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Aust. J. Chem. **2010**, *63*, 169–172

A Unimolecular Half-Subtractor Based on Effective Photoinduced Electron Transfer and Intramolecular Charge Transfer Processes of 1,8-Naphthalimide Derivative

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We report a unimolecular system as a combinatorial logic half-subtractor based on a naphthalimide derivative. Chemical inputs (OH^- and H^+) can significantly change the absorption and fluorescence characteristics through modulating intramolecular charge transfer and photoinduced electron transfer process upon protonation or deprotonation of the molecule. An XOR gate is obtained following the absorbance variations at 485 nm, and an INHIBIT gate is induced when the output signal is monitored at 535 nm in the fluorescence spectra. Large differences in output signals allow unequivocal assignment of logic-0 and logic-1 of both logic gates, which may function in parallel to implement the half-subtractor.

Manuscript received: 31 August 2009.
Manuscript accepted: 21 October 2009.

Introduction

Molecular logic gates that can implement the digital action of Boolean logic are receiving more and more attention.[1] Many examples of molecular logic gates such as OR, NOT, AND, XOR, INHIBIT, and NOR, have been reported by employing a detectable spectroscopic change as output in response to ionic, electronic, or photonic inputs.[2–7] Clearly, input–output homogeneity is not available here, unlike bulk semiconductors that employ all-electronic input and output signals. Fluorescent molecular switches display emission 'off–on' type changes, as a result of the input-induced modulation of the thermodynamics of the photoinduced electron transfer (PET)[8] process. The clear intensity variations are in accordance with the digital action of binary logic, so PET switches are suitable for molecular logic functions. In addition, besides intensity modification of an existing signal, significant input-induced spectral shifts often occur, providing a convenient method to change the logic expression by monitoring the gate at a different wavelength.[1,9] Thus, more than one logic gate can be defined based from the same molecule.

Combinations of molecular logic gates can perform arithmetic operations on binary numbers. The fundamental principles of molecular arithmetic have been carefully demonstrated in previous work, where several examples of addition[10] and subtraction[10b,10f,11] using molecules have been reported. For example, the implementation of a half-subtractor that could carry out elementary subtraction, can be achieved through parallel operation of an XOR gate and an INHIBIT gate, whose output variables produce both the 'difference' digit (D) and the 'borrow' digit (B), respectively.[12] It is worthwhile to note that the logic function of the half-adder and half-subtractor can be implemented using two molecular switches that respond to the same two inputs. In original work by de Silva and coworkers, to demonstrate the proof-of-principle of Boolean algebra, a half-adder was designed relying on two molecules that executed the XOR operation and the AND operation, respectively.[13] However, in the progress of molecular logic gates, it is generally preferable to develop smarter systems that integrate several logic functions into a single molecule.[1,14]

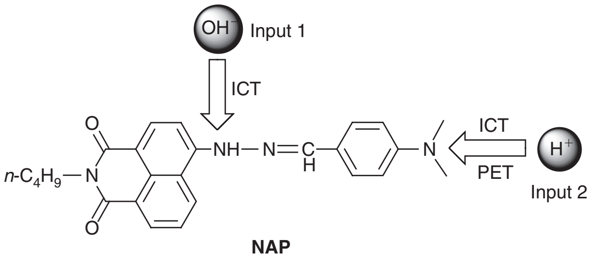

Fig. 1. Acid and base inputs-induced ICT and PET modifications.

With these considerations in mind, we targeted a single molecular entity of naphthalimide-based chromogenic and fluorogenic compound (**NAP**, Fig. 1), which could be used to optically carry out the operation of a half-subtractor in solution using acid and base as two inputs and absorption and fluorescence as two outputs. Naphthalimide derivatives are quite useful fluorescent dyes and have been used to design molecular switches and chemosensors.[15] Typically, strong intramolecular charge transfer (ICT) effect exists within the naphthalimide molecule, leading to considerable dipole character, which permits the significant input-induced spectral shifts upon perturbation of π electron system.[9] Also, we introduced an additional PET-sensitive aniline group to modulate the fluorescence through protonation or deprotonation processes. From the molecular

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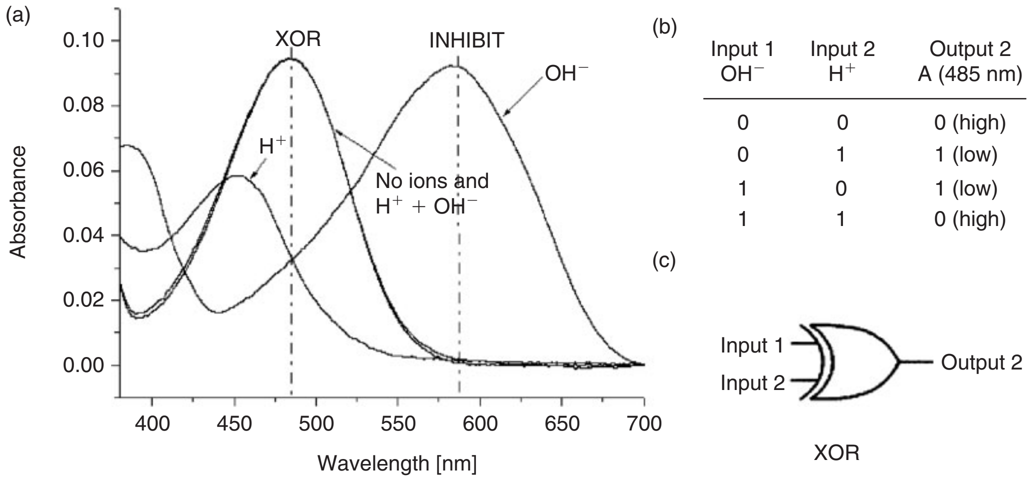
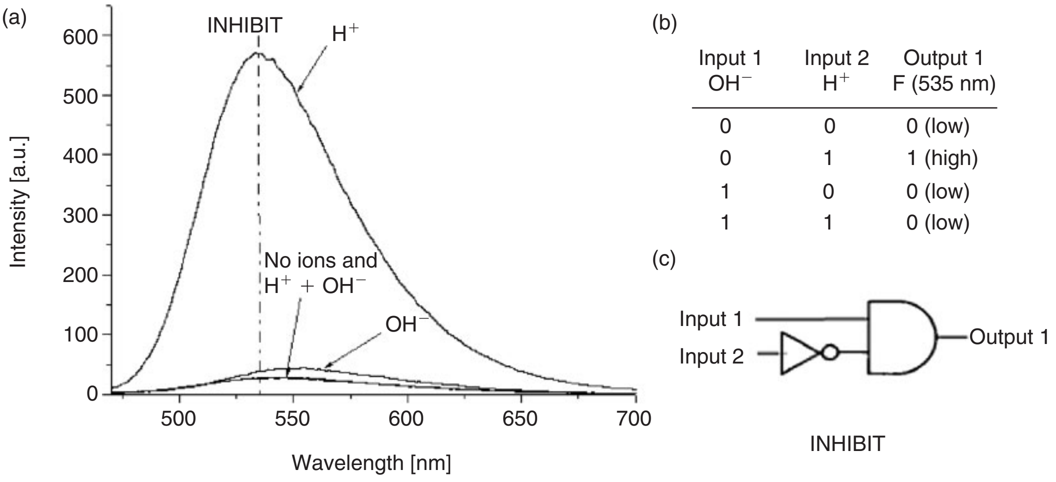


Input 1 OH^-	Input 2 H^+	Output 2 A (485 nm)
0	0	0 (high)
0	1	1 (low)
1	0	1 (low)
1	1	0 (high)

Fig. 2. (a) Absorption spectra of **NAP** (4×10^{-6} M) with or without the addition of 500 mM H^+ and/or 500 mM OH^- in acetonitrile/water (4/1 v/v); (b) truth table for the XOR logic gate; (c) logic circuit.



Input 1 OH^-	Input 2 H^+	Output 1 F (535 nm)
0	0	0 (low)
0	1	1 (high)
1	0	0 (low)
1	1	0 (low)

Fig. 3. (a) Fluorescence spectra of **NAP** (4×10^{-6} M) with or without the addition of 500 mM H^+ and/or 500 mM OH^- in acetonitrile/water (4/1 v/v) ($\lambda_{ex} = 450$ nm); (b) truth table for the INHIBIT logic gate; (c) logic circuit.

structure of **NAP**, the naphthalimide moiety and the aniline moiety were linked by a CH=N group, providing conjugation between these two parts, although the conjugation was not ideal due to lower molecular rigidity.[16] With the same two inputs to switch the absorption and fluorescence, the XOR and INHIBIT gates were constructed and their parallel operation could produce a unimolecular half-subtractor.

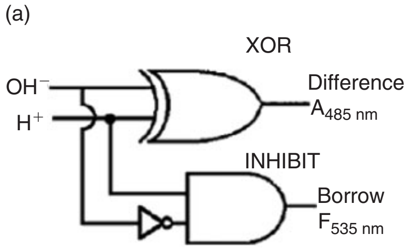
Results and Discussion

Changes of Optical Properties of **NAP** upon Addition of Acid and Base

The absorption and emission bands of naphthalimide derivatives are largely dependent on the electron donating potential of 4-substituents.[9] In the case of an amino group with strong electron-donating ability, the characteristic absorption peaks generally appear at wavelength range from 400 to 450 nm. However, a solution of **NAP** (4×10^{-6} M) in acetonitrile/water (4/1 v/v) showed a red-shifted absorption band centred at 485 nm. The large bathochromic shift was attributed to the lengthening of the conjugated system within the molecule and an increase in the electron-donating ability of the substitute in the *para* position of the benzene ring.[16] It is found that in the presence of a strong base (NaOH), deprotonation of amino moiety on the 4-position of naphthalimide ring could cause a significant increase in the charge density on the amido nitrogen, with associated enhancement in the push–pull effect of the ICT transition (Fig. 1). As a consequence, this enhancement in ICT afforded a red-shifted absorption peak at 587 nm. However, when in the presence of a strong acid (HCl), the protonation of the aniline nitrogen reduced its electron-donating character, weakening the ICT effect within the whole molecule, resulting in a blue-shifted maximum absorption peak at 455 nm. The spectral changes induced by addition of acid and base were investigated and shown in Figs 2 and 3.

Since the naphthalimide portion is not at the same molecular panel with the aniline portion in the **NAP** molecule, the two parts would not be the same conjugated system.[16] As a result, the fluorescence of **NAP** in an acetonitrile/water solution remained yellow in colour with a maxima centred around 535 nm. The colour and position of the emission band were similar to those of 4-amino-1,8-naphthalimide. It should be notable that aniline moiety is an efficient electron donor in the PET process, several

(a)



(b)

Input 1 OH−	Input 2 H+	Output 1 Borrow (B) F (535 nm)	Output 2 Difference (D) A (485 nm)
0	0	0	0
0	1	1	1
1	0	0	1
1	1	0	0

Fig. 4. (a) Logic circuit of the half-subtractor, with 'difference' and 'borrow' outputs collected at 485 nm (absorption) and 535 nm (fluorescence) respectively; (b) truth table for the operation of the molecular half-subtractor.

molecular switches and chemosensors have been designed to display fluorescence 'off–on' type response upon the inhibition of PET through metal ions coordination to an aniline nitrogen.[17] Therefore, the very weak fluorescence of **NAP** was of course expected ($\Phi = 0.024$, Rhodamine B in CH_3CN was used as fluorescence quantum yield standard), considering it an effective PET molecular switch. However, addition of acid protonated the aniline nitrogen, effectively retarding PET, as a result, the fluorescence of **NAP** was switched on at the same wavelength (535 nm). The quantum yield was determined to be 0.39 after acid addition, showing a bright yellow emission. Only a slight increase and small red shift was observed in the case of base addition.

Implementation of Unimolecular Half-Subtractor

Because the absorption wavelength and fluorescence intensity of **NAP** could be well tuned by the simple addition of acid or base, we extended its application to XOR and INHIBIT logic gates based on the switching optical signals at different wavelengths. For this reconfigurable logic system, the strong base (OH^-) and acid (H^+) were used as chemical input 1 and input 2, respectively. The emission and absorption were followed at wavelengths that held the sharp spectral changes, in other words, the emission intensity at 535 nm was defined as output 1 and the absorbance at 485 nm was used as output 2.

As illustrated in Fig. 2a, absorbance at 485 nm was reduced when OH^- or H^+ was applied, whereas in the absence or simultaneous addition of both OH^- and H^+, the absorbance kept a high value. In binary language, the output 2 is in a logic-1 state only when input 1 and input 2 are both in the same 0 or 1 state, while the output 2 is in a logic-0 state when input 1 and input 2 are in different states. So the absorbance output at 485 nm coincided with the XNOR logic gate. It is worthwhile to note that the XOR logic operator can be realized by transformation of XNOR logic. Due to the fact that the inputs and the outputs are of different kind, the negative logic can be applied only to outputs that result in a new XOR logic.[11b,11c] The truth table and logic circuit of the XOR logic gate are shown in Figs 2b and 2c.

The protonation of the aniline nitrogen upon addition of acid led to significant increase of fluorescence intensity at 535 nm. In this case, the input 1 is in the 0 state and input 2 signal is in the 1 state, conferring a 1 state to output 1. All of the other input states are shown to be weakly fluorescent at 535 nm (Fig. 3). The fluorescence behaviour correlates very well with the INHIBIT logic operation. Another INHIBIT logic gate can also be constructed following the absorbance variations at 587 nm. Here, the two inputs nullify each other, so the addition of one input after another to a solution of **NAP** could revert to its original state.

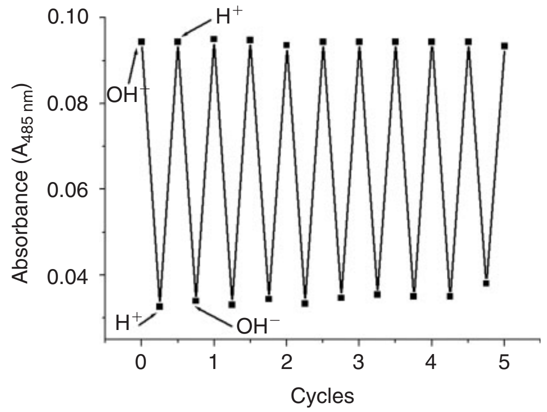


Fig. 5. Modulated absorbance at 485 nm of **NAP** (4×10^{-6} M) in acetonitrile/water (4/1 v/v) during alternating additions of OH^- and H^+.

As demonstrated above, the XOR and INHIBIT gates may function in parallel to implement a half-subtractor. Fig. 4 shows a schematic diagram and truth table of the single molecule-based half-subtractor. In binary subtraction, the XOR gate output corresponds to the 'difference' digit derived from the absorption change at 485 nm, whereas the INHIBIT gate output corresponds to the 'borrow' digit that is derived from the fluorescence change at 535 nm.

Because of the full reversibility of the protonation and deprotonation processes, the chemical input-induced modification of absorption and fluorescence spectra can be repeated. By alternating additions of OH^- and H^+, respectively, we verified that the photochemical processes are highly reproducible over more than five cycles. As Fig. 5 demonstrates, the current half-subtractor has excellent recovery properties and can be used repeatedly, indicating that accumulation of salts formed in the acid-base neutralization did not influence the system performance over several repeated cycles.

Conclusions

A half-subtractor that could carry out elementary subtraction has been implemented utilizing a single molecule with very large differences in absorption wavelengths and emission intensity, from simple protonation and deprotonation processes. This molecular device has the ability to reset the output, such that the half-subtractor can be operated repeatedly. Notably, the realization of binary subtraction operations involving more than one logic expression through a judicial choice of input and output signals has provides a means to design complicated logic circuits based on one molecule, that could inturn effectively enhance the power of the molecular processor.

Experimental

General Procedures

^{1}H NMR and ^{13}C NMR spectra in DMSO-d$_6$ were recorded on a Bruker AM-500 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were obtained with a HITACHI-80 spectrometer. UV-Vis absorption spectra were performed on a Varian Cary 500 spectrophotometer and fluorescence spectroscopy was conducted on a Varian Cary Eclipse fluorescence spectrophotometer. The melting point was measured on an X4 Micro-melting point apparatus. *N*-Butyl-4-hydrazino-1,8-naphthalimide was prepared based on a known method.[15d] All other starting materials and reagents were purchased and used as received.

N-*Butyl-4-(*p-N,N-*dimethylaminobenzylimino) amino-1,8-naphthalimide (***NAP***)*

To a 100 mL round-bottomed flask was added *N*-butyl-4-hydrazino-1,8-naphthalimide (1.0 g, 3.5 mmol), *p-N,N*-dimethylaminobenzaldehyde (0.54 g, 3.6 mmol), and ethanol (60 mL). The mixture was refluxed for 2.5 h. After cooling to room temperature, the precipitated product was filtered and dried. The obtained crude solid was purified by recrystallization from ethanol/acetone (2/1) to afford the *title compound* **NAP** as red-brown crystals (1.2 g, 83%), mp: 267–269°C. δ_H 8.79 (1H, d, *J* 8.47, naphthalene-H), 8.47 (1H, d, *J* 7.26, naphthalene-H), 8.36 (2H, ss, naphthalene-H, NH), 7.77 (1H, t, *J* 8.26, 7.47, naphthalene-H), 7.65 (3H, dd, *J* 8.54, 8.85, naphthalene-H, benzene-H), 6.79 (2H, d, *J* 8.9, benzene-H), 4.03 (2H, t, *J* 7.3, NCH$_2$), 3.00 (6H, s, N(CH$_3$)$_2$), 1.60 (2H, m, CH$_2$), 1.35 (2H, m, CH$_2$CH$_3$), 0.93 (3H, t, *J* 7.3, CH$_3$). δ_C 163.6, 162.8, 147.9, 146.6, 144.9, 133.5, 130.5, 129.2, 128.4, 128.1, 124.4, 122.1, 121.8, 118.4, 111.3, 109.8, 106.1, 40.3, 29.8, 19.8, 13.7 (one signal obscured by overlapping). *m/z* (HR-MS EI); Anal. Calc. for $C_{25}H_{26}N_4O_2$ [M$^+$] 414.2056. Found 414.2057.

Acknowledgements

This work was supported by NSFC/China, National Basic Research 973 Program (2006CB806200) and Scientific Committee of Shanghai.

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