TICT–ICT state change mechanism based acetate fluorescent sensor act as an “Off–On–Off” switch and logic gate

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A B S T R A C T

A novel sensor LX based on the TICT–ICT state change mechanism has been designed and synthesized. The sensor LX can perform as not only an exclusive-NOR (XNOR) logic gate but also an “Off–On–Off” molecular switch triggered by AcO– and H+ ions. By selectivity binding with Y-shape AcO– via double hydrogen bonds, the sensor LX underwent a TICT–ICT state change and induced a dramatic fluorescent response. However, the addition of H+ results in the fluorescence decreasing of LX–AcO–. This “Off–On–Off” switch could be controlled via AcO– and H+ cyclically. Moreover, the sensor LX could instantly detect AcO– in non-aqueous and aqueous solution (water content ≤10%) with specific selectivity and high sensitivity, these sense procedures could not interfered by other coexistent competitive anions (F−, Cl−, Br−, I−, AcO−, H2PO4 −, HSO4 −, ClO4 −, CN−, S2−, HS−, citrate). The detection limits was 4.0 × 10−7 M of AcO−, which is quite low for the detection of AcO− ions found in many chemical and biological systems.

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1. Introduction

Owing to the increasing demands of information technology for miniaturization, a noteworthy trend in the molecular recognition investigations is to design molecular devices, such as molecular switch, logic gates, molecular keypad locks and so on. As one of molecular devices, various molecular logic gates (NOT, AND, OR, NOR, XOR, INHIBIT, etc.) have been developed [1–6]. Among these, intramolecular charge transfer (ICT) and photoinduced electron transfer (PET) based processes have been widely used [7–10]. However, reports on the use of the twisted intramolecular charge transfer (TICT) [11] based processes are extremely rare, possibly due to the difficulty of controlling two crucial factors, the degree of the electron transfer and the change of molecular geometry. Although in principle, the well-designed ones should show very good performance.

Acetate is a critical component of numerous metabolic processes. Recognition of acetate plays a part in the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation [12–15]. For example, the antibiotic ristocetin has been known to efficiently and selectively bind amino acid carboxylates [16–19]. Moreover, the rate of AcO− production and oxidation has been frequently used as an indicator of organic decomposition in marine sediments [20]. To date, considerable effort has been devoted to the development of artificial acetate receptors and carriers, and various binding motifs have been synthesized [21–27]. Unfortunately, these AcO− chemosensors usually also display responses to other basic anions such as H2PO4− and F−.

In view of this, and as a part of our research interest in molecular recognition [28–30], we have attempted to obtain an efficient fluorescent chemosensor for AcO−. In order to achieve the specific recognition, we rational designed the sensor molecule according to the peculiarity of AcO−. Owing to AcO− is a basic anion just like F− and H2PO4−, the common AcO− sensor often been interfered by such basic anions. Fortunately, AcO− possesses a special Y-shape structure, which permit AcO− has a special binding ability. Therefore, AcO− could control the intramolecular twist or rotation of host molecular by form double hydrogen bonds with this host molecule. This property is very suitable for design a TICT–ICT state change mechanism based chemosensor. Thus, we introduced the TICT mechanism to the design of AcO− sensor. Our strategy as follows, firstly, in order to achieve TICT–ICT state change mechanism, the sensor molecular should possess two hydrogen bond donor groups and these two groups could carry out an intramolecular twist or rotation. So, as shown in Scheme 1, we introduced hydroxyl and imine groups to the sensor molecule as binding sites to detect AcO− by double hydrogen-bonding interactions. Secondly, in order to achieve high sensitivity for AcO−, the fluorescent signal report mode has been adopted, because the fluorescent sensors often provide higher sensitivity than other optic sensors [31]. Therefore, we introduced naphthalene and quinoline groups as...
the fluorescence signal group. Finally, the sensor molecular was designed easy to synthesis. As a result, sensor LX could detect ACO− with specific selectivity and high sensitivity. Moreover, the sense procedure could not interfered by other coexistent competitive anions, such as F− and H2PO4−. The sensor LX can perform as not only an exclusive-NOR (XNOR) logic gate but also an “Off–On–Off” molecular switch triggered by ACO− and H+ ions.

2. Experimental

2.1. General information and materials

All reagents for synthesis were of analytical grade, commercially and were used without further purification. All the anions were added in the form of tetra-n-butylammonium (TBA) salts. Which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator. Melting points were measured on an X-4 digital melting point apparatus and were uncorrected. Fluorescence spectra were recorded on a Shimadzu RF-5310. 1H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer with DMSO-d6 as solvent and TMS as an internal reference. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.

2.2. General procedure for fluorescence experiments

The solution of sensor LX (2.0 × 10−4 M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO and water solutions of each anions (1.0 × 10−2 mol L−1) were prepared, respectively, via TBA salts for F−, Cl−, Br−, I−, ACO−, H2PO4−, HSO4−, ClO4− and the sodium salts for CN−, S2−, HSO3−, Citrate. The fluorescence spectra were obtained by excitation at 435 nm. The excitation slit widths were 5 nm and emission slit widths were 5 nm, respectively. Any changes in the fluorescence spectra of sensor LX were recorded upon the addition of salts while keeping the concentration of sensor LX (2.0 × 10−5 M) in all experiments.

2.3. General procedure for 1H NMR experiments

For 1H NMR titrations, sensor LX was prepared in DMSO-d6. (Bu4N)AcO was prepared in DMSO-d6. First of all, only sensor LX in DMSO-d6 were added into NMR tube, and then added ACO− anion at 0.1, 0.3, 0.5, 1.0 and 1.5 equiv sequentially. All solutions were mixed directly in an NMR tube.

2.4. Synthesis of the sensor LX

The structure and synthesis of sensor LX is shown in Scheme 1. 8-Aminoquinoline (0.29 g, 2 mmol), 2-hydroxy-1-naphthaldehyde (0.35 g, 2 mmol) in dry ethanol was stirred under reflux condition for 4 h, and get yellow product (0.51 g, 85% yield) after recrystallization from C2H5OH-DMF.m.p. 227–229 °C IR (KBr, cm−1): ν = 3440(OH), 1624(C=N), 1589(C=C), 1535(C=C). 1H NMR (400 MHz, DMSO) δ 15.91 (d, J = 10.8 Hz, 1H, OH), 9.66–9.51 (m, 1H, =CH), 9.05 (dd, J = 4.1, 1.7 Hz, 1H), 8.47 (dd, J = 14.9, 4.8 Hz, 3H), 7.91–7.16 (m, 7H, Ar–H), 6.72 (dd, J = 9.5, 5.8 Hz, 1H). 13C NMR (151 MHz, DMSO) δ 181.42 (s), 150.17 (s), 147.25 (s), 139.38 (s), 138.74 (s), 136.45 (s), 136.26 (s), 134.24 (s), 129.12 (s), 128.39 (d, J = 6.4Hz), 126.96 (s), 126.29 (s), 125.92 (s), 124.44 (s), 123.46 (s), 122.59 (s), 119.93 (s), 114.63 (s), 108.24 (s). Anal. calcd for C20H14N2O: C 80.52, H 4.73, N 9.39; found: C 80.60, H 4.58, N 9.37. ESI-MS: calcd for [C20H14N2O+H]+ 299.1, found 299.3.

3. Results and discussion

3.1. Fluorescence detection towards ACO−

The sensing abilities of LX towards various anions (F−, Cl−, Br−, I−, ACO−, H2PO4−, HSO4−, ClO4−, CN−, S2−, HSO3− and citrate) were investigated by fluorescence spectroscopy. We carried out experiments in DMSO and DMSO–H2O (v/v = 90:10). Free sensor LX exhibited an emission maximum at 500 nm upon excitation at 435 nm, after addition the DMSO solution of these different anions (c = 1 × 10−3 M) to the DMSO solution of sensor LX (c = 2 × 10−5 M), respectively, a significant fluorescence enhancement and a redshift of approximately 20 nm immediately were only seen in the case of ACO− (Figs. 1 and 2). The other anions did not show any noticeable changes in the emission maximum band under same condition. The plot of changes in the fluorescence intensity at 520 nm upon addition of various anions clearly showed excellent selectivity of sensor LX towards the ACO− (Fig. S1). Furthermore, the similar tests were carried out by adding pure water solutions of above mentioned anions to the DMSO solution of sensor LX, respectively, (total water content ≤ 10%), as shown in Fig. S2 that sensor LX also can selectively detect ACO− in aqueous solution. All of these results suggested that sensor LX displayed an excellent selectivity for ACO− than other anions in non-aqueous and DMSO–H2O medium (total water content ≤ 10%).

Fig. 1. Fluorescent changes of LX after addition of various anions in DMSO, from left to right: none, F−, Cl−, Br−, I−, ACO−, H2PO4−, HSO4−, ClO4−.

Fig. 2. Fluorescence spectra of LX (λex = 435 nm) after addition of various anions (F−, Cl−, Br−, I−, ACO−, H2PO4−, HSO4−, ClO4−) in DMSO.
3.2. Fluorescence titration spectra

For a better understanding of the binding mode, the fluorescence titration experiments were carried out in DMSO and a maximum excitation wavelength of 435 nm was selected. As shown in Fig. 3, there was a ca. 4.3-fold \((I/I_0)\) fluorescent enhancement effect and a red shift of about 20 nm in the emission spectrum when adding 1.2 equiv AcO\(^-\), and further increase in the concentration of AcO\(^-\) led to no change. This observation was consistent with the fact that the AcO\(^-\) interacted with O–H protons of phenolic hydroxyl through hydrogen-binding. The detection limit of the fluorescence spectra changes calculated on the basis of \(3S_B/S\) [32] was \(4.0 \times 10^{-7}\) M for AcO\(^-\) anion, which is quite low for the detection of AcO\(^-\) ions found in many chemical and biological systems [22,24,25,27].

To know stoichiometry between the guest (AcO\(^-\)) and host LX molecule in DMSO solution, Job's plot has been drawn (Fig. 4). It shows the maximum at a molar fraction of 0.5 and clearly demonstrated to be 1:1.

3.3. Time response

As known, chemosensors always have a problem of long response time. In our case, the binding process of AcO\(^-\) to LX was found to be very fast (Fig. 5). After adding AcO\(^-\), the fluorescence emission intensity of LX was increased at 520 nm and reached the plateau region less than 12 s, and remains quite stable, suggesting that the binding process might be completed instantly and the chemosensor has rapid detection ability for acetate anion.

3.4. pH response

The pH dependence of the sensor LX in aqueous media was also checked by fluorescence emission spectroscopy. Acetate ion was added to the DMSO–H\(_2\)O \((v/v=90:10)\) solution of the sensor LX at different pH values from 1 to 12. The result indicated that the binding of sensor LX with AcO\(^-\) only occurred effectively at pH values from 6 to 9 (Fig. S3). Below 6 or above 9, no change due to the addition of acetate ion was observed in emission spectra.

![Image](image_url)
3.5. “Off–On–Off” fluorescent switch and logic gate

It is well known that AcO− has binding ability to H+ to form CH3COOH, so we investigated the fluorescence behaviour of sensor LX between AcO− and H+ ions. The addition of AcO− ions to the solution of sensor LX leads to fluorescence increasing, that is, ‘On state’. The addition of H+ ions to the solution of LX−AcO− complex, that is, ‘On state’ results in the recovery of fluorescence intensity of sensor LX, that is, ‘Off state’. This “Off–On–Off” switching process could be repeated at several times with little fluorescent efficiency loss (Fig. 6).

Thus, depending on the two chemical inputs (AcO− and H+), the sensor LX can switch between different fluorescence emission states, that is, ‘On or Off’. The behaviour of this molecular switch can be demonstrated with the help of binary logic. Binary digits (0 or 1) can be used to represent the two states ‘Off or On’ of each signal. For reversible ‘On–Off’ switch of two inputs (AcO− and H+), the input and output strings of the molecular switch are illustrated in Table 1. The output signal is ‘0’ (weak emission) when input strings ‘00, 11 and 01’ is on (in the absence or presence of both AcO− and H+ ions and only presence H+ ) and output signal is ‘1’ (strong emission) when only AcO− inputs is on in string ‘10’. Such fluorescence changes upon the actions of two chemical inputs mimic the performance of an exclusive–NOR (XNOR) logic gate (Fig. 7). A XNOR logic function is two input device and its output is ‘true’ if the inputs are only ‘10’ and ‘false’ if the inputs are ‘00, 11, 01’.

3.6. Mechanism of the “Off–On–Off” system for sensing of AcO−

To explore the sensing mechanism of sensor LX to AcO−, the 1H NMR titration and ESI-MS were investigated, which illustrated the characteristic structural changes occurring upon interaction with AcO−. As shown in Fig. 8, before the addition of acetate anions, the 1H NMR chemical shifts of the O−H and –HC=N− protons were at δ 15.91 ppm, 9.66 ppm, respectively. Owing to sensor LX could take place an intramolecular rotation and cis–trans transfer as showed in Scheme 2, the O−H and –HC=N− protons signal carry out an obvious split. In this case, the sensor is in the TICT state and show very weak fluorescence. Upon the gradual addition of AcO−, as shown in Scheme 2, the sensor LX formed double hydrogen bonds with AcO−, which restricted the intramolecular rotation of sensor LX, therefore, the split of O−H and –HC=N− protons signal disappeared.

Meanwhile, the formation of double hydrogen bonds induced the signal of O−H and –HC=N− protons underwent a slightly downfield shift and peaks at 9.05 ppm, 6.72 ppm (aromatic protons) were shifted to upfield. At this time, due to the intramolecular rotation was restricted by the double hydrogen bond, the sensor changed to ICT state and shown a strong fluorescence emission at 520 nm. With further adding H+ to solution of [LX−AcO−], the signal of O−H was recovered. These results implied that the interaction of AcO− and H+ can interrupt the hydrogen bond between the sensor LX and acetate ion. Thus, the fluorescence intensity was recovered from a TICT state (Scheme 2).

The results of ESI-MS experiments also support this presumption. In the ESI-MS spectra of sensor LX, the [LX + H+] peak appeared at 299.3 (m/z)calcd = 299.1). However, when 1 equiv. AcO− was added to the solution of LX, a new peak appeared at 619.1, coinciding well with that for the species [LX + AcO− + Bu4N+ + H2O + H+] (m/zcalcd = 618.4) and indicating the formation of the stabilized anionic species LX−AcO−.

4. Conclusion

In summary, we have rational designed and synthesized an AcO− sensor, which could detect AcO− in non-aqueous and aqueous solution via a TICT–ICT state change mechanism. Competitive anions such as F− and H2PO4− with strong basicity did not afford any obvious interference response. An “Off–On” type fluorescent response to AcO− is realized through the AcO− binding induced TICT to ICT state change of sensor LX. Continue to add H+, the “Off–On” response turned into “On–Off” response. This “Off–On–Off” switching process could be repeated at several times with little fluorescent efficiency loss. As a result, sensor LX could detect AcO− with high sensitivity and specific selectivity, moreover, it can be used as a novel NOR logic gate and an “Off–On–Off” molecular switch triggered by AcO− and H+.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.09.004.

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