Molecular half-subtractor based on 3,3′-bis(1*H*-benzimidazolyl-2-yl)[1,1′]-binaphthalenyl-2,2′-diol

Vijay Luxami and Subodh Kumar*

Received (in Durham, UK) 2nd April 2008, Accepted 1st July 2008
First published as an Advance Article on the web 29th August 2008
DOI: 10.1039/b805558k

Title fluorophore (**1**) possessing 2,2′-binaphthol and benzimidazole moieties has been investigated for elaboration of half-subtractor logic operation. For comparison differently substituted systems have been studied. Fluorophore **1** showed strong fluorescence at 585 nm due to ESIPT phenomena which was completely quenched on addition of $HClO_4$ with concomitant appearance of a new emission band at 435 nm with hypsochromic shift of 150 nm. The addition of TBAOH to the solution of **1** gave a new hypsochromically shifted emission band at 515 nm ($\Delta\lambda$ = 70 nm) with concomitant quenching at 585 nm. Thus, fluorophore **1** with large differentials of emission maxima under neutral, acidic and basic conditions provides four opportunities for arithmetic operation half-subtractor. *i.e.* with 435/515 nm (INHIBIT) and 475 nm (XOR) gates and with 435/515 nm (INHIBIT) and 585 nm (XNOR) gates which have been elaborated as combinatorial logic circuits for a molecular half-subtractor with acid and base as input variables. The elaboration of half-subtractor with only XOR logic in the case of fluorophore **2** possessing a molecular structure half that of fluorophore **1** and complete lack of logic gates in fluorophore **5** with change in position of benzimidazole moiety further signify the importance of the structural architecture in fluorophore **1**.

Introduction

In the last decade remarkable progress has been achieved in the development of molecular logic gates[1] and their integration into arithmetic systems has brought chemists closer to the realisation of a molecular scale calculator (a moleculator).[2] These devices, which process chemical or optical inputs and generate light output signals, operate in wireless mode and have the potential for computation on a nanometer scale that silicon based devices cannot address. A number of examples for molecular logic systems which demonstrate AND,[3] XOR,[4] INHIBIT,[5] NOT,[6] OR,[7] NOR,[8] XNOR,[9] NAND,[10] logic operations are available in the literature. However, literature reports on molecular systems that are capable of integrating simple logic gates into combinatorial circuits *viz.* half-subtractor,[11] half-adder[12] and full-adder[13] are relatively scarce. Such operations are important for the realization of complex information processing.

To integrate combinatorial circuits, various entities[3–13] *viz.* light, redox potential, chemical entities such as cations, anions, neutral species, pH [acid (H^+) or base (^-OH/amine)], *etc.* have been used as inputs and the optical (absorption/emission) or electrical outputs when read at different wavelengths or at different potentials can elaborate integrated logic functions. Significantly, de Silva and co-workers[3e,12c] have used Na^+, Ca^{2+}, H^+ *etc.*, the constituents of living cells, in integrating logic circuits and mimicking cell membrane functions. The absorbance of light by three states of a molecular switch emitted from three different fluorophores; use of 12 light sources for achieving 20 AND or OR logic gates capable of processing up to 16 bits of input data and all optical molecular full-adder constitute some of the significant developments in all optical logic circuits created by Raymo,[1b] Szacilowski[3f] and Speiser and co-workers[13b,c]

For using acid (H^+) and base (OH^-) as two inputs to raise characteristically different absorption or emission spectra, the presence of amphiphilic character in a molecular system is essential. A half-subtractor is a combinatorial circuit that subtracts two bits and produces their difference. It needs two outputs: one generates the difference (D), and the other generates the borrow (B). These outputs are generated through XOR/XNOR and INHIBIT gates, respectively.

Here we present that the fluorophore **1** which is amphiphilic in nature, interacting with both acid and base to give three distinctly different emission maxima at 435 nm (in acid), at 515 nm (in base) and at 585 nm (under neutral conditions). These combinations of outputs have been elaborated to form half-subtractor molecular expressions using combinations of INHIBIT logic function with either XOR or XNOR logic functions at two different output emission wavelengths. The acid/base stimulated emissions in the fluorophore **2**, which is exactly half that of the fluorophore **1**, form a molecular half-subtractor with only negative logic. It is noteworthy that fluorophore **5**, which possesses the benzimidazole moiety at C-1 of the naphthalene ring in place of position C-3 in fluorophore **2**, fails to elaborate half-subtractor logic operation.

Results and discussion

Fluorophores **1** and **2** were synthesized by the procedures reported in literature.[14] Fluorophore **5** was synthesized by

Department of Chemistry, Guru Nanak Dev University, Amritsar, 143 005, India. E-mail: subodh_gndu@yahoo.co.in

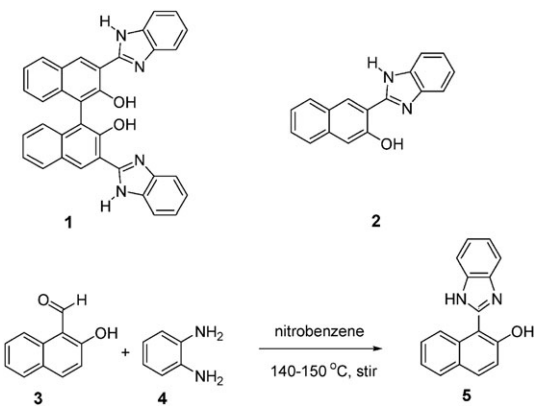
heating a solution of 2-hydroxy-1-naphthaldehyde (**3**) and 1,2-diaminobenzene (**4**) in nitrobenzene (Scheme 1).

Fluorophore **1**[14] (0.5 μM, CH_3CN) on excitation at 330 nm gave emission maxima at 585 nm with a Stokes shift of 255 nm and is attributed to ESIPT from phenolic OH to benzimidazole nitrogen. On addition of perchloric acid ($HClO_4$, as acid) (5 μM), the emission at 585 nm was completely quenched and a new emission band at 435 nm with hypsochromic shift of 150 nm appeared (Fig. 1). On addition of tetrabutylammonium hydroxide (TBAOH, as base OH^-) (5 μM) to the same solution, the emission at 585 nm reappeared. The addition of TBAOH (5 μM) to solution of **1** gave a new hypsochromically shifted emission band at 515 nm ($\Delta\lambda$ = 70 nm) with concomitant quenching at 585 nm. This process was reversed on addition of $HClO_4$ (5 μM) (Fig. 1). The small differences in intensities of spectra a and d in Fig. 1 could be attributed to increased ionic strength and thus polarity of the medium.

Therefore the emission output of **1** at 515 nm is turned "ON" (output = 1) only in the presence of TBAOH as input. For all other circumstances (Fig. 2), the output signal is "OFF" (output = 0). Similarly, the emission output of **1** at 435 nm is turned "ON" (output = 1) only in the presence of $HClO_4$ as input and for all other circumstances (Fig. 1), the output signal is turned "OFF" (threshold value 100) (Fig. 2(Y)). These outputs correlate well with INHIBIT logic gates at 435 nm (with $HClO_4$ turned "ON") and at 515 nm (with TBAOH turned "ON").

To examine that **1** behaves as a XOR gate, the output signal at 475 nm has been monitored. The output at 475 nm is high, *i.e.*, 1, with either of the inputs $HClO_4$ or TBAOH. Further, two simultaneous inputs in the form of H^+ and OH^- annihilate each other's action (Fig. 1) generating the emission spectrum of **1**. This observation correlates well with XOR logic gate as it generates an "ON" output when either input is "ON"; but not when both inputs are either "ON" or both are "OFF". The formation of these logic gates with their threshold values is shown in Fig. 2(X). These observations of XOR (475 nm) and INHIBIT (435 nm) functions have been compiled in truth Table 1 and lead to a molecular half-subtractor. The schematic representation of half-subtractor is given in Fig. 3.

Binary half-subtractor operation of **1** can also be explained by monitoring the emission intensities at two different wavelength 515 nm (INHIBIT) and 475 nm (XOR) (Fig. 1). In these binary subtraction function, XOR gate output (monitoring wavelength: λ_{em} = 475 nm) is the difference digit (D) and the INHIBIT gate (monitoring wavelength: λ_{em} = 515/435 nm) is the borrow digit (B).



Scheme 1

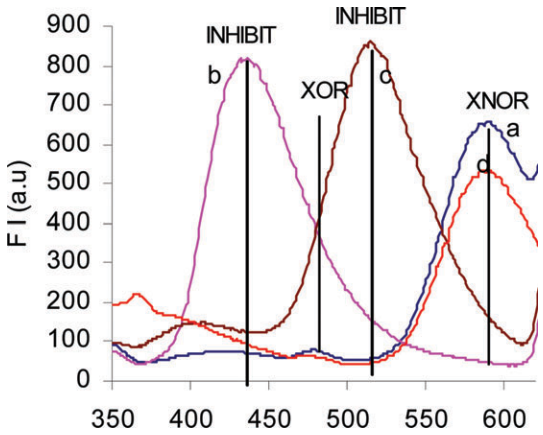


Fig. 1 The effect of acid and base on the fluorescence spectrum of fluorophore **1** in CH_3CN: (a) **1** (0.5 μM), (b) **1** + $HClO_4^-$ (5 μM), (c) **1** + TBAOH (5 μM) and (d) **1** + $HClO_4$ (5 μM) + TBAOH (5 μM).

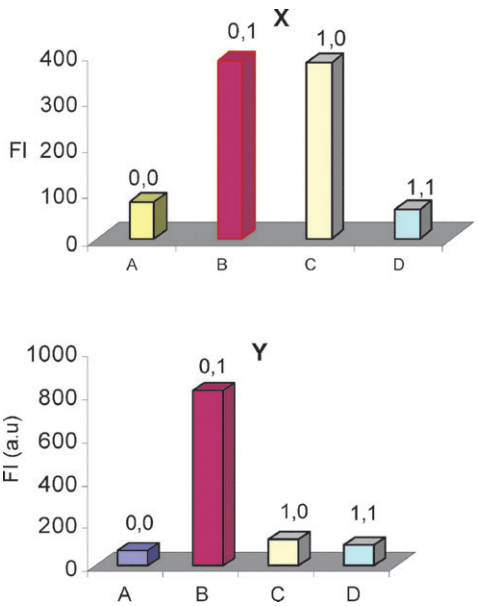


Fig. 2 Bar diagram of half-subtractor showing the fluorescence with different inputs: A, only **1**; B, **1** + $HClO_4$ (5 μM); C, **1** + TBAOH (5 μM); D, **1** + TBAOH (5 μM) + $HClO_4$ (5 μM) ('X' is XOR at 475 nm; 'Y' is INHIBIT at 435 nm).

Table 1 Truth table for fluorophore **1** for the operation of the molecular half-subtractor with INH (B) and XOR (D) combination

Input		Output (emission)		
OH^-	H^+	INH (B) 435 nm	INH (B) 515 nm	XOR (D) 475 nm
0	0	0 (low, 73)	0 (low, 70)	0 (low, 75)
0	1	1 (high, 812)	0 (low, 64)	1 (high, 395)
1	0	0 (low, 126)	1 (high, 850)	1 (high, 395)
1	1	0 (low, 80)	0 (low, 72)	0 (low, 75)

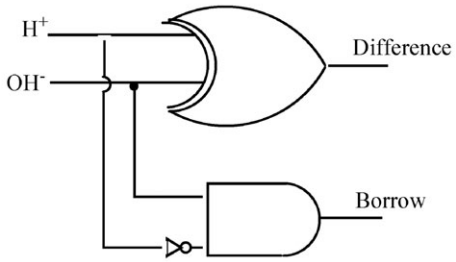


Fig. 3 Schematic representation of the two in-put half-subtractor logic circuit.

Fluorophore **1** on addition of two simultaneous inputs in the form of $HClO_4$ (acid) and TBAOH (base) annihilate each other's action and generate the emission at 585 nm. This results in an XNOR logic gate which is active only if both or neither of inputs are present. The output values of XNOR (585 nm) are simply the inverse of the corresponding output values of XOR (475 nm) (See last columns of Tables 1 and 2). The integration of XNOR logic at 585 nm with INHIBIT gate at 515 nm leads to a half-subtractor. Similarly, XNOR (585 nm) can be combined with INHIBIT at 435 nm to make the combinatorial half-subtractor (Table 2).

Therefore, the present system makes use of ESIPT—a scarcely studied phenomenon for developing logic operations. Here, three different emissive states of molecular switch **1** are created: (i) normal excited state of the molecule, (ii) excited state created through intramolecular proton transfer (ESIPT) from phenol to benzimidazole nitrogen, (iii) modulation of the ESIPT state by the interaction of anion. These molecular states result in emission at three different wavelengths *i.e.* 435, 585 and 515 nm, respectively which could be elaborated as a half-subtractor. It is noteworthy that the presence of more than 40 nm spectral shift in any two nearest emission signals [435 nm (INHIBIT), 475 nm (XOR), 515 nm (INHIBIT), 585 nm (XNOR)] leads to well distinguished different output channels (Fig. 1). Also, more than 300% difference between low and high intensity signals leads to clear binary assignments with low threshold values (Tables 1 and 2).

Fluorophore **2**[13] (1 μM, CH_3CN) on excitation at 330 nm gave two emission maxima at 385 and 585 nm, respectively due to normal emission and excited state intramolecular proton transfer (ESIPT) emission. The addition of tetrabutylammonium hydroxide (TBAOH as base) (5 μM) to a solution of **2** gave two new emission bands at 440 nm and 510 nm. Here, on addition of base, the normal emission band at 385 nm undergoes a bathochromic shift to 440 nm and the ESIPT band at 585 nm undergoes a hypsochromic shift to 510 nm.

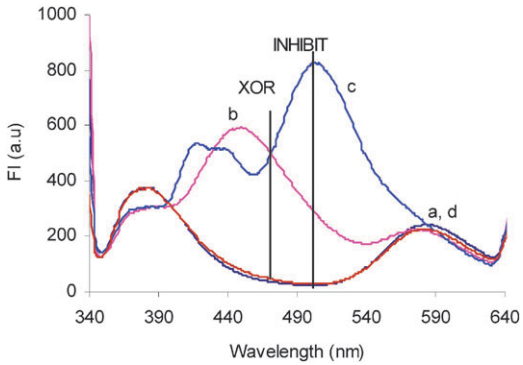


Fig. 4 The effect of acid and base on the fluorescence spectrum of **2** in CH_3CN: (a) **2** (1 μM), (b) **2** + $HClO_4$ (5 μM), (c) **2** + TBAOH (5 μM) and (d) **2** + $HClO_4$ (5 μM) + TBAOH (5 μM).

Both these emission bands were reversed on addition of $HClO_4$ (5 μM). On addition of perchloric acid ($HClO_4$) (5 μM) to a solution of **2** (1 μM, CH_3CN) a new emission band at 455 nm with hypsochromic shift ($\Delta\lambda$ = 130 nm) appeared (Fig. 4). Therefore the emission output of **2** at 510 nm is turned "ON" (output = 1) only in the presence of OH^- as input. For all other circumstances (Fig. 4 and Table 3), the output signal at 510 nm is 0 and thus leads to an INHIBIT gate at 510 nm.

The XOR gate in the case of **2** is elaborated with output signal at 475 nm. The output at 475 nm is high, *i.e.*, 1, with either of the inputs H^+ (acid) or OH^- (base). Further, two simultaneous inputs in the form of H^+ and OH^- annihilate each others action generating the emission spectrum of the fluorophore **2**. Thus this observation correlates well with XOR logic gate as it generates an "ON" output when either input is "ON"; but not when both inputs are either "ON" or both are "OFF". These observations of XOR (475 nm) and INHIBIT (510 nm) functions have been compiled in the truth table and lead to a molecular half-subtractor with negative logic function (Table 3).

Therefore, fluorophore **2**, which is half of the fluorophore **1**, shows significantly different emission behaviour under neutral, basic and acidic conditions than shown by fluorophore **1**. In **1**, the emission at 585 nm under neutral conditions points that only the ESIPT phenomenon is present but in the case of fluorophore **2**, the presence of two emission bands at 385 and 585 nm shows the presence of normal and ESIPT emissions, respectively. As a result, on addition of H^+ or OH^-, the emission bands for **2** are broader and with lower emission intensity than those observed for **1**. Further in **2**, the poor efficiency of ESIPT emission at 585 nm does not allow the XNOR logic operation. All these facts lead to multiple logic

Table 2 Truth table for fluorophore **1** for the operation of the molecular half-subtractor with INH (B) and XNOR (D) combination

Input		Output (emission)		
OH^-	H^+	INH (B) 435 nm	INH (B) 515 nm	XNOR (D) 585 nm
0	0	0 (low, 73)	0 (low, 70)	1 (high, 595)
0	1	1 (high, 812)	0 (low, 64)	0 (low, 50)
1	0	0 (low, 126)	1 (high, 850)	0 (low, 125)
1	1	0 (low, 80)	0 (low, 72)	1 (high, 603)

Table 3 Truth table for fluorophore **2** for the operation of the molecular half-subtractor with INH (B) and XOR (D) combination

Input		Output (emission)	
OH^-	H^+	INH (B) 510 nm	XOR (D) 475 nm
0	0	0 (low, 30)	0 (low, 30)
0	1	0 (low, 245)	1 (high, 523)
1	0	1 (high, 800)	1 (high, 523)
1	1	0 (low, 30)	0 (low, 30)

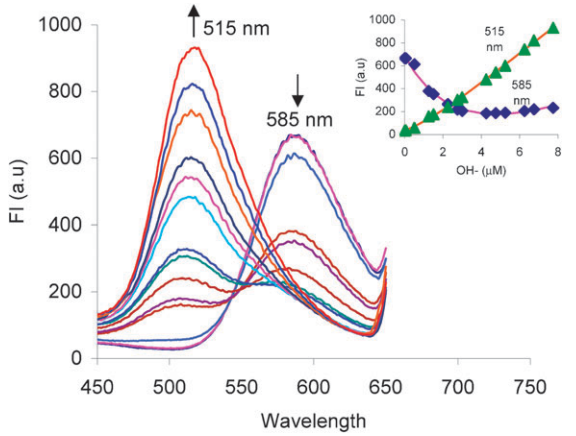


Fig. 5 Effect of incremental addition of TBAOH on the emission spectrum of **1** (CH_3CN, 0.5 μM). Inset: plot of FI *vs.* [TBAOH]; points show the experimental results and the line is the curve fit.

operations with higher sensitivity and efficiency in **1** than for fluorophore **2**.

Further, in order to rationalize the role of spatial placement of 2-hydroxynaphthyl and benzimidazole moieties on elaboration of logic operations, the fluorophore **5** was synthesized. Fluorophore **5** possesses the benzimidazole moiety at position 1 of the 2-naphthol moiety rather than at position 3 in case of fluorophores **1** and **2**. Fluorophore **5** (0.5 μM, CH_3CN) on excitation at λ_{max} 330 nm gave emission maxima at 455 nm which on addition of $HClO_4$ underwent quenching with concomitant appearance of a new emission band at 405 nm. The emission spectrum of **5** on addition of TBAOH (base) showed only enhancement in emission at 455 nm. Therefore, **5** can not be used for elaboration of combinatorial logic gates.

The participation of various species in elaborating a half-subtractor could be rationalised through fluorescence (Fig. 5 and 6) and ^{1}H NMR titrations (Fig. 7 and 8) of **1** with acid and base. The spectral fitting of the emission spectra obtained by titration of fluorophore **1** (0.5 μM, CH_3CN) with $HClO_4$ shows the formation of mono- and di-protonated species **1**·H^+ ($\log \beta_{\mathbf{1}\cdot H^+}$ = 5.8 ± 0.2) and **1**·$2H^+$ ($\log \beta_{\mathbf{1}\cdot 2H^+}$ = 9.8 ± 0.2) and at 5 μM $HClO_4$ a mixture of **1a** (75%) and **1b** (18%) exists. Similarly, the spectral fitting of the emission spectra obtained by titration of fluorophore **1** with TBAOH shows the formation of mono- and di-deprotonated species

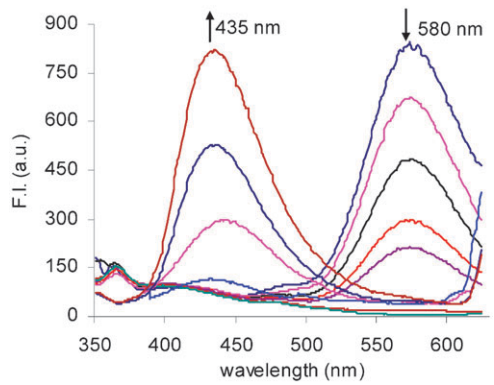


Fig. 6 Effect of incremental addition of $HClO_4$ on the emission spectrum of **1** (CH_3CN, 0.5 μM).

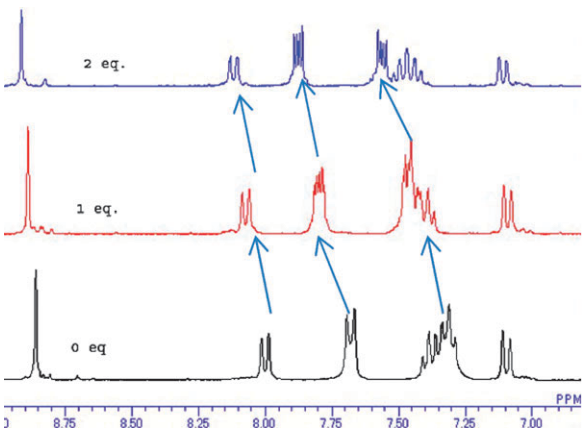


Fig. 7 Effect of $HClO_4$ on the ^{1}H NMR spectrum of fluorophore **1**.

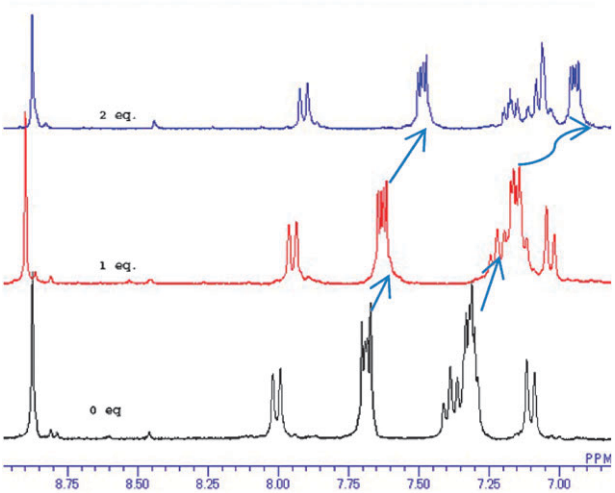
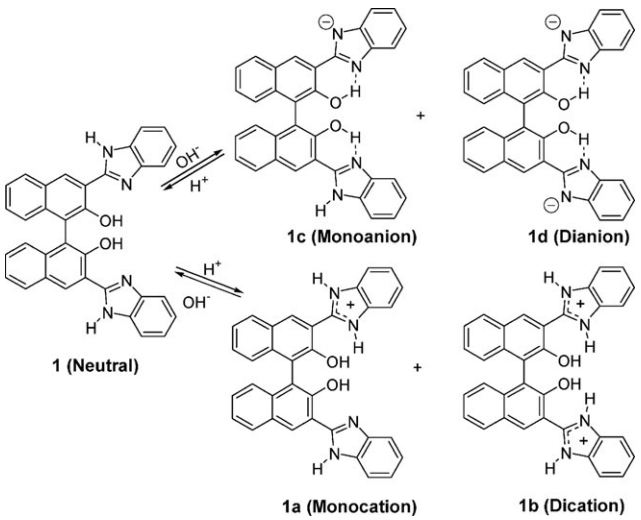


Fig. 8 Effect of TBAOH on the ^{1}H NMR spectrum of fluorophore **1**.

(**1c**) and (**1d**) ($\log \beta_{\mathbf{1}-H}$ = 5.39 ± 0.1 and $\log \beta_{\mathbf{1}-2H}$ = 9.53 + 0.45) and at 5 μM of TBAOH a mixture of **1c** (60%) and **1d** (6%) exists (Scheme 2).



Scheme 2

The structures of **1a–1d** can be rationalized through acid and base titration of **1** using ^{1}H NMR. The ^{1}H NMR titration of solution of **1** (2 mM, DMSO-d_6) with $HClO_4$ showed downfield shift of protons corresponding to the benzimidazole moiety which reaches a plateau after addition of 2 equiv. of $HClO_4$ (Fig. 7). The proton signals due to the 2-naphthol moiety showed insignificant or only a small downfield shift. This downfield shift of protons is in consonance with decreased electron-density on the benzimidazole moiety due to protonation at benzimidazole nitrogen. Similarly, titration of solution of **1** (2 mM, DMSO-d_6) with TBAOH showed upfield shift of signals of both benzimidazole and 2-naphthol moieties but this was more pronounced for the benzimidazole protons than for the 2-naphthol protons (Fig. 8). This could be attributed to the increased electron-density due to negative charge at benzimidazole nitrogen caused by base-mediated deprotonation. Therefore, based on fluorescence and ^{1}H NMR titration studies of **1** with $HClO_4$ and TBAOH, the formation of various species could be rationalized (Scheme 2).

Conclusions

Thus, fluorophore **1** with large differentials of emission maxima under neutral, acidic and basic conditions provides four opportunities for arithmetic operation half-subtractor at the molecular level which is reduced to only one half-subtractor combination in **2**. Fluorophore **3**, though amphiphilic in nature, does not allow elaboration of logic gates. The effect of various structural features on **1** in elaborating logic operations is being investigated.

Experimental

Synthesis of fluorophore 5

A solution of 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) and 1,2-diaminobenzene (108 mg, 1 mmol) in nitrobenzene (5 ml) was heated at 140–150 °C. After completion of the reaction (36 h), the reaction mixture was cooled to room temperature and was diluted with hexane (50 ml). The yellow solid separated was filtered off and was recrystallised from chloroform–methanol (1 : 1) to obtain pure 1-(1*H*-benzimidazole-2-yl)naphthalen-2-ol (**5**), 65%; yellow crystalline solid, mp 260 °C; FAB mass: 261 (M^+); ^{1}H NMR (300 MHz) ($CDCl_3$): δ 7.31–7.36 (m, 3H, ArH), 7.41 (ddd, 1H, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz), 7.61 (ddd, 1H, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz), 7.69 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 2H, ArH), 7.86 (t, J = 6 Hz, 2H, ArH), 8.30 (d, J = 8.4 Hz, 1H, ArH); UV-Vis (CH_3CN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 335 (14 500), 413 (21 000), 462 (14 300). Found: C, 78.65; H, 4.55; N, 10.60%. $C_{17}H_{12}N_2O$ requires C, 78.44; H, 4.65; N, 10.76%.

General procedure for elaboration of logic operations

Fluorescence spectra were recorded on a Shimadzu RF1501 spectrofluorophotometer with a 1 cm quartz cell at 25 ± 1 °C. For performing the studies, solutions of fluorophores, tetrabutylammonium hydroxide (TBAOH) and perchloric acid ($HClO_4$) were prepared in doubly distilled acetonitrile. Solution containing fluorophore **1**, **2** or **5** were taken in a quartz cell and their fluorescence spectra were recorded. The addition of different concentrations of TBAOH and $HClO_4$ was carried out with a micropipette in aliquots of 1.5–3.0 μl in the same cell and each time the solution was allowed to stand for 3 min before recording the fluorescence spectrum. Titration data were fit with program Specfit/32, which analyzes multi-wavelength data using an iterative method to obtain the stoichiometries and association constants.

General procedure for ^{1}H NMR titrations

^{1}H NMR spectra were recorded on a JEOL 300 MHz spectrometer at 25 ± 1 °C. For ^{1}H NMR titrations, the solution of fluorophore **1** (2 mM) was prepared in DMSO-d_6. The addition of different concentrations of TBAOH or $HClO_4$ was carried out with a micropipette in aliquots of 1.5–3.0 μl in the same NMR tube and each time the solution was allowed to stand for 3 min before recording the ^{1}H NMR spectrum.

Acknowledgements

We thank DST for a Rammana Fellowship to S. K., UGC for fellowship to V. L. and CDRI Lucknow for FAB mass spectra.

References

1 (*a*) A. P. de Silva, S. Uchiyama, T. P. Vance and B. Wannalerse, *Coord. Chem. Rev.*, 2007, **251**, 1623–1632; (*b*) F. M. Raymo, *Adv. Mater.*, 2002, **14**, 401–414; (*c*) V. Balzani, A. Credi and M. Venturi, *ChemPhysChem*, 2003, **4**, 49–59; (*d*) J. F. Callan, A. P. de Silva and D. C. Magri, *Tetrahedron*, 2005, **61**, 8551–8588; (*e*) A. P. de Silva and N. D. McClenaghan, *Chem.–Eur. J.*, 2004, **10**, 574–586; (*f*) G. J. Brown, A. P. de Silva and S. Pagliari, *Chem. Commun.*, 2002, 2461–2463; (*g*) A. Okamoto, K. Tanaka and I. Saito, *J. Am. Chem. Soc.*, 2004, **126**, 9458–9463.
2 (*a*) D. Margulies, G. Melman and A. Shanzer, *J. Am. Chem. Soc.*, 2006, **128**, 4865–4871; (*b*) D. Margulies, G. Melman and A. Shanzer, *Nat. Mater.*, 2005, **4**, 768–771.
3 (*a*) H. Wang, D. Zhang, X. Guo, L. Zhu, Z. Shuai and D. Zhu, *Chem. Commun.*, 2004, 670–671; (*b*) H. Xu, X. Xu, R. Dabestani, G. M. Brown, L. Fan, S. Patton and H. F. Ji, *J. Chem. Soc., Perkin Trans. 2*, 2002, 636–643; (*c*) M. N. Stojanovic, T. E. Mitchell and D. Stefanovic, *J. Am. Chem. Soc.*, 2002, **124**, 3555–3561; (*d*) B. Bag and P. K. Bharadwaj, *Chem. Commun.*, 2005, 513–515; (*e*) S. Uchiyama, G. D. McClean, K. Iwai and A. P. de Silva, *J. Am. Chem. Soc.*, 2005, **127**, 8920–8921; (*f*) K. Szacilowski, *Chem.–Eur. J.*, 2004, **10**, 2520.
4 (*a*) A. Credi, V. Balzani, S. J. Langford and J. F. Stoddart, *J. Am. Chem. Soc.*, 1997, **119**, 2679–2681; (*b*) F. Pina, M. J. Melo, M. Maestri, P. Passaniti and V. Balzani, *J. Am. Chem. Soc.*, 2000, **122**, 4496–4498; (*c*) K. Szacilowski, W. Macyk and G. Stochel, *J. Am. Chem. Soc.*, 2006, **128**, 4550–4551.
5 (*a*) M. de Sousa, B. de Castro, S. Abad, M. A. Miranda and U. Pischel, *Chem. Commun.*, 2006, 2051–2053; (*b*) 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; (*c*) S. Banthia and A. Samanta, *Eur. J. Org. Chem.*, 2005, 4967–4970.
6 A. P. de Silva, H. Q. N. Gunaratne and P. L. M Lynch, *J. Chem. Soc., Perkin Trans. 2*, 1995, 685–690.
7 (*a*) P. Ghosh, P. K. Bharadwaj, S. Mandal and S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553–1554; (*b*) M. Yoshizawa, M. Tamura and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 6846–6847.
8 (*a*) B. Turfan and E. U. Akkaya, *Org. Lett.*, 2002, **4**, 2857–2859; (*b*) Z. Wang, G. Zheng and P. Lu, *Org. Lett.*, 2005, **7**, 3669–3672.
9 (*a*) S. H. Lee, J. Y. Kim, S. K. Kim, J. H. Lee and J. S. Kim, *Tetrahedron*, 2004, **60**, 5171–5176; (*b*) M. Asakawa, P. R. Ashton

V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, M. Montalti, N. Spencer, J. F. Stoddart and M. Venturi, *Chem.–Eur. J.*, 1997, **3**, 1992–1996.

10 (*a*) H. T. Baytekin and E. U. Akkaya, *Org. Lett.*, 2000, **2**, 1725–1727; (*b*) G. Zong, L. Xian and G. Lu, *Terahedron Lett.*, 2007, **48**, 3891–3894.

11 (*a*) M. Suresh, D. A. Jose and A. Das, *Org. Lett.*, 2007, **9**, 441–444; (*b*) Y. Liu, W. Jiang, H. Zhang and C. Li, *J. Phys. Chem. B*, 2006, **110**, 14231–14235; (*c*) A. Coskun, E. Deniz and E. U. Akkaya, *Org. Lett.*, 2005, **7**, 5187–5189; (*d*) D. Margulies, G. Melman, C. E. Felder, R. Arad-Yellin and A. Shanzer, *J. Am. Chem. Soc.*, 2004, **126**, 15400–15401; (*e*) S. J. Langford and T. Yann, *J. Am. Chem. Soc.*, 2003, **125**, 11198–11199; (*f*) E. P. Inestrosa, J. M. Montenegro, D. Collado, R. Suau and J. Casado, *J. Phys. Chem. C*, 2007, **111**, 6904–6909; (*g*) U. Pischel, *Angew. Chem., Int. Ed.*, 2007, **46**, 4026–4040; (*h*) M. Suresh, A. Ghosh and A. Das, *Tetrahedron Lett.*, 2007, **48**, 8205–8208; (*i*) U. Pischel and B. Hellerc, *New J. Chem.*, 2008, **32**, 395–400.

12 (*a*) J. Andreasson, G. Kodis, Y. Terazono, P. A. Liddell, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore and D. Gust, *J. Am. Chem. Soc.*, 2004, **126**, 15926–15927; (*b*) Y. Zhou, H. Wu, L. Qu, D. Zhang and D. Zhu, *J. Phys. Chem. B*, 2006, **110**, 15676–15679; (*c*) A. P. de Silva and N. D. McClemaghan, *J. Am. Chem. Soc.*, 2000, **122**, 3965–3966.

13 (*a*) F. Remacle, R. Weinkauf and R. D. Levine, *J. Phys. Chem. A*, 2006, **110**, 177–184; (*b*) O. Kuznetz, H. Salman, N. Shakkour, Y. Eichen and S. Speiser, *Chem. Phys. Lett.*, 2008, **451**, 63–67; (*c*) O. Kuznetz, H. Salman, N. Shakkour, Y. Eichen and S. Speiser, *Mol. Phys.*, 2008, **106**, 531–535; (*d*) H. Lederman, J. Macdonald, D. Stefanovic and M. N. Stojanovic, *Biochemistry*, 2006, **45**, 1194–1199.

14 V. Luxami and S. Kumar, *Tetrahedron Lett.*, 2007, **48**, 3083–3087.