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PAPER

A highly selective colorimetric and "Off-On" fluorescent chemosensor for fluoride ion and its application as a molecular-scale logic devices GuoTao Yan, Hui Li, Yuan Rong Zhu, BingBing Shi, Wenjuan Qu, Qi Lin, Hong Yao, YouMing Zhang,

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A new sensor 2, 2'-((1E, 1'E)-((3, 3'-dimethyl-[1, 1'-biphenyl]-4, 4'-diyl) bis (azanylylidene)) bis (methanylylidene)) diphenol (YT) based on the combination of phenolic hydroxy and imine group was used as an efficient colorimetric and "turn on" fluorescent sensor for fluoride anions. The receptor exhibits high selectivity and sensitivity for sensing F⁻. Furthermore, the enhanced fluorescence caused by 10 fluoride could be recovered upon the addition of calcium ion to this complex solution. The fluorescent changes of YT upon the addition of F^- and Ca^{2+} can be utilized as an INHIBIT logic gate at molecular level, using F^- and Ca^{2+} as chemical inputs and the fluorescence intensity signal as outputs.

Introduction 1.

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The design and development of selective optical sensors and 35 the various fluoride anion sensors, although a hydroxyl group can 15 receptors for anions has gained considerable attentions, as anions play important roles in many areas such as medicinal biological, environmental chemistry and catalysis [1-5]. In recent years, considerable efforts has been devoted to developing fluorescent

- 20 and low detection limit, however, only few of them are "turn on" fluorescent sensors [6-11]. In terms of sensitivity concerns, the recognition process "turn on" fluorescence is advantageous than that of "turn off" event in terms of the detection limit, because
- 25 other quenchers in practical samples [12-13].
 - Fluoride ion (F^{-}) , as the most electronegative atom, being the smallest anion with high charge density plays important roles in environmental, medical and chemical processes [14–17].
- 30 human bodies, result in fluorosis and kidney disorders or even urolithiasis [18]. Therefore, developing new, simple, and highly sensitive F⁻ sensors would be highly demanded.

Till now, a variety of chemosensors for F⁻ based on thiourea[19], amide[20], indole[21], have been reported. Among

also be an excellent hydrogen-bonding donor and its proton even exhibits more acidity compared to the proton of NH unit, far less attention has been paid to the OH based anions receptors and sensors. With these considerations in mind, we developed a anion sensors, due to their simplicity, high degree of specificity 40 structurally simple chemosensor, with a hydroxynaphthalene group as chromogenic signaling subunit and hydroxy as binding sites, which enable dual channel (absorption and fluorescence) detection of F⁻ in DMSO solution. The high selectivity for F⁻ recognition and detection based on noncovalent or covalent fluorescence "turn off" sensors may report false results caused by 45 interactions between the sensor YT and F, employing hydrogen bonding and deprotonation between the hydroxyl group of the receptor and the fluoride. According to these, we reported YT based fluorescent and choromogenic chemosensor, with characteristics of an "OFF-ON-OFF" fluorescence switch. However, an excessive fluoride ion intake may injure animal and 50 Interestingly, the fluoride induced chromogenic process can be totally reversed with addition of Ca²⁺. Based on these, using F⁻ and Ca²⁺ as inputs IFNOT logic operations can be achieved, which allows the design of a molecular-scale sequential memory unit displaying "Writing-Reading-Erasing-Reading" behavior and "Multi-write" functions.

2. **Experimental section**

2.1. Materials and physical methods

- All reagents and solvents were commercially available at 5 analytical grade and were used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AvanceIII 400 MHz spectrometer at 400 MHz and 100 MHz, respectively. 10 downfield from tetramethylsilane (TMS, dscale with solvent resonances as internal standards). UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Mass spectra was recorded on an esquire 50 15 6000 MS instrument equipped with an electrospray (ESI) ion source and version 3.4 of Bruker Daltonics Data Analysis as the
 - data collection system. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected).

2.2. Synthesis of the sensor YT

- 20 Sensor YT could be easily synthesized by condensation of salicylaldehyde (0.5124 g, 4mmol) and 3,3'-dimethylbenzidine (0.45 g, 2.0mmol) in refluxing absolute ethanol (30 mL) (Scheme 1). The reaction mixture was stirred under reflux for 8 h. After
- 25 filtered, washed four times with hot absolute ethanol, then recrystallized with EtOH to give a luminous yellow powder product **YT** (0.72 g) in 85.1% yield (m.p. 220-222 []). ¹H NMR (DMSO-d₆, 400 MHz): δ 13.42 (d 2H, OH), δ 8.99 (d 2H,
- **30** 6.95-7.47 (m 4H, ArH), δ 2.43 (s 6H, -CH₃); ¹³C NMR (DMSO-d₆, 100 MHz): δ /ppm 162.44, 160.31, 145.94, 137.70, 133.04, 132.36, 132.22, 128.39, 124.95, 119.33, 118.90, 118.31, 116.41, 17.71. ESI-MS m/z: $(M+H)^+$ Calcd for $C_{28}H_{24}N_2O_2$ 421.18; Found 421.17; Anal. Calcd for C₂₈H₂₄N₂O₂: C, 79.98; H, 35 5.75; N, 6.66; O, 7.61Found C 79.87; H, 5.68; N, 6.57; O, 7.60.



Scheme 1.Synthetic procedure of YT.

2.3. General procedure for UV-VISIBLE Absorption and Fluorescence experiment

40 All the UV-vis experiments and fluorescence spectroscopy were carried out in DMSO solution on a Shimadzu UV-2550 spectrometer and Shimadzu RF-5301 spectrometer, respectively. Any changes in the UV-vis spectra of the synthesized compound were recorded on addition of tetrabutylammonium salts while Chemical shifts are reported in parts per milliom (ppm) 45 keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. Tetrabutylammonium salt of anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, CN⁻ and SCN⁻) were used for the

UV-vis experiments and fluorescence experiments. 2.4. General procedure for ¹H NMR experiments

For ¹H NMR titrations, sensor **YT** was prepared in DMSO- d_6 , $(Bu_4N)F$ was prepared in DMSO- d_6 . one of them containing host only and the second one containing an appropriate concentration of guest. Aliquots of the two solutions were mixed directly in NMR tubes.

55 **3**. **Results and Discussion**

The selectivity of YT toward different anions was monitored by treating **YT** with excessive F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄, ClO₄, CN⁻ and SCN⁻ in DMSO, respectively. Figure 1 shows the changes in the UV-vis spectra of **YT** $(2.0 \times 10^{-5} \text{ M})$ in completion of the reaction, the obtained yellow precipitate was 60 DMSO after adding 50 equiv. of various anions, when sensor YT was treated with the fluoride anions, the absorbance at 375 nm declined sharply from 1.05 to 0.52, while the one at 454 increased significantly, which induced the color of the solution changes from colorless to yellow, which could be detected by the 'naked -CH=N), δ 7.65-7.76 (m 6H, ArH), δ 7.42-7.54 (m 4H, ArH), δ 65 eve'. In contrast, for the other anions no obvious changes in color were observed (inset of Fig. 1).



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Fig. 1 Absorption spectra change of YT (20 µM) upon addition of selected competing anions (50 equiv). Inset: the corresponding color

changes

In order to further explore sensing ability of the receptor **YT**,

- 5 fluorescence measurements were carried out. As shown in Fig. 2, excitation at 462nm. Treatment with F⁻, resulted in a drastic enhancement of the fluorescence intensity at 552 nm, the fluorescent enhancement observed upon addition of fluoride to
- 10 the sensor YT might be attributed to the intramolecular charge increasingly negative charge density of the phenol oxygen atom promoted the intramolecular charge transfer (ICT) from hydroxyl anion to the aromatic rings. In comparison, the addition of 15 various anions such as Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻,
- changes at 552 nm. Moreover, when being excited by 365 nm UV lamp it emits yellow lights, which acts as a typical of "OFF-ON" based optical response as shown in the photograph inset of Fig. 2. 20 These results clearly indicated that the selectivity of YT toward



Fig. 2 Change in emission spectra of YT (20 µM) upon the addition of 25 different anions (50 equiv) in DMSO. Inset shows the change in color under UV.

The interaction between YT and F⁻ was further investigated through spectrophotometric titration methods by adding a standard solution of corresponding anions to a solution of the

- 30 receptor YT ((2.0×10^{-5} M). Fig. 3 shows absorption spectral changes of receptor YT in the course of titration. Upon successive addition of tetrabutylammonium fluoride (TBAF), the absorption peak initially at 375nm gradually decreased while the absorption intensities at 453 nm increased together with a marked
- YT alone exhibited a very weak fluorescence emission upon 35 red shift. This should be attributed to the strong intramolecular hydrogen-bonding interaction in sensor and the deprotonation of the hydroxyl group coordinated to fluoride anion. As a result, leading to a color change from yellow to red, which could be detected by the 'naked eye'. The binding affinity of sensor YT
- transfer (ICT) transition from the phenolate [22-23]. The 40 with F^- anion was estimated by performing emission titration experiments when excited at 462 nm. As shown in Fig. 4 free probe YT showed weak fluorescence at 552 nm due to the structure of intramolecular hydrogen bond. On further increasing the concentration of F⁻ (4-13.6 equiv.), the original fluorescent CN⁻ and SCN⁻ to the solution of YT exhibited no or small 45 emission peak at 552 nm increased progressively with a 15.3 nm red-shift of the emission maximum. The detection limitation of sensors towards F⁻ was obtained according to fluorescence titration on the basis of $3S_B/S$ [24] was 2.5×10^{-7} M, as shown in (Fig. S1). This value is far below the guideline (211 μ M) of the F⁻ over other competitive anions in DMSO was remarkably high. 50 U.S Environment Protection Agency.



Fig. 3 UV-vis titration spectra of YT (20 µM) upon the addition of F anions (0-118 equiv.) in DMSO solution. Inset: Absorbance at 453 nm versus the number of equiv of F added.

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Page 4 of 8



Fig. 4 Fluorescence titration of YT (20 μ M) with F⁻ (as the TBAF salt from 0 to 13.6 equiv) in DMSO excited at 462 nm.

- The mechanism of the interaction between sensor YT and F 5 was further studied by ¹H NMR titration experiments. Fig. 5 30 shows partial ¹H NMR spectrum of interaction of receptor and F⁻. In the absence of fluoride anion, sensor **YT** showed a single peak at 13.42 ppm in DMSO-d₆, which was confirmed to the proton of OH. In this case, there is a two-stepwise mechanism involving the 10 formation of hydrogen bond between OH and F⁻ first and then deprotonation of the OH by excessive F⁻. With the increasing of the fluoride concentration, the singlet of Ha was downshifted gradually from 13.42 ppm to13.66 ppm by hydrogen bonding with fluoride. After the addition of 6 equiv of fluoride, the singlet
- 15 peak of Ha was broadened, and then completely disappeared by 35 the deprotonation. Furthermore, a new signal appears at 16.12 ppm when 8 equiv. of fluoride was introduced, this peak is indeed suggestive of the formation of bifluoride, HF₂⁻ ion and thus supports the deprotonation of hydroxyl groups [25-26]. The
- suggests that the negative charges generated from the deprotonation of YT by fluoride were delocalized over the receptor molecular. These results corresponded with the spectrophotometric titration results and further suggested that the
- 25 mechanism of the F⁻ sensing process was a combination of an 45 quenching the fluorescence intensity and hence acts as OFF intramolecular hydrogen bond, deprotonation, and P- π conjugation effect. We propose the sensing mechanism of YT to fluoride as shown in Scheme 2.



Fig. 5¹H NMR spectra of YT (1 mg) with the addition of TBAF (DMSO-d₆ solution). (a) **YT** only; (b) $\mathbf{YT} + \mathbf{F}^-$ (0.5 equiv.); (c) $\mathbf{YT} + \mathbf{F}^ (4.5 \text{ equiv.}); (d) \mathbf{YT} + F^{-} (6.0 \text{ equiv.}); (e) \mathbf{YT} + F^{-} (8.0 \text{ equiv.}).$



Scheme 2 Proposed sensing mechanism of YT for fluoride Due to the reversibility is an important aspect for a chemical sensor to be widely employed in the detection of specific analyses, so the reversibility in the response of YT has been further verified during its seven cycles of titrations by alternating

- addition of F⁻ and Ca²⁺ to YT solution. The fluorescence 20 protons of the aromatic rings were shifted to upfield which 40 emission of the tested solution performed alternate enhancing and reviving processes in a sequence as shown in Fig. 6. In addition, the F⁻ exhibits a remarkable fluorescence change by showing ON behavior through complex formation. Upon addition of excess amount of $Ca(ClO_4)_2$ to the mixture of **YT** and F^- results in
 - switch. This "OFF-ON-OFF" switching process could be repeated at several times with little fluorescent efficiency loss. The repeated behavior of the system by fluorescence change clearly suggests that YT is reversible and hence is a reusable

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sensor for F⁻, the possible binding mode between **YT** toward F⁻ is proposed in Scheme 3. Here, the actual results from an experiment are shown in Fig. 7, using F^- and Ca^{2+} act as inputs while the emission intensity at 552 nm (I 552) band acts as output.

- 5 Based on the reversible and reproducible fluorimetric switch, the sensor YT can switch between different fluorescence emission states, i.e. "on" (strong fluorescence emission) or "off" (quenched fluorescence emission), which display "Read-Erase-Write-Read" 30 behavior with the help of reversible logic operations [27]. In this
- 10 concrete system (Fig. 8), the ON state (Output 2 = 1) is defined as the strong fluorescence at 552 nm, whereas the OFF state (Output 2 = 0) corresponds to the weak fluorescence. The two chemical inputs of fluoride and calcium ions are designated as (In F) and $(\ln Ca^{2+})$ for the Set (S) and Reset (R), respectively. The 15 operation of this memory unit is as follows: whenever the Set input is high (S = 1), the system writes and memorizes the binary state 1; on the other hand, when the Reset input is high (R = 1),
 - the 1 state is erased and the 0 state is written and memorized. As shown in Fig. 8a, The reversible and reconfigurable sequences of 35 show the fluorescence output of YT at 552 nm in the presence of
- 20 Set/Reset logic operations in a feedback loop demonstrate the memory feature with "Read-Erase-Write-Read" functions with the optical output signal. Fig. 8b defines the bistability behavior, "ON-OFF" state, of sensor YT and reveals the non-volatile nature of the memory effect. More importantly, the present logic device 25 has a great advantage over early reported relative systems at least

in terms of the reversible and reproducible characteristics.



Scheme 3 The recyable mechnaism of sensor YT toward F after addition of Ca2+.



Fig. 6 Reversible switching cycles of fluorescence intensity ($\lambda_{ex} = 462 \text{ nm}$)

by alternate addition of F⁻ ions and Ca²⁺ in DMSO.



Fig. 7 Performance of YT in the INHIBIT gate mode. The bars

F⁻ and Ca²⁺ as inputs.



Fig. 8 (a) The sequential logic circuit of the memory machine and its truth table. (b) Feedback loop showing reversible logic operations for memory element with "Writing-Reading-Erasing-Reading" functions.

4. Conclusions

In conclusion, we have designed and synthesized a simple colorimetric and fluorescent chemosensor for highly selective recognition of the fluoride anion. Upon interaction with F YT

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showed an obvious color change from colorless to yellow; meanwhile the fluorescence spectra show a 15.3 nm red-shift with enhanced intensity, which makes the receptor YT a dual 40 8 channel sensor for fluoride. More interestingly, the F⁻ induced 5 chromogenic process could be totally reversed by addition of Ca²⁺, this "OFF-ON-OFF" switching process could be repeated at several times with little fluorescence loss. So, the fluorescence responses can be utilized as output to build an INHIBIT logic 45

gate by using F^- and Ca^{2+} as inputs. Base on this, we has 10 designed a molecular-scale sequential information processing circuit displaying "Writing-Reading-Erasing-Reading" functions.

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20 Notes and references

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7

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