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An efficient chloride-selective fluorescent chemosensor based on 2,9-bis(4′-hydroxyphenyl)phenanthroline Cu(II) complex

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Abstract

A new complex Cu(II)/**L**, composed of 2,9-bis(4′-hydroxyphenyl)phenanthroline (**L**) and Cu(II), was synthesized as an efficient chloride-detection fluorescent chemosensor with high selectivity and sensitivity over other halide anions, F^-, Br^-, I^-. The recognition mechanism was discussed primarily.

Keywords: Chloride recognition; Fluorescence on; Phenanthroline derivative; Chemosensor

1. Introduction

Development of new receptors capable of high affinity and adequate selectivity for anions has attracted considerable interest due to the important role anions play in various biological processes in the past decades [1–4]. Anion recognition via fluorescent chemosensor is of particular interest in biology, environmental science and chemical trace detection because of its simplicity and high sensitivity [5–11]. It is known that design of receptors with high sensitivity and selectivity for anions is an ongoing challenge in the course of molecular recognition since the anion recognition is much more difficult to achieve than cation recognition. In order to improve the affinity of receptor to anions, several approaches are generally employed in selective recognition of various anions, such as electrostatic interaction [12,13], hydrogen bonding [14–16], and suitable cavity or framework onto which the structural components can be assembled [17,18]. Indeed, some receptors have been designed for efficient detection of anions [19–22]. For example, an aromatic receptor based on electron-deficient 1,3,5-triazine, which is able to interact with fluoride, chloride, and azide anions was developed [19]. The other strategy for anion recognition is to utilize a functional cavity as suggested by Sato et al. [20]. In the structure of this kind of sensor, a benzene-based tripodal imidazolium receptor is applied to bind halide anions through the hydrogen bonding interaction [21,22]. Another approach is to employ the "cascade" structure, which is able to make the host interact with anionic guest easily [23]. It implies that there are two steps involved in the whole process. Firstly, the sensing molecule acts as a ligand for binding a suitable metal cation to form a metallic complex with positive charge, then, the formed complex interacts selectively with some anions through electrostatic interaction.

Among the molecular recognition community, halide anion recognition represents one of the most challenging works though halides play crucial roles in a range of biological phenomena and many disease states [24]. While many fluoride anion sensors have been developed so far [25–28], however, the sensors for chloride anion detection are scarce due to the inherent property of chloride anion, such as less charge density and large volume compared with fluoride anion [29]. To date, chloride-selective sensors were mainly designed on the basis of size matching and hydrogen bonding interaction. For example, Sessler et al. [30,31] developed an effective chloride-selective receptor based on a flexible calix[4]bipyrrole; Kochi and co-workers [32] employed a series of neutral organic acceptors with electron-deficient olefinic and aromatic centers to recognize larger halides such as Cl^- and Br^-. Multi-hydrogen bonding interaction and size matching make it bind chloride more strongly over other anions [33]. Herein, we employ cascade strategy to develop a highly selective and sensitive light-on chemosenor for chloride anion

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over other halide anions, i.e., F^-, Br^-, I^-. In this case, the emission of ligand 2,9-bis(4′-hydroxyphenyl)-phenanthroline was revived upon addition of chloride anion. The combination of both steric hindrance and ligand substitution is probably the main reason for its high selectivity for chloride anion.

2. Experimental

2.1. Instruments and reagents

All fluorescence spectra in this work were recorded in Hitachi F-4500 fluorescence spectrometer. ^{1}H NMR spectra were recorded at 400 MHz, Bruker-400 instrument. Mass spectra were recorded at Finnigan 4021C MS-spectrometer and Biflex III MALDI-TOF MS-spectrometer. Elemental analysis were recorded at Flash EA 1112 instrument.

Copper(II) perchlorate hydrate and anionic compounds tetra-*n*-butyl ammonium salts of F^-, Cl^-, Br^- and I^- were all purchased from Aldrich and used without further purification. 1,10-phenanthroline was analytical grade from Beijing chemical works and was recrystallized with ethanol once before use. Acetonitrile was chromatographic grade and other reagents were all analytical purity.

2.2. Synthesis

2.2.1. 2,9-Bis(4′-methoxyphenyl)phenanthroline

Lithium (2.6 g, 0.375 mol) and ethyl ether (60 mL) were combined in a 250 mL three-neck flask and aerated by nitrogen-stream for 10 min. The mixed solution was stirred with refluxing condition, then 4-bromoanisole (19 mL, 0.15 mol) was added dropwise within an hour. Continuing to stir the reaction for another 2 h, 4-bromophenoxy lithium was obtained. After that, 1,10-phenanthroline (4.0 g, 22 mmol) and toluene (50 mL) were combined into another three-neck flask under nitrogen atmosphere, then 4-bromophenoxy lithium solution prepared above was added dropwise within half an hour. The reaction was stirred for 48 h and then cooled in ice-bath. Water (40 mL) was added to hydrolyze the reaction and the solution became yellow. Organic product was extracted with dichloromethane and separated from water layer. The organic phase was added to MnO_2 (40 g) and stirred for an hour, then MnO_2 was filtrated and the solvent was evaporated under reduced pressure. The crude product was recrystallized by toluene/petroleum ether = 1/1 (v/v) and colorless needle crystal (2.75 g) was obtained in 45.5% yield (mp: 182–184 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, 2H, ArH), 8.31 (d, 4H, ArH), 8.12 (d, 2H, ArH), 7.78 (s, 2H, ArH), 7.13 (d, 4H, ArH), 3.95 (s, 6H, OCH_3).

2.2.2. 2,9-Bis(4′-hydroxyphenyl)phenanthroline (L)

Pyridine (7 mL), 2,9-bis(4′-methoxyphenyl)phenanthroline (2.75 g, 7.0 mmol) and concentrated HCl (8 mL) were combined and reacted for 3 h at refluxing conditions under nitrogen atmosphere. The reaction was cooled to room temperature and then poured into 100 mL water. During this process, a lot of precipitate appeared. The residue was filtrated and dissolved in ethanol/water = 5/1 (v/v) mixed solvent. The pH value of the solution was modulated to neutral and scarlet precipitate (2.3 g) was obtained in 84% yield. ^{1}H NMR (400 MHz, DMSO) δ 9.90 (s, 2H, ArOH), 8.49 (d, 2H, ArH), 8.37 (d, 4H, ArH), 8.29 (d, 2H, ArH), 7.93 (s, 2H, ArH), 7.01 (d, 4H, ArH). MS (m/e): 364 (347, 335, 333, 281, 273, 226, 158, 151, 94). Anal. Calcd. for $C_{24}H_{16}N_2O_2$: C 79.11%, H 4.43%, N 7.69%, found: C 79.18%, H 4.48%, N 7.53%.

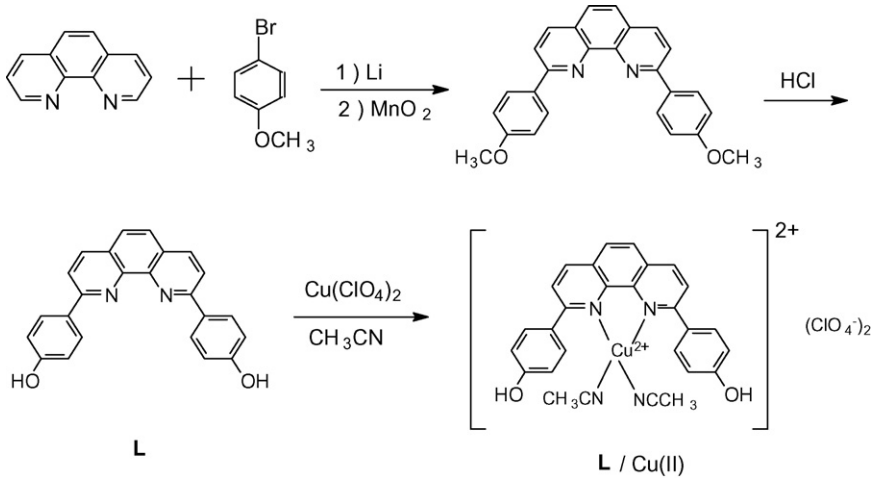
2.2.3. L/Cu(II)

A portion of **L** (364 mg, 1 mmol) and copper perchlorate (370 mg, 1 mmol) were combined in CH_3CN (20 mL), then the solvent was evaporated under reduced pressure. The residue was recrystalled in ethanol/acetonitrile = 10/1 (v/v) mixed solvent and blue crystal was obtained in 27% yield. ^{1}H NMR (400 MHz, DMSO) δ 10.00 (s, 2H, ArOH), 9.09 (s, 2H, ArH), 8.68 (s, 2H, ArH), 8.15 (d, 4H, ArH), 7.99 (s, 2H, ArH), 6.83 (d, 4H, ArH), 5.91(s, 6H, CH_3CN). MALDI-TOF: 708.2. Anal. Calcd. for $C_{28}H_{22}Cl_2CuN_4O_{10}$: C 47.44%, H 3.13%, N 7.90%, found: C 47.67%, H 3.32%, N 7.73%.

3. Results and discussion

Ligand **L** and complex **L**/Cu(II), were synthesized according to the route shown in Scheme 1. Ligand **L** is a strongly emissive compound peaked at 402 nm, whereas complex **L**/Cu(II) is non-emissive because of the photoinduced electron transfer (PET) process [34,35]. In the presence of different anions, the fluorescence intensity of the solution in acetonitrile can be recovered to different extents as the following sequence: $Cl^- > F^- > Br^- > I^-$ (Fig. 1A). Upon addition of 10 equivalents of chloride anion, the fluorescence of complex **L**/Cu(II) at 402 nm was revived, and the fluorescence intensity of this solution is about 70% of the original intensity of ligand **L**. Whereas, at the same conditions, F^-, Br^- and I^- only induced 15, 12 and 10% enhancement, respectively. This result indicates that **L**/Cu(II) may be used as an efficient chemosensor for chloride-selective detection. To confirm our observation, fluorescence titration of **L**/Cu(II) in acetonitrile at different concentrations of $(C_4H_9)_4NCl$ was performed (Fig. 1B). The fluorescence of the solution increases with increasing concentrations of chloride anion regularly. Job's plot shows that **L**/Cu(II) can bind Cl^- in 1:2 stoichiometery (inset in Fig. 1B). The stability constant between **L**/Cu(II) and Cl^- was determined by a nonlinear curve fitting procedure of the fluorescence titration data (Fig. 1B). The value of Kass was calculated to be 2.6×10^8 M^{-2} based on 1:2 stoichiometery, whereas the stability constants for **L**/Cu(II) with other halides are all below 10^3 M^{-2} at the same calculation model [36], indicating its good selectivity for chloride anion over other halide anions, i.e., F^-, Br^- and I^-.

To look into the nature of recognition process, ^{1}H NMR experiments were performed in DMSO-d_6 because of its low solubility in acetonitrile. The ^{1}H NMR spectra of **L**/Cu(II) (Fig. 2a) show dramatic changes upon addition of 10 equivalents of $(C_4H_9)_4NCl$ in DMSO-d_6 (Fig. 2b). H_o, H_m and –OH proton signals show significant downfield shifts ($\Delta\delta$ = +0.22, +0.26 and +0.33, respectively) and $H_{4,7}$ and $H_{3,8}$ proton signals



Scheme 1. Synthetic route of complex **L**/Cu(II).

show obvious upfield shifts ($\Delta\delta = -0.55$ and -0.36, respectively); while $H_{5,6}$ show no obvious change on the basis of comparison of Fig. 2a and b. It implies that the protons of phenanthroline ring become upfield shifts in the prescence of $(C_4H_9)_4NCl$, whereas those of phenyl ring become downfield shifts because of the interaction between **L**/Cu(II) and Cl^-. Furthermore, it is interesting to note that Fig. 2b (^{1}H NMR of **L**/Cu(II) + 10 equiv. $(C_4H_9)_4NCl$ is very similar to Fig. 2c (^{1}H NMR of free **L**). All aromatic protons show no obvious variations except that hydroxyl proton shows an obvious downfield shift ($\Delta\delta = +0.43$, this might be interpreted as the hydrogen bonding interaction between –OH and Cl^-). All these indicate that when $(C_4H_9)_4NCl$ was added to the solution of **L**/Cu(II), two acetonitrile molecules of **L**/Cu(II) were replaced by two chloride anions and a new ternary complex was formed. In addition, from Fig. 2a, CH_3CN proton peak of **L**/Cu(II) was evidently observed, however, when $(C_4H_9)_4NCl$ was added to the solution, this peak was disappeared completely (Fig. 2b). Proton signal of free CH_3CN was shifted to upper yield (2.01 ppm, not shown in Fig. 2b). This observation also suggests that CH_3CN was replaced by chloride anion. The PET process between Cu^{2+} and **L** was believed to be suppressed, thus resulting in an enhancement of the fluorescence intensity of the system (Scheme 2).

To further confirm the significant role acetonitrile molecules play during the recognition process, the following experiment was also carried out. The fluorescence intensity of ligand **L** decreases greatly when a certain amount of $Cu(ClO_4)_2$ was added into its solution in acetonitrile (Fig. 3A). The fluorescence of **L** was quenched completely at the equivalent concentration of $Cu(ClO_4)_2$ to that of **L**. An obvious plateau appears (inset Fig. 3A). This result indicates that ligand **L** can bind Cu(II) with 1:1 molar ratio in acetonitrile (The molecular weight of the complex obtained from TOF-MS analysis is 708, which also supports the formation of complex **L**/Cu(II)/2CH_3CN). The stability constant in CH_3CN is calculated to be $1.2 \times 10^7\ M^{-1}$ (Scheme 3) [17] However, the fluorescence of the solution can be recovered by adding $(C_4H_9)_4NCl$ to the above solution. On the other hand, it is worthy to note that when the titration experiment was performed in CH_2Cl_2, the result is different from the former. From Fig. 3B, it can be found that the amount of $Cu(ClO_4)_2$ added for full quenching of the fluorescence of **L** is the half of that used in acetonitrile. At this concentration, an obvious plateau was observed (inset Fig. 3B). It implies that the molar ratio of complex formed between ligand **L** and Cu(II) in CH_2Cl_2 is 2:1 (the molecular weigh of the complex obtained from TOF-MS analysis is 990, which also confirms the structure of complex

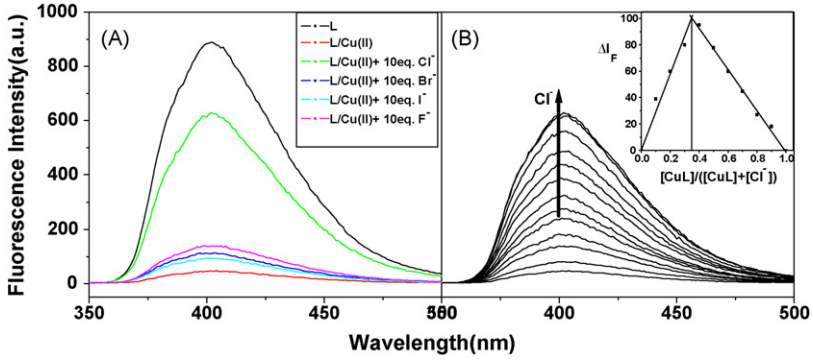


Fig. 1. Fluorescence spectra of **L**/Cu(II) (10 μM) in acetonitrile upon addition of (A) different halide anions ($(C_4H_9)_4NF$, $(C_4H_9)_4NCl$, $(C_4H_9)_4NBr$, $(C_4H_9)_4NI$, 100 μM, respectively) and (B) increasing concentrations of $(C_4H_9)_4NCl$ (5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 100 μM) with an excitation wavelength of 320 nm. Inset: Job's plot for the binding of **L**/Cu(II) with Cl^-.

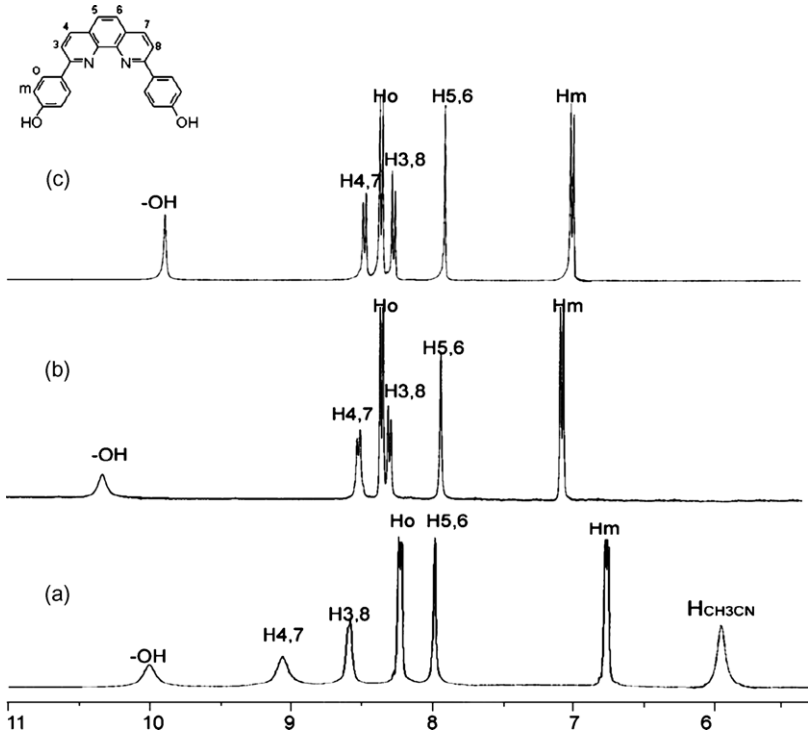
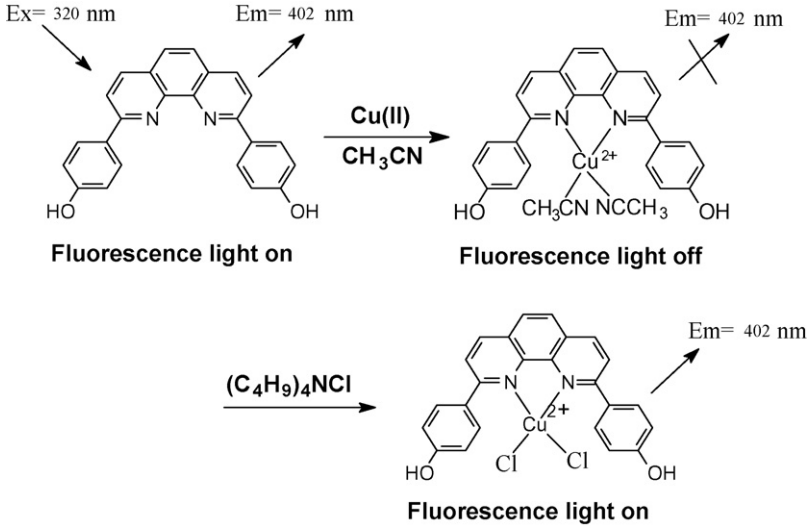


Fig. 2. Partial ^{1}H NMR spectrum of (a) **L**/Cu(II); (b) **L**/Cu(II) + 10 equiv. $(C_4H_9)_4NCl$ and (c) free **L** in DMSO-d_6.

is 2**L**/Cu(II)). Furthermore, no obvious 4fluorescent variation could be observed with addition of Cl^- to the solution. The reason is that CH_3CN molecules act as the additional ligand to form the complex. Therefore, in this case another molecule of **L** is impossible to bind Cu(II), and the bound acetonitrile molecule can be replaced by choride anion due to the stronger interaction between Cu^{2+} and Cl^-. However, in CH_2Cl_2, The formation of a stable 2:1 complex leaves no coordinate position for Cl^-. The stability constant in CH_2Cl_2 is $7.8 \times 10^{10}\,M^{-2}$ (Scheme 3) [36]. It is concluded that acetonitrile molecule plays a pivotal role during the Cl^- recognition process in the present case.

The excellent selectivity of Cu(II)/**L** for chloride anion over other halide anions can be explained by both soft and hard acids and bases rule and steric effect. The stability constants between Cu(II)/**L** and halide anions should be in order of $I^- > Br^- > Cl^- > F^-$ according to Irving–Williams rule [37,38]. However, the complexes between Cu(II)/**L** and Br^- or I^- are difficult to form probably due to the steric hindrance. The radius of Br^- (1.91 Å) and I^- (2.16 Å) are much larger than that of Cl^- (1.81 Å), thus preventing from the formation of stable complexes [39]. The size of chloride anion is more suitable for the pseudocavity of Cu(II)/**L**, therefore, the largest stability con-



Scheme 2. .

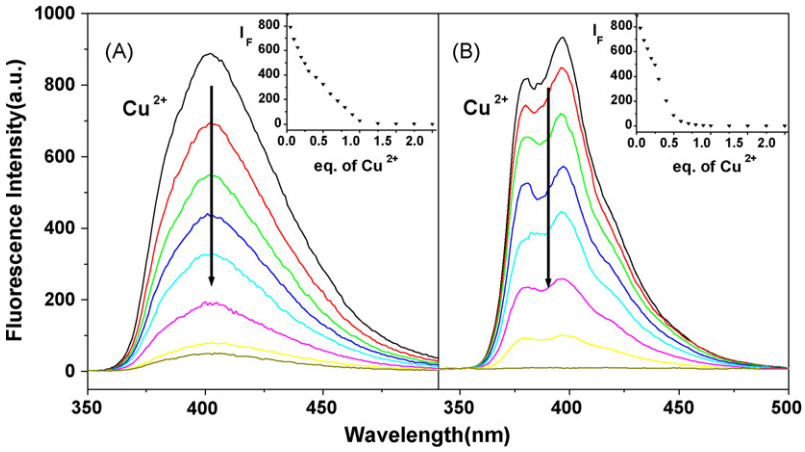
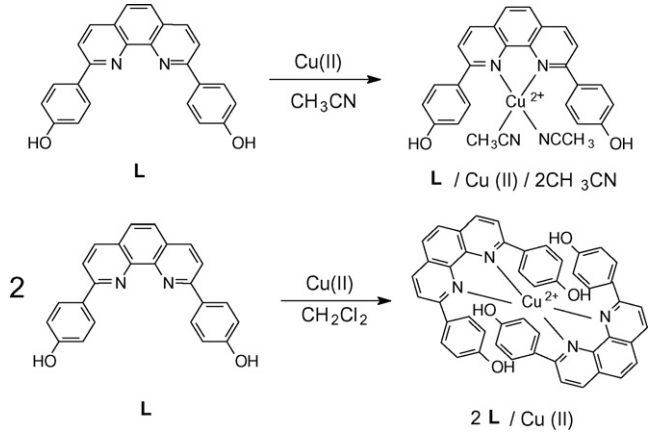


Fig. 3. Variation of fluorescence quenching spectra of ligand **L** (10 μM) with different concentrations of (A) cooper perchlorate (0, 1, 2, 3, 4, 6, 8, 9, 10 μM) in CH_3CN and (B) cooper perchlorate (0, 0.5, 1, 1.5, 2, 3, 4, 4.5, 5 μM) in CH_2Cl_2 with an excitation wavelength of 320 nm. Inset: Fluorescence intensity of **L** vs. equivalents of Cu(II) profile at 402 nm.



Scheme 3. The different complex modes between ligand **L** and Cu(II) in acetonitrile and dichloromethane.

stant between Cu(II)/**L** and chloride anion was observed in our experiment.

4. Conclusions

A novel fluorescent chemosensor **L**/Cu(II), which can recognize Cl^- sensitively and selectively, was synthesized. It is concluded that acetonitrile molecules, which are bound to the complex **L**/Cu(II), play a pivotal role during the Cl^- recognition process in the present case. This may be applicable in design of desirable sensors for anion species recognition.

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