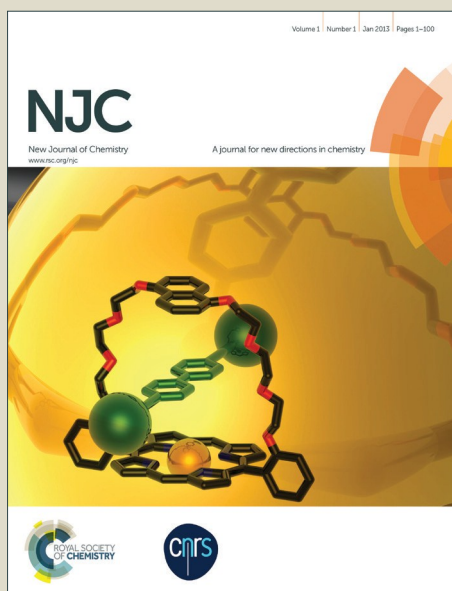


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Cite this: DOI: 10.1039/c0xx00000x

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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**

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5 Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

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.

1. Introduction

The design and development of selective optical sensors and 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 anion sensors, due to their simplicity, high degree of specificity 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 fluorescence “turn off” sensors may report false results caused by 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]. However, an excessive fluoride ion intake may injure animal and 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 the various fluoride anion sensors, although a hydroxyl group can 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 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 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. Interestingly, the fluoride induced chromogenic process can be totally reversed with addition of Ca^{2+} . Based on these, using F^- and Ca^{2+} 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.

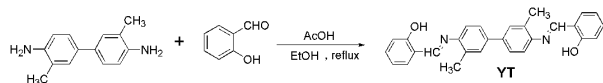
2. Experimental section

2.1. Materials and physical methods

All reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AvanceIII 400 MHz spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) 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 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

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 completion of the reaction, the obtained yellow precipitate was 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 $^{\circ}\text{C}$). ^1H NMR (DMSO- d_6 , 400 MHz): δ 13.42 (d 2H, OH), δ 8.99 (d 2H, -CH=N), δ 7.65-7.76 (m 6H, ArH), δ 7.42-7.54 (m 4H, ArH), δ 6.95-7.47 (m 4H, ArH), δ 2.43 (s 6H, -CH $_3$); ^{13}C NMR (DMSO- d_6 , 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 $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$ 421.18; Found 421.17; Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$: C, 79.98; H, 5.75; N, 6.66; O, 7.61 Found 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

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 keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. Tetrabutylammonium salt of anions (F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- , ClO_4^- , 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 , ($\text{Bu}_4\text{N})\text{F}$ 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.

3. Results and Discussion

The selectivity of **YT** toward different anions was monitored by treating **YT** with excessive F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- , ClO_4^- , CN^- and SCN^- in DMSO, respectively. **Figure 1** shows the changes in the UV-vis spectra of **YT** (2.0×10^{-5} M) in 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 eye’. In contrast, for the other anions no obvious changes in color were observed (inset of Fig. 1).

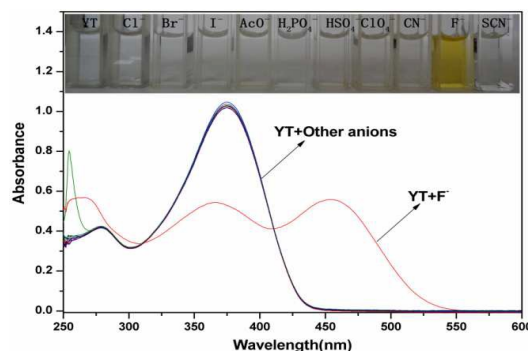


Fig. 1 Absorption spectra change of **YT** (20 μ M) upon addition of selected competing anions (50 equiv). Inset: the corresponding color changes.

In order to further explore sensing ability of the receptor **YT**, 5 fluorescence measurements were carried out. As shown in Fig. 2, **YT** alone exhibited a very weak fluorescence emission upon 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 transfer (ICT) transition from the phenolate[22-23]. The 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^- , $H_2PO_4^-$, HSO_4^- , ClO_4^- , CN^- and SCN^- to the solution of **YT** exhibited no or small 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 F^- over other competitive anions in DMSO was remarkably high. 50 U.S Environment Protection Agency.

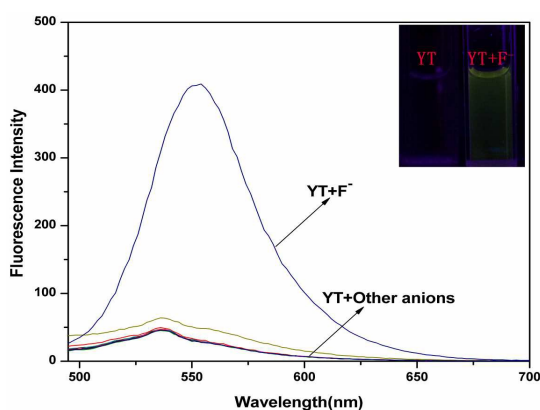


Fig. 2 Change in emission spectra of **YT** (20 μ M) upon the addition of 25 different anions (50 equiv) in DMSO. Inset shows the change in color under UV.

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 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** 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 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 50 U.S Environment Protection Agency.

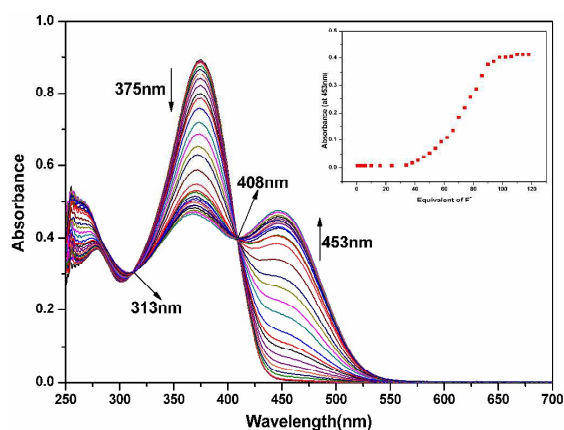


Fig. 3 UV-vis titration spectra of **YT** (20 μ M) upon the addition of F^- 55 anions (0-118 equiv.) in DMSO solution. Inset: Absorbance at 453 nm versus the number of equiv of F^- added.

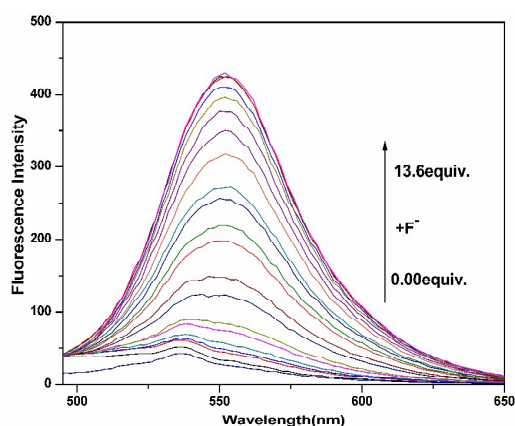


Fig. 4 Fluorescence titration of **YT** (20 μ M) with F^- (as the TBAF salt from 0 to 13.6 equiv) in DMSO excited at 462 nm.

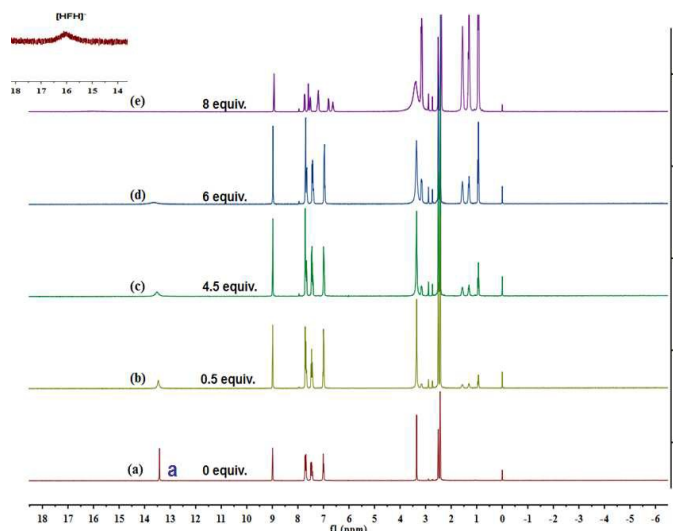
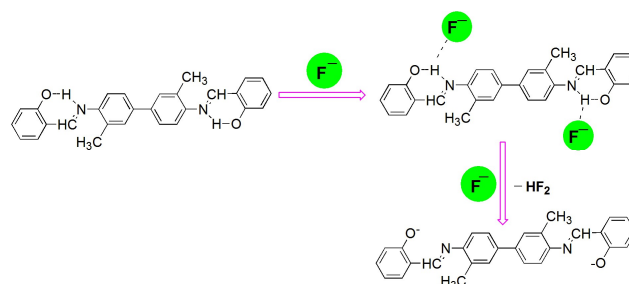


Fig. 5 1H NMR spectra of **YT** (1 mg) with the addition of TBAF (DMSO- d_6 solution). (a) **YT** only; (b) **YT** + F^- (0.5 equiv.); (c) **YT** + F^- (4.5 equiv.); (d) **YT** + F^- (6.0 equiv.); (e) **YT** + F^- (8.0 equiv.).



Scheme 2 Proposed sensing mechanism of **YT** for fluoride

The mechanism of the interaction between sensor **YT** and F^- was further studied by 1H NMR titration experiments. Fig. 5 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- d_6 , which was confirmed to the proton of OH. In this case, there is a two-stepwise mechanism involving the 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 to 13.66 ppm by hydrogen bonding with fluoride. After the addition of 6 equiv of fluoride, the singlet peak of Ha was broadened, and then completely disappeared by 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, HF_2^- ion and thus supports the deprotonation of hydroxyl groups [25-26]. The protons of the aromatic rings were shifted to upfield which 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 mechanism of the F^- sensing process was a combination of an intramolecular hydrogen bond, deprotonation, and P- π conjugation effect. We propose the sensing mechanism of **YT** to fluoride as shown in Scheme 2.

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 Ca^{2+} to **YT** solution. The fluorescence 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 quenching the fluorescence intensity and hence acts as OFF 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

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.

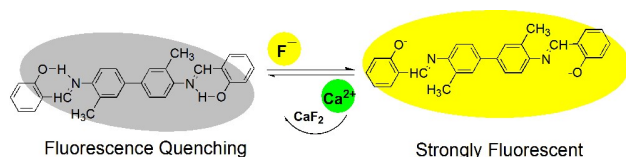
Based on the reversible and reproducible fluorimetric switch, the sensor **YT** can switch between different fluorescence emission states, i.e. “on” (strong fluorescence emission) or “off” (quenched fluorescence emission), which display “Read-Erase-Write-Read”

behavior with the help of reversible logic operations [27]. In this

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 (In Ca^{2+}) for the Set (S) and Reset (R), respectively. The

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

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 has a great advantage over early reported relative systems at least in terms of the reversible and reproducible characteristics.



Scheme 3 The reversible mechanism of sensor **YT** toward F^- after addition of Ca^{2+} .

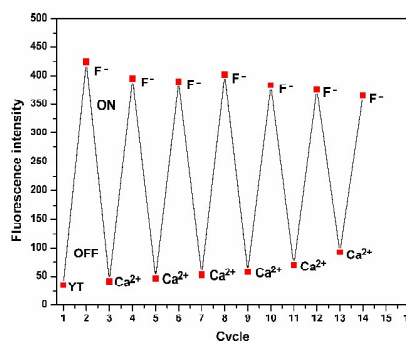


Fig. 6 Reversible switching cycles of fluorescence intensity ($\lambda_{ex} = 462$ nm)

by alternate addition of F^- ions and Ca^{2+} in DMSO.

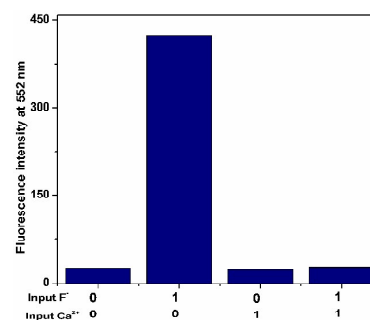


Fig. 7 Performance of **YT** in the INHIBIT gate mode. The bars

show the fluorescence output of **YT** at 552 nm in the presence of F^- and Ca^{2+} as inputs.

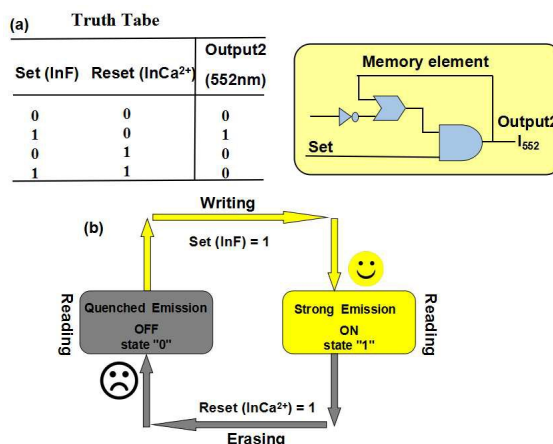


Fig. 8 (a) The sequential logic circuit of the memory machine and its truth table. (b) Feedback loop showing reversible logic operations for memory element with “Writing-Reading-Erasing-Reading” functions.

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**

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 channel sensor for fluoride. More interestingly, the F^- induced chromogenic process could be totally reversed by addition of Ca^{2+} , 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 gate by using F^- and Ca^{2+} as inputs. Base on this, we has designed a molecular-scale sequential information processing circuit displaying “Writing-Reading-Erasing-Reading” functions.

“This work was supported by the National Natural Science Foundation of China (No. 21064006, 21262032 and 21161018), the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (No. IRT1177), the Natural Science Foundation of Gansu Province (No. 1010RJZA018), the Youth Foundation of Gansu Province (No. 2011GS04735) and NWNLU-LKQN-11-32.”

20 Notes and references

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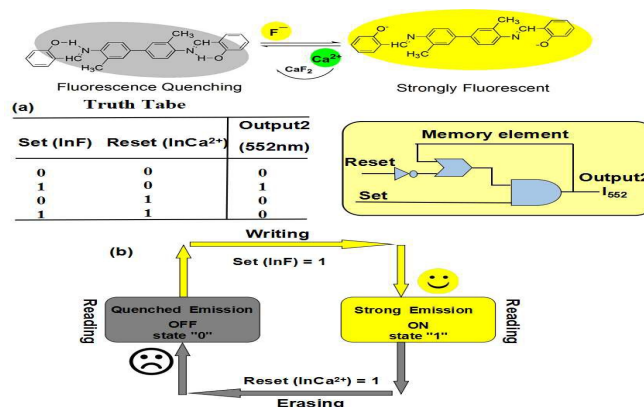
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† Electronic Supplementary Information (ESI) available: [Complete experimental procedures and some of the spectroscopic]. See DOI: 10.1039/b000000x/

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