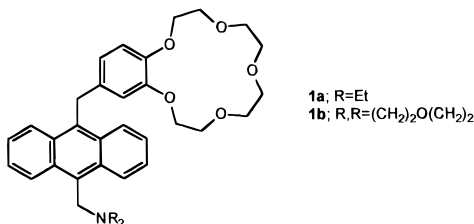# Molecular Photoionic AND Logic Gates with Bright Fluorescence and "Off−On" Digital Action

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Photodriven supramolecular systems[1] are useful for information gathering (sensing),[2] storing,[3] processing,[3b] and transmission.[4] The important goal of molecular arithmetic can be achieved in principle if "off−on" digital[5] AND and XOR logic gates[6,7] with independent inputs are available to operate on binary numbers. Practical considerations would also require strong signals when these gates are in their "on" states. We now demonstrate the first molecular AND gates **1** which satisfy

1a; R=Et
1b; R,R=(CH₂)₂O(CH₂)₂

these criteria. These use two ionic inputs and a fluorescence output, with a design basis of photoinduced electron transfer (PET). Essentially complete digital action is achieved since the "off" states are virtually nonfluorescent under the conditions of operation. The fluorescence efficiency in the "on" state, and hence the signal strength, is high with an emission quantum yield (ϕ_F) of up to 0.24. As a bonus, systems **1** remain functional even in mixed aqueous media. The few available AND gates,[8,9] and systems which can be interpreted as such,[10−12] (a) are poorly emissive,[8] (b) have "on−off" signal intensity ratios that are small,[8,10] or (c) have truth tables that cannot be properly tested[9−12] even though the apparent outcome corresponds to AND logic. The last point arises because most of these require entry of the first ionic input to prepare the system for the reception of the second ionic input. The second ion cannot be entered into the system independent of the first ion. The high performance of **1** is at least partly due to the novel arrangement of photo/ion-responsive modules—a fluorophore flanked by two PET-active and ion-selective receptors with interspersed spacers.[13] This work complements parallel developments in other types of molecular logic gates.[14,15]

System **1** is designed to have no (or weak) PET to the fluorophore from either receptor when they are bound to their appropriate ion (amine/H⁺ and benzo-15-crown-5 ether/Na⁺). This is the "on" state of fluorescence. When the amine group is proton-free, it serves as an efficient PET donor ($\Delta G_{PET} \approx -0.1$ eV)[16] to the fluorophore which is separated by only a methylene group. When protons are present in sufficient concentration and Na⁺ is absent, the protonated aminomethyl moiety behaves as an electron-withdrawing group on the anthracene fluorophore[17] which permits rapid PET from the benzocrown ether moiety ($\Delta G_{PET} \approx -0.1$ eV)[18] a short distance away.

Systems **1a** and **1b** were synthesized as follows. 4-(Anthracen-9′-ylmethyl)benzo-15-crown-5 ether[19] was formylated at the 10′ position under Vilsmeier conditions, reduced with NaBH₄, treated with Ph₃P/Br₂, and aminated with Et₂NH or O(CH₂-CH₂)₂NH, respectively. Systems **1a** and **1b** were fully characterized by elemental analysis and a range of spectroscopies.

The ion-induced fluorescence emission spectral behavior of these systems is illustrated in Figure 1 for the case of **1b**. The

(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis-Horwood: Chichester, 1991.

(2) (a) *Fluorescent Chemosensors of Ion and Molecule Recognition*; ACS Symposium Series 538; Czarnik, A. W., Ed.; American Chemical Society: Washington, DC, 1993. (b) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302. (c) Czarnik, A. W. *Adv. Supramol. Chem.* **1993**, *3*, 131. (d) Fernandez-Gutierrez, A.; Munoz de la Pena, A. In *Molecular Luminescence Spectroscopy. Methods and Applications. Part 1*; Schulman, S. G., Ed.; Wiley: New York, 1985; p 371. (e) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; Sandanayake, K. R. A. S. *Chem. Soc. Rev.* **1992**, *21*, 187. (f) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; McCoy, C. P.; Sandanayake, K. R. A. S. *Top. Curr. Chem.* **1993**, *168*, 223. (g) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; McCoy, C. P.; Maxwell. P. R. S.; Rademacher, J. T.; Rice, T. E. *Pure Appl. Chem.* **1996**, *68*, 1443. (h) Valeur B. In *Topics in Fluorescence Spectroscopy. Vol. 4. Probe Design and Chemical Sensing*; Lakowicz, J. R., Ed.; Plenum: New York, 1994; p 21. (i) Valeur, B.; Bardez, E. *Chem. Br.* **1995**, *31*, 216. (j) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197. (k) Tsien, R. Y. *Chem. Eng. News* **1994**, July 18, 34. (l) Tsien, R. Y. *Am. J. Physiol.* **1992**, *263*, C723. (m) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1910.

(3) (a) Feringa, B. L.; Jager, W. F.; Delange, B. *Tetrahedron* **1993**, *49*, 8267. (b) de Silva, A. P.; McCoy, C. P. *Chem. Ind.* **1994**, 992.

(4) (a) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (b) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519. (c) Wagner, R. W.; Lindsey, J. S.; Seth, T.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996. (d) Harriman, A.; Ziessel, R. *Chem. Comun.* **1996**, 1707. (e) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 595. (f) Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121. Related nonphotonic cases: (g) Gokel, G. W.; Murillo, O. *Acc. Chem. Res.* **1996**, *29*, 425. (h) Voyer, N.; Robitaille, M. *J. Am. Chem. Soc.* **1995**, *117*, 6599. (i) Pregel, M. J.; Jullien, L.; Canceill, J.; Lacombe, L.; Lehn, J.-M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 417. (j) Granja, J. R.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 10785. (k) Fyles, T. M.; James, T. D.; Kaye, K. C. *J. Am. Chem. Soc.* **1993**, *115*, 12315.

(5) For "off−on" digital action in other areas, see: (a) Kimura, K.; Mizutani, R.; Yokoyama, M.; Arakawa, R.; Matsubayashi, G.; Okamoto, M.; Doe, H. *J. Am. Chem. Soc.* **1997**, *119*, 2062. (b) Nabeshima, T.; Furusawa, H.; Yano, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1750.

(6) Molecular arithmetic can also be approached via externally controllable abacuses. See: Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133.

(7) For bulk silicon-based examples, see: Malvino, A. P.; Brown, J. A. *Digital Computer Electronics*, 3rd ed.; Glencoe: Lake Forest, 1992.

(8) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42.

(9) Iwata, S.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1491.

(10) Hosseini, M. W.; Blacker, A. J.; Lehn, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3896.

(11) Huston, M. E.; Akkaya, E. U.; Czarnik, A. W. *J. Am. Chem. Soc.* **1989**, *111*, 8735.

(12) E.g., see: Garcia-Sanchez, F.; Navas, A.; Laserna, J. J. *Talanta* **1982**, *29*, 511.

(13) A related case, targeted for a very different use, possesses only one PET-active receptor. See: de Silva, A. P.; Gunaratne, H. Q. N.; McVeigh, C.; Maguire, G. E. M.; Maxwell, P. R. S.; O'Hanlon, E. *Chem. Commun.* **1996**, 2191.

(14) (a) OR gates: de Silva, A. P.; Gunaratne, H. Q. N.; Maguire, G. E. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1213. (b) Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh, S. *J. Am. Chem. Soc.* **1996**, *118*, 1553.

(15) XOR gates: Credi, A.; Balzani, V.; Langford, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 2679.

(16) $\Delta G_{PET} = -E_{singlet\ fluorophore} - E_{red\ fluorophore} + E_{ox\ receptor} - e^2/\epsilon r$ (Weller, A. *Pure Appl. Chem.* **1968**, *16*, 1150). $E_{singlet\ fluorophore} = 3.08$ eV (model 9,10-dimethylanthracene from Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Dekker: New York, 1993 in this and all other cases), $E_{red\ fluorophore} = -1.87$ V (model 9-methylanthracene), $E_{ox\ receptor} = 1.15$ V (vs SCE) (model triethylamine. Kavarnos, G. J. *Fundamentals of photoinduced electron transfer*; VCH: Weinheim, New York, 1993 gives a more favorable value of 0.96 V), $e^2/\epsilon r = -0.1$ eV (Grabowski, Z. R.; Dobkowski, J *Pure Appl. Chem.* **1983**, *55*, 245). We reiterate that these rough estimates and those in refs 17 and 18, which are necessarily model-based, are sufficient to suggest theoretical feasibility which is clearly borne out by the experimental results.

(17) Protonated 9-[(diethylamino)methyl]anthracene displays PET with electron donors at rates similar to that of 9-cyanoanthracene (Soumillion, J.-P.; Calle, E. Unpublished results). This is also supported by the fact that the CH₂N⁺HMe₂ group has Hammett $\sigma_p = 0.43$ which approaches that of CN ($\sigma_p = 0.66$) whereas the CH₂NMe₂ group has $\sigma_p = 0.01$ (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165).

(18) The Weller equation from ref 16 is applied with $E_{singlet\ fluorophore} = 2.98$ eV (model 9-cyanoanthracene), $E_{red\ fluorophore} = -1.58$ V (model 9-cyanoanthracene), $E_{ox\ receptor} = 1.45$ V (model 1,2-dimethoxybenzene).

(19) de Silva, A. P.; Sandanayake, K. R. A. S. *J. Chem. Soc., Chem. Commun.* **1989**, 1183
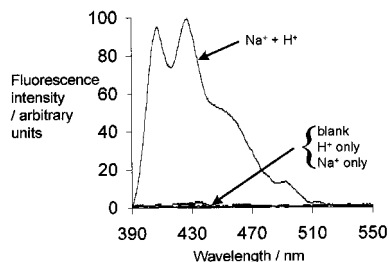
Figure 1. Raw fluorescence emission spectra of gate **1b** in MeOH excited at 377 nm under the four ionic conditions necessary to test its digital AND logic gate function.
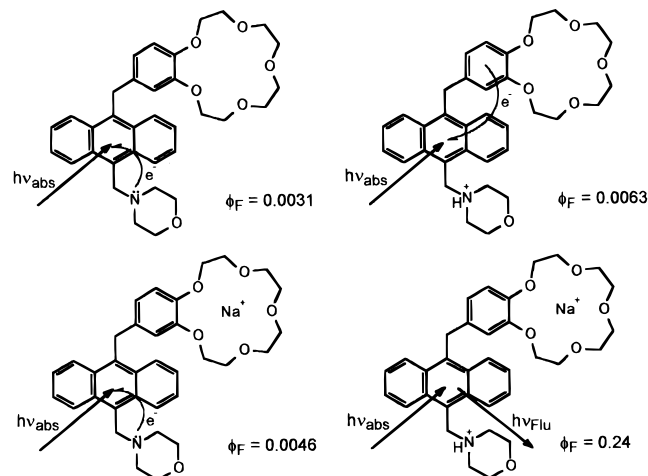

Figure 2. Pictorial form of the truth table for digital AND logic gate **1b**. The PET processes are also shown where they occur. The three low ϕ_F values are upper limits. The curly arrow symbolism should not be taken to imply a through space mechanism for PET.

Table 1. Truth Table and Operating Conditions for Digital AND Gate **1a**[a]

input$_1$ (H$^+$)	input$_2$ (Na$^+$ or K$^+$)	fluorescence output ($\phi_{F,1a}$)[b]
none[c]	none	0.0024[d]
10^{-3} M	none	0.0090[d]
none[c]	10^{-2} M Na$^+$	0.0051[d]
10^{-3} M	10^{-2} M Na$^+$	0.22
none[c]	6 × 10^{-3} M K$^+$	0.0091[d]
10^{-3} M	6 × 10^{-3} M K$^+$	0.10

[a] 10^{-6} M **1a** and **1b** in MeOH excited at the isosbestic point (377 nm). λ_{em} = 406, 428, and 449 (sh) nm when spectra are observable under our instrumental conditions. H$^+$, Na$^+$, and K$^+$ inputs are provided as methanesulfonates. [b] ϕ_F values in this and all other cases are with reference to the primary standard 9,10-diphenylanthracene in deaerated ethanol.[27] [c] In contrast to gate **1b**, the more basic gate **1a** requires 10^{-3} M morpholine as a proton scavenger when the H$^+$ input is to be absent. [d] Upper limits.

resulting corresponding truth table is presented in pictorial form in Figure 2, giving an excellent correlation with the truth table for a digital AND logic gate.[6] The fluorescence is virtually unobservable under our instrumental conditions unless both H$^+$ and Na$^+$ are presented to **1b** in sufficiently high concentration. A large fluorescence enhancement (FE) factor of >37−76 results in the latter case. Smaller FE factors of >16−32 are attained when the more charge diffuse K$^+$ is employed as the alkali metal cation input. In the presence of K$^+$ alone ϕ_F is 0.0042 (upper limit), but rises to 0.10 when H$^+$ is also present. The input ion concentrations and the ϕ_F values for the case of

1a are given in Table 1. Detailed examination of maximum intensities in the fluorescence spectra (I_F) as a function of ion concentration ([M$^+$]) with the aid of eq 1 allows the extraction

$$\log[(I_{F,max} - I_F)/(I_F - I_{F,min})] = -\log([M^+]) - \log \beta_{M^+} \quad (1)$$

of binding constant (β_{M^+}) information. These define the ion concentration thresholds for switching and form part of the operating characteristics of the molecular logic gates. Since fluorescence is only switched "on" in the presence of both ionic inputs (H$^+$ and alkali cation), binding constants are measured for one ion in the presence of the other in excess. log β_{Na^+} is found to be 2.7 for both **1a** and **1b** in the presence of (excess) H$^+$. log β_{K^+} is similarly found to be 2.7 for **1a** and 2.5 for **1b**. These values are close to the corresponding data for the parent benzo-15-crown-5 ether (log β_{Na^+} = 3.1 and log β_{K^+} = 2.9).[20] log β_{H^+} is 4.1 for **1b** in the presence of (excess) Na$^+$ and 4.5 in the presence of (excess) K$^+$. log β_{H^+} is immeasurably high for **1a** in MeOH, but can be measured to be 8.9 in MeOH−H$_2$O (1:1, v/v) in the presence of Na$^+$ and 8.4 in the presence of K$^+$. Under comparable conditions **1b** has log β_{H^+} = 6.1 in the presence of Na$^+$. For comparison, 9-[(diethylamino)methyl]- and 9-(morpholinomethyl)anthracenes have log β_{H^+} = 9.2 and 6.3 in MeOH−H$_2$O (4:1, v/v), respectively.[21]

It is particularly pleasing that these fluorescent gates can potentially be operated at the single molecule level.[22] Another remarkable feature is that these photoionic gates currently operate in wireless mode and self-select their two ionic inputs, photonic power supply, and photonic output into the appropriate molecular compartments with negligible cross-talk. Hard wiring is possible, if necessary, since molecular conduits for photons and ions have been demonstrated.[4] Immobilization of these gates on surfaces is feasible since simpler photoionic PET systems have already been anchored in organic[23,21] and inorganic[24] macromolecular microenvironments.

In conclusion, small supermolecules,[25,26] e.g., **1**, can be persuaded to display digital AND gate action with a strong fluorescence signal. The design basis consists of fluorescence−PET competition and a careful arrangement of the photo/ion-active components.

Supporting Information Available: Details concerning the synthesis and the characterization of **1a** and **1b** (3 pages). See any current masthead page for ordering and Internet access instructions.

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(20) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721.
(21) Bissell, R. A.; Bryan, A. J.; de Silva, A. P.; McCoy, C. P. *J. Chem. Soc., Chem. Commun.* **1994**, 405.
(22) (a) Xie, X. S. *Acc. Chem. Res.* **1996**, *29*, 598. (b) Goodwin, P. M.; Ambrose, W. P.; Keller, R. A. *Acc. Chem. Res.* **1996**, *29*, 607.
(23) Klök, H.-A.; Möller, M. *Makromol. Chem. Phys.* **1996**, *197*, 1395.
(24) Ayadim, M.; Habib-Jiwan, J.-L.; de Silva, A. P.; Soumillion, J.-P. *Tetrahedron Lett.* **1996**, *37*, 7039.
(25) de Silva, A. P.; Gunnlaugsson, T.; McCoy, C. P. *J. Chem. Educ.* **1997**, *74*, 53.
(26) While system **1** may be described as a ditopic receptor from one viewpoint, the presence of three essentially independent components (one fluorophore and two separate receptors for two different guests) within it supports its description as a supermolecule in spite of its small size.
(27) Maciejewski, A.; Steer, R. P. *J. Photochem.* **1986**, *35*, 59.