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Metal ion based chiral fluorescence sensor selective for dihydrogenphosphate

Shyamaprosad Goswami *, Debabrata Sen, Nirmal Kumar Das

Department of Chemistry, Bengal Engg. and Science University, Shibpur, Howrah 711 103, India

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ABSTRACT

A Cu(II) based conformationally restricted chiral fluorescence sensor (receptor **2**) has been designed and synthesized for selective sensing of anions. The anion recognition property of the Cu^{2+}-complex has been studied in acetonitrile by fluorescence methods which show remarkable sensitivity toward dihydrogen phosphate via fluorescence modulation of the Cu^{2+}-complex over the other anions examined.

Anion recognition is an expanding area of research which continues to be of interest in the field of supramolecular chemistry due to its significant role in a wide variety of environmental, clinical, chemical, and biological applications. Hence, considerable attention has been paid for the design of artificial synthetic fluorescent receptors that can selectively recognize and sense the anionic species.[1] Various structural motifs including amide,[2] pyrrole,[3] urea[4], and thiourea[5] along with the positively charged imidazolium,[6] guanidinium[7], and pyridinium[8] having conventional as well as unconventional H-bond donors are noteworthy in anion recognition. Metal ion based fluorescent receptors[9] are relatively new and particularly attractive in this aspect, as the presence of the metal ion not only provides additional binding sites for the guest anion but also pre-organizes the binding sites of the receptor conformationally for optimal anion-binding through hydrogen bonding and metal ion coordination. Such anion-binding directly to a fluorophore by way of a metal often results in high sensitivity as observed in emission spectra.

Fluorescence chemosensors that can selectively bind and detect the phosphate derivatives have actively been investigated for the recent few years.[10] Phosphate anions and their derivatives play a significant role in signal transduction, energy storage, and gene construction in biological systems. Moreover these are the key intermediates for many biochemical reactions and are the main components of biomolecules, for example, DNA and RNA. Pyrophosphate (PPi) is a biologically important target as it is the hydrolysis product of ATP under cellular conditions.

Previously we have reported a Cu(II) based abiotic receptor for selective sensing of acetate.[11] In continuation of our research program in the area of anion sensing, herein we describe a new metal ion based chiral fluorescence sensor, receptor **2** designed for selective sensing of dihydrogenphosphate (DHP).

The rational strategy of designing such metal-based sensors for selective sensing of anions lies in the fact that the anion complexation to a transition metal complex already existing in fluorescence-quenching state could trigger fluorescence emission. Our ultimate goal is to turn the fluorescence on upon binding with an appropriate anion. In this binding phenomenon, the anion would no longer require electron donating or accepting properties to modulate the photo-excited state of the fluorophore. Further, the use of a transition metal would not only quench the emission of the fluorophore but also provide extra binding sites resulting in high sensitivity and selectivity toward the target anion.

In the present design, the mixed donor nitrogen and oxygen atoms of the quinoline fluorophores of the flexible receptor **1** would arrange in such a manner that the fluorophore would directly face its cavity to encircle Cu^{2+}. Hence, the competent electron transfer from donors to electron deficient paramagnetic Cu^{2+} is energetically feasible thereby leaving the resulting Cu^{2+}-complex in fluorescence-quenching state. Now the presence of the metal ion not only imposes a conformational restriction on the fluorescence probe but also organizes the multiple hydrogen bonding donor–acceptor arrays in such a manner that selectively binds and senses the DHP inside the macrocyclic cleft of the metal complex. Additionally, Cu^{2+} complexation offers extra binding sites for the target DHP. Hence, guest DHP is co-ordinated to the metal bound receptor either through electrostatic interaction or covalent bond formation to saturate the co-ordination environment and therefore a structurally rigid receptor–metal–anion complex is formed resulting in expected modulation of the fluorescence. Hence, we may predict that metal and DHP would co-operatively[12] increase each other's respective binding constant (Scheme 1).

The detailed synthetic methods (see Supplementary data) for the preparation of receptor **1** and its Cu^{2+}-complex (receptor **2**) are shown in the following Schemes 2–4. The fluorophore, 8-hydroxyquinoline for this system was first coupled with 2-*N*-pivaloylamino-6-bromomethylpyridine followed by amide hydrolysis of the *N*-pivaloyl group and afforded the compound **a**[13] in 75% yield (Scheme 2). Similar coupling of 8-hydroxyquinoline with methyl 6-(bromomethyl)picolinate[14] (initially obtained from dimethylpyridine-2,6-dicarboxylate) in the presence of dry K_2CO_3

* Corresponding author. Tel.: +91 33 2668 2961x3; fax: +91 33 2668 2916.
E-mail address: spgoswamical@yahoo.com (S. Goswami).

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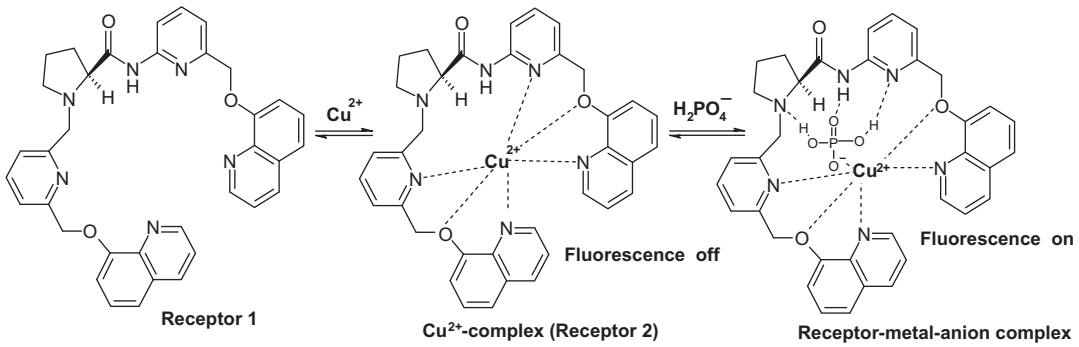
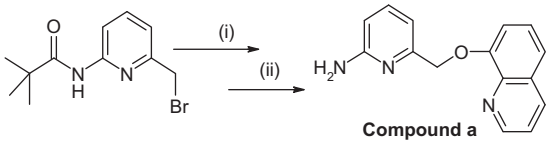


Scheme 1. Equilibrium processes showing the co-operative bindings of Cu^{2+} and DHP to receptor **1**.



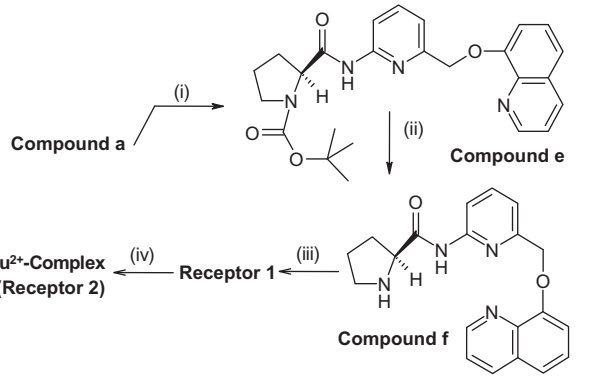
Scheme 2. Reagents and conditions: (i) 8-hydroxyqunoline, K_2CO_3, dry acetone, TBAB, rt, 36 h. (ii) 4(N) KOH/EtOH (1:1), reflux, 18 h.

yielded compound **b**; reduction of the ester intermediate (compound **b**) to the resulting alcohol (compound **c**) followed by bromination in presence of PBr_3 finally afforded the bromo compound **d** in 90% yield (Scheme 3). Now coupling of compound **a** with Boc-(L)-proline in presence of DCC gave the compound **e** which on de-amidation of the *N-tert*-Boc group afforded compound **f** in 70% yield. Receptor **1** was now obtained in 60% yield simply by the treatment of compound **d** with compound **f** in the presence of dry K_2CO_3 in dry dichloromethane (Scheme 4) that was characterized by ^1H NMR and HRMS mass spectra.

Finally the deep green-colored solid Cu^{2+}-complex, receptor **2** was obtained in 70% yield by reacting receptor **1** with $Cu(ClO_4)_2{\cdot}6H_2O$ in dry acetonitrile under refluxing condition (Scheme 4).

The HRMS mass spectrum of the Cu^{2+}-complex of receptor **1** reveals a single mononuclear complex between receptor **1** and Cu^{2+}. The M^+ and $[M-2H]^+$ peaks for the Cu^{2+}-complex are calculated at *m*/*z* 659.9747 and 657.9736 and are found at *m*/*z* 659.9765 and 657.9755, respectively.

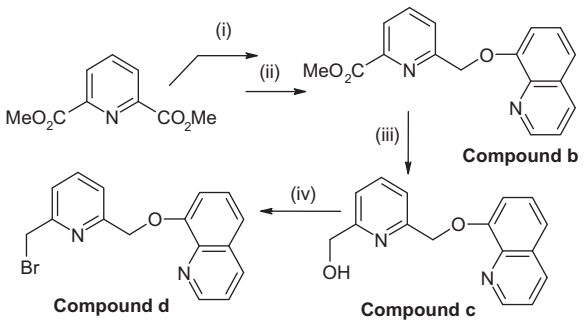
The binding events of receptor **1** and its Cu^{2+}-complex (receptor **2**) have been studied by means of UV–vis and fluorescence spectroscopic methods. All the anions are employed using their tetrabutylammonium salt and dry acetonitrile is used as the spectroscopic



Scheme 4. Synthesis of the receptor **1** and metal complex. Reagents and conditions: (i) Boc-(L)-proline, DCC, DMAP, dry CH_2Cl_2, rt, 20 h. (ii) TFA/CH_2Cl_2 (1:1), rt, 30 min. (iii) Compound **d**, K_2CO_3, dry CH_2Cl_2, rt, 48 h. (iv) $Cu(ClO_4)_2{\cdot}6H_2O$, dry CH_3CN, reflux, 2 h.

solvent. The UV–vis absorption spectra of receptors **1** (Fig. 1a) and **2** exhibit λ_{max} peaks at 285 and 300 nm, respectively. A bathochromic shift ($\Delta\lambda = 15$ nm) is observed for receptor **2** probably due to Cu^{2+} complexation. Gradual addition of DHP solution to receptor **2** produces only a slight decrease in absorption intensity (Fig. 1b) and no other significant spectroscopic change is observed unlike as seen in the emission spectra.

Since the absorption spectroscopy does not provide any useful information for detecting the interaction between DHP and Cu^{2+}-complex, we then move into fluorescence. We first analyzed the interaction between receptor **1** and Cu^{2+} (perchlorate salt is used). Receptor **1** upon excitation at 285 nm gives a broad structure-less emission band centered at 393 nm and the emission intensity



Scheme 3. Reagents and conditions: (i) (a) $NaBH_4$, CH_3OH/CH_2Cl_2 (7:3), rt, 2 h. (b) PBr_3, dry $CHCl_3$, at 0 °C then at rt, 30 min. (ii) 8-Hydroxyqunoline, K_2CO_3, dry acetone, TBAB, rt, 24 h. (iii) $NaBH_4$, CH_3OH, rt, 1 h. (iv) PBr_3, dry $CHCl_3$, at 0 °C then rt, 30 min.

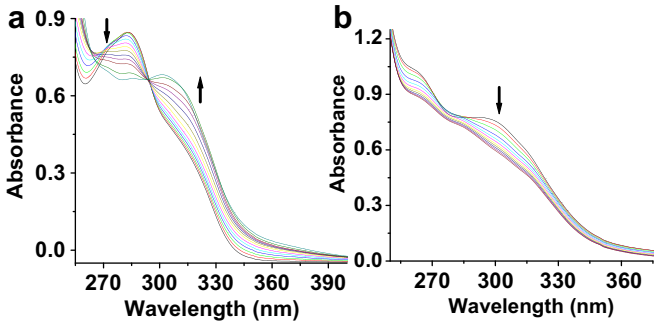


Figure 1. (a) UV–vis absorption spectra of receptor **1** ($c = 3 \times 10^{-5}$ ML^{-1}) upon gradual addition of Cu^{2+} ($c = 3 \times 10^{-4}$ ML^{-1}) in CH_3CN. (b) UV–vis absorption spectra of receptor **2** ($c = 3 \times 10^{-5}$ ML^{-1}) upon gradual addition of DHP ($c = 3 \times 10^{-4}$ ML^{-1}) in CH_3CN.

decreases (Fig. 2) remarkably upon addition of Cu^{2+}. The quenching of emission at 393 nm can be attributed to the paramagnetic Cu^{2+} being brought into the proximity of the quinoline fluorophores when it binds to the receptor **1** and quenches the excited state either by electron or energy transfer process.[15] Binding constant, K_a for the Cu^{2+} complexation is determined[16] by observing the change in fluorescence intensity as a function of Cu^{2+} concentration and the value is $3.0 \times 10^3\ M^{-1}$ (errors <10%). Once the receptor–metal interaction has been established, the anion-binding ability of the Cu^{2+}-complex as a host is analyzed by exciting receptor **2** at 300 nm. Emission maxima of receptor **2** appear at 398 nm and the emission is monitored as a function of increasing the concentration of guest anions. The emission intensity of the Cu^{2+}-complex increases dramatically in presence of DHP (Fig. 3) while a much smaller increase in intensity is observed for other anions such as iodide, bromide, chloride, fluoride, acetate, phosphate, nitrate, benzoate, and (−)-mandelate. Thus the Cu^{2+}-complex (receptor **2**) triggers the selectivity compared to metal-free form receptor **1** toward DHP over the other anions studied. This observation suggests that receptor **2** should be in a quenched state (metal bound to quinoline) for the DHP interaction to modulate the fluorescence.

From the titration experiments, the binding constant (K_a) evaluated[15] of receptor **2** for DHP is found to be $3.33 \times 10^4\ M^{-1}$ (errors <10%). The stoichiometry of the anion complexation is evaluated by the fluorescence titration curve (Fig. 3, inset), the breaking of the titration curve near 1 possibly suggesting a 1:1 (host:guest) binding model between Cu^{2+}-complex and DHP which is further confirmed by Jobs plot diagram (Fig. 4), a maximum at 0.5 mol fraction is observed suggesting a 1:1 complexation.

The fluorescence intensity ratio of the receptor **2** in the presence of different guest anions is displayed in Figure 5. An almost sevenfold increase in emission intensity is clearly observed upon addition of 2.5 equiv of DHP.

Now the observed enhancement in fluorescence of the Cu^{2+}-complex in presence of DHP may be due to the following two reasons. First, and most obvious, is the possibility that the addition of DHP to the Cu^{2+}-complex simply is stripping away the metal from receptor **2** and for that the quinoline fluorophore would no longer need to be quenched and consequently emission intensity gets enhanced upon addition of DHP. It is noteworthy to mention that for receptor **1**, no noticeable change in emission intensity is observed in presence of excess DHP (Fig. 6). So the fact that the emission intensity of receptor **1** in presence of DHP is quenched with progressive addition of Cu^{2+} to near about 90% (Fig. 7) of that found during titration of receptor **1** with Cu^{2+} alone (Fig. 2) contradicts the hypothesis that DHP simply strips away the metal from

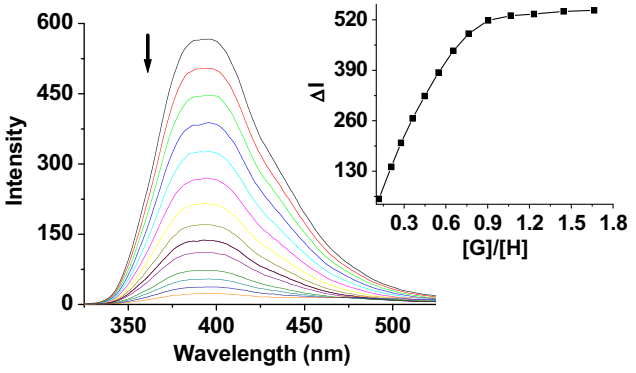


Figure 2. Emission spectra of receptor **1** ($c = 3 \times 10^{-5}\ ML^{-1}$) upon gradual addition of Cu^{2+} ($c = 3 \times 10^{-4}\ ML^{-1}$) in CH_3CN. Inset, titration curve of receptor **1** with Cu^{2+}, where ΔI is the change of emission intensity and G, H represent the concentration of $Cu^{2+}$and receptor **1**, respectively.

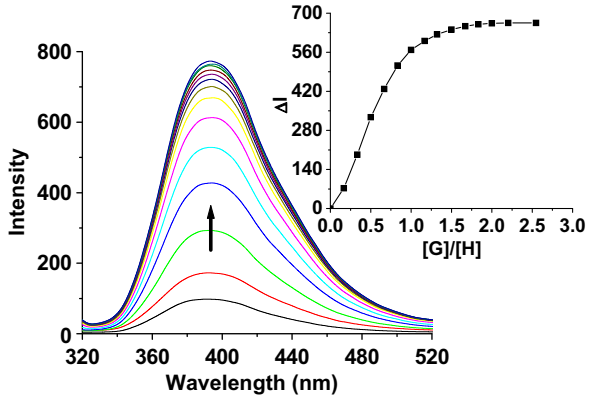


Figure 3. Emission spectra of receptor **2** ($c = 3 \times 10^{-5}\ ML^{-1}$) upon gradual addition of DHP ($c = 3 \times 10^{-4}\ ML^{-1}$) in CH_3CN. Inset, titration curve of receptor **2** with DHP, where ΔI is the change of emission intensity and G, H represent the concentration of DHP and receptor **2**, respectively.

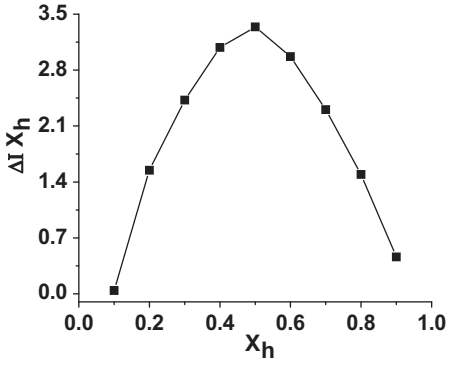


Figure 4. Jobs plot diagram of the Cu^{2+}-complex for DHP determined by fluorescence method in CH_3CN (where X_h is the mole fraction of the host and ΔI is the change of emission intensity).

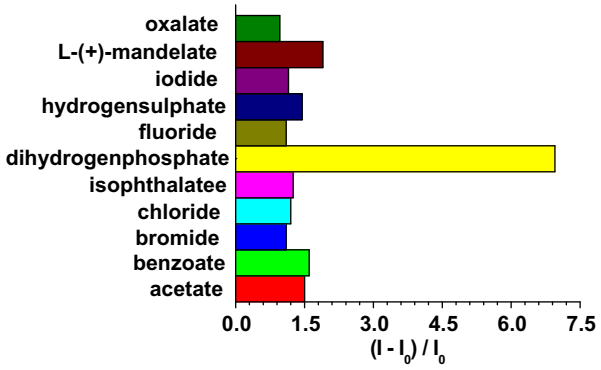


Figure 5. Fluorescence ratio of receptor **2** ($c = 3 \times 10^{-5}\ ML^{-1}$) upon addition of 2.5 equiv tetrabutylammonium salt of a particular anion in CH_3CN.

receptor **2**. Another possibility is that Cu^{2+} still remains co-ordinated with the quinoline moieties so addition of DHP causes binding not only to the metal center but also to the rest binding sites of the fluorophore. In fact, the metal complex formed a suitable cavity for the selective inclusion of DHP possibly due to complementary size and shape of the host and guest. As a consequence of anion co-ordination, the rigidity of the formed complex increases making the non-radiative decay from the excited state less probable; hence, the emission intensity increases.[17] Selective enhancement in emission intensity in presence of DHP is due to increase in

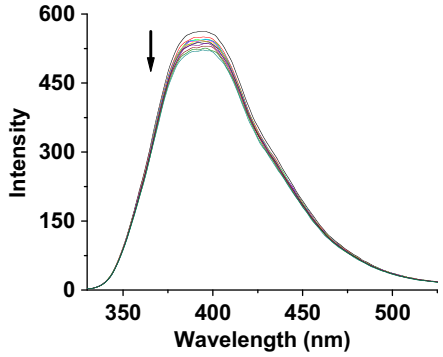


Figure 6. Emission spectra of receptor **1** ($c = 3 \times 10^{-5}$ ML^{-1}) upon addition of 4 equiv of DHP ($c = 3 \times 10^{-4}$ ML^{-1}) in CH_3CN.

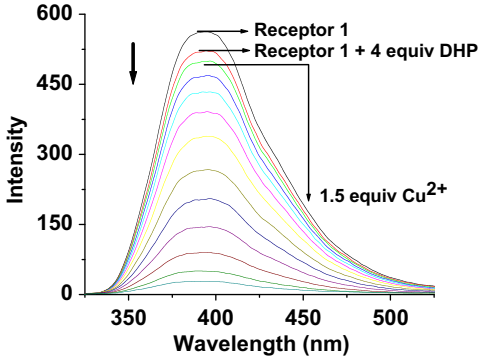


Figure 7. Fluorescence emission spectra of receptor **1**–DHP complex in presence of increasing amount of Cu^{2+} ($c = 3 \times 10^{-4}$ ML^{-1}) in CH_3CN.

electron density of the metal thereby changing the oxidation–reduction potential of the metal. In addition, anion complexation with metal suppresses the extent of electron transfer between quinoline fluorophores and Cu^{2+}, so the responsible mechanism of fluorescence quenching from free metal–receptor substrate to metal–receptor–DHP substrate in the excited state is possibly restricted. Consequently, emission intensity is reaching its maximum value until the metal–receptor complex is possibly converted to a structurally rigid metal–receptor–DHP complex.

In summary, herein we report the successful design and synthesis of a metal ion based chiral fluorescence sensor selective for DHP over the other anions studied. The remarkable sensitivity of the Cu^{2+}-complex toward DHP in fluorescence is a consequence of better encapsulation of DHP inside the open cavity of the metal templated pre-organized macrocyclic receptor. Anion induced fluorescence activation of such metal complexes (in quenched state) have some advantageous features in that the guest anion would no longer need to possess electron donor or acceptor properties, but simply activate the coupling between a metal quencher and fluorophore in a co-operative manner and consequently the enhancement in fluorescence is expected.

Acknowledgments

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Supplementary data

Supplementary data (^{1}H NMR, ^{13}C NMR and HRMS spectra of receptors **1** and **2** along with other intermediates, general procedure of titrations, detailed experimental procedures, and detailed synthetic methods) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.034.

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