An effective Cu(II) quenching fluorescence sensor in aqueous solution and 1D chain coordinative polymer framework

Zeng-chen Liu, Zheng-yin Yang*, Tian-rong Li, Bao-dui Wang, Yong Li, Dong-dong Qin, Ming-fang Wang, Mi-hui Yan

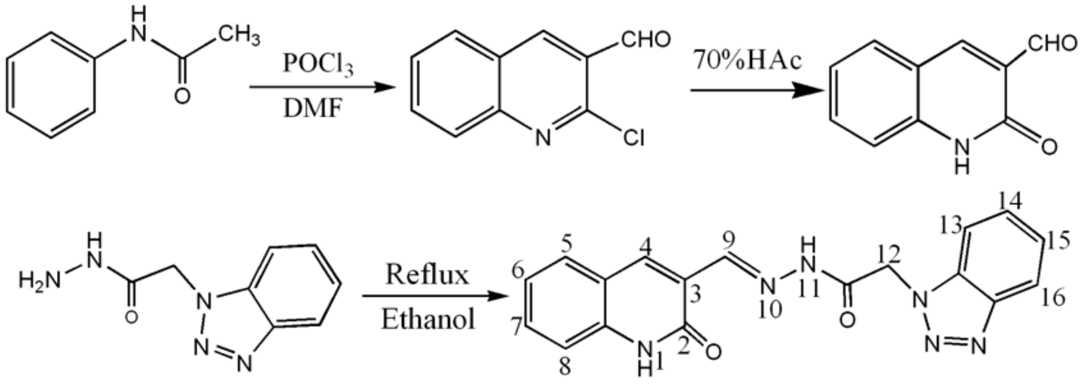
College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilizati-on of Gansu Province, Lanzhou University, Lanzhou 730000, PR China

Instruments and Materials

^{1}H-NMR spectra were recorded on a Varian VR300-MHz spectrometer with TMS as an internal standard. The melting points of the compound were determined on a Beijing XT4-100X microscopic melting point apparatus. The UV-Vis spectra were recorded on a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrophotometer at room temperature. ESI-MS was recorded on an Esquire 6000 mass spectrograph. IR spectra were recorded on a Thermo Mattson FT-IR instrument using KBr discs in the 4000-400 cm^{-1} region.

All the used metal ions are from nitric acid salt. All spectroscopic measurements were performed in MeOH-H_2O (9:1) solution. All materials and solvents were of analytical reagent grade quality and were used without further purification.



Scheme S1. The synthesis route of fluorescence chemosensor L.

Synthesis of fluorescence probe (2-oxo-quinoline-3-carbaldehyde-1H-benzotriazol-1-acetic acid hydrazone)

As shown in Scheme S1. 3-formyl-quinoline-2(1H) one was prepared according to the literature.[1-2] 1H-benzotriazol-1-acetic acid hydrazide was synthesized by the reported method.[3] Then an ethanol solution (15 mL) containing 1H-benzotriazol-1-acetic acid hydrazide (0.445 g) was added to another ethanol solution (50 mL) containing 3-formyl-quinoline-2(1H) one (0.4 g). The mixture was refluxed for twelve hours with stirring and a yellow precipitate was separated out. The precipitation was filtrated under decompression and washed with ethanol. Recrystallization from DMF/H_2O (V:V = 1:1) gave the ligand L, which was dried under vacuum . Yield, 73%. m.p.: 307-310 °C. ^{1}H-NMR (DMSO-d_6, ppm): δ 12.10 (1H, s, –N^1–H), δ 12.03 (1H, s, –N^{11}–H), δ 8.60 (1H, s, –CH=N), δ 8.34 (1H, s, –C^4–H), δ 8.06–8.08 (1H, m, –C^{13}–H), δ 7.87–7.89 (1H, m, –C^{16}–H), δ 7.76–7.87 (1H, m, –C^8–H), δ 7.53–7.54 (1H, m, –C^{14}–H), δ 7.55–7.58 (1H, m, –C^{15}–H), δ 7.41–7.44 (1H, m, –C^7–H), δ 7.34–7.36(1H, m, –C^5–H), δ 7.22-7.25 (1H, m, –C^6–H). δ 6.13 (2H, s, –C^{12}–H).

Crystal structure description

The single crystal of Cu(II) complex was gained in the methanol-H_2O solution using volatilizing method. The crystal of the Cu(II) complex was green. The crystal data and structure refinement of Cu(II) complex were listed in Table S1. And the selected bond lengths (Å) and angles (°) for the Cu(II) complex were listed in Table S2. A green crystal of Cu(II) complex (0.32 × 0.28 × 0.25 mm) was measured on a Bruker Smart-1000 CCD diffractometer with graphite monochromatic Mokα radiation (λ=0.71073Å) at 293(2) *K*. $2.38^{\circ} < \theta < 21.08^{\circ}$ for *hkl* ($-15 \leq h \leq 10$, $-17 \leq k \leq 17$, $-16 \leq l \leq 18$) in the triclinic P-1 space group. The positions and anisotropic thermal parameters of all non-hydrogen atoms were refined on F^2 by full-matrix least-squares techniques with the SHELX-97 program package (G.M. Sheldrick, Bruker AXS, Madison, WI, 2001). Absorption correction was employed using Semi-empirical methods from equivalents.

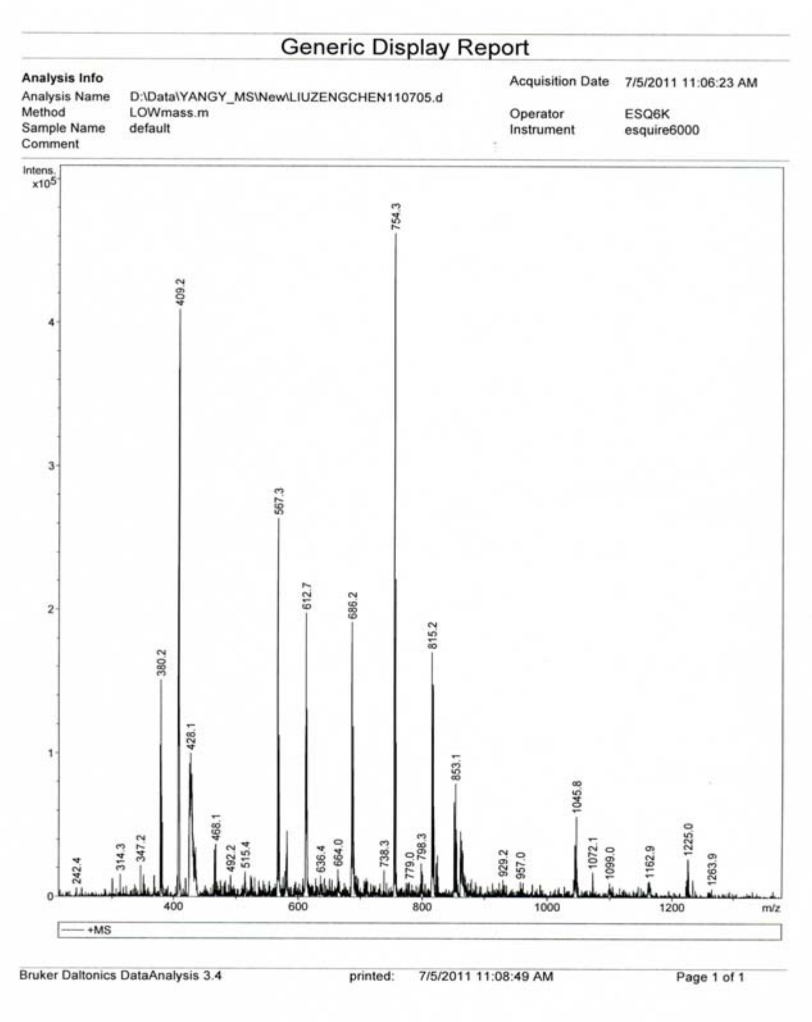
In the crystal structure, the two Cu(II) atoms is all five coordinated form and adopts pyramid geometry, however, the summit atom of pyramid is different, Cu1 coordinates by oxygen atom from methanol, but Cu2 coordinates with oxygen atom of H_2O. In addition, through the bridge linking of 1H-benzotriazol-1-acetic acid hydrazine, one Cu(II) center coordinates to one nitrogen atom from the ligand, which leads to a interesting 1D polymeric chain architecture. Moreover，the distances between Cu(II) center are 7.932 Å and 7.903 Å, respectively. Simultaneously, the C=O bond from 1H-benzotriazol-1-acetic acid hydrazine has been found to be enolic to achieve charge balance.

	Cu(II) Complex
Empirical formula	C37 H31 Cu2 N14 O12
FW	990.84
Crystal color	green
Crystal size	0.32 × 0.28 × 0.25 mm
Crystal system	Triclinic
Space group	p-1
a (Å)	13.031(3)
b (Å)	14.668(3)
c (Å)	14.887(3)
α	101.44(3)
β	112.36(3)
γ	102.56(3)
Volume (Å^3)	2440.9(8)
Z	2
D_{calc} (Mg/m^3)	1.348
Abs coeff (mm^{-1})	0.940
F(000)	1010
$\theta_{\text{min and max(deg)}}$	2.38-21.08
Reflections collected/ Unique	13165/9088 [R(int)=0.0416]
Final R indices [I>2σ(I)]	R_1= 0.0609 wR_2= 0.1406
R indices (all data)	R_1= 0.1229 wR_2= 0.1584

Table S1. Crystal data and structure refinement of the Cu(II) complex.

Bond names	**Bond lengths(Å)**	**Bond angles**	**Angle(°)**
Cu(1)-N(6)	1.932(4)	N(6)-Cu(1)-O(4)	80.89(16)
Cu(1)-O(4)	1.953(3)	N(6)-Cu(1)-O(3)	91.30(16)
Cu(1)-N(9)	1.985(4)	O(4)-Cu(1)-O(3)	172.11(15)
Cu(1)-O(3)	1.975(3)	N(6)-Cu(1)-N(9)	161.29(18)
Cu(1)-O(11)	2.261(5)	O(4)-Cu(1)-N(9)	95.54(15)
Cu(2)-O(1)	1.939(3)	O(3)-Cu(1)-N(9)	91.50(15)
Cu(2)-O(2)	1.940(3)	N(6)-Cu(1)-O(11)	99.16(18)
Cu(2)-N(1)	1.949(4)	O(4)-Cu(1)-O(11)	87.05(18)
Cu(2)-N(3)	1.999(4)	O(3)-Cu(1)-O(11)	95.39(18)
Cu(2)-O(10)	2.252(5)	N(9)-Cu(1)-O(11)	98.99(18)
N(14)-O(9)	1.222(6)	O(1)-Cu(2)-O(2)	172.46(15)
N(5)-N(4)	1.337(5)	O(1)-Cu(2)-N(1)	91.67(15)
N(3)-N(4)	1.317(5)	O(2)-Cu(2)-N(1)	81.15(15)
N(1)-N(2)	1.398(5)	O(1)-Cu(2)-N(3)	91.29(15)
N(9)-C(7)	1.390(6)	O(2)-Cu(2)-N(3)	94.75(16)
N(6)-C(10)	1.295(6)	N(1)-Cu(2)-N(3)	160.51(19)
N(6)-N(7)	1.399(5)	O(1)-Cu(2)-O(10)	91.36(19)
N(2)-C(11)	1.313(6)	O(2)-Cu(2)-O(10)	92.24(19)
N(8)-C(5)	1.356(6)	N(1)-Cu(2)-O(10)	101.0(2)
N(8)-C(12)	1.377(6)	N(3)-Cu(2)-O(10))	98.2(2)
N(7)-C(13)	1.310(6)	C(5)-O(3)-Cu(1)	126.9(3)
N(15)-O(5)	1.099(11)	C(13)-O(4)-Cu(1)	109.3(3)
C(39)-C(40)	1.406(11)	C(11)-O(2)-Cu(2)	109.4(3)

Table S2. The Selected bond lengths (Å) and angles (°) for the Cu(II) complex.



Generic Display Report

Analysis Info

Analysis Name D:\Data\YANGY_MS\New\LIUZENGCHEN110705.d
Method LOWmass.m
Sample Name default
Comment

Acquisition Date 7/5/2011 11:06:23 AM
Operator ESQ6K
Instrument esquire6000

Bruker Daltonics DataAnalysis 3.4 printed: 7/5/2011 11:08:49 AM Page 1 of 1

Fig. S1. ESI-MS of the Cu(II) 1D chain polymer ([CuL]n) in Methanol-H_2O (9:1) solution.

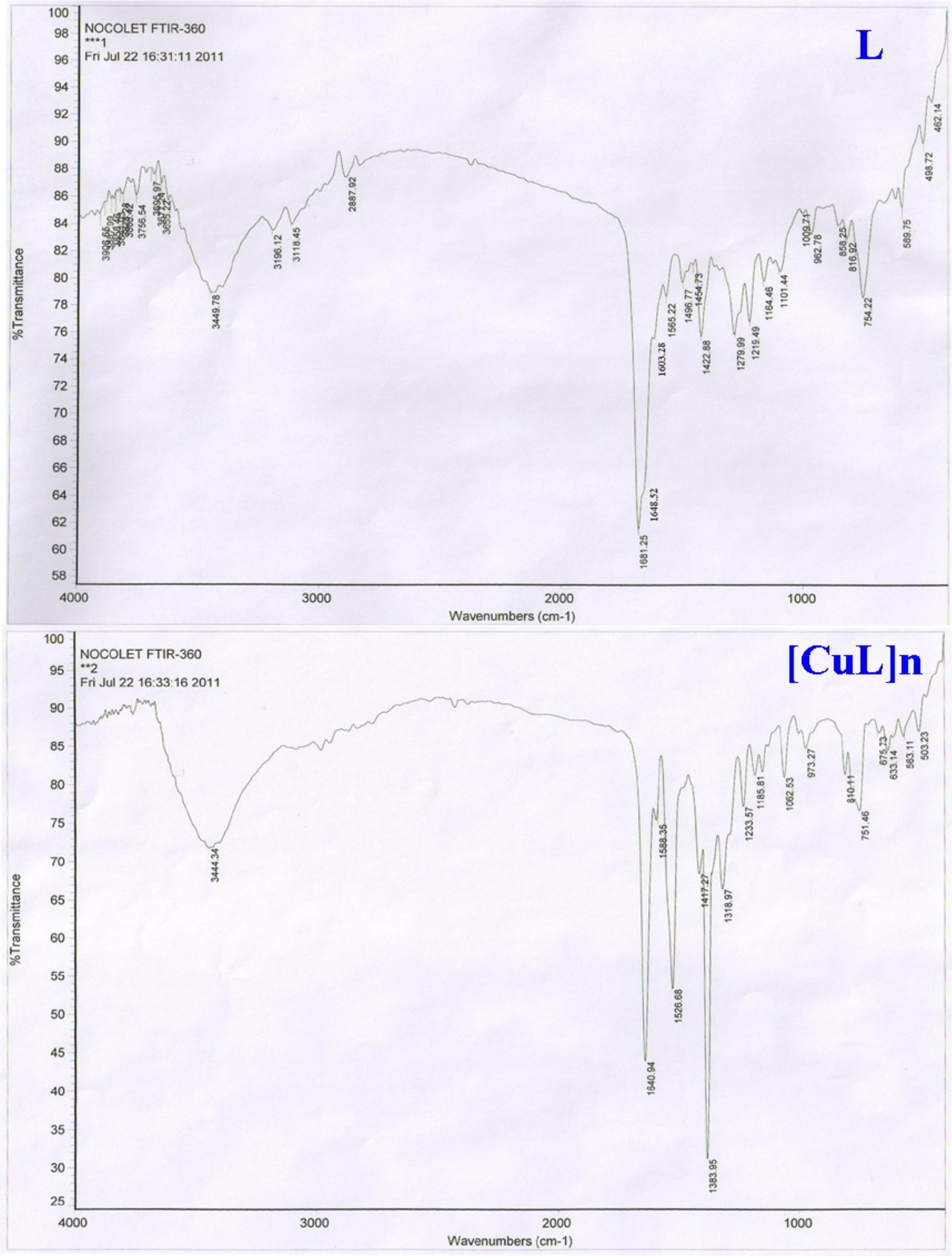


Fig. S2. FT-IR spectra of fluorescence chemosensor L and the Cu(II) 1D chain polymer ([CuL]n).

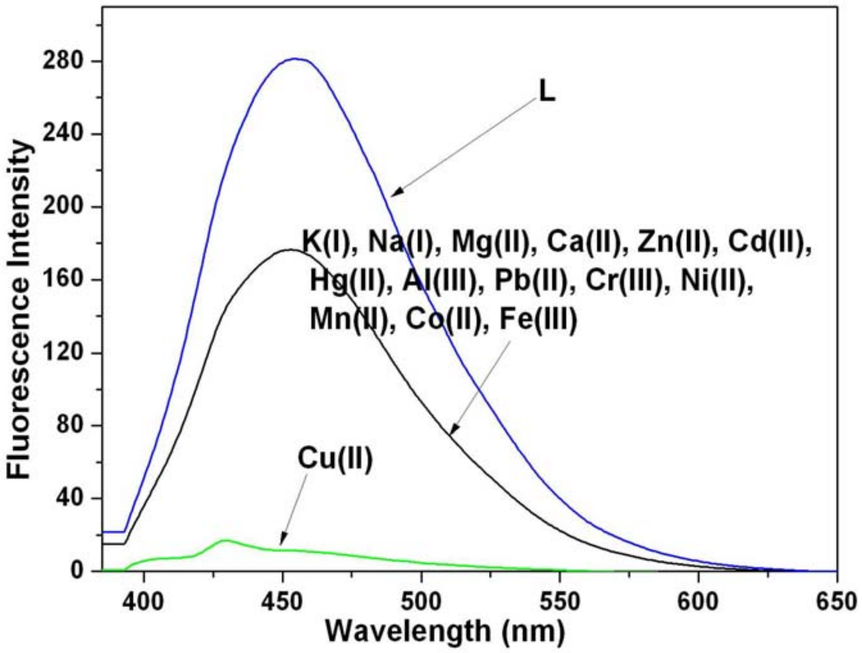


Fig. S3. The fluorescence intensity changes of complex real sample in Methanol-H_2O (9:1) solution. Blue line represents the fluorescence intensity of L (10 μM) without metal ions, Black line represents the fluorescence intensity change of L (10 μM) with addition of the coexistence system of K(I), Na(I), Mg(II), Ca(II), Zn(II), Cd(II), Hg(II), Al(III), Pb(II), Cr(III), Ni(II), Mn(II), Co(II), Fe(III) (10 μM).Green line represents the fluorescence intensity change of L-metal ions coexistence system upon addition of Cu(II) (10 μM).

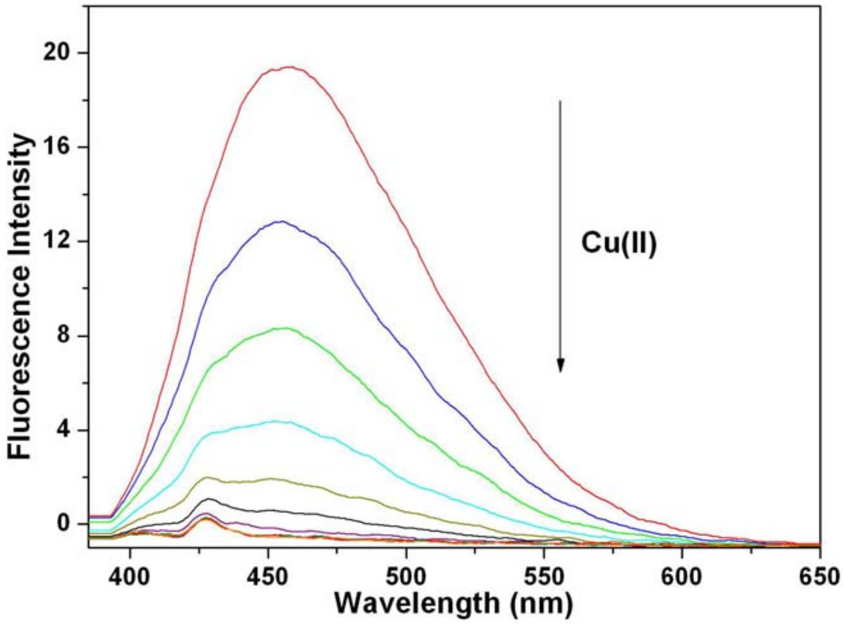


Fig. S4. Fluorescence emission changes of sensor L (10^{-6} M) upon addition of Cu(II) (by 0.2 ppm) in MeOH-H_2O (9:1) solution. Slit: Exication / emission = 5.0 / 5.0.

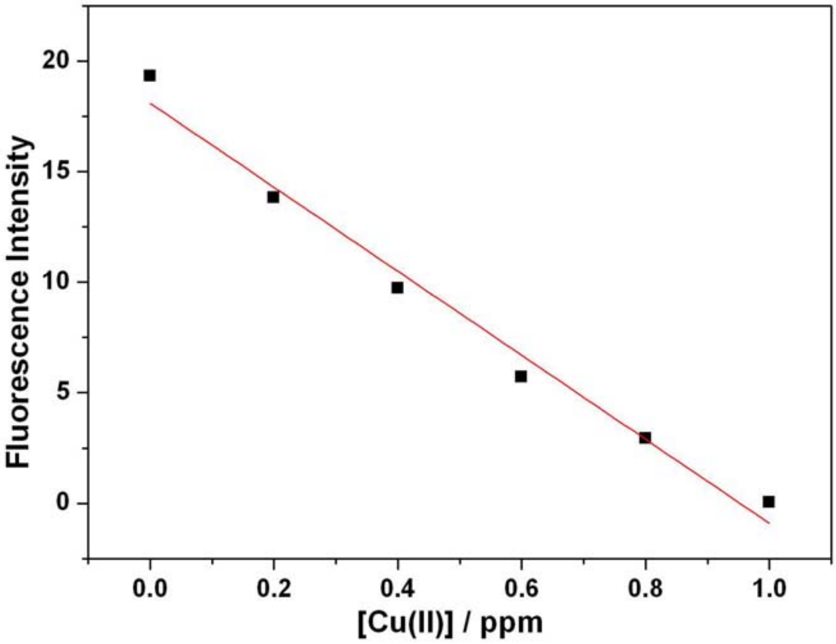


Fig. S5. The fluorescence intensities of sensor L at 460 nm.

Notes and references

[1] M. K. Singh, A. Chandra, B. Singh, R. M. Singh, Tetrahedron Lett., 2007, 48, 5987.

[2] R. K. Kalita, B. Baruah, P. J. Bhuyan, Tetrahedron Lett., 2006, 47, 7779.

[3] S. M. El-Khawass, N. S. Habib, J. Heterocyclic Chem., 1989, 26, 177.