Multiple molecular logic functions and molecular calculations facilitated by surfactant's versatility†

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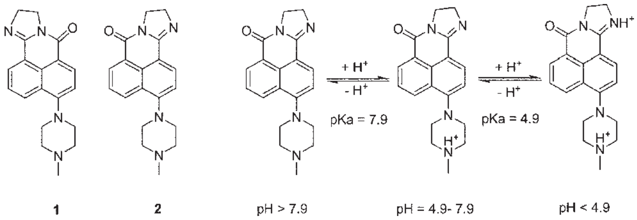
Two isomeric compounds 1 and 2, combining intramolecular charge transfer (ICT) and photoinduced electron transfer (PET) mechanisms together, were designed and used as logic gates with configurable multiple outputs; ten different logic functions (AND, NAND, OR, NOR, XNOR, INHIBIT, YES, NO, PASS 1 and PASS 0) were achieved by varying the inputs threshold or by altering the inputs; furthermore, half addition and half subtraction were performed within 2 (or 1); the concept demonstrated here may provide a strategy for constructing more integrated molecular level devices with multiple functions.



Scheme 1 Molecular structures of the isomers and protonation processes for **2**.

Design and synthesis of molecular devices for molecular-scale information processing has attracted much attention since the creation of the first molecular AND logic gate.[1,2] The realization of XOR and INHIBIT (or AND) functions within one two-input system makes molecular calculation possible.[3] However, restricted by fewer types of configurable logic functions, the researches of incorporating a half-adder (full-adder) and half-subtractor (full-subtractor) in a single fluorescent molecule are limited.[4] So, construction of molecular systems with multiple logic functions is of particular interest.[5,6]

Surfactants, with versatility related to their concentrations, have been used in many scientific researches. Some logic functions are realized in surfactant systems facilitated by the amplifying effect on the local ion concentration or the low polarity within the small nanospace of micelles and de Silva and co-workers demonstrated for the first time that a molecular logic gate can operate in micelles.[7] Pina and co-workers constructed a logic gate assisted by anionic surfactant sodium dodecyl sulfate (SDS) due to the higher concentration of protons around it.[8] Moreover, organic fluorescent molecules (OFMs) can associate with surfactant by electrostatic and hydrophobic interactions, and may form OFM–surfactant mixed aggregates or be solubilized in surfactant micelles depending on the surfactant concentration.[9] Different photophysical properties will be produced according to the aggregation state of the OFM. As a consequence, logic functions may be realized with OFMs by altering the threshold of surfactant.

Herein, compounds **1** and **2** bearing a new fluorophore, dihydrogen imidazo[2,1-α]benz[*d*,*e*]isoquinolin-7-one, were designed, synthesized and used as logic gates with multiply configurable multiple outputs. Ten logic functions, AND, NAND, OR, NOR, XNOR, INHIBIT, YES, NO, PASS 1 and PASS 0 can be achieved with **2** by altering the input or by varying the input threshold. Based on these functions, half addition and half subtraction can also be performed. Remarkably, several logic functions and calculations are performed with different concentrations of surfactant as inputs, which benefit from the formation of SDS–**2** (or **1**) complex and the amplifying effect on the local ion concentration of the SDS micelle. This is the first time so complicated a molecular calculation has been accomplished, assisted by surfactant, and **2** might be the first molecule to perform ten logic gates at the same time.

1 and **2**, combining intramolecular charge transfer (ICT) and photoinduced electron transfer (PET) mechanisms together,[10–13] both have three H^+ receptors: the imine (C=N), the appended tertiary amine and the aminonaphthalene nitrogen (Scheme 1), but the latter can not be protonated at pH >3. Protonation of the second site will restrain PET from the tertiary amine to the fluorophore and so switch on the fluorescence. Further addition of acid protonates the imine, which enhances the "push–pull" character of the ICT process and results in a considerable red-shift (+39 nm) in absorption, that is, its maximum shifts from 386 to 425 nm (Table 1). However, the protonation of the imine leads to fluorescence quenching caused by the non-radiative deexcitation pathway, such as solvation by water. In addition, the equilibrium between the hydrophobicity from the aromatic ring together with alkyl side chain and hydrophilicity from the protonated imine or/and tertiary amine, will lead to versatile properties for **1** and **2** with polar/apolar solvents.

Table 1 reveals that isomers **1** and **2** show distinct differences in their photophysical properties: (1) the fluorescence quantum yield of **1** (0.218) is much higher than that of **2** (0.055) in neutral water; (2) the molar absorption coefficient of **1** was smaller in acid solution than in basic solution, while that of **2** was larger in acid solution; (3) the maxima of both emission and absorption spectra of **1** were red-shifted in response to H^+, whereas the addition of protons resulted in a red-shift in absorption and a blue-shift in emission of **2**, and an unusual large Stokes shifts (about 180 nm) of **2** in basic solution was observed. The above differences were

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Table 1 Photophysical data for **1** and **2** under different conditions

	λ_{abs}/nm			log ε			λ_{em}/nm			Φ_F[a]		
Compound	Acid	Neutral	Base	Acid	Neutral	Base	Acid	Neutral	Base	Acid	Neutral	Base
1	426	388	394	4.15	4.20	4.26	578	508	513	0.060	0.218	0.010
2	425	386	388	4.24	4.08	4.06	509	545	572	0.008	0.055	0.013

[a] The fluorescence quantum yields (Φ_F) were estimated with quinine sulfate ($\Phi_F = 0.55$ in 50 mM H_2SO_4 solution) as standard.

caused by the geometry distinctions, which lead to different distributions of electron density.[14]

However, when **1** and **2** were used as molecular logic devices, they can implement similar logic functions and calculations.

We can demonstrate the half subtraction logic operation with H^+ and OH^- as inputs, and A_{425} and fluorescence quantum yield as outputs, respectively. Fig. 1 shows the fluorescence characteristics of **2** in aqueous solution under four different conditions. As shown in Fig. 1, a strong fluorescent signal is observed when both two inputs are kept high or low. In contrast, the fluorescence is weak in the other cases. The fluorescence quantum yield (Φ_F) in the former case is over three times higher than in the latter case. The absorbance at 425 nm is high only when H^+ is added to the solution. In contrast, it is very low in the other three cases. So, the INHIBIT and XNOR functions are realized with A_{425} and Φ_F as outputs, respectively. A half-subtractor can be implemented with a combinatorial logic circuit composed of a XOR gate and an INHIBIT gate. The XOR gate is obtained by using Φ_F with negative logic convention as output.[3d] Therefore, half subtraction is achieved as shown in Fig. 1.

When we respectively use SDS [0 (low), 8.4 mM (high)] and OH^- [10^{-7} M (low), 10^{-4} M (high)] as inputs, A_{425} and fluorescence quantum yield with negative logic convention as outputs, half subtraction can also be executed (Fig. 2). Here, the effect of SDS is the same as that of H^+ due to the "proton sponge effect" of SDS micelles.[8]

Scheme 1 demonstrates the protonation process of **2**. As shown in Scheme 1, **2** exists as monocationic species in neutral water. When negatively charged surfactant SDS (4.2 mM) was added to the solution of **2**, SDS–**2** complex formed due to the electrostatic and hydrophobic interactions between SDS and **2**. The red-shift in absorption maximum (+11 nm) and the reduced fluorescence quantum yield (from 0.055 to 0.035, Fig. S5, ESI†) indicated the formation of **2**–SDS complexes.[9d,e] Some of SDS–**2** complexes were insoluble in water because of their decreased overall charge density, which led to a lower concentration of **2** in bulk solution, as a result, the absorption intensities at the maxima in the original spectra decreased.[9a,b]

Further addition of SDS to 8.4 mM, led to disassociation of SDS–**2** complexes to form SDS micelles.[15] The hydrophobic and the electrostatic interactions between SDS and **2** caused the latter to be located in SDS micelles. The molecules of **2** associated with SDS were re-solubilized in SDS micellar solution, so, the absorbance was enhanced. It is of note that in the presence of 8.4 mM SDS (pH = 7.0), **2** has an absorption band centered at 425 nm whereas its absorption peak is centered at 386 nm at pH 7.0 without SDS (Fig. 3). As we know that anionic surfactant SDS can adsorb counter ion H^+, so the H^+ concentration is much higher at the micelle surface than in bulk solution, which makes the imine in **2** located in SDS micelles more easily protonated and causes a considerable red shift in absorption wavelength in SDS micelles.

Fig. 3 shows the absorption spectra and the truth table of **2** in different conditions, in which SDS concentration is 0 (low) or 4.2 mM (high). The absorbance at 425 nm is high only in the case of both inputs kept high. The absorbance at 400 nm is high when two inputs are kept the same. So, AND gate and XNOR gate are obtained when the outputs are A_{425} and A_{400}, respectively. With the transmittance at 400 nm used as output, the XOR gate is also achieved. Therefore, half addition is carried out when both inputs are SDS. It should be mentioned that SDS concentrations used in both inputs are the same,[4b,c] which is different from many known gates and makes the design of logic circuit simpler. The same logic calculations can also be performed with compound **1** (Fig. S2–4, ESI†).

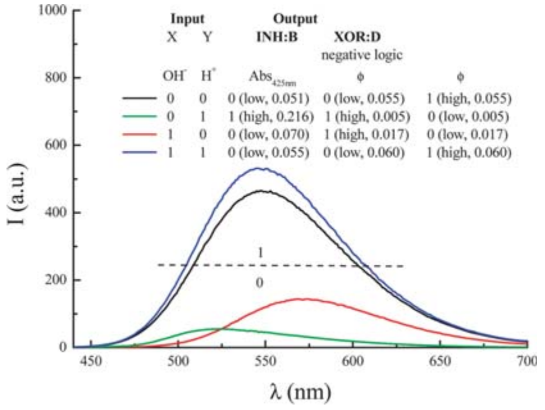

Fig. 1 Emission spectra and the truth table of **2** in water in the presence of chemical inputs, with excitation at the isosbestic point of 395 nm.

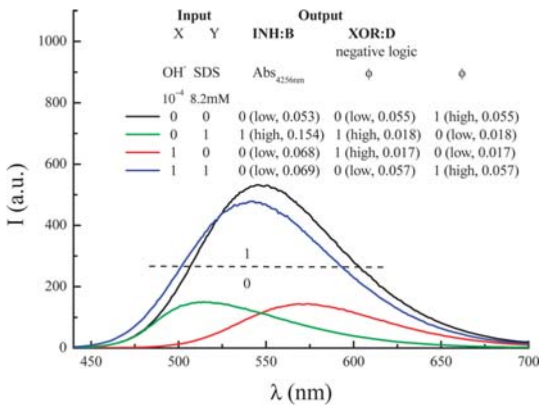

Fig. 2 Emission spectra and the truth table of **2** in the presence of chemical inputs, with excitation at the isosbestic point of 395 nm.

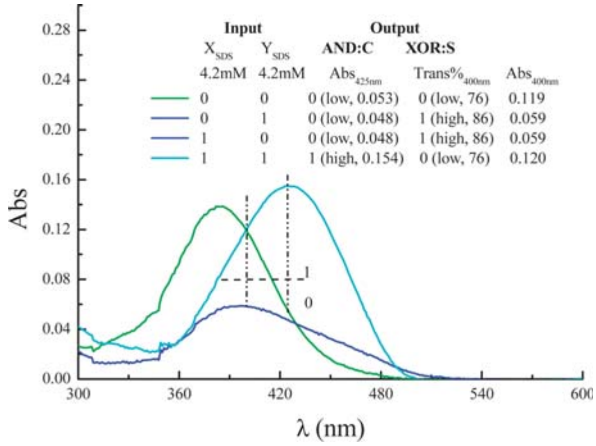

Fig. 3 Absorption spectra and the truth table of **2** in different conditions.

Similarly, different logic functions can be realized by varying the input threshold of SDS concentration. When 4.2 mM SDS and H^+ were used as inputs, YES logic gate is obtained with A_{425} as output whereas OR logic gate is achieved with the same output simply by increasing the threshold of SDS concentration to 8.4 mM (Fig. S6, ESI†).

Three-input systems with simple logic functions are relatively few.[16] However, three inputs provide much more information and can show interesting behavior, such as the consequence of chemical congregations.[17] Based on the above two-input systems, we have also developed three-input NOR and INHIBIT gates with **1**, which arise from the distinct spectral changes induced by SDS at different concentrations (Table S3 and S4, ESI†).

In conclusion, a new fluorophore with the assistance of surfactant affords multiple molecular logic functions and molecular calculations by altering the inputs or by varying the input threshold. Although there are some questions needing to be solved (for example, logic operation to be reset by removal of surfactant from solution), surfactant, with its versatile properties, has provided a new platform for operating molecular calculations and molecular logic gates. This investigation might be able to extend solution phase events to semi-solid (micelle) ones and pave the way for one to use this and similar technologies as a strategy of advancing the field of molecular logic.

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