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Three-input–three-output logic operations based on absorption and fluorescence dual-mode from a thiourea compound†

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A simple organic molecule of 2-naphthol-1-aldehyde-conjugated thiourea (denoted as receptor **1**) is designed and prepared. Absorption and fluorescence spectra response profiles of receptor **1** with different ionic inputs vary significantly in a DMSO–H_2O solution (V/V = 9 : 1) through modulating intramolecular charge transfer (ICT) processes. In particular, the changes of the dual-modal spectra when anions, such as F^-, AcO^- or $H_2PO_4^-$, are introduced in such an aqueous solution indicate that receptor **1** could be tolerant to H_2O at least to some extent in recognizing anions. On the basis of the above results, binary logic operations (OR, NOR and INHIBIT) and their multiply-logic functions with different combinations have been achieved at the molecular level by changing different chemical inputs. The output signals can be encoded as absorption and fluorescence dual-mode, depending on the choice of 2-naphthol as the chromophore and fluorophore core.

Introduction

The signal communication at molecular level is important and necessary in the development of innovative materials for data storage and processing. In 1988, Aviram suggested the use of "molecules for memory, logic and amplification" in the context of molecular electronics.[1] Ever since the pioneering work on molecular AND logic gates in 1993 by de Silva and coworkers,[2] the design and construction of molecular systems capable of performing binary arithmetic and logical operations has been explored extensively.[3] The molecular approach to logic devices is usually associated with the mimicry of functions performed by silicon-based microprocessors, by moving beyond silicon-based technology simultaneously. The elementary logic operations,[4] such as logic gates, encoders/decoders, molecular digital demultiplexers, and keypad locks, central to the functioning of electronic circuitry, can be performed by cleverly designing organic molecules, and can access those areas inaccessible by even the smallest electronics.

Logic gates, as a class of important and basic logic operations, are switches whose output state (0 or 1) depends on input conditions (0 or 1).[3e] Generally, one output mode shows one logic function by a combination of two certain chemical inputs. More recently, construction of molecules, whose multi-output logic functions can be modulated by multi-input combinations, has induced great interest.[5] It would be possible to extend the information processing and computing to molecular level if only molecular logic gates are available, which could perform binary arithmetic and logical operations. Besides, receptor molecules obtained through simple synthetic protocols but capable of performing multiple logic operations are the first choice for any supramolecular chemist towards the construction of molecular devices and machines.

The construction of logic gates at molecular level can be carried out by using chemical and/or optical inputs and optical outputs.[6] Typically, in these systems, addition of acid/base, metal ions, and/or anions leads to changes in the absorption spectrum (*i.e.*, color changes) or alterations of fluorescence properties (*i.e.*, change of intensity or band shifts) of the molecule which can be detected and influenced by a quite small but extremely versatile toolbox of excited state processes, such as photoinduced electron transfer (PET),[7] intramolecular charge transfer (ICT),[8] and fluorescence resonance energy transfer (FRET).[9]

Keeping these considerations in mind, we have designed a single molecule, 2-naphthol-1-aldehyde-conjugated thiourea

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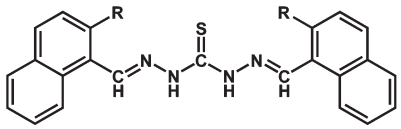
†Electronic supplementary information (ESI) available: Job's plots for determining the stoichiometry of receptor **1** with various ions, spectra responses of receptor **1** in the presence of various interference ions, spectra responses of receptor **2** in the presence of anions, reversibility of receptor **1** with various ions, ^1H NMR spectra of thiocarbohydride, receptors **1** and **2**. See DOI: 10.1039/c2dt31808c



1: R=OH
2: R=H

Scheme 1 Molecular structure of receptors **1** and **2**.

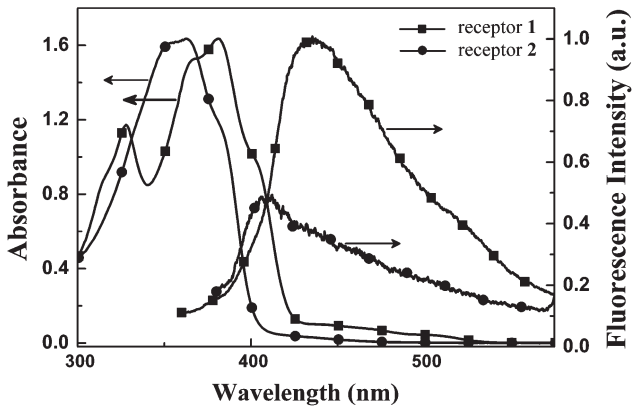


Fig. 1 The absorption and normalized emission spectral overlay of receptors **1** (■) and **2** (●) in a DMSO–H_2O solution (V/V = 9 : 1).

ligand **1** (denoted as receptor **1**), and studied the logic responses of receptor **1** by using appropriate combinations of anions and cations as inputs based on absorption and fluorescence dual-mode in a DMSO–H_2O solution (V/V = 9 : 1). The thioamide moiety, linked with 2-naphthol by a CH=N group, has often been used as a binding group for anion and cation chemosensors[10] because the thiourea group offers an ideal binding and signal transduction unit. However, it has been considerably less used as a logic device.[6f]

Results and discussion

A. Absorption and fluorescence spectra

A.1 Absorption and fluorescence spectra of pure 1. Receptor **1** was synthesized with a very simple protocol as shown in Scheme 1. The 2-naphthol moiety in receptor **1** serves as the chromophore and fluorophore core. The amine and hydroxyl groups in receptor **1** serve as chelating sites for anions and cations. Due to the electron-donating property of 2-naphthol and the electron-withdrawing property of the thioketone group, receptor **1** gives a "push–pull" based excited state.

The absorption spectrum of receptor **1** as shown in Fig. 1 is recorded in a DMSO–H_2O solution (V/V = 9 : 1), which displays an ICT band at 381 nm and a shoulder band at 367 nm, mainly due to the Ar–CH=N–NH conjugation.[10a] Receptor **1** in the DMSO–H_2O solution exhibits an emission band centered at 437 nm upon excitation at 342 nm (Fig. 1). Compared with the control receptor **2**, the red-shifted absorption and fluorescence of receptor **1** is mainly due to the electron-donating ability of the hydroxyl substituent. Furthermore, the fluorescent intensity of receptor **1** is also enhanced by the electron-donating nature of the hydroxyl substituent.

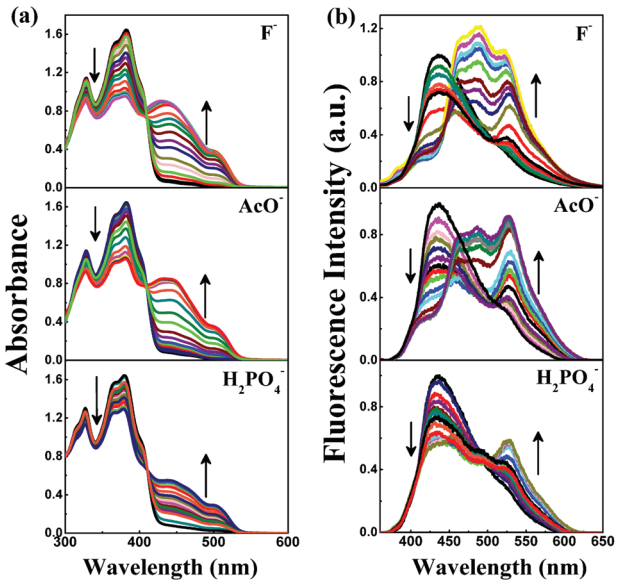


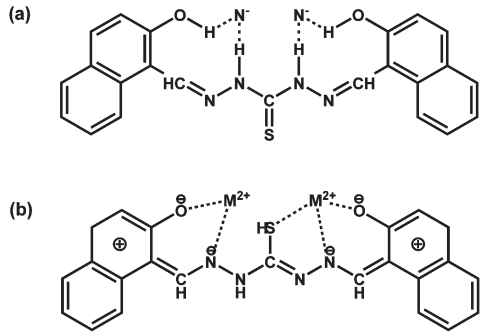
Fig. 2 Absorption (a) and normalized fluorescence spectra (b, λ_{ex} = 342 nm) of receptor **1** (50 μM) in the presence of anions of increasing concentration from 0 to 20 equiv. in a DMSO–H_2O solution (V/V = 9 : 1).

Table 1 Binding constants (K_s) of anions and cations with receptor **1** in a DMSO–H_2O solution (V/V = 9 : 1)

Ions	λ_{abs} (nm)	K_s (M^{-2})
F^-	439	$(2.13 \pm 0.11) \times 10^8$
AcO^-	441	$(1.18 \pm 0.01) \times 10^8$
$H_2PO_4^-$	439	$(1.53 \pm 0.05) \times 10^7$
Zn^{2+}	439	$(5.83 \pm 0.20) \times 10^7$
Cu^{2+}	442	$(9.94 \pm 0.33) \times 10^9$
Ni^{2+}	450	$(3.20 \pm 0.07) \times 10^8$
Co^{2+}	456	$(7.43 \pm 0.09) \times 10^8$

A.2 Absorption and fluorescence spectra of receptor 1 in the presence of anions. The binding behavior of receptor **1** with various anions (such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^-) is firstly monitored by visual observation in a DMSO–H_2O solution (V/V = 9 : 1) (Fig. 2a and S1†). As shown in Fig. 2a, the intensity of an ICT band at 381 nm decreases gradually and a new absorption band appears with a maximum absorption at 439 nm upon increasing the concentration of F^-.

Contemporarily, a well-defined isosbestic point emerges at 408 nm during absorption spectral titration, which indicates the formation of a stable complex with a certain stoichiometric ratio between receptor **1** and F^- through hydrogen bond interaction. Similar phenomena are also observed with the isosbestic point at 411 nm for AcO^- and 408 nm for $H_2PO_4^-$, respectively. Job's plots indicate the formation of a 1 : 2 complex between receptor **1** and anions (Fig. S2†). The association constants (K_s) of receptor **1** for F^-, AcO^-, and $H_2PO_4^-$ are calculated from eqn (1) and their results are summarized in Table 1. On the other hand, the addition of other anions to the receptor **1** solution gives no spectral change (Fig. S1†).



Scheme 2 Proposed structures of the hydrogen bonding [N_2**1**] complex (a) and the doubly deprotonated [M_2**1**] complex (b) (N = anion; M = metal ion).

For a better understanding of the binding mode, fluorescence variations of receptor **1** in the DMSO–H_2O solution (V/V = 9 : 1) in the presence of all the above anions are studied. It is evident from Fig. 2b that the emission of receptor **1** displays red shifts towards F^-, AcO^- and $H_2PO_4^-$, which should be attributed to the enhanced ICT efficiency caused by the hydrogen-bonding interaction between receptor **1** and above anions (Scheme 2a). The addition of other anions to receptor **1** causes insignificant changes in its fluorescence spectra (Fig. S1†).

As is well known, only aprotic solvents are usually permitted for the hydrogen-bonding-based anion chemosensors. In protic solvents such as H_2O or MeOH, the hydrogen-bonding of the sensor with anions would be completely quenched because anions give priority to the interaction with protic solvent molecules.[11] However, the thioamide group could be tolerant to H_2O to some extent due to the high acidity of NH protons,[10a] and the hydroxyl group could further enhance such ability. So detection of anions is expected to be carried out in the solution of DMSO–H_2O (V/V = 9 : 1). To further prove the tolerant ability of receptor **1** towards water, receptor **2** which has a similar molecular structure to that of receptor **1** is synthesized and investigated. With receptor **2** (50 μM), no hydroxyl substituent compared to receptor **1**, addition of various anions does not induce any discernible spectral changes in the same solution (Fig. S3†). However, a problem worthy to point out is that receptor **2** would also be tolerant to H_2O to some extent when its concentration is high.

Considering that the addition of the F^- ion to the solution of receptor **1** can lead to representative spectral changes, it is thus chosen as the input for studying logic operations of receptor **1** in subsequent experiments.

A.3 Absorption and fluorescence spectra of receptor 1 in the presence of cations. The interaction of receptor **1** with metal ions Zn^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} is demonstrated by its absorption and fluorescence responses of receptor **1** (50 μM) in the DMSO–H_2O solution (V/V = 9 : 1) (Fig. 3).

As for UV-Vis spectra, the ICT band of receptor **1** at 381 nm is gradually reduced upon addition of the above metal ions, a series of new bands appear at 439 nm, 442 nm, 450 nm and 456 nm, respectively (Fig. 3a). The appearance of the isosbestic points in titration traces suggests the formation of well-defined

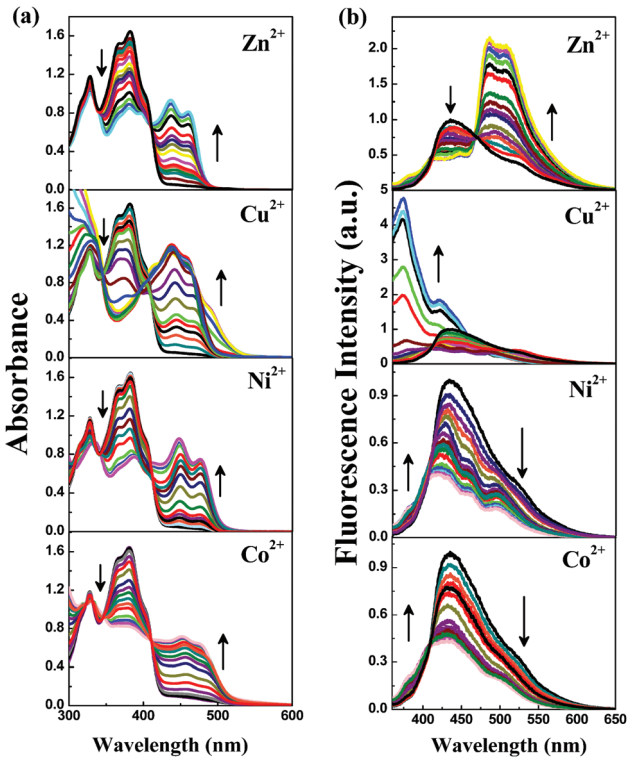


Fig. 3 Absorption (a) and normalized fluorescence spectra (b, λ_{ex} = 342 nm) of receptor **1** (50 μM) in the presence of cations of increasing concentration from 0 to 20 equiv. in a DMSO–H_2O solution (V/V = 9 : 1).

binding complexes between receptor **1** and the above tested metal ions, which thereby allows their binding constants (K_s) to be fitted by a nonlinear fitting procedure for 1 : 2 binding complexes (Table 1, Scheme 2b).[10e]

The changes of fluorescence spectra of receptor **1** along with concentration increase of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} are shown in Fig. 3b. Upon titration of Zn^{2+}, a gradual decrease in fluorescence intensity at 437 nm and simultaneous appearance of a new red-shifted emission band at 486 nm are observed with an isoemission point at 467 nm. The distinctive red-shift on the maximum absorption peak is caused by the enhanced ICT process due to the chelation of receptor **1** with Zn^{2+}, as an electron-deficient group, different from that between **1** and anions. In contrast, the coordination of Cu^{2+}, Co^{2+} or Ni^{2+} with receptor **1** blocks the ICT process and causes a significant blue-shift in the fluorescent peak because they can lead to an energy transfer from the excited naphthalene unit to the low-lying empty d orbital of the ions.[12] What deserves to be mentioned is that the capture of Cu^{2+} by receptor **1** produces a new band at 375 nm and the fluorescence increases sharply, while Co^{2+} and Ni^{2+} only have little fluorescence increase below 400 nm without appearance of a new band. For most receptors, the communication between them and transition metal ions is too strong compared with the other interactions, which is believed to be the main reason for the quenching of fluorescence. In our work, receptor **1** forms a proper cavity and shows the strongest binding with Cu^{2+} among the tested metal

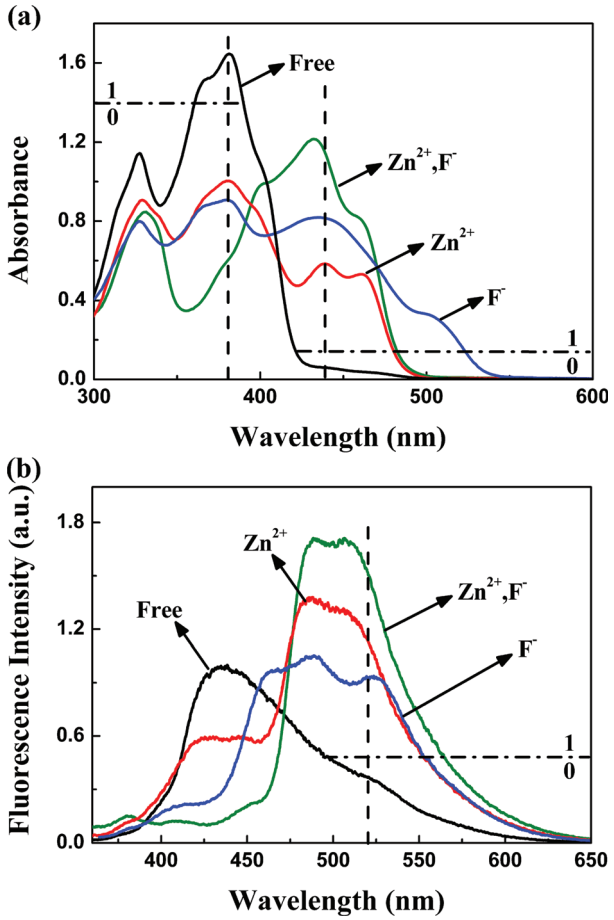


Fig. 4 (a) Absorption and (b) fluorescence (λ_{ex} = 342 nm) spectra about different situations of receptor **1** with Zn^{2+} (IN1, 5 equiv.) and F^- (IN2, 5 equiv.).

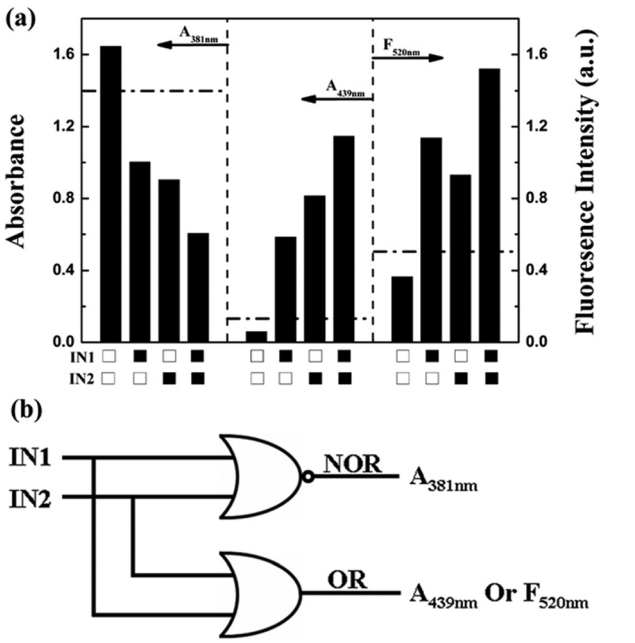


Fig. 5 (a) The changes of absorbance at 381 nm and 439 nm and fluorescence intensity at 520 nm for receptor **1** with Zn^{2+} (IN1, 5 equiv.) and F^- (IN2, 5 equiv.). (□ represents inputs that are 0, ■ represents inputs that are 1). (b) The logic circuit for the NOR/OR logic gates.

cations. According to a literature report, the Cu^{2+}–fluorophore interaction might be suppressed with the increasing concentration of the Cu^{2+}–receptor. As a result, fluorescence of receptor **1** is maintained.[13] It should be emphasized that other metal ions, such as Na^+, K^+, Cd^{2+}, Mg^{2+}, Al^{3+}, Pb^{2+} and Ca^{2+}, were also tested, but no obvious influence on absorption and fluorescence spectra of receptor **1** is detected (Fig. S1†).

As two representative metal ions, Zn^{2+} and Cu^{2+} are chosen as two of the signal inputs for studying the logic operations of receptor **1** in the subsequent experiment.

A.4 Reversibility of receptor 1 binding to various ions. In the recognition of specific analytes, the reversibility of a chemical responding system is a very important factor. In this work, the reversibility of receptor **1** after immersion in F^-, Zn^{2+}, or Cu^{2+} is examined, respectively. The interactions between receptor **1** and these ions are chemically reversible, which can be verified by the introduction of Ca^{2+} into the system for F^- and EDTA (sodium salt) for Zn^{2+}/Cu^{2+}, respectively (Fig. S4–S6†).[14] The corresponding absorption and fluorescent spectra of receptor **1** binding to F^-, Zn^{2+} and Cu^{2+} could all immediately be restored.

These processes could all be repeated for at least three times. These regenerations indicate that receptor **1** could be reused with proper treatment.

B. Logic gating behavior of receptor 1 with anions and cations as inputs

On the basis of above-mentioned results, different spectral outputs of receptor **1**, encoded as absorption and fluorescence dual-mode, can provide an entry for developing multiple logic operations at molecular level using various ions as inputs. These inputs and outputs can be encoded with binary digits by applying positive logic conventions (off = 0, on = 1).[10b]

Monitoring changes of absorption and fluorescence as outputs this molecule can operate simultaneously as NOR and OR logic gates when Zn^{2+} (IN1) and F^- (IN2) are used as inputs, as shown in Fig. 4 and 5. The absorption value at 381 nm can only be monitored when there is no chemical input, which leads to a NOR logic gate. Without the two inputs of IN1 and IN2, the absorption value at 439 nm or the fluorescence intensity at 520 nm of receptor **1** is relatively low, so the output is read as "0". Whereas the two values are both obviously enhanced in the presence of individual or both of the two inputs, giving the output of "1", and this behavior can be described as two OR logic gates. Since there are two OR gates with different responses to the inputs, the order can be exchanged when needed.

With the introduction of Cu^{2+} as the third input (IN3), the molecular device can achieve a more complicated logic function. With the similar behaviors on the absorption of receptor **1** upon addition of Cu^{2+} compared with Zn^{2+} and F^-, as we mentioned above, the NOR and OR gates are both retained when Cu^{2+} (IN3) acts on the combination of Zn^{2+} (IN1) and F^- (IN2) (Fig. 6). On the other hand, as shown in Fig. 7, the fluorescence intensity at 520 nm would be quenched by the

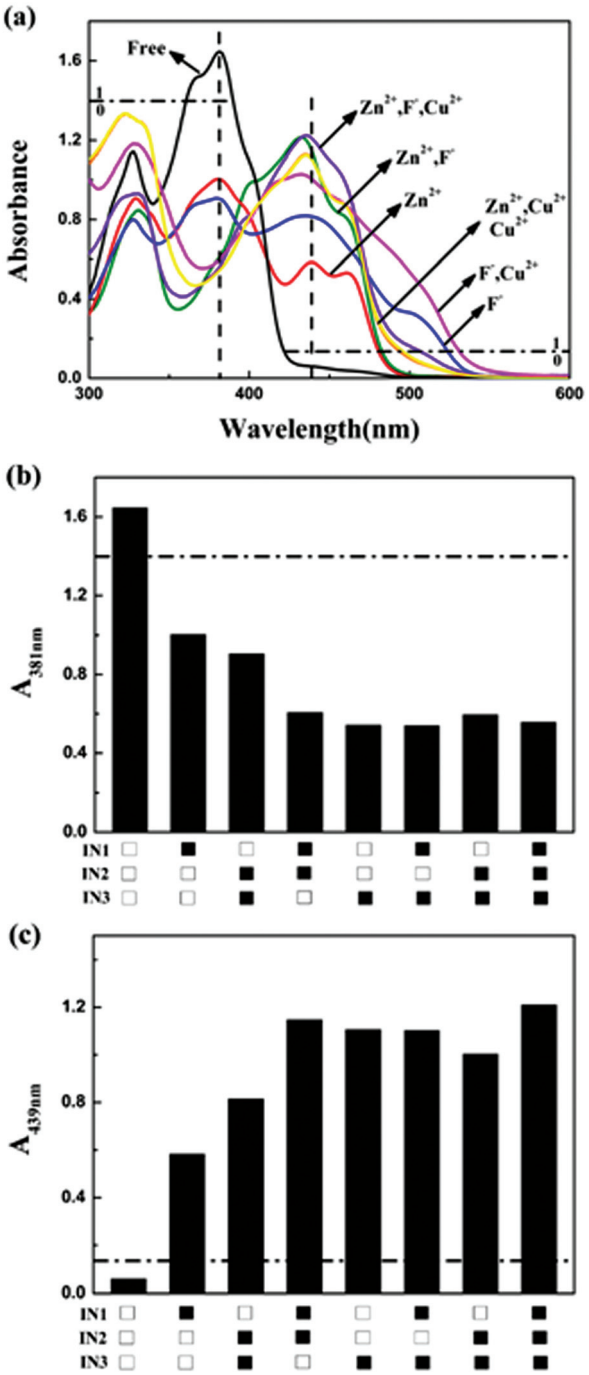


Fig. 6 (a) Absorption about different situations of receptor **1** with Zn^{2+} (IN1, 5 equiv.), F^- (IN2, 5 equiv.) and Cu^{2+} (IN3, 5 equiv.). (b) and (c) The changes of absorbance at 381 nm and 439 nm, respectively (□ represents inputs that are 0, ■ represents inputs that are 1).

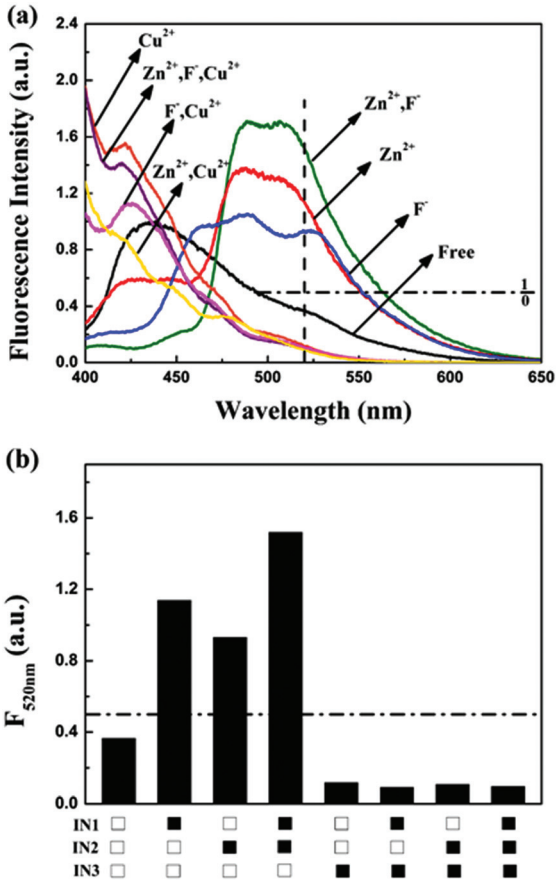


Fig. 7 (a) Fluorescence spectra (λ_{ex} = 342 nm) about different situations of receptor **1** with Zn^{2+} (IN1, 5 equiv.), F^- (IN2, 5 equiv.) and Cu^{2+} (IN3, 5 equiv.). (b) The changes of fluorescence intensity at 520 nm (□ represents inputs that are 0, ■ represents inputs that are 1).

introduction of Cu^{2+} (IN3) no matter with or without Zn^{2+} (IN1) and/or F^- (IN2), which is read as "0". The spectral changes in response to the three inputs are in accordance with an INHIBIT logic gate, which is integrated with an OR gate and a NOT gate. According to the three histograms (Fig. 6b, c and 7b), the truth table (Fig. 8a) can be achieved. It can be seen that this chemical system responds to an input string of

(a)

Input			Output		
IN1	IN2	IN3	OUT1	OUT2	OUT3
Zn^{2+}	F^-	Cu^{2+}	A_{381nm}	A_{439nm}	F_{520nm}
0	0	0	1	0	0
1	0	0	0	1	1
0	1	0	0	1	1
1	1	0	0	1	1
0	0	1	0	1	0
1	0	1	0	1	0
0	1	1	0	1	0
1	1	1	0	1	0

(b)

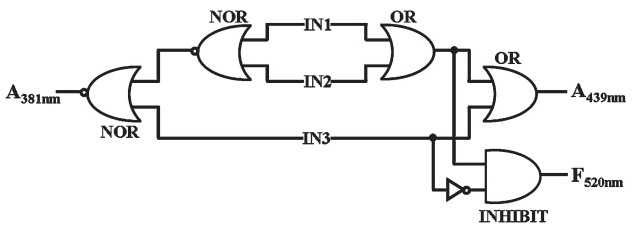


Fig. 8 A three-input, three-output molecular switch: (a) truth table for a three-input situation. (b) Combinatorial logic scheme.

three binary digits (IN1, IN2, IN3) with an output string of three binary digits (OUT1, OUT2, OUT3). Consequently, this chemical system can be integrated to a combinational logic circuit at monomolecular level with a NOR gate, an OR gate and an INHIBIT gate (Fig. 8b). It is worth noting that all these logic types can be observed simultaneously if required.

Conclusions

In this work, a thiocarbazone derivative bearing 2-naphthol as the chromophore and fluorophore core, denoted as receptor **1**, has been synthesized and characterized. The absorption and fluorescence spectra response profiles of receptor **1**, which are sensitive towards anions and metal cations, have been investigated in a DMSO–H_2O solution (V/V = 9 : 1). We find that receptor **1** can proceed upon logic operations with multiply-configurable dual outputs by selecting different ionic inputs through modulating ICT processes. As a result, binary logic operations (OR, NOR and INHIBIT) and combinational logic circuits have been achieved at molecular level. Since all logic operations mentioned above can be operated with two/three inputs by a single molecule, the system of receptor **1** reported here shows high versatility. We believe that the present system will provide useful information on the range of optical devices that can operate at molecular level.

Experimental

General considerations

Analytical grade solvents and compounds were used for all preparations. Anions and metal ions were used as the tetrabutylammonium salts and nitrates, respectively. The water used in our present work was deionized. UV/Visible (UV/Vis) absorption spectra were obtained on a Shi-madzu-UV-3101 scanning spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The excitation and emission wavelength bandpasses were both set at 5 nm. All spectral titrations were carried out by keeping the concentration constant (50 μM) while varying ion concentrations (0–1 mM) in a 1 cm quartz cell. The binding constants K_s of the complex **1**–X_n were determined by direct spectrophotometric titrations as a function of [X] in a DMSO–H_2O solution (V/V = 9 : 1) at room temperature, using the UV-Vis absorption spectra. The absorbance data are fitted with eqn (1):[15]

$$\frac{A - A_{\min}}{A_{\max} - A} = K_s[X]^n \quad (1)$$

In the equation, A denotes the absorbance at [X], whereas $A_{\min}$ and $A_{\max}$ are the limiting absorbance values of a free (minimal [X]) and abound (saturating [X]) indicator, respectively. ^{1}H NMR spectra were recorded using a mercury-300BB spectrometer (Varian, USA) operated at 300 MHz with tetramethylsilane (TMS) as an internal standard.

Synthesis of receptors 1 and 2

The compounds of **1** and **2** were synthesized according to the procedure described in the literature.[10a]

Thiocarbohydride. CS_2 (13 mL) was added dropwise to a solution of excess hydrazine hydrate (80%, 60 mL) in water (70 mL). After the addition, the mixture was refluxed with stirring for 4 h and then cooled for 30 min in an ice-water bath. The product was filtrated and washed with ethanol and ether. A white solid of thiocarbohydride was obtained by recrystallization in dilute hydrochloric acid. Yield: 71%; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 4.50 (4H, NH_2, s), 8.71 (2H, NH, s).

2-Naphthol-1-aldehyde-conjugated thiourea (1). A solution of 2-naphthol-1-aldehyde (0.43 g, 2.5 mmol) or 1-naphthaldehyde (0.39 g, 2.5 mmol) in ethanol (20 mL) was added slowly to a solution of thiocarbohydride (0.1062 g, 1 mmol) in water (10 mL). The heterogeneous mixture was refluxed with stirring for 5 h. Then the mixture was cooled to room temperature and filtered. The precipitate was washed with ethanol and dried under vacuum to afford receptor **1** in quantitative yield. Yield: 65%; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 12.89 (2H, NH, br s), 12.09 (2H, OH, s), 9.17–9.63 (2H, CH═N, d), 8.20–8.54 (2H, ArH, d), 7.88–7.96 (4H, ArH, q), 7.60–7.65 (2H, ArH, t), 7.39–7.44 (2H, ArH, t), 7.23–7.26(2H, ArH, d).

1-Aldehyde-conjugated thiourea (2). The synthesis procedure of receptor **2** is same as that of receptor **1**. Yield: 73%; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 11.83–12.03 (2, NH, d), 9.16 (2H, CH═N, br s), 8.31–8.45 (2H, ArH, d), 8.02–8.08 (6H, ArH, t), 7.59–7.72 (6H, ArH, m).

Acknowledgements

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References

1 A. Aviram, *J. Am. Chem. Soc.*, 1988, **110**, 5687–5692.
2 A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Nature*, 1993, **364**, 42–44.
3 (*a*) A. P. de Silva, I. M. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell and T. E. Rice, *J. Am. Chem. Soc.*, 1999, **121**, 1393–1394; (*b*) D. H. Qu, Q. C. Wang and H. Tian, *Angew. Chem., Int. Ed.*, 2005, **44**, 5296–5299; (*c*) A. P. de Silva, Y. Leydet, C. Lincheneau and N. D. McClenaghan, *J. Phys.: Condens. Matter*, 2006, **18**, S1847–S1872; (*d*) D. Margulies, C. E. Felder, G. Melman and A. Shanzer, *J. Am. Chem. Soc.*, 2007, **129**, 347–354; (*e*) K. Szacilowski, *Chem. Rev.*, 2008, **108**, 3481–3548; (*f*) C. H. Xu, W. Sun, Y. R. Zheng, C. J. Fang, C. Zhou, J. Y. Jin and C. H. Yan, *New J. Chem.*, 2009, **33**, 838–846; (*g*) M. Kumar, A. Dhir and V. Bhalla, *Org. Lett.*, 2009, **11**,

2667–2570; (*h*) J. Andréasson and U. Pischel, *Chem. Soc. Rev.*, 2010, **39**, 174–188; (*i*) M. Kumar, R. Kumar and V. Bhalla, *Org. Biomol. Chem.*, 2011, **9**, 8237–8245.

4 (*a*) N. Kaur, N. Singh, D. Cairns and J. F. Callan, *Org. Lett.*, 2009, **11**, 2229–2232; (*b*) J. Andréasson, S. D. Straight, T. A. Moore, A. L. Moore and D. Gust, *J. Am. Chem. Soc.*, 2008, **130**, 11122–11128; (*c*) M. Amelia, M. Baroncini and A. Credi, *Angew. Chem., Int. Ed.*, 2008, **47**, 6240–6243; (*d*) Y. H. Wang, Y. Q. Huang, B. Li, L. M. Zhang, H. Song, H. Jiang and J. Gao, *RSC Adv.*, 2011, **1**, 1294–1300.

5 (*a*) Y. Shiraishi, Y. Tokitoh and T. Hirai, *Chem. Commun.*, 2005, 5316–5318; (*b*) L. Y. Zhao, D. Sui, J. Chai, Y. Wang and S. M. Jiang, *J. Phys. Chem. B*, 2006, **110**, 24299–24304; (*c*) D. Zhang, J. H. Su, X. Ma and H. Tian, *Tetrahedron*, 2008, **64**, 8515–8521; (*d*) G. Q. Zong and G. X. Lu, *Tetrahedron Lett.*, 2008, **49**, 5676–5679; (*e*) G. Q. Zong and G. X. Lu, *J. Phys. Chem. C*, 2009, **113**, 2541–2546; (*f*) S. C. Wang, G. W. Men, L. Y. Zhao, Q. F. Hou and S. M. Jiang, *Sens. Actuators, B*, 2010, **145**, 826–831; (*g*) K. C. Chang, I. H. Su, Y. Y. Wang and W. S. Chung, *Eur. J. Org. Chem.*, 2010, 4700–4470; (*h*) Y. Liu, M. Y. Li, Q. Zhao, H. Z. Wu, K. W. Huang and F. Y. Li, *Inorg. Chem.*, 2011, **50**, 5969–5977.

6 (*a*) D. Margulies, G. Melman and A. Shanzer, *J. Am. Chem. Soc.*, 2006, **128**, 4865–4871; (*b*) S. D. Straight, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore and D. Gust, *Adv. Funct. Mater.*, 2007, **17**, 777–785; (*c*) B. Leng and H. Tian, *Aust. J. Chem.*, 2010, **63**, 169–172; (*d*) A. F. Li, Y. B. Ruan, Q. Q. Jiang, W. B. He and Y. B. Jiang, *Chem.–Eur. J.*, 2010, **16**, 5794–5802; (*e*) O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci and E. U. Akkaya, *J. Am. Chem. Soc.*, 2010, **132**, 8029–8036; (*f*) W. Lu, M. Y. Zhang, K. Y. Liu, B. Fan, Z. Xia and L. M. Jiang, *Sens. Actuators, B*, 2011, **160**, 1005–1010; (*g*) M. Shahid, P. Srivastava and A. Misra, *New J. Chem.*, 2011, **35**, 1690–1700; (*h*) R. K. Mishra and K. K. Upadhyay, *Eur. J. Org. Chem.*, 2011, 4799–4805.

7 D. C. Magri and A. P. de Silva, *New J. Chem.*, 2010, **34**, 476–481.

8 A. P. de Silva and N. D. McClenaghan, *Chem.–Eur. J.*, 2002, **8**, 4935–4945.

9 M. J. Yuan, W. D. Zhou, X. F. Liu, M. Zhu, J. B. Li, X. D. Yin, H. Y. Zheng, Z. C. Zuo, C. B. Ouyang, H. B. Liu, Y. L. Li and D. B. Zhu, *J. Org. Chem.*, 2008, **73**, 5008–5014.

10 (*a*) F. Han, Y. H. Bao, Z. G. Yang, T. M. Fyles, J. Z. Zhao, X. J. Peng, J. L. Fan, Y. K. Wu and S. G. Sun, *Chem.–Eur. J.*, 2007, **13**, 2880–2892; (*b*) F. Otón, A. Espinosa, A. Tárraga, I. Ratera, K. Wurst, J. Veciana and P. Molina, *Inorg. Chem.*, 2009, **48**, 1566–1576; (*c*) M. M. M. Raposo, B. García-Acosta, T. Ábalos, P. Calero, R. Martínez-Máñez, J. V. Ros-Lis and J. Soto, *J. Org. Chem.*, 2010, **75**, 2922–2933; (*d*) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962–2964; (*e*) D. Maity and T. Govindaraju, *Chem.–Eur. J.*, 2011, **17**, 1410–1414; (*f*) J. L. Wu, Y. B. He, Z. Y. Zeng, L. H. Wei, L. Z. Meng and T. X. Yang, *Tetrahedron*, 2004, **60**, 4309–4314; (*g*) S. Y. Liu, L. Fang, Y. B. He, W. H. Chan, K. T. Yeung, Y. K. Cheng and R. H. Yang, *Org. Lett.*, 2005, **7**, 5825–2828; (*h*) A. F. Li, J. H. Wang, F. Wang and Y. B. Jiang, *Chem. Soc. Rev.*, 2010, **39**, 3729–3745; (*i*) F. Wang, W. B. He, J. H. Wang, X. S. Yan, Y. Zhan, Y. Y. Ma, L. C. Ye, R. Yang, F. Cai, Z. Li and Y. B. Jiang, *Chem. Commun.*, 2011, **47**, 11784–11786; (*j*) W. W. Huang, Z. Chen, H. Lin and H. K. Lin, *J. Lumin.*, 2011, **131**, 592–596; (*k*) L. Wu, L. Liu, R. Fang, C. Deng, J. Han, H. W. Hu, C. Lin and L. Y. Wang, *Tetrahedron Lett.*, 2012, **53**, 3637–3641.

11 Y. Sun, Y. L. Liu, M. L. Chen and W. Guo, *Talanta*, 2009, **80**, 996–1000.

12 H. X. Wang, H. X. Wu, L. Xue, Y. Shi and X. Y. Li, *Org. Biomol. Chem.*, 2011, **9**, 5436.

13 Z. C. Xu, Y. Xiao, X. H. Qian, J. N. Cui and D. W. Cui, *Org. Lett.*, 2005, **7**, 889–892.

14 (*a*) D. Maity, A. K. Manna, D. Karthigeyan, T. K. Kundu, S. K. PaTi and T. Govindaraju, *Chem.–Eur. J.*, 2011, **17**, 11152–111161; (*b*) Z. X. Li, L. F. Zhang, L. N. Wang, Y. K. Guo, L. H. Cai, M. M. Yu and L. H. Wei, *Chem. Commun.*, 2011, **47**, 5798–5800.

15 N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**, 1130–1172.