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An efficient multiple-mode molecular logic system for pH, solvent polarity, and Hg^{2+} ions

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ABSTRACT

A novel fluorophore 1,3-bis(1,1,3-trimethyl-1*H*-benzo[*e*]indol-2(3*H*)-ylidene)propan-2-one (**L**) was synthesized and fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray single-crystal structural analysis. Compound **L** is a pH-controlled molecular switch due to its protonation. The fluorescence change in protic polar solvents means that this compound also could be used as a protic solvent polarity sensor. Among the considered metal ions, the fluorescence of compound **L** could be quenched completely by Hg^{2+} ions with a high selectivity. Based on these fluorescence characters, this fluorescent dye **L** has promising applications as a multiple-mode molecular logic system.

1. Introduction

Developing a wide variety of supramolecular systems performing as elementary electronic devices, such as switches, sensors, logic gates, and molecular-level machines, is an intense research area and of tremendous significance to the development of miniaturized device components.[1] Potential applications of these components in optical and electronic molecular-scale computational devices have attracted considerable effort to this research area.[2]

A significant amount of work has been devoted to obtain specific molecule that is able to change one or several macroscopic properties in response external inputs.[3] The design of fluorescent signaling molecules has attracted a great deal of attention.[4] Many supramolecular systems, the emission properties of which can be modulated by external inputs, such as temperature, pH, redox potential, solvent polarity, and metal ions, have been reported.[5–9] There are few molecular systems behaving as 'multiply configurable' fluorescent indicators.[10]

Merocyanine dyes are heterocyclic chromophores that are extensively used in a number of areas (i.e., as photographic sensitizers, for nonlinear optics, and in chemotherapy).[11] Recently, they have also been employed as sensors of protein conformation and protein interactions in live cell imaging.[12] Here, we design a merocyanine dye, **L** (Scheme 1), which has a carbonyl bearing two benzo[*e*]indoline fragments at both ends. At both sides, **L** has nitrogen atoms (trialkylamine moiety), which could be protonated. In fact, basic donor amino groups can also act as fluorescence quenchers.[13] On account of the nitrogen atoms with lone electron pairs, which can form coordinate bonds, **L** is propitious to recognize special metal ion with high selectivity due to its structure. Based on these results, a pH switch was achieved. Meanwhile, a highly fluorescent material displaying novel solvent polarity-tunable blue-green fluorescence emission was presented, which was clearly different from the behaviors of solvent polarity sensors previously reported. Otherwise, this molecule has a selective detection of Hg^{2+} ions.

As a class of molecular devices, fluorescent logic gates play a pivotal role in molecular computation because they are detectable as a single molecule and can simultaneously treat multiple inputs.[14,15] Within the past decade, many fluorescent logic gates showing NOT, AND, OR, XOR, NOR, NAND, and INHIBIT operations, and combinational logic circuits incorporating single logic gates have been reported.[16] In the same way, the molecule we reported here could demonstrate three different logic functions (NAND, NOR, and INHIBIT) operated by solvent polarity, proton (H^+), and Hg^{2+} as inputs.

2. Results and discussion

The synthetic route to the merocyanine receptor (**L**) is illustrated in Scheme 1. 1,1,2,3-Tetramethyl-1*H*-benzo[*e*]indolinium iodide (**1**) and 2-methylene-1,1,3-trimethyl-1*H*-benzo[*e*]indoline (**2**) were prepared according to the literature method.[17] Treatment of **2** with an appropriate amount of triphosgene and $AlCl_3$ afforded the symmetrical structural **L**. Compounds **1**, **2**, and **L** have been

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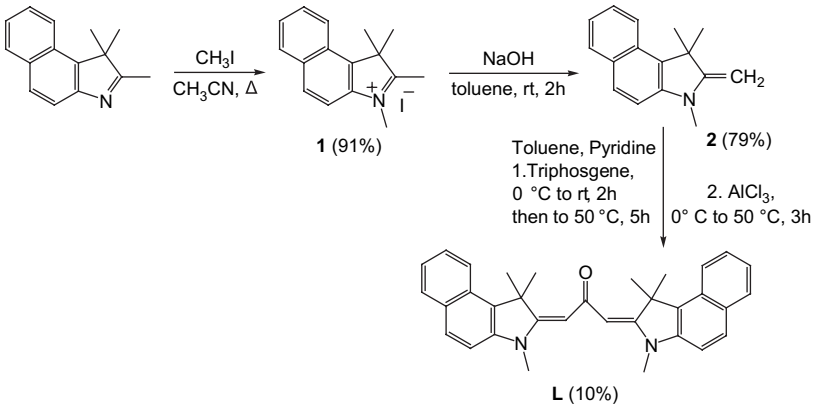


Scheme 1. Synthesis of merocyanine receptor **L**.

characterized by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and HRMS (ESI) spectrometry. Compound **L** was also characterized crystallographically.

2.1. pH switch

Molecular systems behaving as a fluorescent indicator of the pH window have attracted much attention, because the proton (H^+) concentration is simply and easily controlled.[18] Due to the very low solubility of **L** in water, its properties as a base have been examined in a THF/H_2O mixed solvent. A 50% THF solution of **L** (1.0×10^{-5} M) was titrated with H^+ ($HClO_4$). After addition of H^+, the yellow solution of **L** turned colorless (see the photograph in Fig. 1a). The color bleaching resulted from the progressive disappearance of the absorption band at 441 nm. Meanwhile, upon addition of H^+, a new smaller absorption band with a peak at 393 nm forms and develops, as shown in Figure 2. The absorption makes a blue shift of 48 nm. There is no absorption from 500 to 700 nm, so this segment is not shown in Figure 2.

As shown in the photograph (Fig. 1b), the solution of **L** in 50% THF emits blue fluorescence, which can be considered as 'switched on'. Upon addition of H^+, the blue fluorescence was quenched gradually. It was quenched completely at pH=2, which is considered as 'switched off' as shown in Figure 3. Since compound **L** is not 'ideal' polymethine, the mirror-image relationship of absorption and fluorescence is often abrogated.

In this pH sensing system, with a decrease in pH of the solution, the color was bleached and the fluorescence quenched. This change occurs because of the protonation of the nitrogen atoms (two trialkylamine moieties). The nitrogen atoms change from electron-contributing groups to electron-withdrawing units. After the protonation, the whole conjugated system of the molecule has been separated. Thus, the merocyanine-like chromophore was broken up, which resulted in the blue shift of the absorption spectrum and the quenching of the fluorescence.

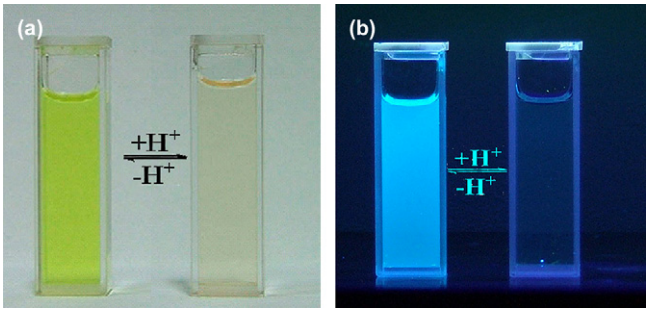


Figure 1. The color change (a) and fluorescence emission (b) responses of **L** (1.0×10^{-5} M in THF/H_2O=1:1) on addition of H^+. Left to right: in the absence (pH=8) and presence (pH=2) of H^+ in KCl (0.1 M) solution at 298 K.

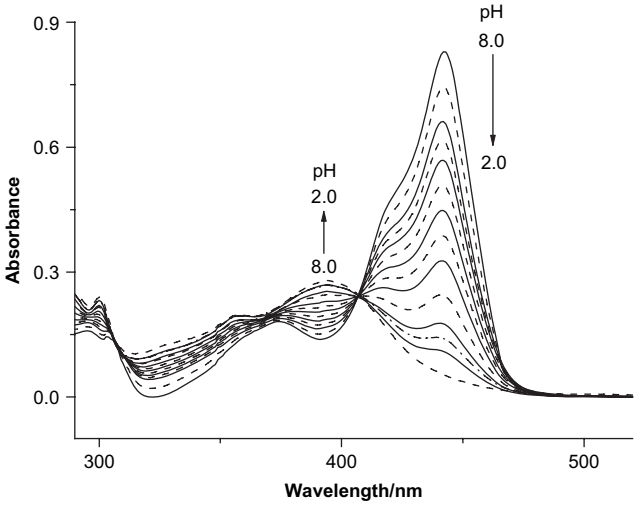


Figure 2. UV–vis spectra in the course of titration of the aqueous THF solution (1.0×10^{-5} M) of **L** with H^+, at 298 K.

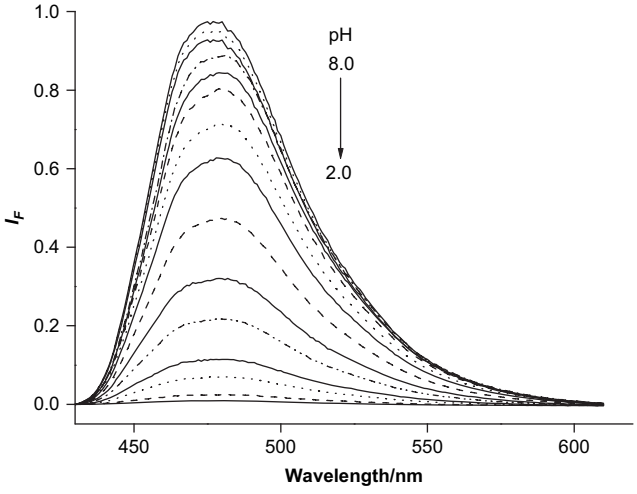


Figure 3. Change in fluorescence spectra (λ_{ex}=410 nm) of **L** (10 μM) with pH in aqueous KCl (0.1 M) solution with 50% THF at 298 K.

2.2. Polar fluorescence

There have been several experimental and theoretical studies on the solvatochromic behavior of merocyanine dyes.[11a,19] As a merocyanine dye, the spectral character of compound **L** may be largely influenced in solvents of different polarities. We took the binary mixed solvents, THF with relative lower polarity and H_2O with higher polarity, to adjust the polarity of solvent. The emission spectra of **L** were recorded with different fractions of THF in distilled water (Fig. 4).

As the addition of a high-polarity solvent (H_2O) to a low-polarity one (THF), enhancement of the solvent polarity causes a significant quenching of the fluorescence of **L** coupled with the appearance of a new band centered at 520 nm. A dramatic fluorescence change from blue (95% THF) to green (5% THF) could be clearly seen (Fig. 5).

The dual emission character of this compound shows an obvious red shift. A well-defined isoemissive point at 508 nm can be clearly observed (Fig. 4). This could be interpreted in terms of two emissive species with a relationship, as one of the proofs for the formation of the exciplex with a polar solvent.[20] We have measured the fluorescence spectrum of **L** in different polar mixed solvents (Fig. 6).

Due to the low solubility of **L**, its fluorescence spectra were measured in different polar solvents containing 5% THF. Upon enhancement of the solvent polarity (THF→CH_3CH_2OH→CH_3OH→H_2O), the fluorescence of **L** makes a red shift and the intensity is weakened. This is probably due to the interaction between the solvent and the merocyanine molecule. These indicated that **L** might be used as a solvent polarity sensor.

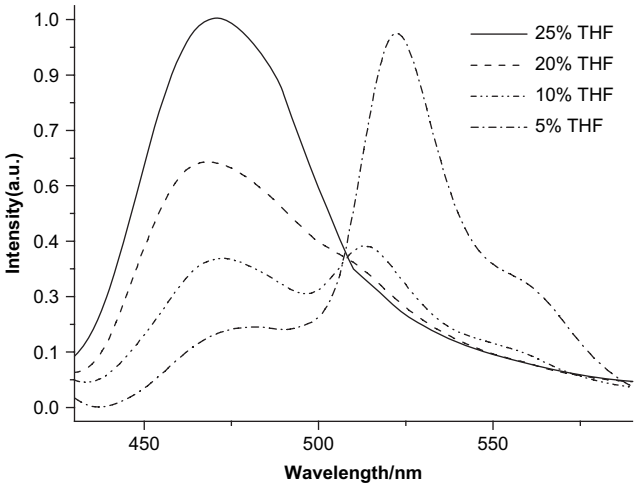


Figure 4. Emission spectra of **L** (1.0×10^{-5} M, at 298 K) in H_2O with different amount of THF excited at 410 nm.

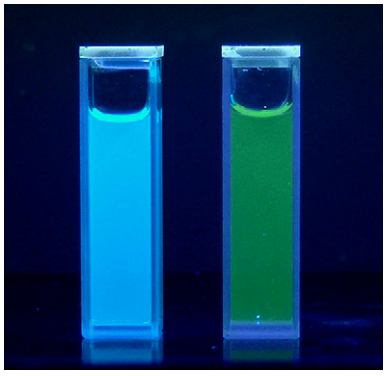


Figure 5. Photograph of **L** in 95% THF (left) and 5% THF (right), excited at 410 nm (1.0×10^{-5} M, at 298 K).

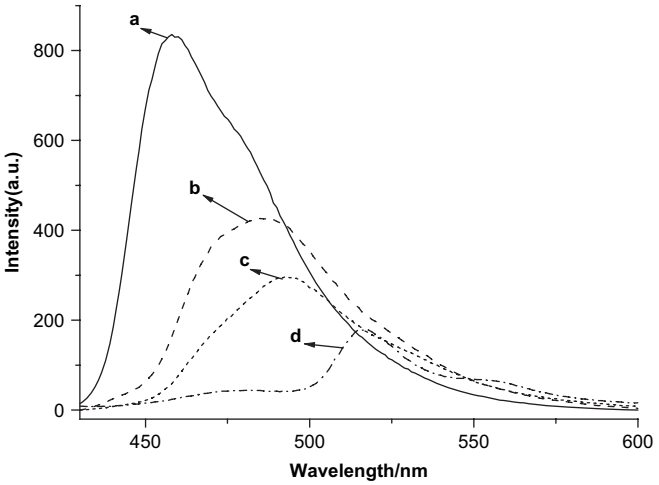


Figure 6. Emission spectra of **L** in mixed solvents with different polarities excited at 410 nm (1.0×10^{-5} M, at 298 K). From left to right: (a) pure THF; (b) 95% ethanol+5% THF; (c) 95% methanol+5% THF; (d) 95% H_2O+5% THF.

2.3. Metal ions

Sensing harmful species is critical to the environment. Elementary mercury and Hg^{2+} salts, which are dangerous for human health, should be detected effectively.[21] Hg^{2+} is able to quench the fluorescence of **L** when forming the corresponding complex giving rise to the appearance of CHEQ (chelation enhanced quenching) effect. The selective properties of **L** were determined toward representative alkali (K^+), alkaline earth (Ca^{2+} and Ba^{2+}), and transition-metal ions (Cd^{2+}, Co^{2+}, Ag^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+}). Upon interaction with 100 equiv of various metal ions, only Hg^{2+} ion exhibited effective fluorescence quenching among the tested metal ions (Fig. 7a), even in the presence of other cations (e.g., Ca^{2+} and Cd^{2+}, see Supplementary data).

This compound therefore possesses an efficient Hg^{2+} selective ON–OFF type signaling behavior, which can be explained by the existence of deactivation channels involving the metal orbital. The fluorescence quenching effect clearly indicates the coordination of Hg^{2+} at the receptor unit of **L**. Obviously, Hg^{2+} binds to the two nitrogen atoms, which have a lone electron pair. From the X-ray single-crystal structure of **L** (Fig. 8), the space length between the two nitrogen atoms (trialkylamine moiety) was found, which indicated that **L** could form a complex only with particular ions that have appropriate dimensions. Selected bond distances and angles are tabulated in Table 1. The dimensions of Hg^{2+} are fit to form a complex with **L**, but other metal ions do not have the suitable size. The stoichiometry of the **L**–Hg^{2+} complex was estimated to be 1:1 by ^{1}H NMR titration (Fig. 9) and a nonlinear curve fitting of the fluorescence titration results (Fig. 10).

As shown in the ^{1}H NMR spectra of Figure 9, **L** alone shows the symmetrical planar structure, which can also be seen from the single crystal (Fig. 8). Treatment with Hg^{2+} ions resulted in destroy of structural symmetry, which led to 10 signals (Fig. 9, up) from original 5 signals (Fig. 9, down) in the range of 7.2–8.2 ppm.

To gain more insight into the chemosensing properties of **L** toward Hg^{2+} ions, fluorescence titrations were carried out (Fig. 10). In high-polar solvent (5% THF+95% H_2O, Fig. 10), this system exhibited very efficient fluorescence quenching, and over 85% of the total fluorescence intensity change was observed with addition of 3 equiv of Hg^{2+} ions. The association constant, K_{assoc}, was estimated

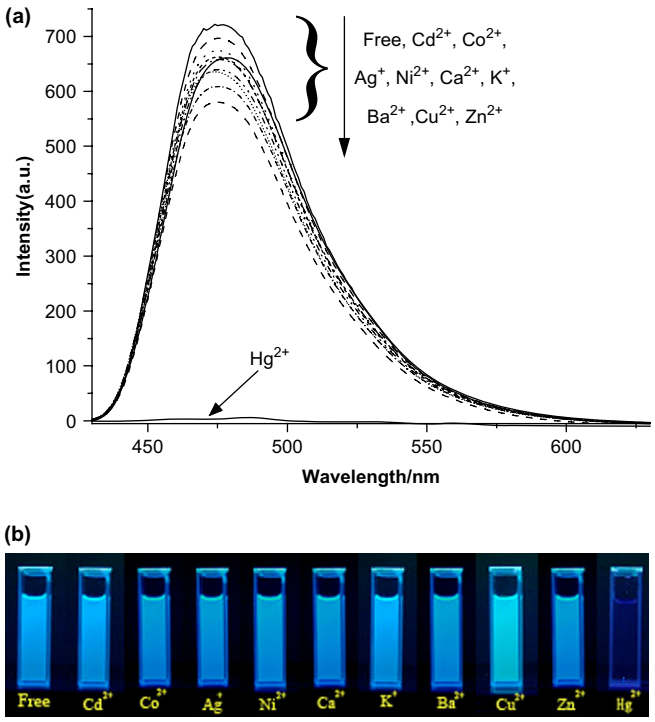


Figure 7. (a) Fluorescence spectra (λ_{ex}=410 nm) and (b) photograph (irradiated at 365 nm using UV lamp) of **L** (10 μM) with various metal ions in 50% THF solution at 298 K.

by the nonlinear curve-fitting procedure[22] of fluorescence titration data and was 5.3×10^4 M^{-1}. The detection limit[23] was also estimated from the titration results and was 2.1×10^{-6} M.

2.4. Logic gates

Compound **L** behaves as a pH-controlled molecular switch, solvent polarity sensor, as well as Hg^{2+} sensor, which constitutes the basis for a molecular logic gate with three different logic functions (NAND, NOR, and INHIBIT) in response to solvent polarity, proton, and Hg^{2+} ion.

2.4.1. NAND gate based on a polarity–CHEQ pair

In Figure 10, we represent the quenching of fluorescence emission of **L** with Hg^{2+} in two different polarity solutions. When the solvent polarity is low (50% THF+50% H_2O, Fig. 10), relative abundant Hg^{2+} (100 equiv) was needed to quench the fluorescence

Table 1
Selected bond distances (Å) and bond angles (°) for **L** with estimated standard deviations in parentheses

N(1)–C(3)	1.377(2)	C(1)–C(18)	1.459(2)
N(1)–C(17)	1.445(2)	C(1)–C(2)	1.459(2)
N(2)–C(19)	1.3769(19)	C(2)–C(3)	1.355(2)
N(2)–C(33)	1.440(2)	C(18)–C(19)	1.360(2)
C(3)–N(1)–C(17)	124.44(14)	C(2)–C(3)–N(1)	122.59(16)
C(19)–N(2)–C(33)	125.13(15)	C(19)–C(18)–C(1)	129.41(17)
C(18)–C(1)–C(2)	113.94(16)	C(18)–C(19)–N(2)	121.41(16)
C(3)–C(2)–C(1)	128.75(17)		

of **L** completely. On the other hand, when the solvent polarity is high (5% THF+95% H_2O, Fig. 10), only 3 equiv of Hg^{2+} could quench the fluorescence intensity of **L**.

Several previous reports have designed switching systems based on external inputs.[18] The emission performances of chemosensors are used as the example for mimicking the logic gates. Due to the dependence of the fluorescence intensity of **L** on the external stimulations, visible light (410 nm for excitation), metal ion (Hg^{2+}), and polarity of solvent (THF/H_2O), it is possible to mimic the function of an integrated two-input NAND logic gate (Fig. 11).

In the present system, excitation at 410 nm is the power supply. We consider the polarity of the solvent as one input—the high polarity (5% THF+95% H_2O) standing for 1 and the low one (50% THF+50% H_2O) standing for 0. The other input is the addition of 3 equiv of Hg^{2+} ions (symbol 1) or nonaddition (symbol 0). The fluorescence emission intensity (λ=520 nm) was used as the output signal as follows: if the emission reaches more than 70% of the maximum emission intensity of the free ligand in low-polarity solvent (50% THF+50% H_2O) at 520 nm, the output is considered as digital 1; if the emission lies below 10% of the maximum emission intensity, the output is considered as digital 0. The symbol of two-input NAND logic gate and the truth table is given in Figure 11.

2.4.2. NOR and INHIBIT dual-output gates based on polarity–protonation pair

Compound **L** presents a red shift of fluorescence in different polarity solvents. Meanwhile, the protonation of **L** could quench the fluorescence emission. Based on these results, compound **L** could be applied as dual-output logic gate with NOR (Out_1) and INHIBIT (Out_2) functions.

The two input signals are Input1 (high- or low-polarity solvent) and Input2 (H^+), and the two output signals are the fluorescence emissions: Output1 (λ=470 nm) and Output2 (λ=520 nm). We consider final outputs with digital 1 when the intensity of the fluorescence emission goes over 0.8 relative units, and with digital 0 when the relative intensity of the emission is below 0.3 (see Fig. 12).

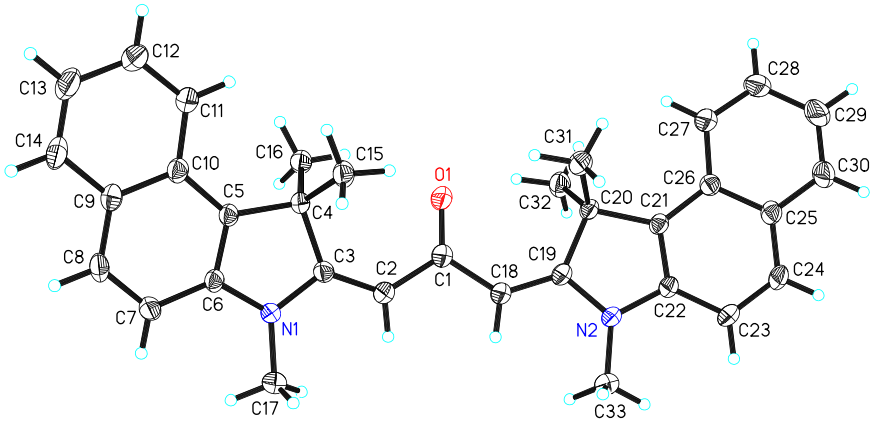


Figure 8. Perspective drawing of compound **L** with atomic numbering scheme. Thermal ellipsoids were shown at the 50% probability level.

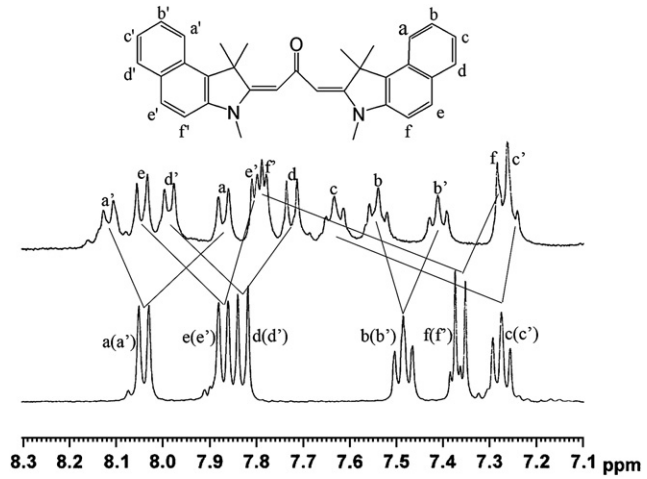


Figure 9. ^{1}H NMR spectra of **L** blank (down) and in the presence of Hg^{2+} ions (up) in DMSO-d_6. All spectra were obtained at 298 K.

When low-polarity (95% THF+5% H_2O) solvent is used (standing for 0) and at pH=8 (without H^+, standing for 0), **L** shows only short-wavelength emission at λ=470 nm. Hence, two outputs monitoring at 470 (Out_1) and 520 nm (Out_2) result in 1 and 0, respectively.

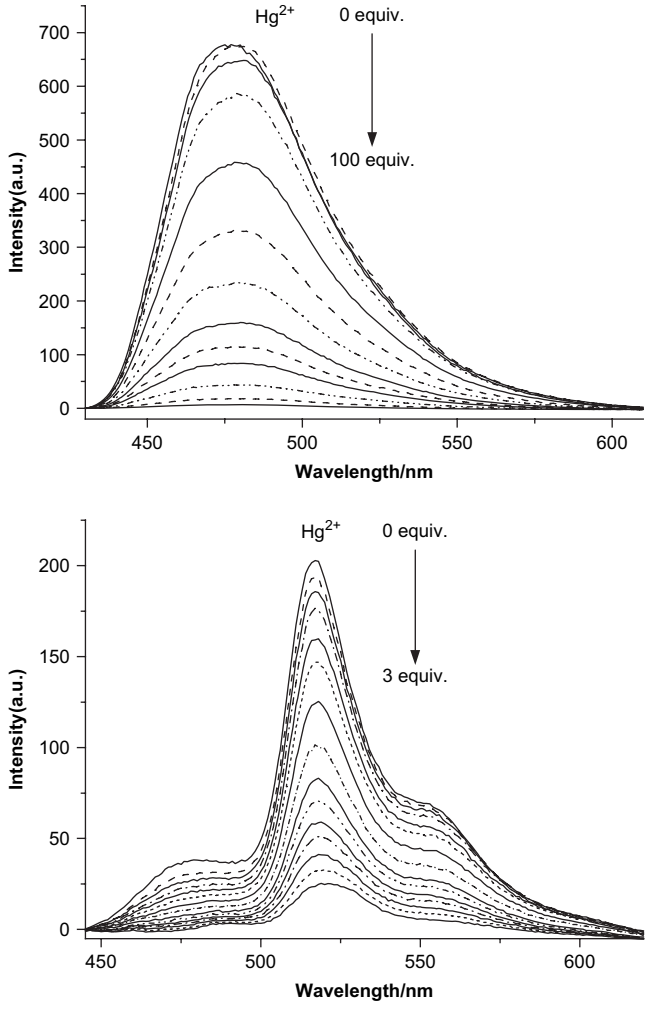


Figure 10. Change in fluorescence spectra (λ_{ex}=410 nm) of **L** (10 μM) with Hg^{2+} in low-polarity solvent (50% THF+50% H_2O, up) and high-polarity solvent (5% THF+95% H_2O, down) at 298 K.

Addition of H^+ to the solution (pH=2, Input2 is 1) leads to the protonation of **L**, which brings on quenching of fluorescence emission, resulting in 0 (Out 1) and 0 (Out 2) outputs. On the other hand, when high-polar (5% THF+95% H_2O) solvent is employed (polarity Input is 1), **L** shows long-wavelength emission at 520 nm (Output2=1). Based on this diversification, a binary logic gate comes into being as shown in Figure 12.

We demonstrate that a simple-structured molecule, **L**, functions as a fluorescent molecular logic gate with multiple outputs. The most interesting feature of the present system is the fact that it can operate with solvent polarity, and, therefore, this opens new possibilities in the design of molecular logic devices. Solvent polarity, as one input, could be reset by adjusting reapportionment of different polar solvents or evaporating and re-dissolving with another polar solvent. Adding acid (e.g., $HClO_4$) and base (e.g., NaOH) could achieve the reversibility of protonation. Due to the fact that EDTA has stronger complexation ability with Hg^{2+}, it could be used for de-complexation of **L**–Hg^{2+} complex. However, after several operations, this system will be saturated with acid and base, as well as Hg^{2+} and EDTA. It is the ubiquitous problem for most chemical computers, which should be resolved with our efforts in the future.

3. Conclusion

A new simple and easily made merocyanine dye **L** described here displays multiple-mode fluorescence response driven by pH, solvent polarity, and Hg^{2+} ions. Controlling the multiple-mode fluorescence by simple chemical inputs resulted in three different logic functions (NAND, NOR, and INHIBIT). The potential use of this simple molecule as an efficient luminescent chemosensor as well as a molecular logic system was demonstrated.

4. Experimental section

4.1. General

The pH values were measured by using PHS-3C pH meter. ^{1}H NMR and ^{13}C NMR spectra were obtained by using a Bruker AV 400 spectrometer. Mass spectra were performed with an HP5989 mass spectrometer and UV–vis spectra on a Varian Cary 500 spectrophotometer (1-cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Toluene was distilled from calcium hydride.

*4.1.1. 1,1,2,3-Tetramethyl-1H-benzo[e]indolinium iodide (**1**)[17]*

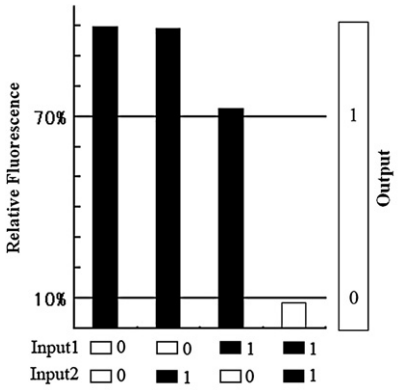
A mixture of 60 g (0.287 mol) 1,1,2-trimethyl-1*H*-indole and 84 g (0.6 mol) methyl iodide was refluxed in 200 ml acetonitrile for 2 h. Upon cooling to room temperature, compound **1** was precipitated and filtered off and washed with cold diethyl ether, giving white powder. Yield: 91 g; 91%; mp 219–220 °C.

*4.1.2. 2-Methylene-1,1,3-trimethyl-1H-benzo[e]indoline (**2**)[17]*

A mixture of 20 g (0.057 mol) **1** and 7 g (0.125 mol) potassium hydroxide was stirred vigorously at room temperature in 40 ml water and 100 ml toluene for 2 h. Upon standing, the organic phase was isolated, dried ($MgSO_4$), and then concentrated under reduced pressure. The product was then recrystallized from ethanol to give **2** as olivine flakes. Yield: 10 g; 79%; mp 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 1.69 (s, 6H, CH_3), 3.15 (s, 3H, N–CH_3), 3.95 (d, 2H, CH_2, J=26.4 Hz), 7.01 (d, 1H, J=4.8 Hz), 7.21 (s, 1H), 7.41 (s, 1H), 7.72 (d, 1H, J=5.2 Hz), 7.78 (d, 1H, J=4.8 Hz), 7.98 (d, 1H, J=5.6 Hz).

*4.1.3. 1,3-Bis(1,1,3-trimethyl-1H-benzo[e]indol-2(3H)-ylidene) propan-2-one (**L**)*

Compound **2** (5 g, 0.0224 mol) was stirred in 60 ml dry toluene and the temperature was kept below 5 °C. Dry pyridine (15 ml) was



Input1 [Polarity]	Input2 [Hg2+]	Output emission λ_{em}=517 nm
0	0	1 (high, > 70%)
0	1	1 (high, > 70%)
1	0	1 (high, > 70%)
1	1	0 (low, < 10%)

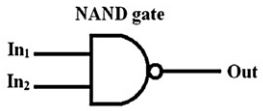
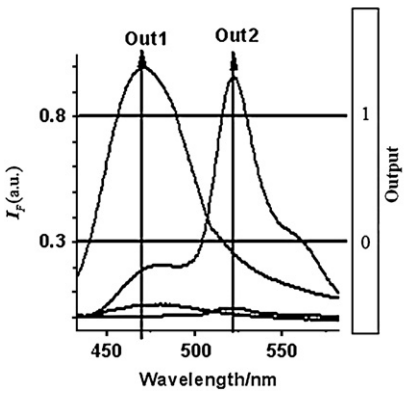


Figure 11. Bar graph representation of the output (relative fluorescence at 520 nm) of the NAND gate (excited at 410 nm at 298 K), truth table, and logic scheme.



		NOR	INH
Input1 (Polarity)	Input2 (H^+)	Output1 (λ=470nm)	Output2 (λ=520nm)
0	0	1 (high, > 0.8)	0 (low, < 0.3)
0	1	0 (low, < 0.3)	0 (low, < 0.3)
1	0	0 (low, < 0.3)	1 (high, > 0.8)
1	1	0 (low, < 0.3)	0 (low, < 0.3)

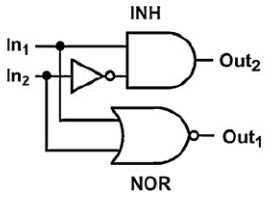


Figure 12. Fluorescence spectra (λ_{ex}=410 nm) of **L** (0.1 M) in the absence and presence of H^+ in KCl (0.1 M) solution at 298 K, truth table, and logic scheme.

added to the mixture under stirring and isolated from water vapor. A solution of 1.11 g triphosgene (0.0112 mol) dissolved in 15 ml dry toluene was subsequently added dropwise at 0–5 °C. After the dropwise addition, the mixture was stirred at room temperature for 2 h and then heated at 50 °C for 5 h. Then at 0–5 °C, 2.5 g anhydrous aluminum chloride (0.0187 mol) was added and heated at 50 °C for 3 h. After cooling to room temperature, 150 ml NaOH (0.1 mol l^{-1}) was added and stirred for 10 min. Upon standing, the organic phase was isolated, washed with water (3×100 ml), dried ($MgSO_4$), and then concentrated under reduced pressure to 10 ml solution. After cooling, yellow solid (0.6 g) was precipitated and filtered off. The product was washed with ethyl acetate (20 ml) and then recrystallized from dichlorobenzene to give pure **L** as brilliant flakes. Yield: 0.52 g; 10%; mp 253–254 °C; IR (KBr, cm^{-1}): 3044, 2968, 2929, 1625, 1593, 1546, 1514, 1047, 943; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.05 (s, 12H, CH_3), 3.28 (s, 6H, N–CH_3), 5.61 (t, 2H, CHCO), 7.27 (t, 2H, Ar–H), 7.36 (d, 2H, J=8.8 Hz, Ar–H), 7.48 (t, 2H, Ar–H), 7.85 (m, 4H, Ar–H), 8.04 (d, 2H, J=8.8 Hz, Ar–H); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 22.95 (4C, CH_3), 30.02 (2C, N–CH_3), 49.13 (2C, $C(Me)_2$), 99.86 (2C), 110.41 (2C), 122.31 (2C), 122.79 (2C), 127.16 (2C), 127.33 (2C), 128.71 (2C), 129.46 (2C), 129.66 (2C), 130.05 (2C), 130.18 (2C), 141.76 (1C, CO), 169.18 (2C); HRMS (ESI), m/z: 473.2577 $[\mathbf{L}+H]^+$.

Table 2
Crystal data and structural refinement data for **L**

Empirical formula	$C_{33}H_{32}N_2O$
Formula weight	472.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	a=10.4999(10) Å, α=90°
	b=7.4272(7) Å, β=91.258(2)°
	c=32.916(3) Å, γ=90°
Volume	2566.3(4) $Å^3$
Z	4
Calculated density	1.223 g cm^{-3}
Absorption coefficient	0.073 mm^{-1}
F(000)	1008
Crystal size	0.481 mm×0.412 mm×0.387 mm
θ Range for data collection	2.02–27.00°
Limiting indices	$-13\le h\le 13$, $-5\le k\le 9$, $-40\le l\le 41$
Reflections collected/unique	14,507/5593 [R(int)=0.0809]
Completeness to θ=27.00°	99.4%
Absorption correction	Empirical
Max and min transmission	1.0000 and 0.7535
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5593/0/331
Goodness-of-fit on F^2	0.922
Final R indices [$I>2\sigma(I)$]	$R1$=0.0535, $wR2$=0.1232
R indices (all data)	$R1$=0.0818, $wR2$=0.1350
Largest diff. peak and hole	0.222 and −0.222 e $Å^{-3}$

4.2. Crystal structural determination

Single crystals of **L** were obtained by slow evaporation of dichloromethane/ethanol solution. A yellow glassy crystal of dimensions 0.481 mm×0.412 mm×0.387 mm was used for data collection at 20 °C (λ=0.71073 Å). Crystal data (CCDC 662222) and structural refinement data are given in Table 2. These data can be

obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.05.048.

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