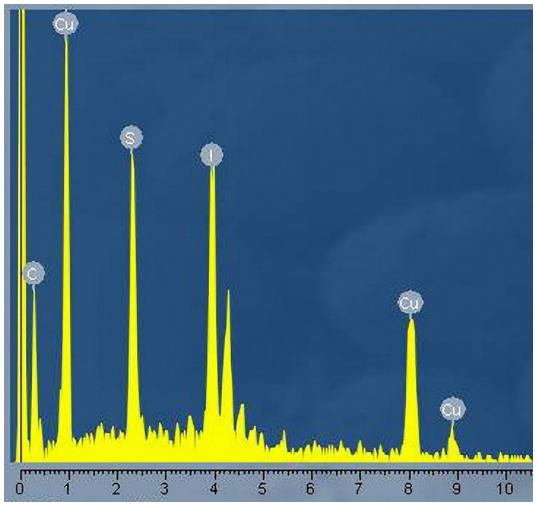
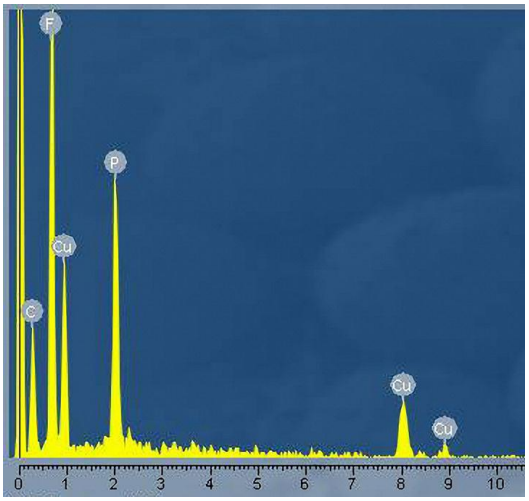
C	47.72	48.39
H	3.96	4.11
N	11.11	10.38



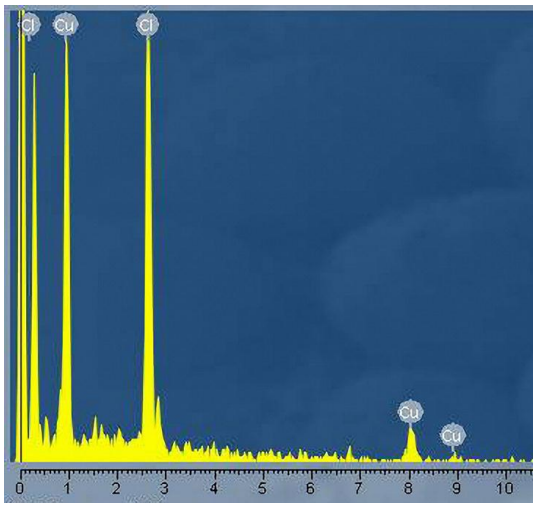
Products of 05’		
Element	Calcd (%)	Found (%)
C	49.15	48.80
H	4.01	4.49
N	11.75	11.58



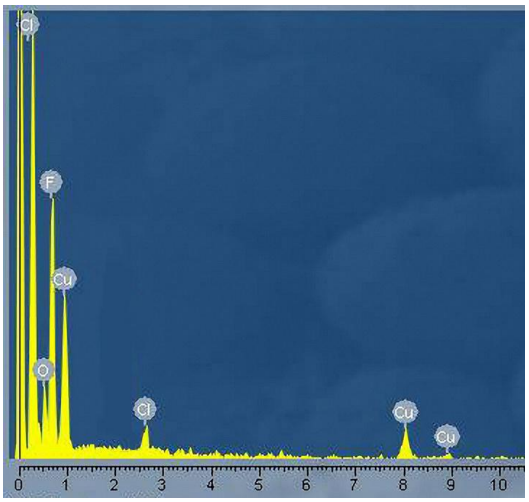
Products of 04’		
Element	Calcd (%)	Found (%)
C	48.45	47.88
H	3.98	4.24
N	11.43	11.36



Products of 06’		
Element	Calcd (%)	Found (%)
C	46.98	47.27
H	3.87	4.43
N	10.76	10.82



Products of 07’		
Element	Calcd (%)	Found (%)
C	49.52	49.86
H	4.08	4.40
N	10.99	11.32



Products of 09’		
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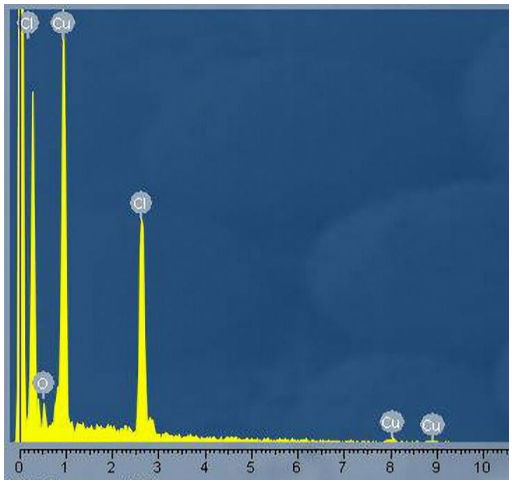
C	48.12	48.58
H	3.97	4.49
N	11.15	10.87



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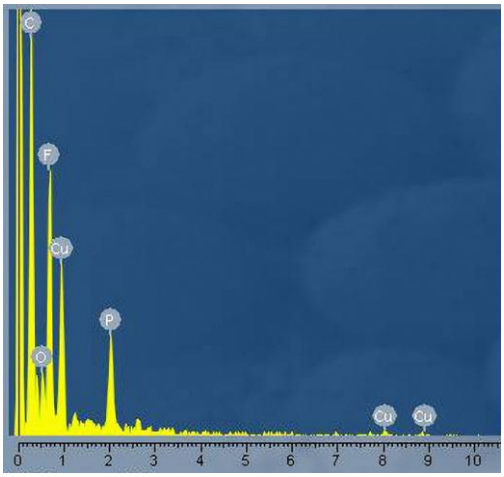
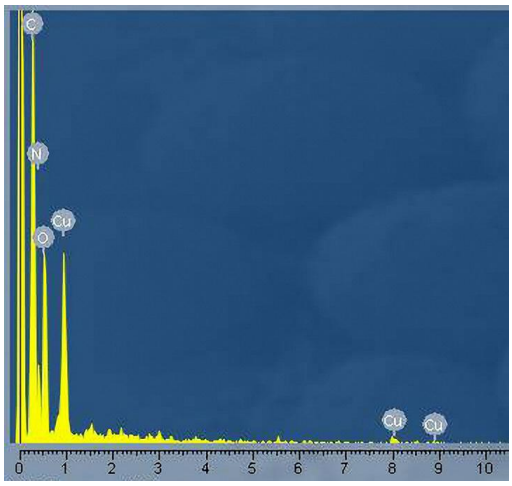
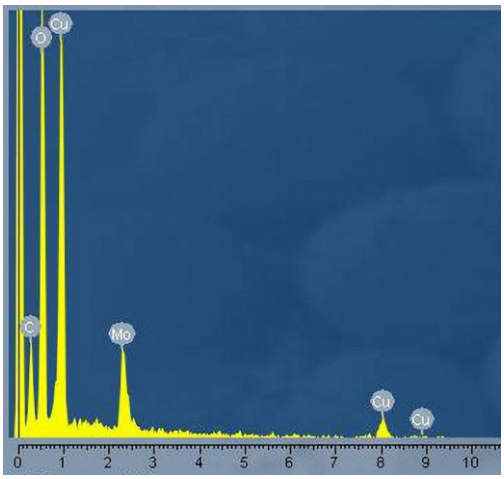
C	49.43	50.16
H	4.08	4.38
N	11.06	11.09



Products of 10’		
Element	Calcd (%)	Found (%)
C	46.98	47.39
H	3.87	4.47
N	10.76	11.25



Products of 11’		
Element	Calcd (%)	Found (%)
C	48.88	48.17
H	4.03	4.37
N	11.80	11.25



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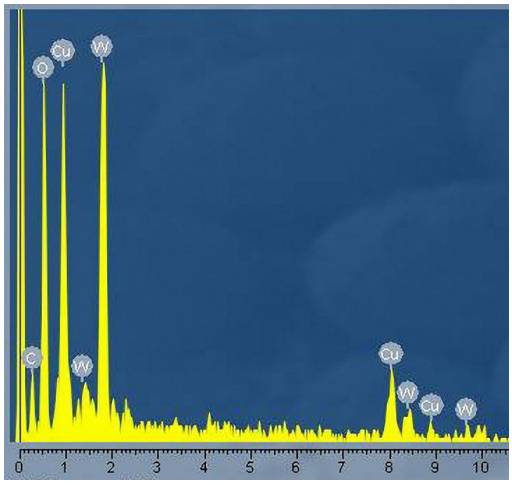
C	47.67	48.25
H	3.93	4.67
N	11.05	11.53



Products of 12’		
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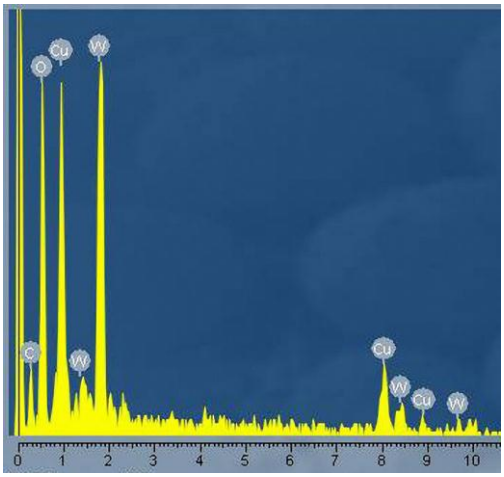
C	47.66	46.89
H	3.93	4.35
N	11.05	11.59



Products of 14’		
Element	Calcd (%)	Found (%)
C	47.63	47.69
H	3.93	4.76
N	11.03	11. 79