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A novel colorimetric and fluorescence anion sensor with a urea group as binding site and a coumarin group as signal unit

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ABSTRACT

A novel colorimetric and fluorescent anion sensor based on urea substituted with a coumarin moiety and a pendant phenylazo unit was synthesized and evaluated according to the binding site-signalling subunit approach. The azo group was exploited as the chromogene, the urea moiety providing the anion binding site and the coumarin system was responsible for fluorescence. As such, the dye enabled visual detection of acetate ion in DMSO (color change light yellow to red) without resorting to spectroscopic instrumentation. More importantly, the sensor displayed significant fluorescence enhancement response to anions such as acetate, because of complex formation.

1. Introduction

In recent years, considerable attention has attended the development of colorimetric and fluorescent chemosensors for sensing anionic species [1–5]. Commonly, such sensors offer many advantages such as high sensitivity and simplicity, especially for real-time and on-line analysis of analytes [6,7]. Anions are widely found in the environmental and biological systems, as exemplified by fluoride, which is commonly used in dental care applications and exhibits inhibition of certain enzyme functions [8]; however, overexposure to fluoride can also result in the most widespread side effect of fluoride (*fluorosis*) [9] which induces nephrotoxic changes in both humans and animals and leads to urolithiasis [10]. Acetate ion has been found to be a possible tracer for malignancies and has been extensively investigated in prostate cancer and its metastases [11]. Accordingly, the determination of anionic species and their concentration is of interest in many areas, including food processing, environmental evaluation and clinic analysis [12–14], in which context, the development a novel colorimetric and fluorescent chemosensor for the rapid and convenient detection of biologically important anions such as fluoride and acetate [15–17] is required.

Hitherto, numerous colorimetric and/or fluorescent chemosensors for anions, cations or neutral molecules have been reported; however, almost all of these are designed to rely upon the same principles namely, that the functional moiety is covalently (binding site-signalling subunit approach) [18–21] or non-covalently (displacement approach) [22,23] linked to the signal moiety (eg chromogene, electrochemical group, fluorescent group). The functional moiety is responsible for binding guests and the signalling moiety acts as a signal transducer, that converts binding events into an optical signal expressed as a change in either color, electrochemistry or fluorescence [24]. Mechanisms that involve the photophysics of fluorogenic anion sensors, include photoinduced electron transfer (PET) [25], photoinduced charge transfer (PCT) [26] and excimer/exciplex formation [27]. In general, a PET fluorescent sensor displays an 'ON–OFF' response towards anionic guests [28] and a fluorescent sensor based on PCT or excimer/exciplex formation shows a ratiometric response towards anions, which can quantify the analyte concentration by using the ratio of intensities [29,30]. However, despite many advantages, excimer/exciplex formation or PCT-based fluorogenic sensors for anions are not common in the literature.

This paper concerns a novel colorimetric and fluorescent anion sensor **1** that comprises a urea group (anion binding site) coupled to with a 6-(phenylazo)-coumarin group (chromogenic and fluorescence unit). The behaviour of this new compound towards anions eg acetate, was investigated by UV–vis and fluorescence spectroscopy in DMSO.

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2. Experimental section

2.1. Apparatus

^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elementar vario EL. UV–vis spectra and fluorescence spectra were recorded on a Shimadzu UV2450 Spectrophotometer and a Shimadzu RF-5301PC fluorimeter, respectively, at 298.2 ± 0.1 K.

2.2. Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetra-n-butylammonium (TBA) salts, which were purchased from Chemical Company Ltd., stored in a vacuum desiccator containing self-indicating silica and dried fully before use. DMSO was dried with CaH_2 and then distilled under reduced pressure.

2.3. General method

All titration experiments were carried out at 298.2 K, unless otherwise mentioned. UV–vis spectra and fluorescent spectra were measured using a Shimadzu UV2450 Spectrophotometer and a Shimadzu RF-5301PC fluorimeter, respectively. A 5.0×10^{-5} M solution of the compound 1 in dried DMSO and solutions of 0.10 M tetrabutylammonium (TBA) salts of the respective anions were prepared in dried DMSO and were stored under a dry atmosphere. These solutions were used for all spectroscopic studies after appropriate dilution. Then, a given amount of the solution of 1 was added to the quartz cuvette and the increased amount of anions tested (0.1 M in DMSO-*d*6) was added to the solution. The absorbance/emission spectra were then recorded immediately. The slit width used for fluorescence measurements was 5 mm.

2.4. Synthesis

2.4.1. 5-Phenylazo-salicylaldehyde (**2**)

The route to **1** is shown in Figs. 1 and **2** was prepared according to the reported method [21,31]. To a solution of aniline (5 ml; 0.05 mol) in a small quantity of water was slowly added 6 ml of 37% aq HCl solution at 0–5 °C with stirring. 20 ml of 20% aq $NaNO_2$ solution was added to the mixture and the resulting solution was stirred for 1 h, affording a bright yellow solution. salicylaldehyde (5 ml; 0.05 ml) was dissolved in a solution comprising 18 g $NaCO_3$ and 150 ml H_2O and the resulting solution of salicylaldehyde was added dropwise to the bright yellow coloured solution over 1 h. After stirring for 4 h, the reaction mixture was neutralized with HCl, the brown crude solid was filtered and recrystallized from ethanol to afford a pure yellow product. Mp: 120 °C (Fig. 2).

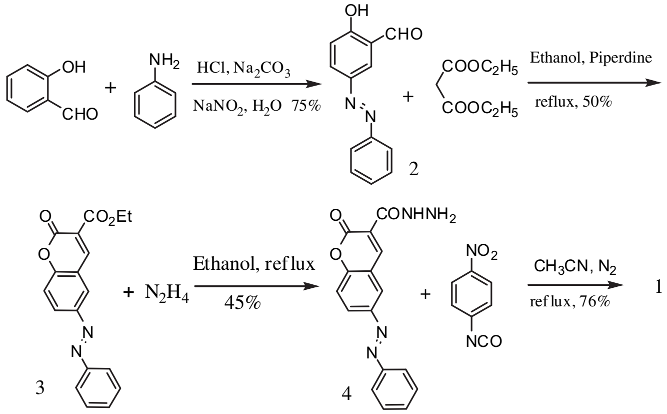

Fig. 1. Synthesis of *N*-(6-phenylazo-coumarin-3- formyl)-*N*′-4-nitrophenylurea (**1**).

2.4.2. 6-Phenylazo-coumarin-3-formylethylester (**3**)

3 was synthesized according to the literature [32]. In a 250 ml round-bottomed flask was added **3** (4.52 g, 20.0 mmol), **5** (3.2 g, 20.0 mmol), a catalytic amount of piperdine and ethanol (140 mL). The resulting mixture was heated to reflux under magnetic stirring for 6 h after which the solution was cooled to room temperature over 10 h and the brown precipitate which appeared was collected by filtration, washed with ethanol and recrystallized from ethanol to give the pure brown coloured product (3.24 g). Yield = 50%.

2.4.3. 6-Phenylazo-coumarin-3- formylhydrazine (**4**)

4 (0.644 g, 2 mmol) was dissolved in ethanol (40 ml), to which was added hydrazine in ethanol (5 ml) dropwise and the ensuing mixture was stirred at reflux for 4 h. The reaction solution was cooled to room temperature and the brown precipitate was filtered, washed with ethanol and used in the next step without further purification.

2.4.4. N-(6-Phenylazo-coumarin-3-formyl)-N′-4-(nitrophenyl)urea (**1**)

1 was prepared according to the literature procedure [14,33]. **2** (0.31 g, 1.0 mmol) was dissolved in hot CH_3CN (25 mL) to which was then added, dropwise, 4-nitrophenylisocyanate (0.16 g, 1.0 mmol) and the ensuing mixture was stirred under an inert atmosphere at reflux for 5 h. The reaction mixture was cooled to room temperature and the brown precipitate formed was filtered and washed with CH_3CN, yield = 0.36 g, 76%. ^{1}H NMR (400 MHz; DMSO-d_6; Me_4Si): δ_H 11.07 (s, –NH, 1H), 10.98 (s, –NH, 1H), 9.71 (s, –NH, 1H), 8.65 (s, Ar–H, 1H), 8.41 (s, Ar–H, 1H), 8.24 (d, $J = 9.2$ Hz, Ar–H, 2H), 8.01 (d, $J = 9.2$ Hz, Ar–H, 2H), 7.88 (d, $J = 7.6$ Hz, Ar–H, 2H), 7.83 (m, Ar–H, 1H), 7.62 (m, Ar–H, 2H), 7.56 (d, $J = 7.2$ Hz, Ar–H, 1H), 7.10 (d, $J = 8$ Hz, Ar–H, 1H); ESI-mass: m/z calcd. for $C_{23}H_{16}N_6O_6$ [M] 472.41, found: 473.13; Elemental analysis calcd for $C_{23}H_{16}N_6O_6$: C 58.48%, H 3.41%, N 17.79%, found: C 58.21%, H 3.32%, N 18.01%.

3. Results and discussion

Coumarin derivatives have been extensively investigated for electronic and photonic applications, such as fluorescence probes, charge-transfer agents, solar energy collectors, and nonlinear optical properties due to their inherent photochemical characteristics, reasonable stability, good solubility and their relative ease of synthesis [4,34–36]. A great number of fluorescent probes based on coumarin derivatives for various transition-metal ions have been developed in recent years [37,38], however, fluorescent anion sensors derived from coumarins have been scarcely reported [39]. In addition, the urea group has been proven to be an excellent hydrogen bonding donor exploited in design and synthesis of anion sensors [40–42]. Bearing these in mind, we

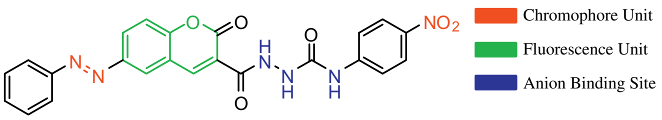

Fig. 2. Structure of the sensor 1.

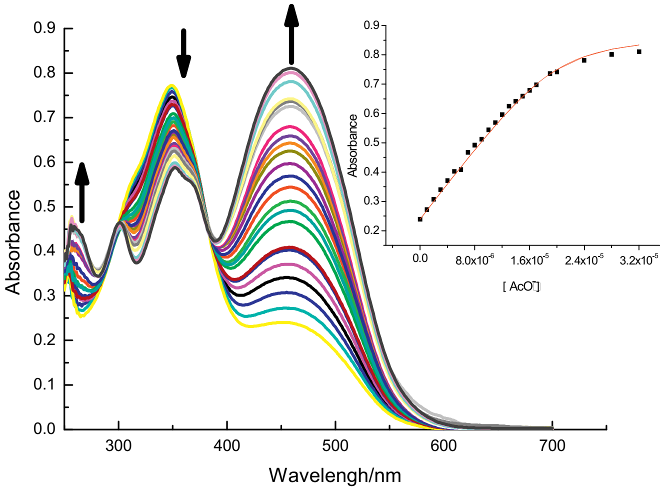

Fig. 3. Variation in the absorption spectra of 1 (2×10^{-5} M) in DMSO with increasing concentrations of AcO^-. Inset: The titration curves for AcO^- show the 1:1 stoichiometry.

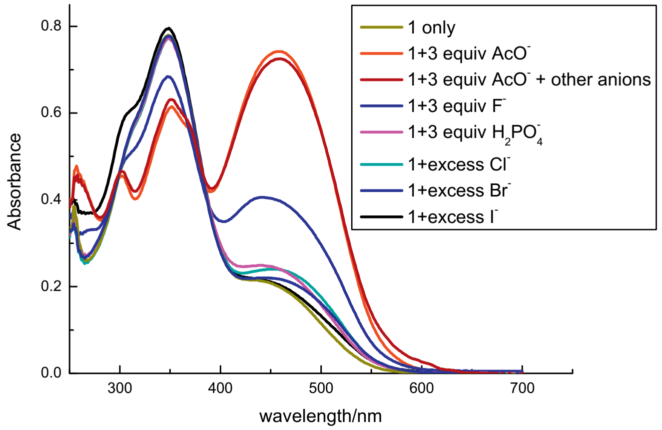

Fig. 5. Variation in the absorption spectra of 1 (2×10^{-5} M) induced by different anions in DMSO.

introduced an azo moiety (a chromophore unit) to the coumarin derivative (a fluorescence unit) and thus the intermediate (3-substituted-6-(phenylazo)-coumarin) was obtained. Then, the colorimetric and fluorescent anion sensor 1 was successfully prepared through coupling the urea group with the intermediate.

Firstly, the anion binding and sensing ability of 1 was investigated in detail in DMSO. Fig. 3 demonstrates the changes in the absorption spectrum of 1 (2×10^{-5} M) in DMSO in the absence and the presence of AcO^-. The free compound 1 exhibited one main band at 348 nm with a shoulder band at 458 nm, which could be attributed to π–π^* transition of the azo moiety. As soon as the acetate ion was added at room temperature, the absorption maximum of 1 at 348 nm decreased gradually whereas the absorption at 259 nm and a new absorption maximum at 458 nm increased. The color changes of sensor 1 were also observed by eye simultaneously from light yellow to red in presence of AcO^- (see Fig. 4). Additionally there were two well-defined isosbestic points at 301 nm and 385 nm, respectively, indicating that a stable complex having a certain stoichiometric ratio between 1 and AcO^- formed in solution. The titration profile of 1 with AcO^- shown in inset of Fig. 3 demonstrated 1 equiv of AcO^- reacting with 1 equiv of 1 could quickly reached an equilibrium, indicating the formation of a 1/AcO^- complex of 1:1 stoichiometry.

The sensor 1 gave a similar spectral response towards F^- ion. The presence of the other anions (Cl^-, Br^- and I^-) with weak basicity resulted in negligible changes in UV–vis spectra of 1, which could be seen from Fig. 5. Surprisingly spectral changes were induced by addition of $H_2PO_4^-$ ions, which possibly resulted from an uncertain stoichiometric ratio between 1 and $H_2PO_4^-$ (see Fig. 6). Fig. 4 displayed color changes of 1 (2×10^{-5} M, DMSO) in presence of the different anions tested. Obviously, addition of AcO^-, F^- and $H_2PO_4^-$ ions induced similar color changes from light yellow to red and no significant color changes were seen when Cl^-, Br^- and I^- ions were added, which was consistent with results observed from spectral titrations. In particular, the selectivity for acetate anion over a complex background of potentially competing species was of interest and was thus evaluated (see Fig. 5). Obviously, the spectral changes of 1 resulting from AcO^- were influenced slightly by the subsequent addition of miscellaneous anions.

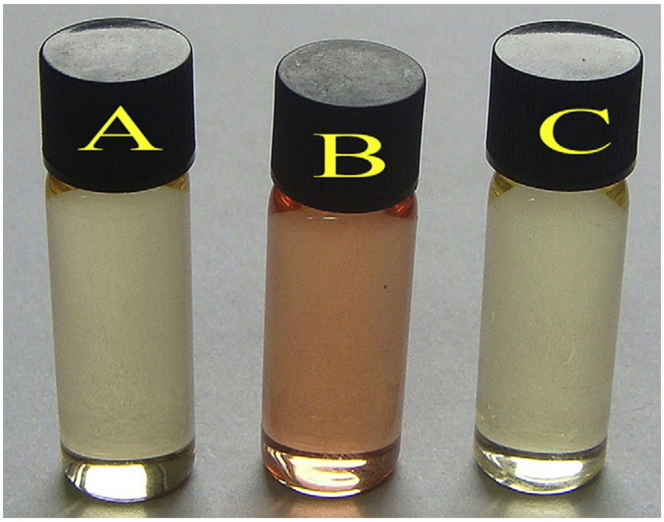

Fig. 4. Color changes of the sensor 1 (2×10^{-5} M) in absence and presence of different anions (A: the free 1; B: 1 + 5 equiv AcO^-, F^- or $H_2PO_4^-$; C: 1 + excessive equiv Cl^-, Br^- or I^-).

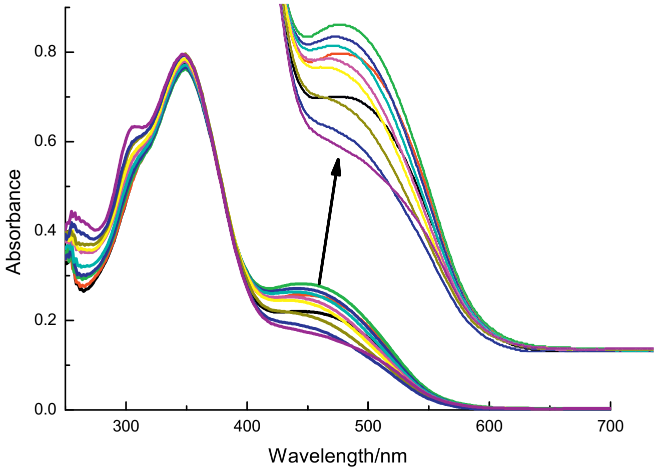

Fig. 6. Variation in the absorption spectra of 1 (2×10^{-5} M) in DMSO with increasing concentrations of $H_2PO_4^-$.

Table 1
Equilibrium constants (K_s mol^{-1} L) of the sensor 1 with anions in DMSO at 298.2 ± 0.1 K.

Anions[a]	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
K_s (M^{-1})	9.87×10^5	8.29×10^3	_[b]	_[c]	_	_
R^2	0.996	0.994	_	_	_	_

[a] All the anions were added in the form of tetrabutylammonium salts.
[b] The titration profile was not suitable for determination of the equilibrium constant.
[c] The equilibrium constants could not be determined due to slight spectral changes.

The equilibrium constants (K_s) of 1 with different anions were determined by nonlinear fitting analyses of the titration curves according to the Eq. (1), 1:1 host–guest complexation [43].

$$A = A_0 + \frac{(A_{\lim} - A)\left\{c_H + c_G + 1/K_s - \left[(c_H + c_G + 1/K_s)^2 - 4c_Hc_G\right]^{1/2}\right\}}{2c_H} \quad (1)$$

Where, c_G and c_H are the concentration of guest and host, respectively and A is the intensity of absorbance at a certain concentration of host and guest. A_0 is the intensity of absorbance of host only and $A_{\lim}$ is the maximum intensity of absorbance of host when guest is added. K_s is the equilibrium constant. The equilibrium constant (K_s) could be determined from the plot of A against [Anion] and the high value (R^2) of the plots (Table 1) confirmed a 1:1 complex formation between 1 and anions. This further corroborates 1:1 complex formation that we have concluded based on the spectral titration profile.

The selectivity of the host for a specific anion of interest could be rationalized on the basis of not only the guest basicity but also complementary shape between the host and the anionic guests [44]. In particular, multiple hydrogen-bonding interactions were necessary in high-affinity anion binding sites. Consequently, it was reasonable that the sensor 1 showed a high selectivity for acetate ion among the other anions tested such as F^- and $H_2PO_4^-$ (see Fig. 7). The proposed binding mode of the host 1 with AcO^- ion in solution was described in Fig. 7, which corresponds with observations from previous studies [45].

The fluorescence properties of 1 upon binding with anions were studied in DMSO. The sensor 1 gave a weak emission at 389 nm with a tail at 447 nm (Fig. 8). When AcO^- ion was added, a hypsochromic shift (~10 nm) was observed for the 389 nm band and synchronously there were significant increases in fluorescence intensity. Moreover, the tail emission band at 447 nm was fully quenched. The proposed mechanism for the enhancement was based upon binding-induced conformational restriction of a fluorophore [46]. In solution, the N–N bond of 1 could freely vibrate and rotate, which enabled vibrational and rotational relaxation modes of the non-radiative decay. As a consequence of the anion coordination, the rigidity of the formed complex increased rendering the non-radiative decay from the excited state less probable; consequently, the emission intensity increased (see Fig. 8).

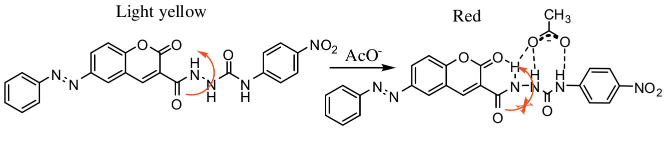

Fig. 7. The proposed host–guest interaction mode in the solution.

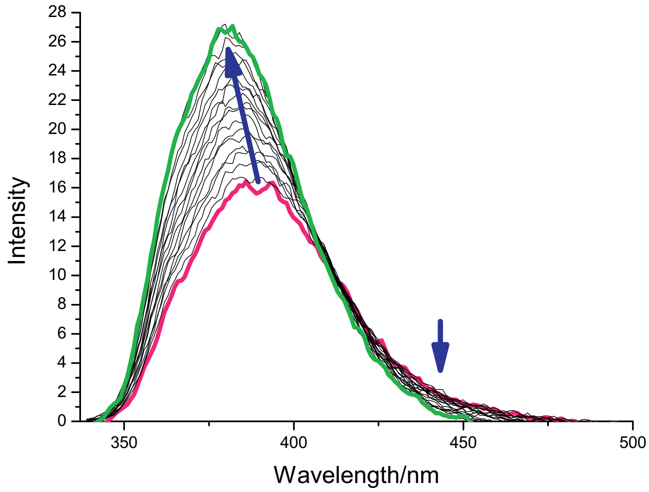

Fig. 8. Variation in the emission spectra of 1 (2×10^{-5} M) in DMSO with increasing concentrations of AcO^- (λ_{exc} = 382 nm).

4. Conclusion

In summary, a colorimetric and turn-on fluorescence anion sensor was designed and synthesized according to the binding site-signalling subunit approach. The urea group was exploited as an anion binding site in 1 and 6-(phenylazo)-coumarin moiety acted as both a fluorescence unit and a chromophore unit. In addition, the fluorescence enhancement in the emission spectra of 1 were observed due to anion-induced conformational restriction.

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