Supporting Information

1. Chemicals and instrumentation

Copper(II) chloride dehydrate (CuCl$_2$·2H$_2$O, 99%), 2,5-dicarboxylic acid-3,4-ethylene

dioxythiophene (H$_2$L, >95%), N,N-dimethylacetamide (DMA, >99%), N,N-

dimethylformamide (DMF, >99%) were purchased from commercial suppliers

(aladdin-reagent, TCL-reagent and macklin-reagent) and were used as received

without further purification. All solutions were prepared with ultrapure water. The

phases were analyzed by X-ray powder diffraction (XRD) using a D/Max-2500 X-ray

diffractometer with Cu Kα radiation. The FT-IR spectra were measured with a Bruker

Tensor 27 spectrophotometer on KBr disks. TGA experiment was performed on a

NETZSCH TG 209 instrument with a heating rate of 10 °C min^{-1}. Ultraviolet-visible

(UV-Vis) spectra were recorded on a Hitachi U-3900 spectrometer. A PO-120 quartz

cuvette (10 mm) was purchased from Shanghai Huamei Experiment Instrument Plants,

China. The ultrasonicate process was handled with an ultrasonic cleaning machine

(Elma, S100H). All electrochemcial experiments were performed by a Chi660e

electrochemical workstation (China).All the studies were carried out at room

temperature and under nitrogen surroundings. For the pH measurements a pH meter

with a combined glass electrode was used. Ultra-pure water (ulup, 18.2 MΩ cm, 25 ℃)

was used to prepare all electrolyte solutions.

2. General measurements

Prior to be used, a glass carbon electrode (GCE, Φ = 1 mm) was carefully polished

with an alumina slurry (0.5 μm particle size) until a mirror-like surface was obtained, then rinsed ultrasonically with ultrapure water, nitric acid (1:1, v/v), sodium hydroxide (0.1 mol•L^{-1}) and ethanol in turn to remove any alumina residue from the electrode surface.

Diffraction intensity data for single crystals of **Cu-1** and **Cu-2** was collected on a Agilent Technologies SuperNova Single Crystal Diffractometer at 293 (2) K equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL[1] (full matrix least-squares techniques) in the Olex2 package[2].

3. Direct synthesis of {[CuL(DMF)]·MeCN}$_n$(Cu-2)

A mixture of 34.10 mg (0.2 mmol) CuCl$_2$·2H$_2$O and 46.04 mg (0.2 mmol) H$_2$L was dissolved in a mixture of 5 mL DMF, 5 mL DMA, 5 mL H$_2$O and 5 mL acetonitrile, and then heated for 2 days at 90 ℃ in a Parr Teflon-lined stainless steel vessel (23 mL), then cooled to room temperature slowly in 2 days. Dark Green diamond-like crystals of **Cu-2** were collected at the bottom of the glass vessel. Yield: 77.1 mg (75.8 %). Anal. Calc for C$_{13}$H$_{14}$CuN$_2$O$_7$S. C, 38.47; H, 3.48 (%); Found: C, 38.62; IR (KBr disk/cm^{-1}) 3323.66 m, 2961.15 m, 1603.28 s, 1451.22 m, 1387.15 s, 1350.26 s, 1200.57 w, 1100.17 s, 848.01 w, 793.57 w, 734.69 w, 538. 48 w.

Table S1. Crystal data and structure refinements for **Cu-1**and **Cu-2**

	Cu-1	Cu-2
Formula	$C_8H_6CuO_7S$	$C_{13}H_{14}CuN_2O_7S$
M, g mol^{-1}	309.72	405.87
Temp （K）	123(2)	123(2)
Cryst. syst.	tetragonal	monoclinic
space group	*Cmm2*	*P2$_1$/n*
a / Å	28.034 (3)	10.7512(4)
b / Å	28.097 (3)	13.6515(6)
c / Å	7.6489 (8)	10.9769(5)
α / deg	90	90
β / deg	90	94.102(4)
γ / deg	90	90
V / Å^3	6025.0 (12)	1606.96(11)
Z	8	4
GOF	1.168	1.041
reflns collected	2480	2927
unique reflns	2488	6188
R1 [I > 2σ(I)]	0.0756	0.035
wR2 (all data)	0.2378	0.0825
CCDC *number*	2175361	2175362
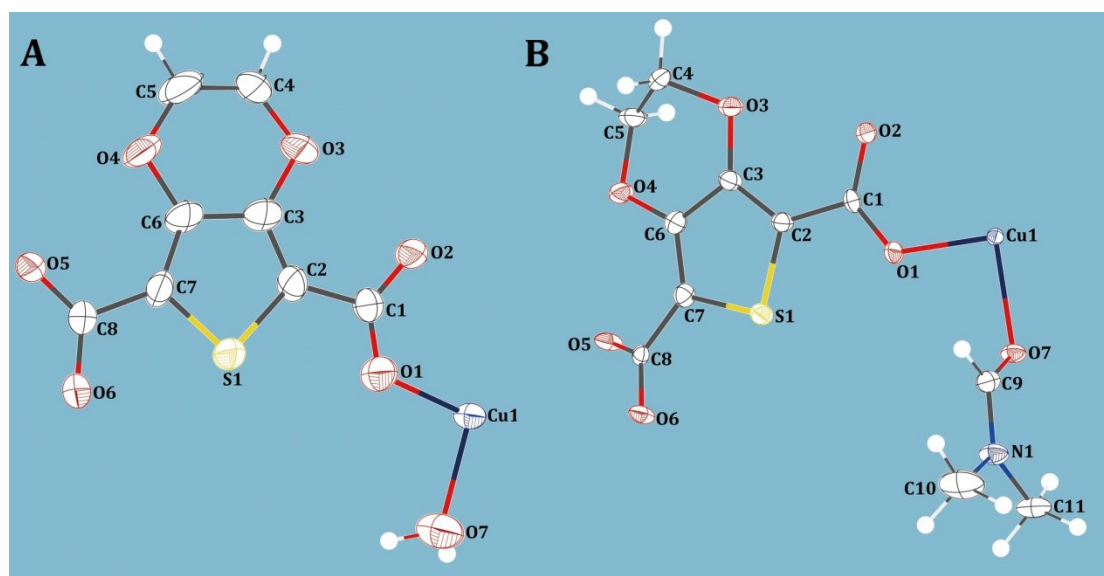
Fig.S1 (A) thermal ellipsoid diagram of **Cu-1**; (B) thermal ellipsoid diagram of **Cu-2**(without solvent molecule).
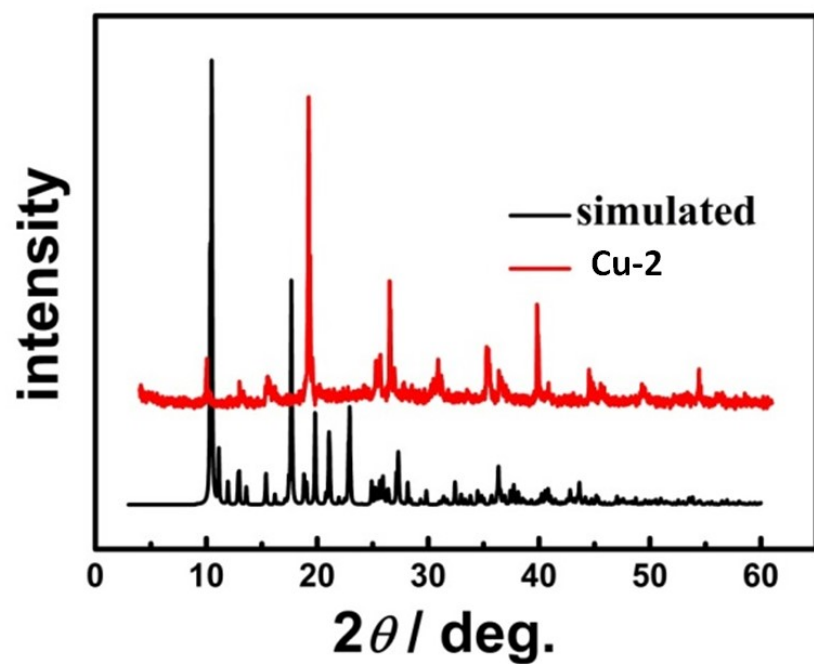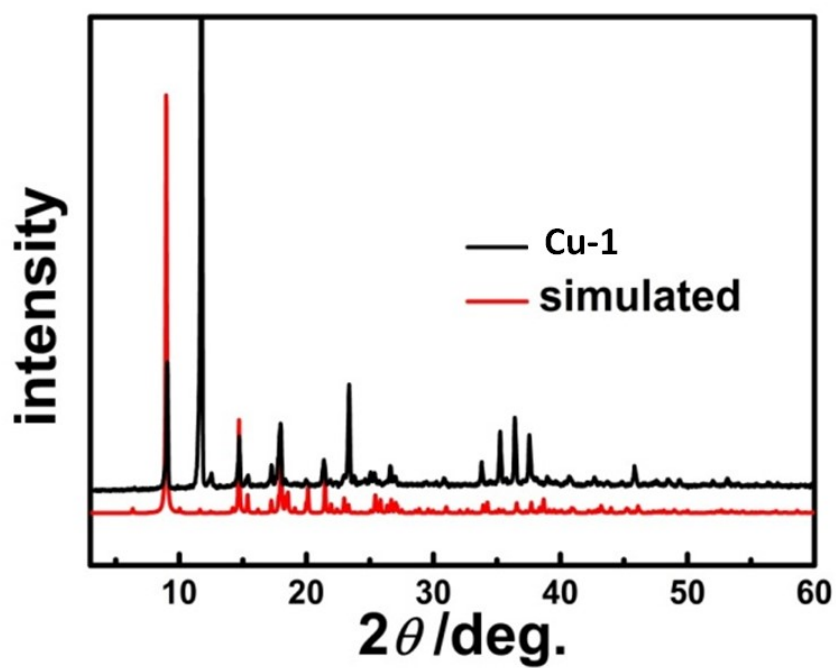
Fig. S2 PXRD patterns of **Cu-1** or **Cu-2** compare with the simulated one from single-crystal date of **Cu-1** or **Cu-2**, respectively.
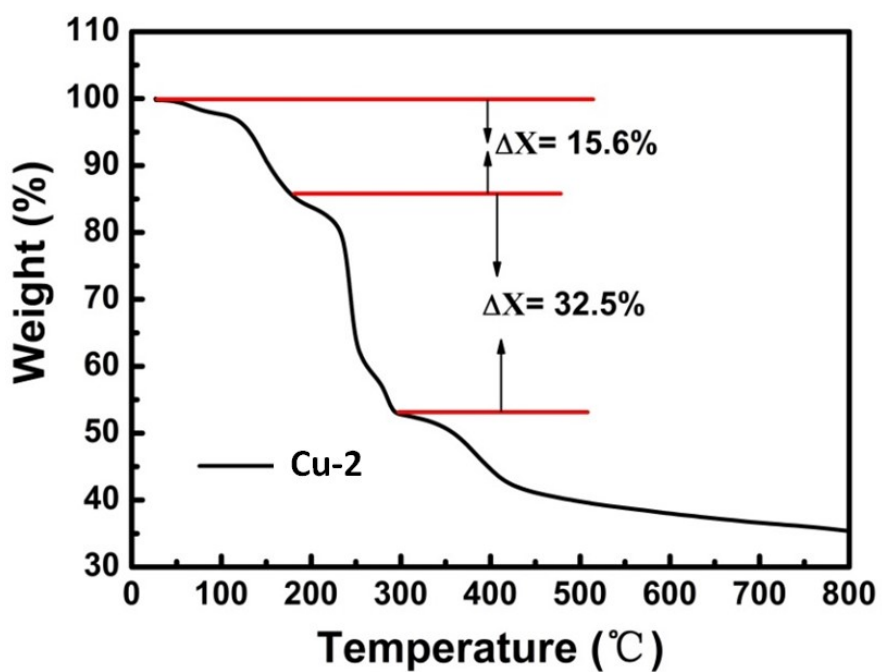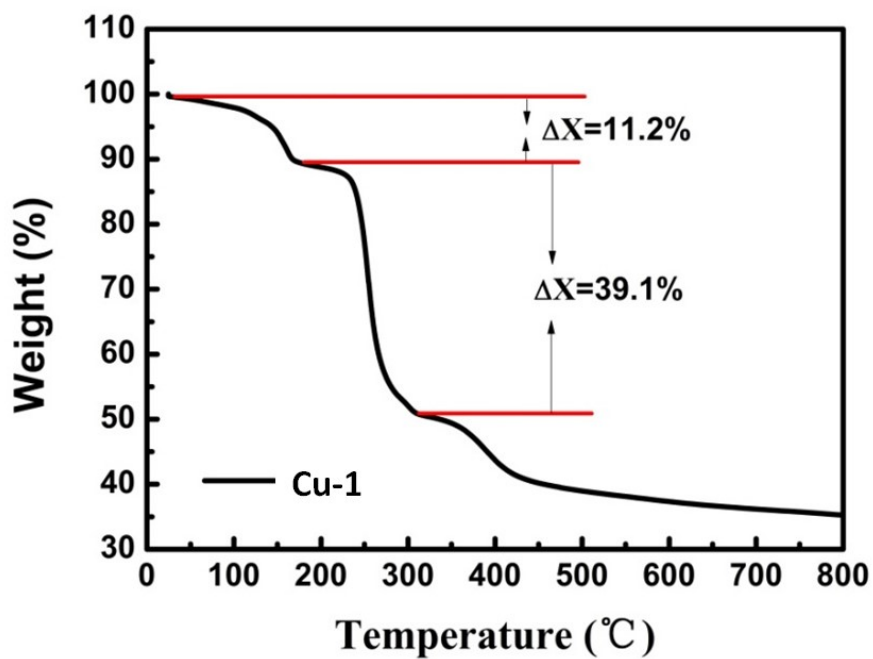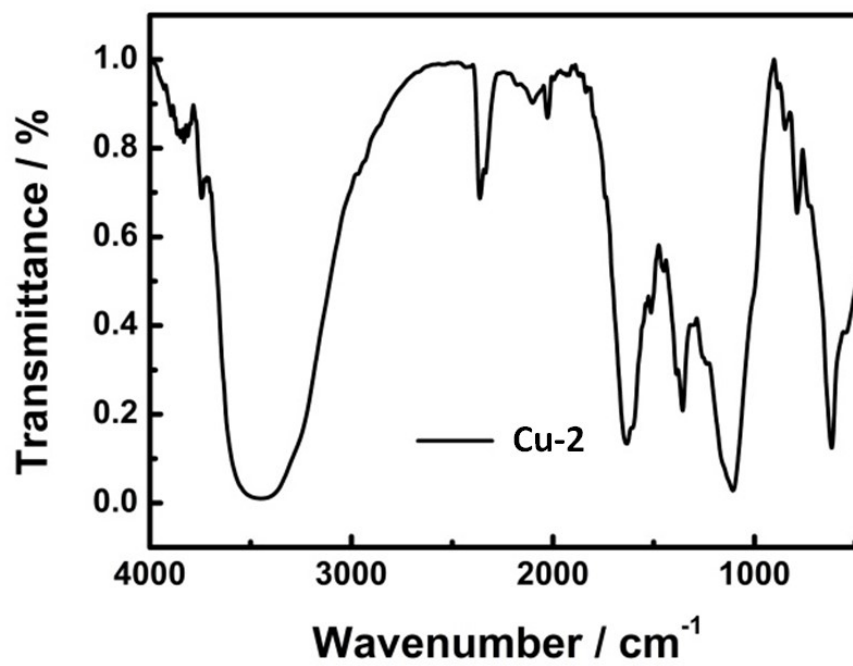
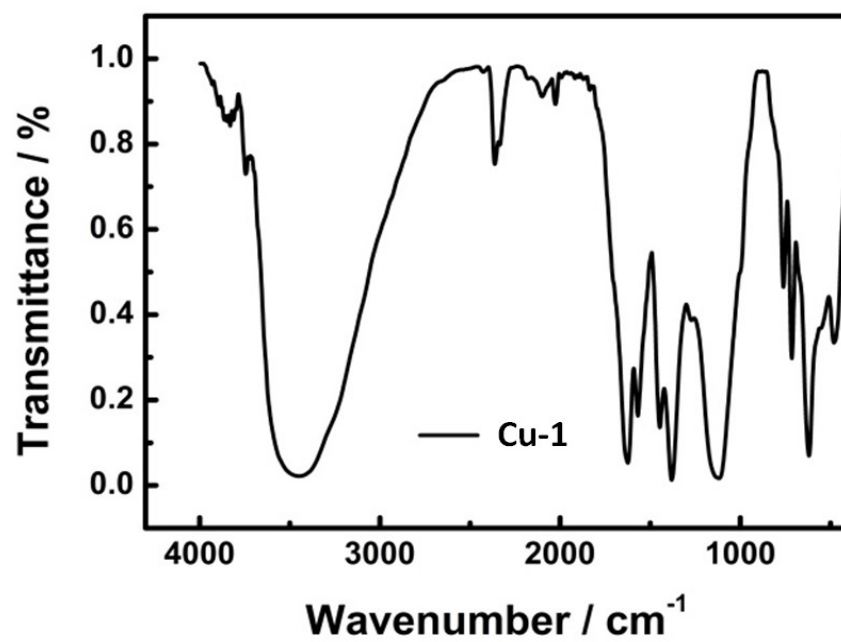**Figure S3.** Thermal gravimetric analyses (TGA) of **Cu-1** and **Cu-2.**

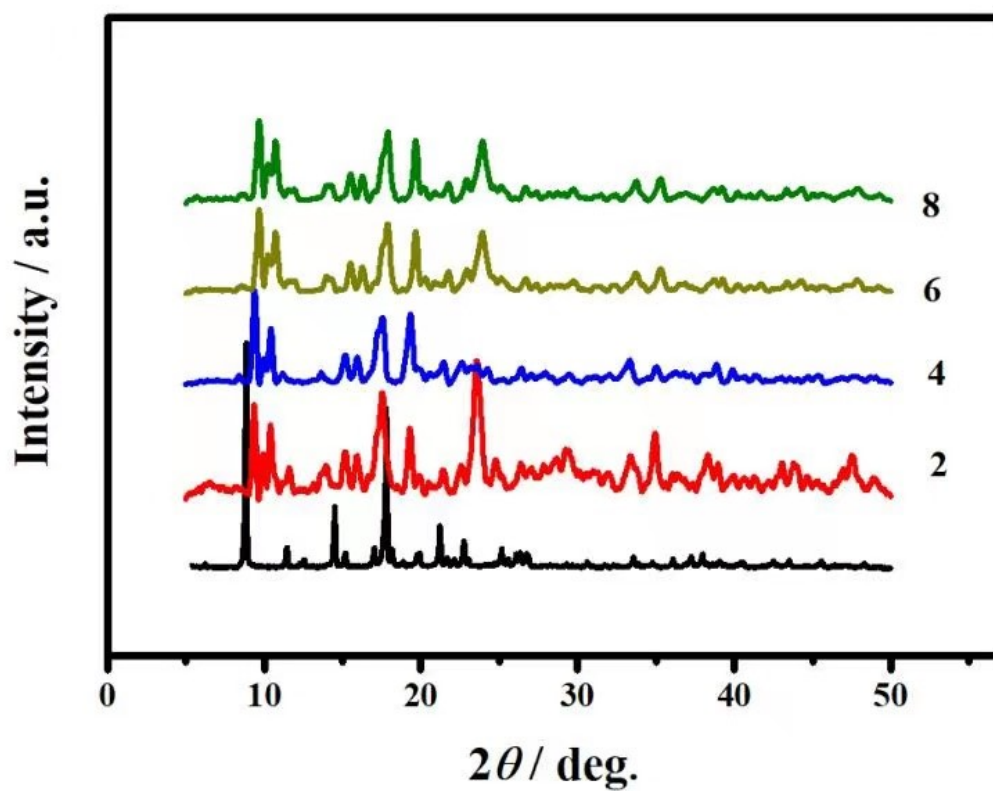**Fig. S4.** IR data for **Cu-1** and **Cu-2**.

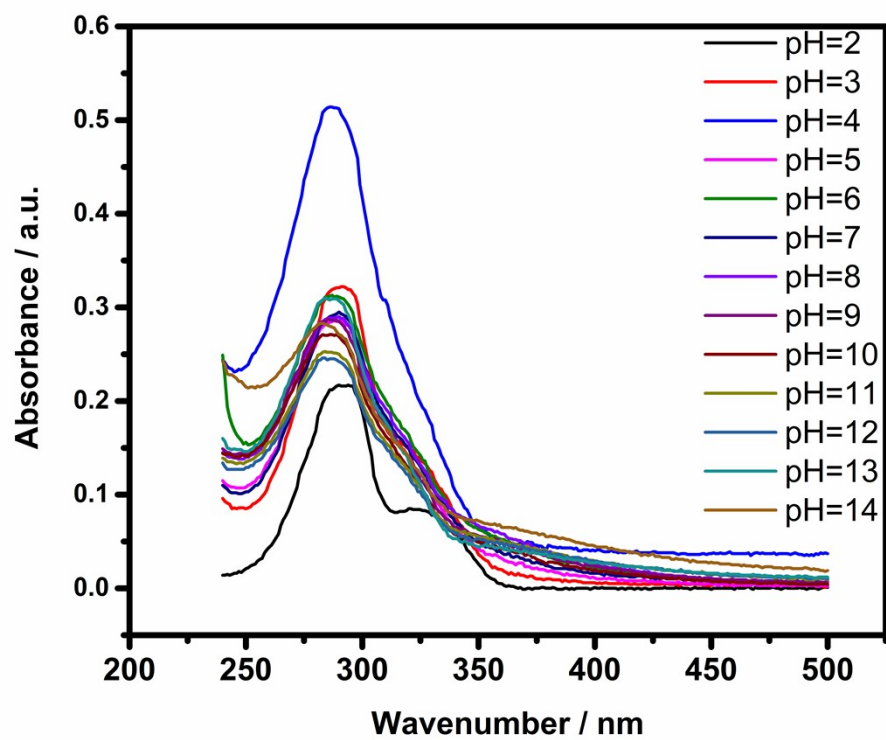**Fig. S5**   PXRD diagram of **Cu-1** afer immersing in different pH.solution

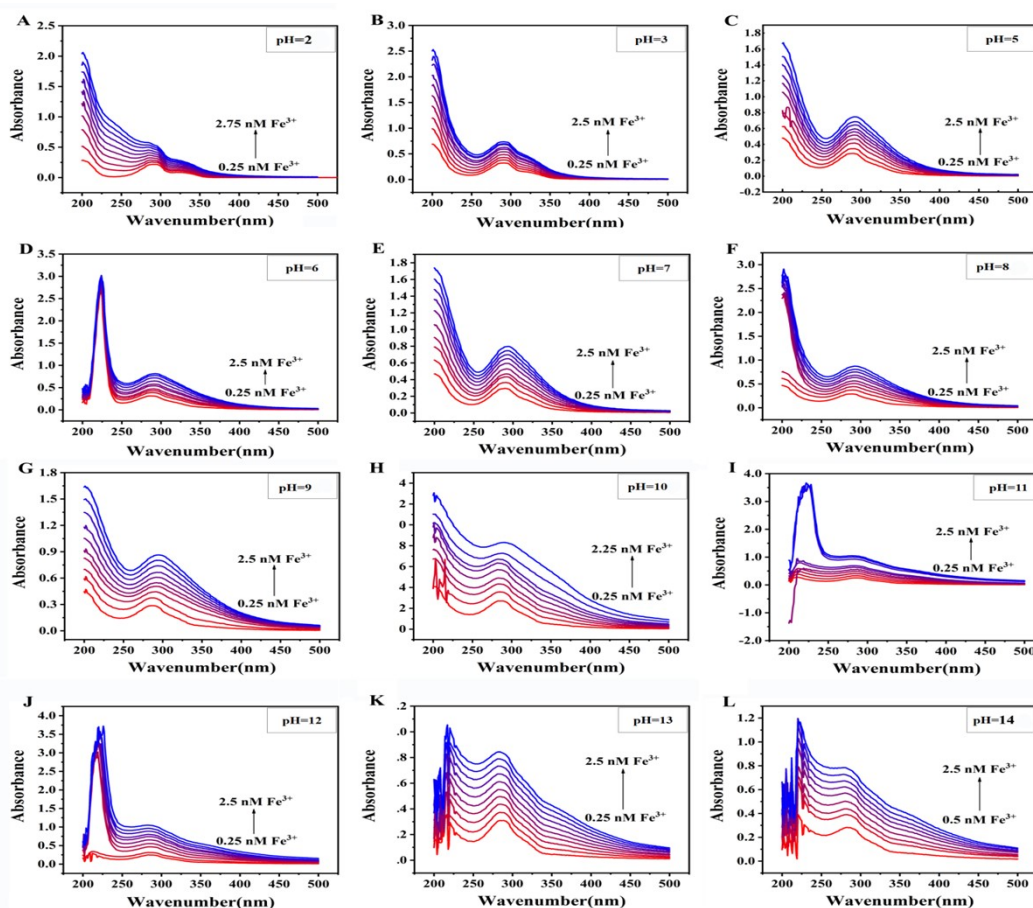**Fig. S6.** UV spectra of **Cu-1** in different pH aqueous solution

Fig. S7. UV spectra of **Cu-1** in different pH aqueous solution for detecting Fe^{3+}: (A) pH=2, concentration range 0.25~2.75 nmol/L; (B) pH=3, concentration range 0.25~2.5 nmol/L; (C) pH=5, concentration range 0.25~2.5 nmol/L; (D) pH=6, concentration range 0.25~2.5 nmol/L; (E) pH=7, concentration range 0.25~2.75 nmol/L; (F) pH=8, concentration range 0.25~2.75 nmol/L; (G) pH=10, concentration range 0.25~2.5 nmol/L; (H) pH=10, concentration range 0.25~2.25 nmol/L; (I) pH=11, concentration range 0.25~2.75 nmol/L; (J) pH=12, concentration range 0.25~2.75 nmol/L; (K) pH=13, concentration range 0.25~2.75 nmol/L; (L) pH=14, concentration range 0.5~2.5 nmol/L.
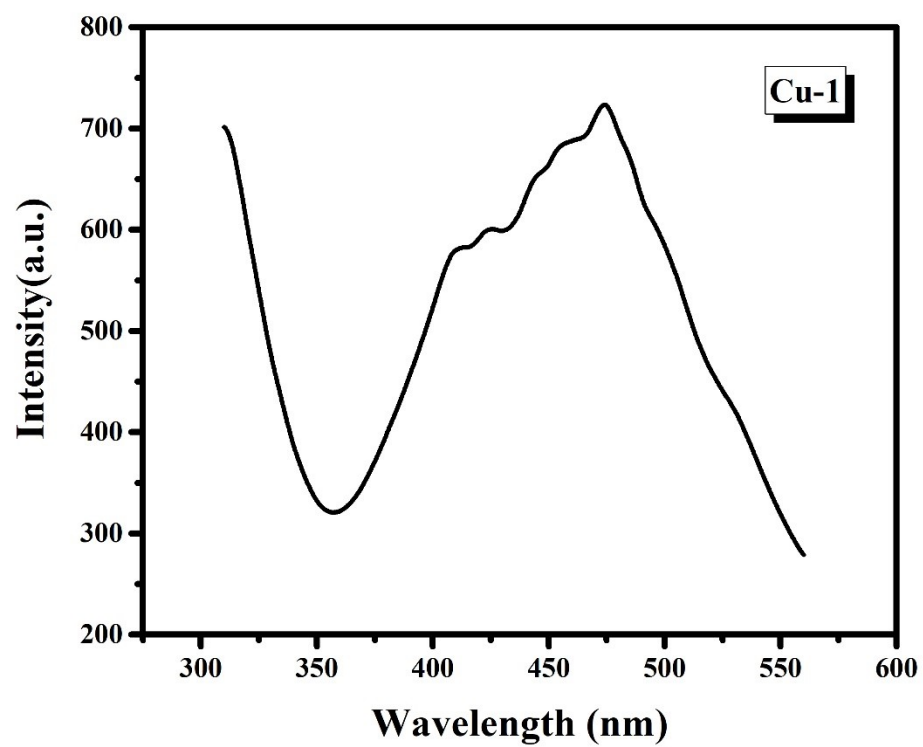
Fig. S8. The solid-state fluorescence spectra of **Cu-1** at room temperature.
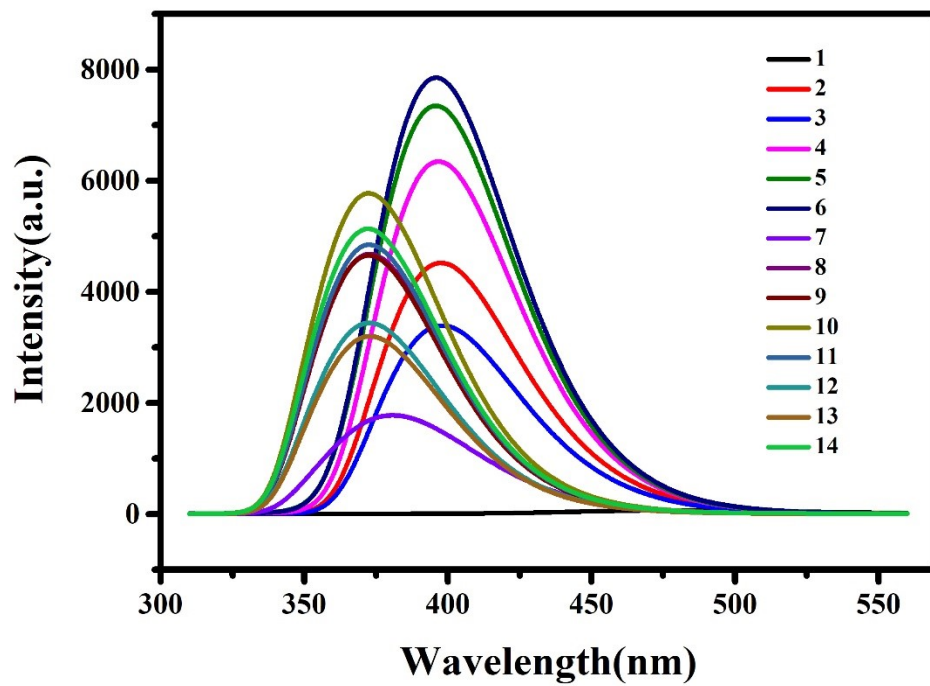
Fig. S9. Fluorescence spectra of **Cu-1** in different pH aqueous solution.

Table S2. ICP-MS results of **Cu-1** and **Cu-1**@Fe.

	Cu content(mmol/g)	Fe content(mmol/g)	Cu:Fe(molar ratio)
Cu-1	5040.257871	82.55161996	61.05583238
Cu-1@Fe	659.6489779	4003.072212	0.16478568

[1]O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

[2]G. Sheldrick, *Acta Cryst.*, 2008,**A64**, 112-122.