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New diaminomaleonitrile derivatives containing aza-crown ether: Selective, sensitive and colorimetric chemosensors for Cu(II)

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1. Introduction

Copper is one of a relatively small group of trace metal nutrients that are essential to sustain normal human health [1]. Copperdependent enzymes act as catalysts to help a number of body functions to provide energy for biochemical reactions, transform melanin for pigmentation of the skin, assist the formation of crosslinks in collagen and elastin, and thereby maintain and repair connective tissues [2]. However, copper in excessive amounts can be toxic and cause oxidative stress and disorders associated with neurodegenerative diseases including Alzheimer's, Parkinson's, Menke's, Wilson's, and prion diseases [3]. Due to the extensive application of copper (II) ions in life science, medicine, chemistry and biotechnology, it has become one of the important environmental pollutants. Therefore, it is important to design and develop Cu(II) sensors with high sensitivity and selectivity. However there are lots of impressive reports on fluorescent as well as colorimetric sensors for Cu(II), most of them showed poor solubility in water [4], low sensitivity [5] and poor selectivity over other metals [6].

ABSTRACT

Two novel soluble chemosensors based on Schiff-base diaminomaleonitrile derivatives which were modified by an aza-crown ether moiety have been synthesized. These chemosensors were fully characterized by ¹H NMR, ¹³C NMR spectroscopy, mass spectrometry, IR, DSC and single crystal X-ray diffraction. The recognition abilities of the sensors with a range of metal ions were evaluated and their photophysical properties have been systematically investigated. DFT theoretical calculations were employed to understand the behavior of the sensors toward the Cu(II). The sensing mechanism was derived through experimental and theoretical calculations. The results consistently indicated that the monoaza-10-crown-5 species was the ideal sensor, which can be utilized to monitor Cu(II) in solution over a wide pH range.

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To date, a wide range of analytical methods have been employed for chemoselective screening of Cu(II) ions in a variety of complex environments, such as atomic absorption/emission spectroscopy, inductively-coupled plasma mass spectroscopy, inductivelycoupled plasma atomic spectroscopy inductively coupled plasma (ICP) spectroscopy, and voltammetric sensors [7]. Although all of these conventional strategies are beneficial because of their superior sensitivity, they are limited by matrix interference, complicated sample-pretreatment procedures, and analysis time [8]. Optical signals based on changes of absorption wavelength are an area of significant interest because of their low detection limits, high sensitivity, simplistic operation and good selectivity. In this respect, we have been interested in developing a selective colorimetric sensor for the visual detection of metal ions due to their simplicity.

In this article, modified diaminomaleonitrile bearing aza-crown ether in different size was synthesized and characterized (Fig. 1). The diaminomaleonitrile (DMN) was chosen not only for its ability to act as diamine and form simple schiff-base ligands but also for the fact that the electron-withdrawing CN groups, which clearly affect the coordinating capacity of DMN itself [9]. In addition, azacrown ether group which was easily dissolved in aqueous solution and lipid solution was brought in to improve the solubility of the

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Fig. 1. Structures of L1 (left) and L2 (right).

sensors and enlarge its extent of application, concurrently modulate the coordinating properties of molecules cooperatively with DMN [10].

The sensor L1 is able to selectively detect Cu(II) over environmentally relevant ions including Ag(I), Ba(II), Ca(II), Cd(II), Co(II), Hg(II), Pd(II), Mg(II), Ni(II), Zn(II), Fe(III), Cr(III). The response upon exposure to Cu(II) is fast and can be used to detect Cu(II) visually in the concentration of 1×10^{-5} M in solution and the detection limit is decreased down to 2×10^{-7} M by spectroscopy. By contrast L2 offered quiet poor selectivity to Cu(II), and its detection limit of Cu(II) is much higher than that of L1. From the analysis of these data, L1 was taken as the better sensor.

2. Experimental section

2.1. Materials and instruments

Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Dimethylformamide (DMF) was distilled and dried over potassium hydroxide. Sodium hydride and 2,2'-(phenylimino)bisethanol were purchased from Aldrich. Diethylamine, triethylene glycol, etracthylene glycol, 4-fluorobenzaldehyde, phosphorus oxychloride and diaminomaleonitrile were available commercially. DMSO, THF and CH₃CN were spectrometric grade. Metal salts LiNO₃, NaNO₃, KNO₃, Mg(NO₃)₂, Ca(NO₃)₂, Ba(NO₃)₂, Cu(NO₃)₂, Zn(NO₃)₂, Co(NO₃)₂, Ni(NO₃)₂, Cd(NO₃)₂, AgNO₃, Hg(NO₃)₂, Pd(NO₃)₂, Fe(NO₃)₃.9H₂O, Cr(NO₃)₃ were purchased from Aldrich and used as received. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker Avance 400 MHz NMR spectrometer using CDCl₃ as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), or multiplet (*m*). The mass spectra were measured with an LTQ Orbitrap XL and AXIMA-CFR plus MALDI-TOF MS. IR data were got from FT-IR Nicolet NEXUS 870 FT-IR-NEXUS. Melting points were measured with DSC Q2000 V24.9 build 121.

The one-photon absorption (OPA) spectra were recorded on the UV-265 spectrophotometer. The one-photon excited fluorescence (OPEF) spectra measurements were performed using the Hitachi F-7000 fluorescence spectrophotometer. OPA and OPEF were measured in the concentration of 10 μ M. The quartz cuvettes used were of 1 cm path length.

2.2. Materials

Aza-crown ether substituted benzaldehyde was synthesized in high yield according to reported procedures [11]. Chemosensors were synthesized through condensation of diaminomaleonitrile and aza-crown ether substituted benzaldehyde (Scheme 1). Products were characterized by ¹H NMR, ¹³C NMR, Mass Spectroscopy and single-crystal X-ray diffraction. Single crystals of both L1 and L2 were obtained by diffusion of EtOH to solutions of L1 and L2 in dichloromethane. Sensors L1 and L2 crystallize in the monoclinic form with space group $P2_{(1)}/c$. The single crystal structures of L1 and L2 are shown in Fig. 2 respectively, and the data are collected in Table 1. A large planar can be seen between benzene and DMN in L1 from Fig. 2, for the bond lengths which are between the single bond lengths and double single lengths, are quite conjugated, N(2)-C(17)(1.278 Å), N(2)–C(19) (1.393 Å), C(18)–C(19) (1.362 Å), N(3)–C(18) (1.351 Å), C(14)–C(17) (1.436 Å). And the same phenomenon can been observed in L2 (Table 2). But the conformations of the whole molecules of L1 and L2 were quiet distorted clearly shown in Fig. 2. From the side view of the planar of benzene and DMN, obvious differences between L1 and L2 were observed, L1 looking like a couch while L2 resembling a key (Fig. 2, right).

2.3. Synthetic methods

2.3.1. Synthesis of 1-[4-(1, 4, 7, 10-tetraoxa-13-aza

cyclopentadecyl) benzyl]-2-aminomalonitrile (L1)

4-(1, 4, 7, 10-tetraoxa-13-aza cyclopentadecyl) benzaldehyde (1.0 g, 3.0 mmol) was added to a benzene solution (100 mL), containing diaminomaleonitrile (0.32 g, 3.0 mmol) and several drops of piperidine, which had been vigorously stirred for 30 min. The mixture was then refluxed by stirring for 8 h. Water was removed using a Dean–Stark trap. The reaction mixture was then cooled to room temperature. The precipitated crude product was separated



Scheme 1. Synthetic route of sensors L1 and L2.



Fig. 2. The front view of the single crystal structure of L1 (left top); the side view of the single crystal structure of L1 (right top); the front view of the single crystal structure of L2 (left bottom); the side view of the single crystal structure of L2 (right bottom).

Table 1	
Single crystal data of L1 and L2.	

Compound	L1	L2
Empirical formula	C43 H56 Cl2 N10 O8	C ₂₃ H ₃₁ N ₅ O ₅
Formula weight	911.88	457.53
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{(1)}/c$	$P2_{(1)}/c$
a [Å]	11.2247(2)	10.362(5)
b [Å]	9.9154(2)	18.502(5)
c [Å]	21.3063(5)	13.007(5)
α [°]	90.000	90.000(5)
β [°]	98.9120(10)	97.346(5)
γ [°]	90.000	90.000(5)
V [Å ³]	2342.71(8)	2373.2(17)
Ζ	2	4
T [K]	296(2)	298(2)
D _{calcd} [Mg m ⁻³]	1.290	1.229
$\mu [mm^{-1}]$	0.2	0.088
θ_{range} [°]	1.84-25.05	1.92-25
Total no. data	15,932	17,432
No. unique data	4142	4352
No. params refined	299	298
R ₁	0.0789	0.057
wR ₂	0.2572	0.1496
GOF	1.106	1.008

Ta	abl	le	2	
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Selected bond lengths of L1 and L2 (Å).

L1		L2	
N(2)-C(17)	1.278 (4)	N(2)-C(19)	1.291 (3)
N(2)-C(19)	1.393 (4)	N(2)-C(20)	1.394 (3)
C(18)-C(19)	1.362 (4)	C(20)-C(22)	1.361 (4)
N(3)-C(18)	1.351 (4)	N(3)-C(22)	1.339 (3)
C(14)-C(17)	1.436 (4)	C(16)-C(19)	1.443 (4)

by filtration and washed with cold toluene, then recrystallized from ethane:dichloromethane (1:3). Reddish brown needle product was obtained (0.95 g, 2.29 mmol) in 76.3% yield. ¹H NMR (400 MHz, CDCl₃): δ = 8.0941 (*s*, 1H), 7.8032 (*J* = 8 Hz, *d*, 2H), 7.4719 (*s*, 2H), 6.7154 (*J* = 8 Hz, *d*, 2H), 3.6678−3.5089 ppm (*m*, 20H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.6261, 151.1498, 131.3454, 122.8801, 121.9788, 114.3847, 112.9222, 111.5593, 109.7210, 71.2420, 70.2975, 69.9655, 68.2697, 52.8783 ppm. MALDI-TOF MS [M + 1]⁺: 414.17. IR (selective peak): 3391.14 cm⁻¹, 3302.34 cm⁻¹ corresponds to amido-group N−H stretching vibration, 2228.20 cm⁻¹, 2198.62 cm⁻¹ corresponds to cyano-group C≡N stretching vibration. Mp: 162.628 °C.



Fig. 3. Absorption of L1 in different pH values at 420 nm.



Fig. 4. (a) Solutions of L1 upon addition of different metal ions. (b) Absorption changes of L1 in CH₃CN (1.0×10^{-5} M) upon addition of 1 equiv of different nitrate salts (1.0×10^{-5} M). (c) Absorption of L1 at 336 nm upon addition of different cations.



Fig. 5. Top: UV–vis titration curves of L1 in CH₃CN (1.0×10^{-5} M) in the presence of different amounts of Cu(II) (0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2×10^{-5} M), bottom: FL titration curves of L1 in CH₃CN (1.0×10^{-5} M) in the presence of different amounts of Cu(II).

2.3.2. Synthesis of 1-[4-(1, 4, 7, 10, 13-pentaoxa-16-aza cycloctadecyl) benzyl]-2-aminomalonitrile (L2)

Compound L2 was obtained as orange powders in 61.4% by following a procedure similar to that of L1. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.2512(s, 1H)$, 7.6639 (d, 2H), 6.7058 (J = 12 Hz, t, 2H), 5.1402 (J = 12 Hz, d, 2H), 3.7218–3.6580 ppm (m, 24H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2597$, 151.3713, 131.3140, 122.9994, 122.9733, 122.3487, 114.4846, 113.0713, 111.4838, 70.6253, 68.4661, 51.0916 ppm. MS (ESI): $[M + 1]^+$ 458.23. IR (selective peak): 3391.14 cm⁻¹, 3302.34 cm⁻¹ corresponds to amido-group N-H stretching vibration, 2228.20 cm⁻¹, 2198.62 cm⁻¹ corresponds to cyano-group C \equiv N stretching vibration. Mp: 142.979 °C.



Fig. 6. Job's plot of L1 and Cu(II) ($\lambda_{ex} = 300$ nm). The total concentrations of L1 and Cu(II) are 1 μ M. The experiments were measured at room temperature in CH₃CN.



Fig. 7. Benesi–Hildebrand plot of the Cu(II)–L1 complex in acetonitrile solution.



Fig. 8. Absorption of L2 in different pH values at 425 nm.

3. Results and discussion

3.1. UV-vis spectroscopic recognition of L1 and L2 toward metal ions

The visible spectra of the chemosensors L1 and L2 in acetonitrile solutions (1×10^{-5} M) were characterized by two bands at 290 nm and 420 nm, respectively. The band located at 290 nm corresponds to the $\pi - \pi^*$ absorbance of diaminomaleonitrile and the band centered at about 420 nm can tentatively be assigned to a charge-transfer band from the donor to the acceptor [12].

Fig. 3 shows that L1 is stable within a wide pH range of 5.5–10.5, and the following tests are in the range of pH. The response of solutions of L1 to a series of individual metallic cations was investigated. Addition of equimolar quantities of Ag(I), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), K(I), Hg(II), Pd(II), Mg(II), Li(I), Na(I), Ni(II), Zn(II), Fe(III), Cr(III) to solutions of L1 respectively, it was found that both Cu(II) and Hg(II) induced a rapid color change, but obvious difference in color between the L1–Cu(II) and L1–Hg(II) still can be found clearly. The solution of L1–Cu(II) turned to colorless while that of L1–Hg(II) turned to pale yellow. The changes attributed to metal coordination with the donor nitrogen atom of aniline group [13] and the difference between Cu(II) and Hg(II) owed to the different binding affinity with L1 [20]. The other ions failed to show any significant interference as shown in Fig. 4b and c.

To elicit the interactions between L1 and Cu(II), UV–vis absorption spectrum of L1 $(1 \times 10^{-5} \text{ M})$ in acetonitrile solution was titrated with Cu(II) from 0 to 1.2×10^{-5} M. As shown in Fig. 5, the maximum absorbance at 420 nm gradually decreased, and a new band centered at 336 nm was increased. An isosbestic point was clearly observed at 366 nm. The presence of this isosbestic point is indicative of the formation of only one complex [14]. Job's plot (Fig. 6) analysis indicated that when the Cu(II) molar fraction reaches 0.5, the maximum absorbance is obtained, indicating a 1:1 binding model between L1 and Cu(II). On the basis of 1:1 stoichiometry, the stability constant of the complex between L1 and Cu(II)



Fig. 9. (a) Solutions of L2 upon addition of different metal ions. (b) Absorption changes of L2 in CH₃CN (1.0×10^{-5} M) upon addition of 1 equiv of different nitrate salts (1.0×10^{-5} M). (c) Absorption of L2 at 360 nm upon addition of different cations.



Fig. 10. Titration curves of L2 in CH₃CN (1.0 × 10⁻⁵ M) in the presence of different amounts of Cu(II) (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0×10^{-5} M). Insert: Titration curves of L1 in CH₃CN (1.0 × 10⁻⁵ M).

was estimated to be $1.04\times10^4~M^{-1}$ by plotting $1/\Delta A$ against 1/ [Cu(II)] according to the Benesi–Hilderbrand equation (Fig. 7). The limit detected concentration of Cu(II) is about $2\times10^{-7}~M$ in acetonitrile.

In contrast L2, with a larger cavity, is also stable within a pH range of 5.5–10.5 (Fig. 8). When an equimolar quantity of Ag(I), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), K(I), Hg(II), Pd(II), Mg(II), Li(I), Na(I), Ni(II), Zn(II), Fe(III), Cr(III) was added to the solution of L2 respectively, it shows three different behaviors (Fig. 9), a slight intensity enhancement of the band at 420 nm in the presence of Ca(II), appearance of a new band at about 360 nm and obvious intensity decrease of the band centered at 420 nm in the presence of Ba(II), Cu(II), Hg(II), Fe(III), Cr(III) respectively, and no changes upon addition of the other ions. To investigate the difference between L1 and L2, L2 was titrated with Cu(II) from 0 to 3.0×10^{-5} M. With progressive addition of Cu(II) (Fig. 10), the UV-vis absorptions of L2 at 300 and 420 nm were diminished. The well located isosbestic points at 373 nm and 316 nm indicated new compounds produced. After more than 0.8 equivalents of Cu(II) were added, however, the absorption at 260 nm emerged and intensified gradually with a new isosbestic point at 297 nm. The dramatic difference in results of the stepwise UV–vis changes may be due to the competition between aza-crown ether and DMN which was demonstrated by theoretical calculations. The limit detected concentration of Cu(II) is about 1×10^{-6} M in acetonitrile, much lower than the value of L1.

From the results, L1 and L2 showed dramatically different selectivity and sensitivity to Cu(II), which arises as a consequence of their structures (cavity size). From L1, only one isosbestic point was clearly seen. But to L2, there were three isosbestic points formed. This may because in L1, Cu(II) can only combine with DMN, while in L2 it can combine with DMN and the large cavitied aza-18-crown-6-ether.

The correct combination of ring and cation size would result in a suitable coordination to the nitrogen atom of the macrocycle group, thus inducing the intensity of the charge-transfer band decreasing [15]. The data demonstrated that the two binding sites in L2 have more fierce competition in capturing cations while L1 has a stricter standard and a better specify in selecting the cations based on the two bonding sites cooperating operation.

3.2. Theoretical calculation study

In order to further understand the behavior of L1 and L2 with the Cu(II), DTF calculations have been carried out. As Cu(II) is known for its 4-coordination complex, the input structures were designed in a way to have bidentate coordination with the DMN, whereas the other two coordination sites were occupied by the solvent molecule (Fig. 11). The structural optimization was done using the Gaussian 03 package adopting the B3LYP method with 6– 31G as basic set [16]. TD-DFT calculations were carried out for the first 25 excitation to investigate the change of the absorption spectra upon addition of Cu(II). Electron density of HOMO and LUMO of both L1 and L2 lies on the electron-withdrawing part. From the energy level diagram (Fig. 12), it can be seen that addition of the metal ions leads to the stabilization of the HOMO and LUMO of the sensors (Table 3).

From the calculated results, energy levels of HOMO and LUMO of L1 decreased more dramatically than that of L2 after addition of Cu(II), namely L1 was more selective and sensitive to Cu(II) [17], which was in line with the experimental results. From Table 4, we see nitrogen atoms in L1 have higher electron density than that of L2, which indicated that L1 was more sensitive to Cu(II) [18]. And this result confirmed that L1 was the better sensor for Cu(II) again.



Fig. 11. Optimized structures of L1 with Cu(II) (left), L2 with Cu(II) (right).



Fig. 12. (a) Energy levels of various HOMO and LUMO's of L1 in the absence and the presence of Cu(II); (b) Energy levels of various HOMO and LUMO's of L2 and compound coordinated with DMN; (c) Energy levels of various HOMO and LUMO's of L2 and compound coordinated with crown ether.

Table 5 shows the electronic density assigned in oxygen atoms and nitrogen atoms was merely equal in L2. So we calculated the energy of the complex Cu(II) coordinated with the crown ether (L2-Cu-E) to realize the possible reasons of the multi-isosbestic points. From Fig. 12(b, c), we found HOMO orbital of the complex coordinated with DMN (L2-Cu-N) had much lower energy. But the energy of (HOMO-1) of L2-Cu-E was next to the HOMO of L2-Cu-N, as well as the LUMO orbital of the two complexes. Because the energies have little difference, we speculated that two formations of complexes may change from one form to another.

All the results consistently indicate that L1 is the ideal chemosensor for Cu(II) which has higher sensitivity and selectivity.

Table 3

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Energies of HOMO and LUMO of the ligands and complexes (a.u.).

	L1	L1 + Cu(II)	L2	L2 + Cu(II)
HOMO	-3.702	-7.272	-4.10	-5.040
LUMO	-1.935	-4.092	-1.837	-2.056
Δ	1.767	3.180	2.261	2.985

lable 4	
Electronic density of nitrogen a	atoms in L1 and L2.

L1		L2	
N1	-0.4541	N4	-0.2482
N2	-0.5184	N11	-0.2083
N11	-0.4912	N20	-0.4984
N23	-0.6715	N32	-0.2366
N41	-0.5403	N48	-0.2048

3.3. Solvatochromin and cations interference of L1 reacting with Cu(II)

In order to research sensor L1 more thoroughly the response of L toward Cu(II) in different solvents e.g. THF and THF/H₂O (20:80) was studied. The titrations were done to find out the limit sensitivity concentration (Figs. 13 and 14). The results indicated that the highest sensitivity with the value of 2×10^{-7} M and binding constant 4.97×10^6 M were obtained in THF/H₂O (20:80) solution. This result can be explained by the possible reasons. As reported, the main driving forces to construct these complexes including hydrogen bond, $\pi - \pi$ stacking and charge transfer interaction [19]. In the structures of THF and H₂O, there is an oxygen atom with a pair of lone electrons respectively. Nitrogen and oxygen will compete to obtain the hydrogen ions. The pK_a of cyanoamide protons is in the range of 9.95–11.0, and the pK_a values of H₂O and THF are 15.7 and 3.70 respectively. From the data, we speculated that the hydrogen of cyanoamine could be taken by oxygen atom easily. As a result, the sensor L1 selected Cu(II) more sensitively and bound with it more tightly.

Table 5	
Electronic density of nitrogen and oxygen atoms in L2	•

L2			
01	-0.2186	N4	-0.2482
02	-0.2172	N11	-0.2083
03	-0.2181	N20	-0.4984
06	-0.2170	N32	-0.2366
064	-0.2542	N48	-0.2048



Fig. 13. (a) Titration curves of L1 in THF (1.0×10^{-5} M) in the presence of different amounts of Cu(II) (0, 0.01, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.8, 2.0 × 10^{-5} M); (b) Benesi–Hildebrand plot of the Cu(II)–L1 complexes in THF.



Fig. 14. (a)Titration curves of L1 in THF/H₂O (1/4) in the presence of different amounts of Cu(II) (0, 0.001, 0.002, 0.006, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0, 3.4, 3.8, 4.2, 4.6 \times 10⁻⁵ M); (b) Benesi–Hildebrand plot of the Cu(II)–L1 complexes in THF/H₂O (1/4).



Fig. 15. Absorbance of L1–Cu(II) at the new band upon addition of various cations. The low bars represent L1 $(1.0 \times 10^{-5} \text{ M})$ with cations $(5.0 \times 10^{-5} \text{ M})$ without Cu(II); the high bars represent L1 $(1.0 \times 10^{-5} \text{ M})$ with cations $(5.0 \times 10^{-5} \text{ M})$ upon the subsequent addition of Cu(II) $(1.0 \times 10^{-5} \text{ M})$. (a), (b), (c) is the diagram of CH₃CN, THF/H₂O (20:80), THF, respectively.



Fig. 16. pH titration of Cu(II) binding with chemosensor L1 (10^{-5} M) in a THF-H₂O solution (v/v = 4/1, 20 mM buffer). Concentration of Cu(II) was 10^{-5} M.

Lastly, to study the influence of other metal ions on Cu(II) binding with L1, the research performed competitive experiments with other metal ions (5 \times 10⁻⁵ M) in the presence of Cu(II) (1 \times 10⁻⁵ M) (Fig. 15). Absorption changes caused by the mixture Cu(II) with most other metal ions were similar to that caused by Cu(II) alone.

3.4. pH titration on L1–Cu(II)

To demonstrate the Cu(II)-induced deprotonation of the amide group in chemosensor L1, pH titration experiments were carried out (Fig. 16). First, the influence of pH on chemosensor L1 was studied using UV-vis spectroscopy. Over a pH range of 6-8, the visible absorption band centered at about 300 nm was in accordance with the results obtained in Cu(II) titration test. A decrease in pH from 5 to 1 engendered a shift in the maximum absorption wavelength to 350 nm and peak values banded at 300 approximated to sensor L1. The possible reason could be due to protonation of the amide group which lowered its coordination ability [20]. And when pH values changed from 9 to 12 obvious decrease of the peak located at 425 nm and increase of the peak banded at 300 nm were observed. This can be explained by the fact that in strong alkalisolution the hydrogen ion was deprotonate more easily and this leaded to a stronger binding affinity with Cu(II) [20]. The results indicated that the formation of L1-Cu(II) complexes was a deprotonation process, which was consistent with the presumption when discussing solvatochromin above.

4. Conclusions

In conclusion, two sensors with different aza-crown-ether moieties were readily synthesized in good yield and the recognition of Cu(II) was studied. The mechanisms were offered through experiment and theoretical calculations. L1 displayed Cu(II)-selective chromogenic behavior whose detection limit of Cu(II) is about 10^{-6} M by naked-eye and accurate detection limit is 2×10^{-7} M by UV–vis measurement. A series of advantages such as high selectivity, good solubility, strong stability in a wide pH range and high binding constant values indicate that L1 has potential applications in environment and biological chemistry. The results may guide us to design ideal sensors through the modulation of substituents.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig. 2013.01.018.

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