Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 47 (2006) 8165–8169
Tetrahedron Letters

Colorimetric and fluorescence sensing of anions using thiourea based coumarin receptors

Kumaresh Ghosh* and Suman Adhikari

Department of Chemistry, University of Kalyani, Kalyani, Nadia 741 235, India

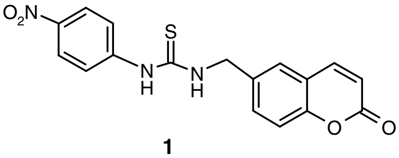
Received 21 June 2006; revised 28 August 2006; accepted 7 September 2006
Available online 4 October 2006

Abstract—Thiourea-containing coumarins **1**, **2** have been designed and synthesized via reaction of 6-aminomethylcoumarin and the corresponding isothiocyanates. Their anion-binding ability has been examined using UV–vis, fluorescence and ^{1}H NMR. The anion recognition takes place through charge neutral thiourea receptor sites with concomitant fluorescence quenching of the coumarin moiety with **1** showing a strong binding to $C_6H_5COO^-$ over F^- with a distinct change in color.

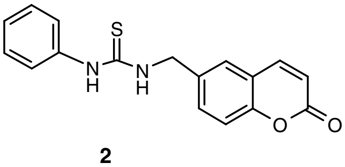
The design of host molecules that can recognize and sense anions selectively through visible, electrochemical and optical responses has received considerable interest in recent years because of the important roles played by the anions in biological, industrial, and environmental processes.[1] Molecules that possess functional groups such as amides,[2] ureas/thioureas,[3] guanidinium[4] and ammonium[5] derivatives have proven to be particularly effective in this regard as they are able to bind anions using directional hydrogen bonding interactions. The attachment of such functional groups with a suitable chromophoric part either covalently or intermolecularly provides a complete receptor that can intimate binding information either by a color change, fluorescence or both. Several reviews on anion binding in this regard using luminescent sensors have appeared.[1b,6] Despite the significant development in this domain, the search for new luminescent sensors with structural simplicity and easy synthesis has recently been of keen interest in molecular recognition research.

In pursuit of developing anion receptors during the course of our work on molecular recognition,[7] we present coumarin-based chemosensors **1** and **2** for the selective recognition of anions employing the criteria of PET sensing using the '*fluorophore-spacer-receptor*' model developed by de Silva for the detection of cations.[8] Although several PET sensors for anions are known,[9] no such thiourea-linked coumarin systems, employing neutral anion receptors, have been reported that exhibit an ideal PET behavior and color changes as signaling events, detectable by the naked eye, upon binding of anions.

Chemosensors **1** and **2** were easily synthesized in good yields from readily available starting materials, following Scheme 1. 6-Aminomethylcoumarin **7**, was synthesized via a series of reactions on 4-hydroxybenzaldehyde as indicated in Scheme 1, was reacted in dry THF (containing few drops of dry DMF due to insolubility) at room temperature under an inert atmosphere with an equimolar amount of isothiocyanate to afford **1** or **2** as pale



1

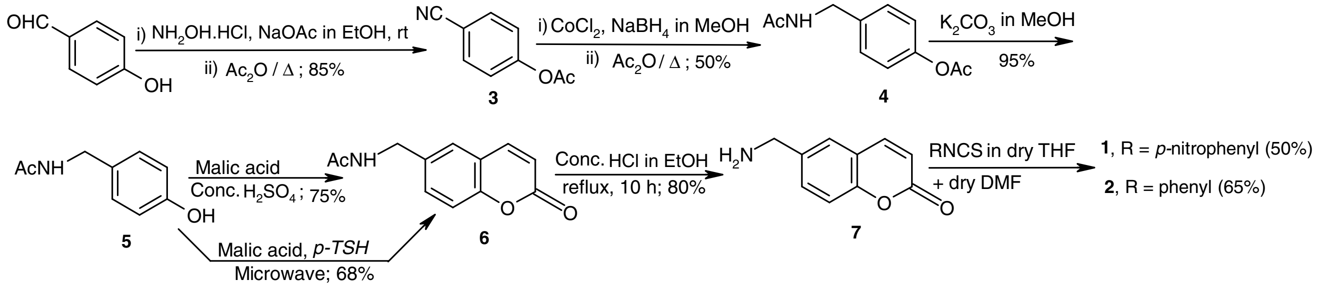


2

Keywords: Anion binding; Colorimetric; Selective binding; Fluorescence quenching; Fluoride binding; Benzoate binding.

* Corresponding author. Tel.: +91 33 25828282/306; fax: +91 33 25828282; e-mail: ghosh_k2003@yahoo.co.in

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.09.035



Scheme 1. Syntheses of receptors **1** and **2**.

yellow and white solids, respectively. The crude products were purified by column chromatography and were analyzed by conventional methods.[10] It is also worth noting that the amide derivative **6** was successfully synthesized in 68% yield under solvent-free conditions using microwave irradiation.

The anion-binding properties of **1** and **2** were investigated by observing the changes in their fluorescence emission, absorption spectra in CH_3CN and by ^1H NMR in $CDCl_3$. The UV–vis experiments were carried out in CH_3CN (containing 0.08% DMSO for homogeneity of the solution). The titration of **1** ($c = 5.63 \times 10^{-5}$ M), which exhibits a broad strong absorption band at 330 nm due to the coumarin moiety, was carried out with anions such as tetrabutylammonium fluoride, bromide, iodide, hydrogen sulfate and benzoate. Upon the addition of fluoride, the intensity of the absorption peak at 330 nm was remarkably reduced with a simultaneous growth of a new peak at 455 nm (Fig. 1) and the almost colorless solution turned yellow brown (Fig. 4c). In the case of benzoate, the absorption peak at 330 nm was shifted to 348 nm ($\Delta\lambda = 18$ nm) with a concomitant decrease in the intensity of the absorption (Fig. 2) and the solution turned light green in color (Fig. 4b). The presence of isobestic points during titration with both F^- and $C_6H_5COO^-$ revealed the formation of 1:1 complexes. No significant change in absorption or a noticeable color change was observed for other anions such as Br^-, I^- and HSO_4^-.

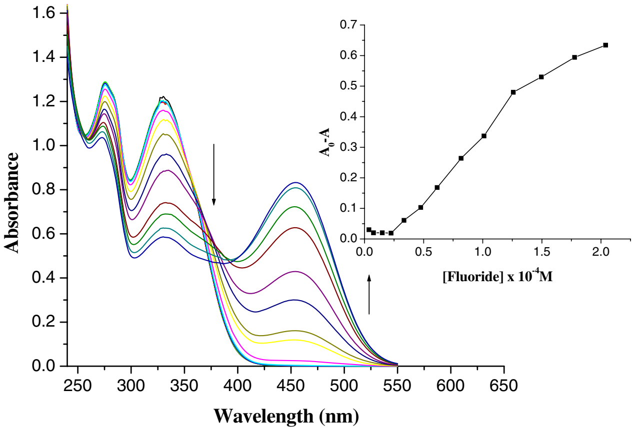


Figure 1. Changes in UV–vis spectra for **1** ($c = 5.63 \times 10^{-5}$ M) in CH_3CN upon the addition of tetrabutylammonium fluoride. Inset: differences in absorbances versus concentration of fluoride.

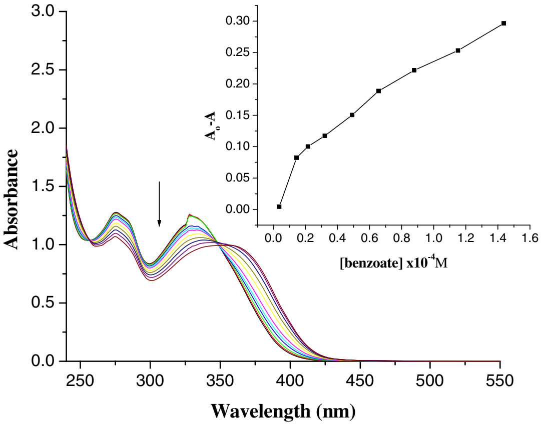


Figure 2. Changes in UV–vis spectra for **1** ($c = 5.63 \times 10^{-5}$ M) in CH_3CN upon the addition of tetrabutylammonium benzoate. Inset: differences in absorbances versus concentration of benzoate.

The study of the fluorescence of **1** also showed a similar trend. The fluorescence emission spectra of **1** ($c = 4.51 \times 10^{-4}$ M) consisted of a broad band at 420 nm when excited at 380 nm (red edge excitation). With the addition of monodentate anions such as $C_6H_5COO^-$ and F^- as $N(C_4H_9)_4^+$ salts, the emissions were ca. 88 and 99.6% '*switched off*' or quenched, due to the formation of anion-receptor hydrogen-bonded complexes (Fig. 3). During the titration there were no other observable changes in the emission spectra (Figs. 5 and 6). Upon the addition of HSO_4^-, the emission spectra were hardly affected suggesting its weak interaction with the receptor site. The addition of other spherical ions such as Br^-, I^-, etc did not cause any significant quenching of the emission, thereby ruling out quenching by the heavy atom effect. The Stern–Volmer plot (Fig. 7) illustrates the quenching process.

The analogous thiourea receptor **2** was evaluated to establish the role of the acidity of the thiourea protons in binding with the putative anions. The addition of F^-, $C_6H_5COO^-$, Br^-, I^- and HSO_4^- as tetrabutylammonium salts to a solution of **2** in CH_3CN (containing 0.08% DMSO) resulted in a minor change in the UV–vis spectrum of receptor **2** and did not result in any new peaks at higher wavelengths or color changes of the solution. The fluorescence changes of **2** upon addition of F^- and $C_6H_5COO^-$ were significant, but smaller compared to **1**. The fluorescence emissions at 369 nm ($\lambda_{ex} = 320$ nm) were ca. 12% and 19% '*switched*