



## Cu(II) complex of an abiotic receptor as highly selective fluorescent sensor for acetate

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### ABSTRACT

A copper complex having quinoline moiety as fluorophore has been synthesized. The anion recognition behavior of the receptor and its copper complex has been studied in acetonitrile and in acetonitrile:H<sub>2</sub>O (95:5 v/v). The copper complex shows high selectivity toward acetate over other anions studied such as F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, OAc<sup>-</sup>, DL-malate, L-mandelate, benzoate, isophthalate, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>.

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The design and synthesis of abiotic receptors for anion recognition is a rapidly expanding area of interest.<sup>1</sup> Since anions play an important role in many biological and environmental processes,<sup>2</sup> selective recognition of a particular anion is an important challenge in the field of supramolecular chemistry. Anions are mainly recognized through hydrogen-bonding interactions,<sup>3</sup> electrostatic interactions,<sup>4</sup> coordination through metal ions,<sup>5</sup> etc. Development of metal-based receptors<sup>6</sup> has recently been the center of interest as metal ions pre-organize the binding sites structurally for optimal anion-binding through hydrogen bonding and metal ion coordination, resulting in strong affinities than purely organic receptors.

Binding of anion through hydrogen bonding is really difficult in water as anions become highly solvated in water and there exists a competition of water and anions toward binding with the host molecules. Additional binding sites like metal coordination may help in recognizing anions in the presence of water.

Selective sensing of acetate is particularly topical<sup>7</sup> due to its significance in numerous metabolic processes for example, a significant number of metal enzymes having cations in their active sites influence various hydrolysis processes. The rate of acetate production and sedimentation has frequently been used to indicate the organic decomposition in marine sediments. Carboxylate anions play an important role in nylon industry. They are also used in the manufacture of paper, plastics, dyes and paints.

We herein report a new metal (copper)-based receptor which selectively binds acetate anion. The receptor employs nitrogen atoms as donor centers. Here, quinoline moiety acts as a fluoro-

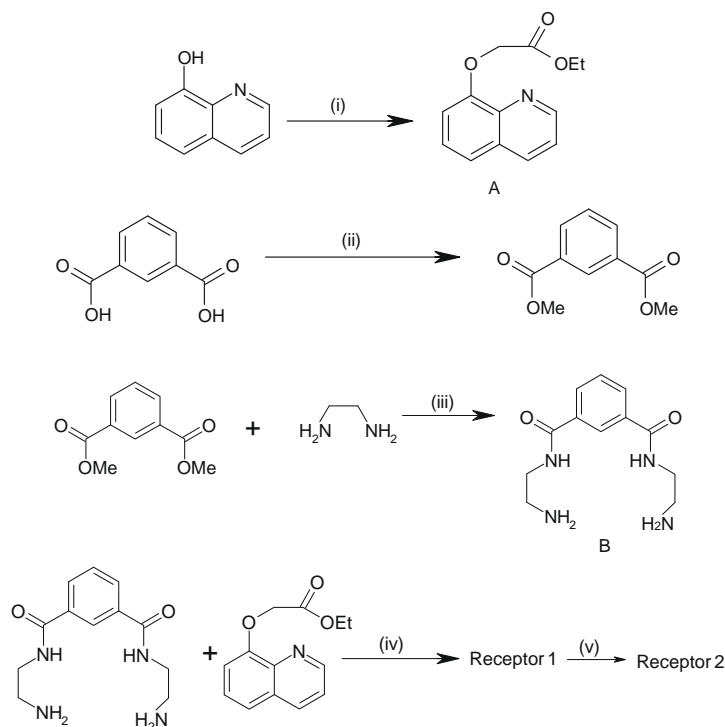
phore. The formation of copper complex locks the cavity and organizes the molecule to selectively bind acetate anion. Again the copper cation provides additional binding site to the acetate anion resulting in high selectivity measured in fluorescence spectra.

The receptors **1** and **2** were synthesized as shown in Scheme 1. Isophthalic acid upon esterification yielded the corresponding dimethyl ester. The diester was then refluxed with ethylenediamine to afford the diamido diamine (**B**). We prepared receptor **1** directly from compound **B** and compound **A** under reflux in about 27% yield. The <sup>1</sup>H NMR spectrum of receptor **1** revealed the presence of two NH protons at 8.66 and 7.82 ppm. Complex **2** was prepared from compound **1** when it was reacted with Cu(ClO<sub>4</sub>)<sub>2</sub>.

The green-colored complex **2** was synthesized by reacting receptor **1** (yellow) with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Scheme 1) in dry acetonitrile at refluxing condition. The HRMS mass spectrum reveals the formation of complex **2** [*m/z* = 684.6462 (found), the calculated value is 684.6458]. The attempts to grow single crystals of complex **2** which are suitable for X-ray structure determination were not successful.<sup>8</sup> Energy minimization using PCMODEL Serena software helped us to understand the interactions between the Cu(II) and receptor **1**. Previously reported copper containing receptors<sup>9</sup> which recognize anions show current interest and progress in the area of anion recognition research.

The photophysical behavior of receptors **1** and **2** was investigated using acetonitrile as a solvent. The emission maximum for receptor **1** appears at 399 nm when it is excited at 298 nm, but for complex **2**, the emission maximum appears at 411 nm at an excitation wavelength of 305 nm using acetonitrile as a solvent. When acetonitrile:H<sub>2</sub>O (95:5 v/v) is used (receptor **2**), the emission maximum gets shifted to 390 nm at an excitation wavelength of 302 nm. The appearance and nature of the emission bands of

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**Scheme 1.** Reagents and conditions: (i) ethyl chloroacetate, dry  $K_2CO_3$ , dry acetone, TBAB (0.5 mol %); (ii) dry MeOH, conc  $H_2SO_4$  (two drops), reflux; (iii) and (iv) acetonitrile, reflux; (v)  $Cu(ClO_4)_2 \cdot 6H_2O$ , acetonitrile, reflux.

receptors **1** and **2** indicate the coordination of copper with the quinoline moiety because the two receptors were taken in equal concentrations.

The anion-binding ability of the receptors **1** and **2** has been studied by UV–vis and fluorescence methods (Fig. 1) using tetrabutylammonium salt of particular anions in acetonitrile and acetonitrile–water (for **2**). The change of fluorescence intensity of receptor **1** after addition of anions as their tetrabutylammonium salts is very small. After addition of a large amount of acetate the intensity decreases in acetonitrile–water (9:1 v/v) solvent. Other anions influence no noticeable changes. However due to the addition of very larger amounts of anion salts the fluorescence intensity of receptor **1** decreases in very small amounts like acetate. The intensity changes (of receptor **2**) in acetonitrile (Supplementary data) and acetonitrile–water after addition of particular anion solutions are depicted in Figure 1. Figure 1 shows that there was no significant change after addition of other anions studied ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ , DL-malate, L-mandelate, benzoate, isophthalate,  $H_2PO_4^-$ ,  $NO_3^-$  and  $HSO_4^-$ ). Thus complex **2** can be used for selective recognition of acetate.

The fluorescence ratio of receptor **2** displayed in Figure 2 also displayed the enhancement of emission spectra in the cases of iodide, acetate, DL-malate, L-mandelate, benzoate, isophthalate,  $H_2PO_4^-$  and  $NO_3^-$ . Slight decrease takes place in the cases of  $F^-$ ,  $Cl^-$  and  $Br^-$  (decrease with red shift in case of  $HSO_4^-$ ) in acetonitrile.

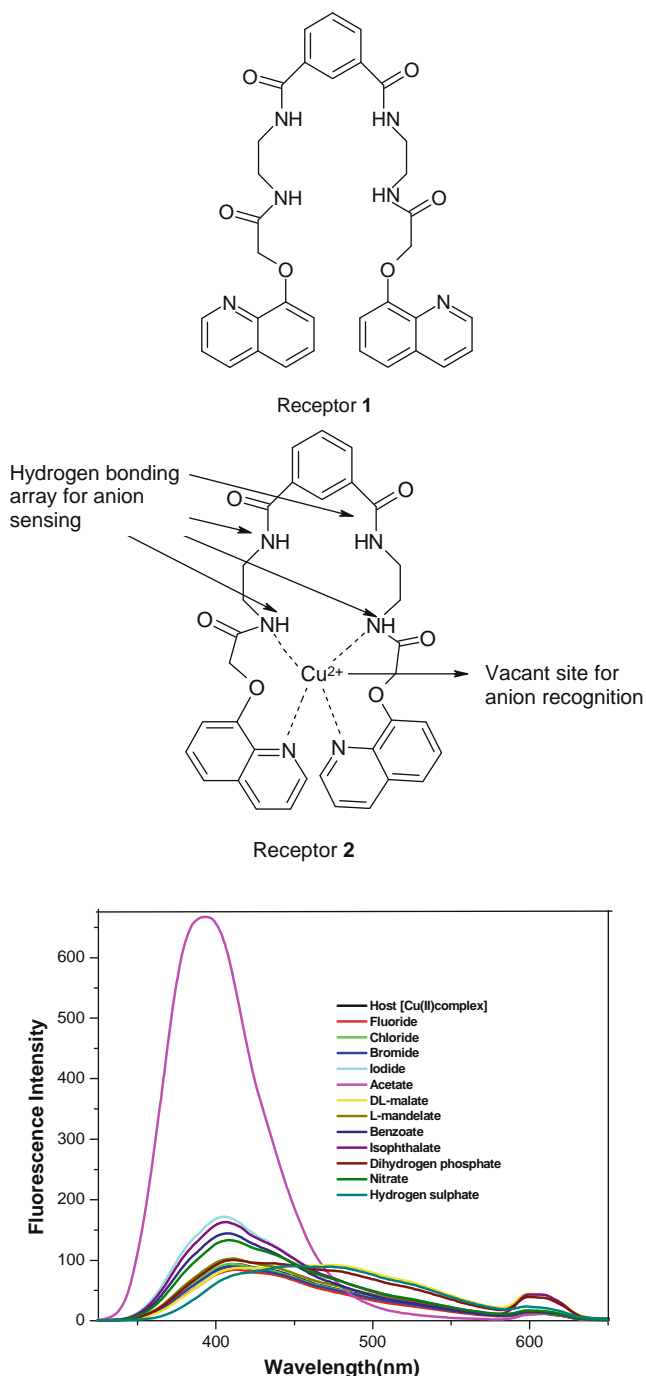
The preference of acetate over other anions may be due to the size and shape of the host and guest being complementary to each other. The acetate anion was encapsulated within the cavity formed after complexation of receptor **1** with copper cation in a better way as compared to the other anions studied. Marked and selective enhancement in the fluorescence emission intensity was observed in presence of acetate ion. This effect is probably due to a consequence of the strong complexation (of acetate with the copper complex) with a decrease in non-radiative rate constant.<sup>10</sup> Again besides the size and shape selectivity, the presence

of a metal center ( $Cu^{2+}$ ) provides additional binding site to the anion either through electrostatic or covalent bond formation resulting in high selectivity of **2** toward acetate in acetonitrile as well as in acetonitrile–water mixture (9:1 v/v). Similarly the cavity of **2** selectively binds  $OAc^-$  over  $C_6H_5COO^-$  which may be due to the steric hindrance of the phenyl ring at the binding site of the copper complex.

The photophysical property of copper complex as a selective host for acetate was studied in detail by titration of host and acetate in acetonitrile and in acetonitrile–water (95:5 v/v) using tetrabutylammonium acetate. The fluorescence intensity increased gradually (SI: Fig. S3) as we added the guest solution. The association constant  $K_a$  of complex **2** for acetate in acetonitrile–water was found to be  $5.11 \times 10^5 M^{-1}$  which was calculated using the reported literature method.<sup>11</sup>

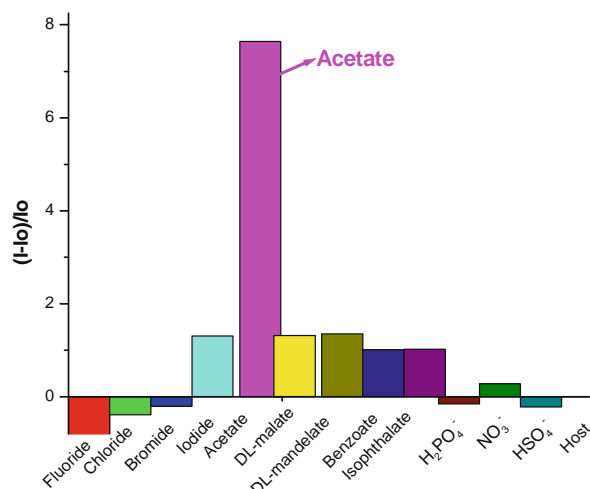
From the fluorescence spectra, it is clear that the complex shows sensitivity toward acetate by increasing the emission intensity. The stoichiometry of complexation can be determined by JOB plot (Fig. 3a). The JOB plot between the copper complex and acetate shows maxima at mol fraction 0.5, suggesting 1:1 complexation. Another typical experiment for evaluation of the selectivity of acetate over other anions was carried out for receptor **2** in acetonitrile and in acetonitrile–water mixture. In this experiment, other anions which may interfere were added in 10 times higher concentration with respect to acetate, and the fluorescence intensities were measured. The fluorescence intensities almost remain unchanged as shown in Figure 3b. Slight interference can be seen in the case of  $HSO_4^-$  when concentration of acetate anion is very less  $\sim 10$ – $30 \mu M$  in acetonitrile. But in the case of acetonitrile–water mixture, such kind of interferences was almost negligible. This experiment was also carried out in the case of receptor **1** to clarify any interference of other anions. Here, we noticed no appreciable positive results (SI: Fig. S10).

To understand the binding behavior of receptor **2** with anions, we performed model study<sup>12</sup> (see Supplementary data) using

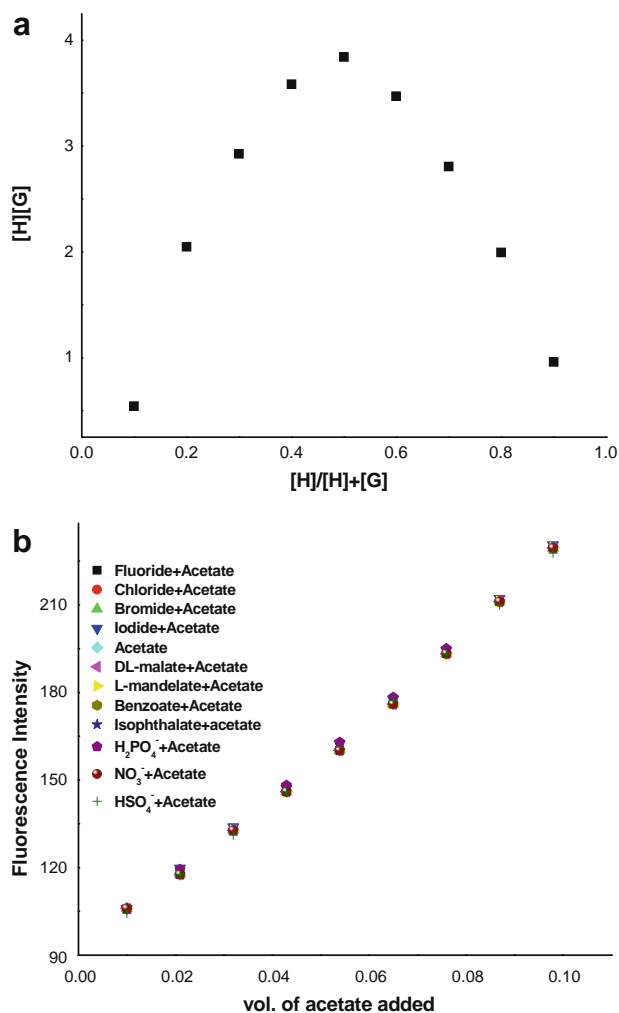


**Figure 1.** Fluorescence spectra of receptor 2 after addition of 1 equiv of guest substrates in acetonitrile–water (95:5 v/v).

PCMODEL Serena Software where we can see that the minimum energy ( $E_{\min}$ ) determined in this method is 60.2, 40.5, and  $-23.7$  (in  $\text{KJ mol}^{-1}$ ) respectively (Fig. S15). The  $E_{\min}$  values revealed that copper complex of receptor 1, that is, complex 2 is more stable than receptor 1. Again complex 2 forms a more stable complex with acetate ion as the energy value is further lowered after binding with acetate ion. Due to the more organized structure of the copper complex, stabilization energy in the case of 2 decreases upon complexation of 1 with copper. The inclusion of acetate anion into the rigid pre-organized cavity of the Cu(II) complex induced a rigidification with the consequence of the decrease of the  $E_{\min}$  value observed.



**Figure 2.** Fluorescence ratio ( $I_0 - I/I_0$ ) of complex 2 at 411 nm upon addition of 20  $\mu\text{M}$  of a particular anion in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (95:5 v/v).



**Figure 3.** (a) Job plot between complex 2.Cu(II) and acetate in acetonitrile–water (95:5 v/v). The concentration of  $[\text{HG}]$  was calculated by the equation  $[\text{HG}] = \Delta I/I_0 \times [\text{H}]$ ; (b) Estimation of acetate in the presence of other anions (10 times) in  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  (95:5 v/v) (at 390 nm).

In conclusion, we have reported the design and synthesis of receptor 1 and its copper complex (receptor 2) for selective

fluorescence sensing of anions. The fluorescent Cu(II) complex **2** for the selective recognition of acetate anion has been designed and studied in CH<sub>3</sub>CN and in CH<sub>3</sub>CN–H<sub>2</sub>O (95:5 v/v). The rigid pre-organized cavity of the Cu(II) complex leads to the selective inclusion of the acetate anion into its cavity with the consequence of the observed emission enhancement.

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### Supplementary data

Supplementary data (<sup>1</sup>H NMR, <sup>13</sup>C spectra, of receptor **1** and the mass spectra of receptors **1** and **2**, general procedure of titrations, detailed experimental procedure and energy minimized structures of receptors) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.021.

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