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Direct detection of ion pairs by fluorescence enhancement

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Received (in Cambridge, UK) 14th May 2003, Accepted 30th June 2003
First published as an Advance Article on the web 10th July 2003

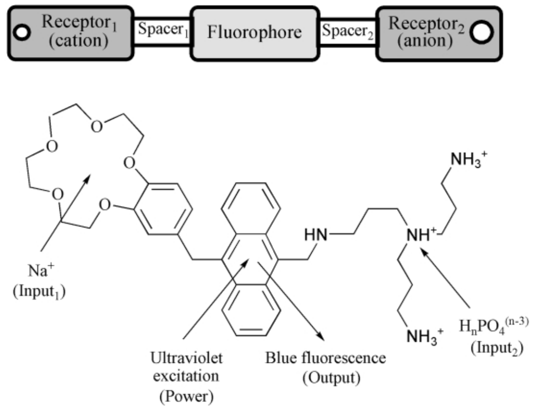
DOI: 10.1039/b305262a

Sensor 1 signals the simultaneous presence of sodium and phosphate with an increased fluorescence signal in the manner of a photoionic AND logic gate.

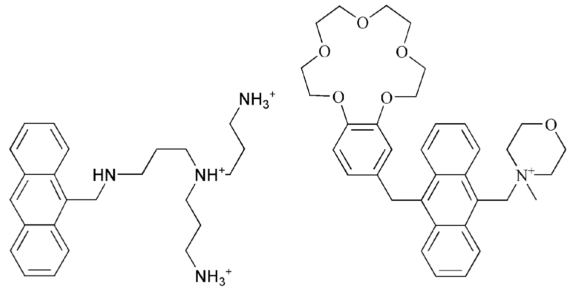
Ion pairs have played formative roles in many branches of chemistry.[1] Ion pair recognition is therefore a subject of great interest in supramolecular chemistry[2] and several examples of heteroditopic receptors for anions and cations have been reported so far.[3] Most of these systems have been used as extraction or transport agents for ion pair species of environmental or biological importance,[4] but only a few of them are able to signal the complexation of the ion pair by means of a change in an easily detectable photophysical property such as absorption[5] or fluorescence.[6] We now present a sensor behaving as an AND logic gate,[7,8] having sodium and phosphate as chemical inputs and fluorescence enhancement as output.

For this purpose system **1**† (Scheme 1) is constructed according to the 'receptor$_1$–spacer$_1$–fluorophore–spacer$_2$–receptor$_2$' format. A benzo-15-crown-5 ether is chosen as receptor for sodium for its well-known binding properties in mixed solvent, while a polyamine is chosen as receptor for phosphate. Czarnik and co-workers reported the example of the anthrylpolyamine **2** (Scheme 2) that shows a fluorescence enhancement upon binding of monohydrogen phosphate in water at pH 6.[9a]

Anthracene, which is known to participate in PET processes from amino groups and benzocrown ethers under appropriate conditions,[8a] is selected as fluorophore. The synthesis of **1** is achieved by reaction of 4-(10-bromomethylanthracen-9-ylmethyl)benzo-15-crown-5-ether[8a] with an excess of tris(3-aminopropyl)amine. System **1** is represented as a trication (Scheme 1) because this is the ionic species that can act as an anion binder.[9] To test its logic characteristics, the fluorescence of **1** is measured at different pH values under all the four possible input conditions, using methanol : water 1 : 1 (v/v) as solvent (Fig. 1).



Scheme 1 Schematic and molecular structure of AND logic gate **1**.



2 **3**

Scheme 2

In absence of any input the fluorescence output is always low. At alkaline pH the fluorescence is quenched by a PET process from the benzylic amine lone pair to anthracene,[10] whereas at acidic pH this PET process is eliminated because of the protonation of the free benzylic amine, enabling a second PET process from the benzocrown ether to the fluorophore.[8a] In the presence of a high concentration of both sodium and phosphate, which is the input condition obtained by addition of 0.1 M NaH_2PO_4, the fluorescence output is high until pH 8.5 and then decreases at higher pH values. The first PET process is eliminated by an intracomplex proton transfer from the phosphate OH group to the benzylic amine,[9a] while the binding of a sodium ion to the benzocrown ether suppresses the second PET.[8a] The decrease of fluorescence at higher pH values is due to the re-activation of the first PET process as the phosphate OH is deprotonated. The input conditions corresponding to the presence of one ion and absence of the other were realized by adding a salt of the desired ion with an 'innocent' counter-ion. Tetramethylammonium is chosen as counter-ion for phosphate and chloride is selected as counter-ion for sodium. Chloride was found to be an innocent anion by Czarnik with his sensor for phosphate in water.[9a] If only phosphate is present, the fluorescence output is low, because the PET process from the benzocrown ether can still quench the anthracene fluorescence at acidic pH. PET from the amine can do the same when the alkaline pH deprotonates the phosphate OH group. When only sodium is present the fluorescence output was predicted to be high only at acidic pH (due to sodium and protons blocking PET processes from the benzocrown ether and the amine respectively), and low at the other values of pH, but it is found to

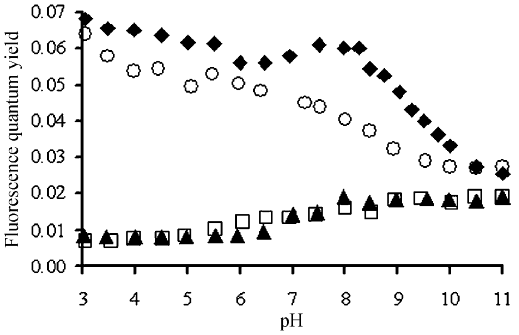


Fig. 1 pH dependence of the fluorescence emission of **1** (□), **1** and 0.1M H_3PO_4 (▲), **1** and 0.1M NaCl (○), **1** and 0.1M NaH_2PO_4 (◆) in MeOH : H_2O = 1 : 1 (v/v), λ_{exc} = 376 nm, λ_{em} = 428 nm. The positions and shapes of the fluorescence bands are essentially constant as expected for PET systems.[10]

Table 1 Truth table, operating conditions and binding constants for AND logic gate **1** in MeOH : H_2O = 1 : 1 (v/v) at pH 8.0

Input$_1$ Na^+	Input$_2$ $H_nPO_4^{(n-3)}$	Fluorescence output (ϕ_F)[a,b,c]	log β[d]
0 (low)	0 (low)	0 (low; 0.016)	—
0 (low)	1 (high; 0.1 M)	0 (low; 0.019)	2.1[e]
1 (high; 0.1 M)	0 (low)	0 (low; 0.040)	1.1[f]
1 (high; 0.1 M)	1 (high; 0.1 M)	1 (high; 0.060)	1.2[g], 2.5[h]

[a] Output is taken as high if $\phi_F > 0.050$ and as low otherwise. [b] Fluorescence quantum yield values (ϕ_F) obtained by comparison with that of 9,10-bis[di(hydroxyethyl)aminomethyl]anthracene in MeOH : H_2O = 1 : 4 (v/v) at pH 3.0, whose ϕ_F value is 0.66.[10b] [c] The relative quantum yields have an uncertainty of 6%. [d] Determined from the dependence of ϕ_F on $[X] = [Na^+]$ or $[H_nPO_4^{(n-3)}]$ according to the equation $\log[(\phi_{Fmax} - \phi_F)/(\phi_F - \phi_{Fmin})] = \log[X] - \log\beta_x$.[10] [e] For **2** with respect to phosphate. [f] For **3** with respect to sodium. [g] With respect to sodium. [h] With respect to phosphate.

be higher than expected. Chloride is bound to the triprotonated polyamine receptor in the mixed organic solvent, thus enhancing the basicity of the benzylic amino group and promoting its protonation at neutral pH. Other anions such as fluoride and tetrafluoroborate show the same effect, confirming its non-specific nature. Nevertheless we can find a value of pH (8.0) at which the fluorescence enhancement due to the presence of both sodium and phosphate is significantly higher than those observed in all the other three input conditions.

Table 1 shows the AND logic truth table which can be obtained in this way. This prototype should be open to further improvement of its gate characteristics by employing stronger receptor modules for sodium which operate in neat water[11] and thus eliminate the non-specific anion effect observed in mixed organic solvents. Table 1 also gives the relevant input ion binding constants (log β) which are the thresholds that must be exceeded before the ion input can be considered as being high. Solubility limits prevent full fluorescence switching ‘on’ by sodium. Due to the AND logic nature of **1**, the log β values corresponding to the second and third rows of the truth table cannot be obtained directly since the relevant ion is incapable of switching ‘on’ the fluorescence by itself. These data can be easily obtained by examining the model ‘fluorophore–spacer–receptor’ systems **2**[9a] and **3** respectively, whose logical fusion led to the design of **1** in the first place. The log β_{Na^+} value is unaffected whether phosphate is present or not. The log $\beta_{H_nPO_4^{(n-3)}}$ value is similarly unaffected within experimental error by the presence of sodium. So system **1** has no cooperativity between the two receptors, which is unsurprising given the rather significant inter-receptor separation.

In conclusion, system **1** behaves as an AND logic gate having sodium and phosphate as ionic inputs and fluorescence enhancement as output. This system simultaneously recognizes an anion and a cation.

We thank the Department of Employment and Learning in Northern Ireland and the European Union (HPRN-CT-2000-00029) for support.

Notes and references

† Selected data for **1**: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.53 (m, 4H; CH_2 amine), 1.74 (m, 2H; CH_2 amine), 2.42, (t, *J* 7.4, 4H; CH_2 amine), 2.48 (t, *J* 7.2, 2H; CH_2 amine), 2.65 (t, *J* 6.9, 4H; CH_2 amine), 2.93 (t, *J* 6.9, 2H; CH_2 amine), 3.71 (m, 8H; CH_2 crown), 3.80–3.85 (m, 4H; CH_2 crown), 3.95–3.97 (m, 2H; CH_2 crown), 4.03–4.04 (m, 2H; CH_2 crown), 4.73, (s, 2H; CH_2 spacer), 4.92 (s, 2H; CH_2 spacer), 6.52 (dd, *J* 8.2 and *J* 1.9, 1H; phenyl), 6.66 (d, *J* 8.3, 1H; phenyl), 6.72 (s, 1H; phenyl), 7.45 (t, *J* 6.8, 2H; anthr.), 7.52 (t, *J* 6.5, 2H; anthr.), 8.23 (d, *J* 8.8, 2H; anthr.), 8.40 (d, *J* 8.8, 2H; anthr.). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 27.58, 30.83, 33.38, 40.65, 46.19, 49.23, 51.86, 52.41, 53.42, 69.09, 69.23, 69.60, 69.67, 70.58, 71.02, 114.37, 114.47, 120.79, 124.89, 125.43, 125.62, 128.55, 130.21, 130.41, 131.53, 132.25, 134.16, 147.44, 149.20. MS (ESI): m/z (%) = 342 (100) $[MHNa^{2+}]$, 659 (47) $[MH^+]$.

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