Communication

Molecular Logic: A Half-Subtractor Based on Tetraphenylporphyrin

Steven J. Langford, and Trevor Yann

J. Am. Chem. Soc., **2003**, 125 (37), 11198-11199• DOI: 10.1021/ja036909+ • Publication Date (Web): 23 August 2003

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Molecular Logic: A Half-Subtractor Based on Tetraphenylporphyrin

Steven J. Langford* and Trevor Yann

School of Chemistry, Monash University, Victoria, Australia, 3800

Received June 26, 2003; E-mail: s.langford@sci.monash.edu.au

Demonstrating the fundamental principles of Boolean algebra through a detectable spectroscopic change upon an ionic, electronic, or photonic input[1−5] has led to the interpretation of complex logic functions such as AND,[6,7] XOR,[7,8] and INHIBIT[6a,9] at the molecular level. In some instances, the conjoined use of such logic functions has been utilized to perform arithmetic operations involving two binary digits (bits), the so-called half-adder.[10] A half-adder requires two binary inputs and two binary outputs: the input variables designate the augend and addend bits; the output variables produce the sum (S) and carry (C). This additive output is generated through XOR and AND gates, respectively. While addition is an important operation, digital computers also perform a variety of other information processing tasks. For example, it is also possible to implement subtraction with logic circuits in the same direct manner as addition. A half-subtractor is a combinational circuit that subtracts two bits and produces their difference.[11] A half-subtractor, like a half-adder, needs two outputs. One generates the difference (D), and the second generates the borrow (B). These outputs are generated through XOR and INHIBIT gates, respectively. The truth table for the input/output relationships for a half-adder and half-subtractor is shown in Figure 1. A full-subtractor is a combinational circuit that performs a subtraction between two bits, taking into account that a “1” may have been borrowed by a lower significant stage.

The realization that it is possible to simutaneously multiply configure a system, so that complex operations involving more than one Boolean expression are possible through the judicial choice of input and output signals, has brought with it an even greater realization that single molecular entities might serve as suitable combinational circuits.[7] However, there are a number of important and practical issues that still need to be addressed before the realization of a pragmatic molecular logic device. The use of UV light, which is relatively high in energy, as either an excitatory (input) or a diagnostic (output) source will undoubtably limit the lifetime of the device. Second, the generation of regular and addressable arrays of the logic device is still desired. To these ends, porphyrin systems, which absorb strongly in the visible region[12] (in low incident light) and can be manipulated to form regular arrays on a variety of substrates,[13] might provide a practical approach. Here, we describe how a simple porphyrin system, 5,10,15,20-tetraphenylporphyrin, (TPPH$_2$), can be used to optically demonstrate the operation of a half-subtractor in solution using acid and base input variables and transmittance and fluorescence as the output variables.

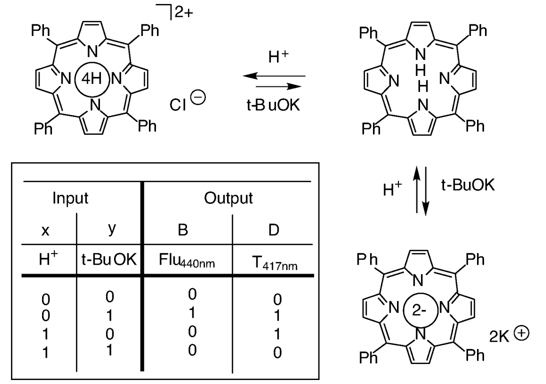
(a)

x	y	C	S
0	0	0	0
0	1	0	1
1	0	0	1
1	1	1	0

(b)

x	y	B	D
0	0	0	0
0	1	1	1
1	0	0	1
1	1	0	0

Figure 1. Truth table for the input−output relationships of (a) a half-adder and (b) a half-subtractor. Note that the XOR logic operation for output D in the half-subtractor is the same as that for output S in the half-adder.



Input		Output	
x	y	B	D
H$^+$	t-BuOK	Flu$_{440nm}$	T$_{417nm}$
0	0	0	0
0	1	1	1
1	0	0	1
1	1	0	0

Figure 2. The amphophilic nature of tetraphenylporphyrin (TPPH$_2$) results in significant changes in the transmittance (Soret) and emission bands upon the addition of acid or base. These changes can be interpreted in a truth table using acid and base as the inputs. The results display a combinational circuit that subtracts.

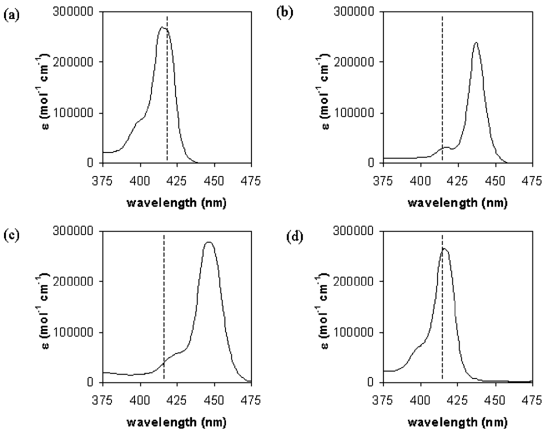


Figure 3. Changes in the absorption bands of (a) TPPH$_2$ upon the addition of (b) 0.1 M *t*-BuOK, (c) 0.1 M aq HCl, and (d) a 1:1 mix of 0.1 M *t*-BuOK and 0.1 M aq HCl in DMF solution ([TPPH$_2$] = 10^{-5} M). The XOR function is derived by monitoring the transmittance at 417 nm.

Free base porphyins such as TPPH$_2$ can be regarded as being amphophilic, because the two pyrrolenine nitrogen atoms are capable of accepting protons and the two inner peripheral NH groups are capable of losing protons (Figure 2).[12] The weakly acidic nature of the porphyrin (pK_a > 16) means that sodium alkoxides are required to allow spectroscopic observation of the dianion TPP^{2-}. The generation of TPPH$_4^{2+}$ can be observed in dilute mineral acids. The electronic absorption spectra of TPPH$_2$ in DMF (10^{-5} M) exist as the etio-type, with a single Soret band (λ_{max} 417 nm, log ϵ = 5.4) and four weaker Q-bands (I−IV) occurring at higher wavelength (500−700 nm, log ϵ < 4). The sequential addition of inputs H$^+$ and ^{t}BuOK to TPPH$_2$ causes significant changes to the position of the Soret band (Figure 3a−c) and the number and position of the Q-bands within the electronic absorption

10.1021/ja036909+ CCC: $25.00

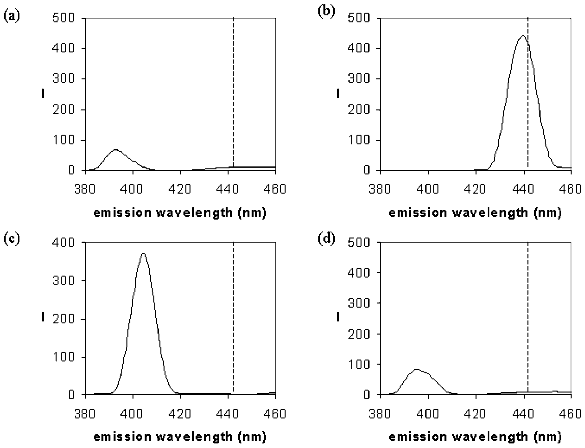


Figure 4. Changes in the emission bands of (a) $TPPH_2$ upon the addition of (b) 0.1 M *t*-BuOK, (c) 0.1 M aq HCl, and (d) a 1:1 mix of 0.1 M *t*-BuOK and 0.1 M aq HCl in DMF solution ($[TPPH_2] = 10^{-5}$ M, $\lambda_{ex} = 397 \pm 2$ nm.). The INHIBIT function is attributed to the emission band at 440 nm.

spectra of $TPPH_2$. The spectra of either the porphyrin dianion (Figure 3b) or the dication (Figure 3c) show little absorption in the region 400−420 nm when compared to $TPPH_2$. The resultant change in maxima of the Soret band can be used to derive a truth table based on the chemical inputs H^+ and ^{t}BuOK and transmittance as the output variable (Figure 2).[14] The result of this table is a demonstration of the highly desirable XOR function, which has proved to be one of the more difficult to implement on a molecular level. An XOR function is complicated by the fact that it excludes the combination of both inputs (x and y) being equal to 1. Hence, the presence of only one input registers a high output value. The XOR gate is of significant value to a combinational circuit that performs both addition and subtraction of the two binary digits (or bits). While the present example involving $TPPH_2$ expresses a correct truth table, the output variables do rely on a situation where the two inputs annihilate each other's action. This situation, however, does not exclude incorporation of the porphyrin into a more advanced system.

The same set of inputs (H^+ and ^{t}BuOK) give rise to significant changes in the fluorescence spectrum of $TPPH_2$ in DMF solution (Figure 4a−d). The spectra are dominated by the intensity and well-resolved nature of the emission bands for TPP^{2-} ($\lambda_{max} = 440$ nm, Figure 4b) and $TPPH_4^{2+}$ ($\lambda_{max} = 405$ nm, Figure 4c). Monitoring the fluorescence at 440 nm upon the addition of acid, base, and an equimolar mix of acid and base simultaneously yields a truth table (Figure 2) that leads to an INHIBITION function. Although INHIBITION is neither communicative nor associative, it can be viewed as a two-input AND gate, one of whose input lines contains an inverter. The strength of the INHIBIT gate is acknowledged in combination with an XOR gate, leading to a circuit able to function as a half-subtractor. What complicates a half-subtractor over a half-adder is the fact that to perform $x - y$, the relative magnitudes of x and y need to be accounted. In practice, if $x \geq y$, then three possibilities exist: $0 - 0 = 0$, $1 - 0 = 1$, and $1 - 1 = 0$. In these cases, the borrow (B) is a 0. If $x < y$, then the expression becomes $0 - 1$, and it is necessary to borrow a 1 from the next higher stage. The borrowed 1 has the effect of adding 2 to the minuend bit. With the minuend equal to 2, the difference becomes $2 - 1 = 1$. Alternatively, monitoring the change in emission at $\lambda_{max} = 405$ nm would yield the same truth table through the interchange of inputs x and y.

In conclusion, we hope to have drawn attention to the use of porphyrins as a viable component in the pursuit of logic-based devices by demonstrating the first molecular half-subtractor.[15] Moreso, we have illustrated how cheap and readily accessible materials can be employed as a potential cost-effective logic gate displaying complicated operations. We are now investigating whether other chemical inputs, for example, metalation and subsequent axial ligation, in conjunction with electronic or photonic inputs, give rise to other combinational circuits, including a full-subtractor.

Acknowledgment. This work was supported by the Australian Research Council through the Discovery Scheme (DP0210193).

Supporting Information Available: A representation of an electronic circuit implementing INHIBIT and XOR logic as well as details of the measurements undertaken (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42−44. (b) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445−455. (c) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines − A Journey into the Nanoworld*; Wiley-VCH: Weinheim, 2003; Chapter 9.

(2) (a) Credi, A.; Balzani, V.; Langford, S. J.; Montalti, M.; Raymo, F. M.; Stoddart, J. F. *New J. Chem.* **1998**, 1061−1065. (b) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig, G.; Mathews, O. A.; Montalti, M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *Chem.-Eur. J.* **1997**, *3*, 1992−1996.

(3) Kompa, K. L.; Levine, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 410−414.

(4) (a) Lukas, A. S.; Bushard, P. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 2440−2441. (b) Raymo, F. M.; Giordani, S. *Org. Lett.* **2001**, *3*, 1833−1836. (c) de Silva, A. P.; McClenaghan, N. D.; McCoy, C. P. *Electron Transfer Chem.* **2001**, *5*, 156−185. (d) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401−414.

(5) Woo, Raymond; Pati, R.; Karna, S. P. *Appl. Phys. Lett.* **2002**, *81*, 1872−1874.

(6) (a) Xu, H.; Xu, X.; Dabestani, R.; Brown, G. M.; Fan, L.; Patton, S.; Ji, H.-F. *J. Chem. Soc., Perkin Trans. 2* **2002**, 636−643. (b) Stojanovic, M. N.; Mitchell, T. E.; Stefanovic, D. *J. Am. Chem. Soc.* **2002**, *124*, 3555−3561.

(7) de Silva, A. P.; McClenaghan, N. D. *Chem.-Eur. J.* **2002**, *8*, 4935−4945.

(8) (a) Balzani, V.; Credi, A.; Langford, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 2679−2681. (b) Pina, F.; Melo, M. J.; Maestri, M.; Passaniti, P.; Balzani, V. *J. Am. Chem. Soc.* **2000**, *122*, 4496−4498.

(9) Gunnlaugsson, T.; MacDonaill, D. A.; Parker, D. *Chem. Commun.* **2000**, 93−94.

(10) (a) Stojanovic M. N.; Stofanovic, D. *J. Am. Chem. Soc.* **2003**, *125*, 6673−6676. (b) de Silva, A. P.; McClenaghan, N. D. *J. Am. Chem. Soc.* **2000**, *122*, 3965−3966. (c) Remacle, F.; Speiser, S.; Levine, R. D. *J. Phys. Chem. B* **2001**, *105*, 5589−5591. For an example of a full-adder, see: Remacle, F.; Weinkauf, R.; Steinitz, D.; Kompa, K. L.; Levine, R. D. *Chem. Phys.* **2002**, *281*, 363−372.

(11) Mano, M. M. *Digital Design*, 2nd ed.; Prentice Hall: New Jersey, 1991.

(12) Smith, K. M. *Porphyrins and Metalloporphyrins*; Elsevier: Amsterdam, 1975.

(13) (a) De Feyter, S.; De Schryver, F. C. *Chem. Soc. Rev.* **2003**, *32*, 139−150. (b) Drain, C. D.; Nifiatis, F.; Vasenko A.; Batteas, J. D. *Angew. Chem.* **1998**, *37*, 2344−2347.

(14) Transmittance, as an output variable, may only be practical if compounds exhibit large differences in the extinction coefficients at the addressable wavelength for "0" and "1" states.

(15) A half-subtractor based on the use of a spin-$^7/_2$ Cs-133 nuclei in a liquid-crystalline medium has been described, see: Murali, K. V. R. M.; Sinha N.; Mahesh T. S.; Levitt M. H.; Ramanathan K. V.; Kumar A. *Phys. Rev. A* **2002**, *66*, 022313.

JA036909+