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Fluorescence anion sensors based on combination of conformational restriction and photo-induced electron transfer

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ABSTRACT

Six fluorescence and colorimetric sensors (1–6) were designed and synthesized through a facile method. These compounds, whose structures were characterized by ¹H NMR, elemental analyses and MS, could be easily prepared by simple synthesis method. In these sensor molecules, azo group and conjugated di-benzene unit acted as a chromophore and a fluorophore; respectively, and phenol moieties are anion binding sites. In dry DMSO solution, significant red shifts in UV–vis spectra with visible color changes were observed when the sensors were exposed to anions with strong base. Particularly, the simple compounds gave interesting fluorescence changes upon presence of anions, which probably resulted from electronic effects of the substituent. The sensors (1–3) with the nitro group exhibited ‘turn-on’ fluorescence responses to anions due to conformational restriction and 4–6 with absence of –NO₂ group showed ‘turn-off’ fluorescence responses to anion owing to photo-induced electron transfer.

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1. Introduction

Considering the important roles that anion play in the areas of medicinal, biochemistry, and environmental chemistry, the development of chemosensors for the selective detection of biologically important anions is of great importance [1–3]. For example, acetate and dicarboxylates are involved in numerous metabolic processes [4]. Organic decomposition in marine sediments can be indicated frequently by acetate production and oxidation rate [5]. In addition, fluoride ion is used to prevent dental caries and treat osteoporosis and also has its detrimental (e.g., fluorosis) roles [6]. Accordingly, recognition and detection of the biologically important anions is still an urgent task for chemistry researchers.

With a view to binding sites, those are classified basically into electrostatic interactions [7,8], formation of hydrogen bonds [1–3,9,10], and interactions with metal [11] and so on. However, anion chemosensors with hydrogen bonding donors as anion binding sites have high selectivity for anions owing to that H-bonds are directional, a feature which allows the design of receptors having ability to differentiate between anions with different geometries and hydrogen-bonding requirements [12]. In general, hydrogen-bonding groups widely used in design of anion sensors are (thio) ureas [13–15], calyx [4] pyrroles [16],

pyrrole subunit [17], amides [18] and so on. Recently, more and more anion chemosensors with phenolic hydroxyl group are also reported. For example, Shao and the co-workers [19–21] reported a series of anion colorimetric sensors based on substituted-salicylaldehyde derivatives and some of them could work even in aqueous media, indicating that phenol moiety is a strong hydrogen bond donor. Jose et al. [22] reported two ruthenium (II) polypyridyl complexes with pendant phenol/catechol functionality that act as colorimetric sensors for fluoride ions. However, anion binding properties of the sensor bearing phenol moiety are often studied by UV–vis spectral titrations. Therefore, it is necessary that the fluorescence responses of new compounds derived from phenol to anions should be studied and shown.

As far as signaling mechanisms of fluorescent sensors are concerned, there are photo-induced charge transfer (PCT) [23], photo-induced electron transfer (PET) [24], binding-induced rigidity changes [25] and so on. However, most of the fluorescence sensors reported previously was only based on one of these signaling mechanisms [23–25]. We reported that one sensor displays positive and negative fluorescence responses to anions with different basicity due to PET and binding-induced conformational restriction, respectively [26]. Mello and co-workers [27] reported fluorescent chemosensors for Ca²⁺ with the combination of conformational restriction and induced charge transfer as signaling mechanism. With these in mind, we designed and synthesized six fluorescence host molecules (1–6) with phenol moiety as anion binding sites. These fluorescence sensors were based on the combination of

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conformational restriction and photo-induced electron transfer and showed different fluorescent responses.

2. Experimental

2.1. Apparatus and materials

^1H NMR spectra were obtained on a Varian UNITY Plus-300 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elemental vario EL. UV-vis spectra were recorded on a TU-1810 Spectrophotometer equipped with temperature control device made by Beijing Puxi Tongyong apparatus company with quartz cuvette (path length=1 cm), and fluorescence spectra were recorded on a F96 Spectrophotometer equipped with temperature control device made by Shanghai Lengguang Technology Co., Ltd. The width of the slits is 10 nm.

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

2.2. General method

All titration experiments were carried out at 298.2 K, unless otherwise mentioned. A 5.0×10^{-4} M solution of the host compounds in dried DMSO and solutions of the respective anions were prepared in dried DMSO and stored under a dry atmosphere. These solutions were used for all spectroscopic studies after appropriate dilution. Then, given amount of the solution of sensors was added to the quartz cuvette and the increased amount of anions tested (0.1 M in DMSO) was added to the solution above-mentioned, whose absorbance/emission spectra were tested immediately.

^1H NMR titration experiments were carried out in the DMSO- d_6 solution (TMS as an internal standard). A 1.0×10^{-2} M solution of the host compounds in DMSO- d_6 was prepared. Then, the increased amount of fluoride anion solution (1.0 M in DMSO- d_6) was added to the solution above-mentioned and ^1H NMR of the anion-sensor system was tested.

2.3. Synthesis of sensor molecules

The two starting materials: N-(2-hydroxy-5-substituted-dibenzophenone)-1,2-diaminobenzene (7) [28] and 5-(4-substituted-phenylazo)-salicylaldehyde (8) [21] were synthesized according to the reported methods. Synthetic routes for the compounds 1–6 were showed in Scheme 1. To a solution of the compound 7 (1 mmol) in ethanol (20 mL) was added the compound 8 (1 mmol). The mixture was stirred and heated to reflux for 2 h. Then the reaction mixture was cooled to room temperature and the precipitates formed. The pure compounds were obtained by filtering and washing with ethanol.

The sensor 1: 0.42 g, yield=73%. ^1H NMR(DMSO- d_6 , 300 MHz) δ : 14.82 (s, 1H, OH), 13.94 (s, 1H, OH), 9.99 (s, 1H, N=CH), 9.15 (d, $J=14.1$, 1H, ArH), 8.38 (m, 3H, ArH), 8.04 (m, 2H, ArH), 7.76 (t, 1H, ArH), 7.50 (m, 3H, ArH), 7.36 (m, 1H, ArH), 7.14 (m, 5H, ArH), 6.83 (m, 3H, ArH); ESI-mass: $\text{C}_{32}\text{H}_{22}\text{ClN}_5\text{O}_4$, $m/z=576.30$ $[\text{M}]^+$; Anal. for ($\text{C}_{32}\text{H}_{22}\text{ClN}_5\text{O}_4$), Calc. C, 66.73; H, 3.85; N, 12.16; Found: C, 66.22; H, 3.67; N, 12.69.

The sensor 2: 0.49 g, yield=79%. ^1H NMR (DMSO- d_6 , 300 MHz) δ : 14.81 (s, 1H, OH), 13.96 (s, 1H, OH), 10.02 (s, 1H, N=CH), 9.15

(d, $J=12.3$, 1H, ArH), 8.42 (m, 3H, ArH), 8.04 (m, 3H, ArH), 7.76 (m, 1H, ArH), 7.54 (m, 3H, ArH), 7.14 (m, 7H, ArH), 6.74 (m, 1H, ArH); ESI-mass: $\text{C}_{32}\text{H}_{22}\text{BrN}_5\text{O}_4$, $m/z=618.0$ $[\text{M}]^-$; Anal. for ($\text{C}_{32}\text{H}_{22}\text{BrN}_5\text{O}_4$), Calc. C, 61.95; H, 3.57; N, 11.29; Found: C, 61.42; H, 3.87; N, 12.56.

The sensor 3: 0.43 g, yield=77%. ^1H NMR(DMSO- d_6 , 300 MHz) δ : 14.28 (s, 1H, OH), 13.67 (s, 1H, OH), 9.12 (s, 1H, N=CH), 8.38 (m, 3H, ArH), 8.04 (m, 3H, ArH), 7.76 (s, 1H, ArH), 7.47 (m, 2H, ArH), 7.33 (m, 2H, ArH), 7.04 (m, 6H, ArH), 6.67 (m, 2H, ArH), 2.05 (d, 3H, CH_3); ESI-mass: $\text{C}_{33}\text{H}_{25}\text{N}_5\text{O}_4$, $m/z=556.2$ $[\text{M}]^+$; Anal. for ($\text{C}_{33}\text{H}_{25}\text{N}_5\text{O}_4$), Calc. C, 71.34; H, 4.54; N, 12.61; Found: C, 71.12; H, 4.88; N, 12.15.

The sensor 4 reported previously [29]: 0.42 g, yield=77%. ^1H NMR (DMSO- d_6 , 300 MHz) δ : 14.47 (s, 1H, OH), 13.98 (s, 1H, OH), 9.13 (s, 1H, N=CH), 8.27 (d, $J=13.5$, 1H, ArH), 7.97 (m, 1H, ArH), 7.86 (m, 2H, ArH), 7.74 (s, 1H, ArH), 7.55 (m, 6H, ArH), 7.36 (s, 1H, ArH), 7.12 (m, 5H, ArH), 6.85 (m, 3H, ArH); ESI-mass: $\text{C}_{32}\text{H}_{23}\text{ClN}_4\text{O}_2$, $m/z=529.1$ $[\text{M}]^-$; Anal. for ($\text{C}_{32}\text{H}_{23}\text{ClN}_4\text{O}_2$), Calc. C, 72.38; H, 4.37; N, 10.55; Found: C, 72.62; H, 4.85; N, 10.93.

The sensor 5: 0.44 g, yield=76%. ^1H NMR (DMSO- d_6 , 300 MHz) δ : 14.45 (s, 1H, OH), 13.99 (s, 1H, OH), 9.11 (d, $J=9.11$ Hz, 1H, N=CH), 8.27 (d, $J=12.6$ Hz, 1H, ArH), 7.98 (m, 1H, ArH), 7.86 (m, 2H, ArH), 7.75 (d, $J=4.5$ Hz 1H, ArH), 7.55 (m, 6H, ArH), 7.36 (s, 1H, ArH), 7.26 (d, $J=5.1$ Hz 1H, ArH), 7.12 (m, 5H, ArH), 6.96 (s, 1H, ArH), 6.74 (m, 1H, ArH); ESI-mass: $\text{C}_{32}\text{H}_{23}\text{BrN}_4\text{O}_2$, $m/z=388.10$ $[\text{M}]^-$; Anal. for ($\text{C}_{32}\text{H}_{23}\text{BrN}_4\text{O}_2$), Calc. C, 66.79; H, 4.03; N, 9.74; Found: C, 66.26; H, 4.45; N, 9.56.

The sensor 6: 0.38 g, yield=75%. ^1H NMR(DMSO- d_6 , 300 MHz) δ : 13.97 (s, 1H, OH), 13.70 (s, 1H, OH), 9.09 (s, 1H, N=CH), 8.26 (d, $J=13.8$, 1H, ArH), 7.98 (m, 1H, ArH), 7.85 (s, 2H, ArH), 7.75 (s, 1H, ArH), 7.53 (m, 5H, ArH), 7.33 (t, 2H, ArH), 7.10 (m, 4H, ArH), 6.93 (m, 2H, ArH), 6.74 (m, 2H, ArH), 2.04 (d, 3H, CH_3); ESI-mass: $\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_2$, $m/z=511.3$ $[\text{M}]^+$; Anal. for ($\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_2$), Calc. C, 77.63; H, 5.13; N, 10.97; Found: C, 77.22; H, 5.58; N, 10.55.

3. Results and discussion

3.1. UV-vis spectral titrations and colorimetric experiments

The anion binding ability of the sensors (1–6) was investigated using UV-vis spectral titrations in dry DMSO solution. Fig. 1 and S-Fig. 1 (in Supporting Information) showed UV-vis spectral changes of the sensors (1–6, 2×10^{-5} M) induced by addition of acetate ions. Obviously, the free 1 exhibited a main absorption band centered at 384 nm with a shoulder at 500 nm, which was assigned to the charge transfer of the azo moiety [21]. As the concentration of acetate ion was increased, the absorption intensity at 384 nm gradually decreased and a new absorption peak appeared at 578 nm with an isosbestic point at 441 nm. The increase in intensity of 578 nm resulted from acetate-induced deprotonation of the hydroxy protons, which could be further proven by ^1H NMR titrations of 1 with acetate ions and the UV-vis spectral titration of 1 with OH^- as its tetrabutylammonium (TBA) salt (see Fig. 2). Just as Table 1 and S-Fig. 1 showed, the presence of the nitro group in 1, 2 and 3 improved the charge transfer of the azo moiety and therefore resulted in ca. 35 nm red shift in absorption compared to that of 4, 5 and 6. Meanwhile, 1, 2 and 3 exhibited more significant red shifts (about 190 nm) in UV-vis spectrum induced by addition of acetate ion than 4, 5 and 6 (about 110 nm).

The naked-eye detection ability of the sensor was preferred on account of resort to no spectroscopic instrument. So, visible detection experiments of the sensors were also carried out in DMSO. Fig. 3 demonstrated the color changes of 1–6 (2×10^{-5} M, DMSO) in the absence and the presence of 50 equiv of different

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