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A fluorescent 'off-on-off' proton switch with an overriding 'enable-disable' sodium ion switch

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A molecular photoionic switch that responds to three cationic inputs with a primary 'off-on-off' and a secondary overriding 'enable-disable' fluorescence output, *via* the control of three separate photoinduced electron transfer (PET) processes is described.

The design of photoresponsive supramolecular systems has developed rapidly over the past two decades leading to molecules that can be used for a variety of purposes such as sensors, switches, triggers, logic gates and molecular level machines.[1] Some of these systems utilize photoinduced electron transfer (PET) as a means of translating a molecular recognition event into an optical signal such as a fluorescence signal.[2] The signaling process of luminescent PET sensors depends on a molecular recognition event to inhibit, or initiate PET between a covalently linked chromophore and a receptor, leading to the generation, or quenching of fluorescence. During the past fifteen years luminescent PET sensors have evolved from simple first generation systems that respond to one cationic input[3] to higher generation systems that require several specific inputs to elicit a luminescence signal. The ability to modulate a luminescence signal by several inputs has led to PET systems that exhibit logic gate behaviour on a molecular scale ranging from two input AND gates to three input INHIBIT gates.[4] We, and others, have shown that it is possible to achieve complex luminescence switching in higher generation PET systems with variation of pH when the cationic inputs are protons.[5] All PET systems reported so far are capable of handling up to two PET processes to generate a luminescence signal.

In this paper, we report PET system **1** that functions as a fluorescent 'off-on-off' proton switch with an overriding 'enable-disable' sodium ion switch. This complex fluorescence signal modulation is achieved by using three PET processes that are controlled by three cation binding events.

System **1** follows the basic design concept of utilizing a chromophore–spacer–receptor assembly to generate a luminescent signal that competes with a PET process between the chromophore and the receptor.[2] In designing system **1**, we have combined the proton receptors of our fluorescent 'off-on-off' switch for protons,[5a] and the sodium ion receptor of a fluorescent AND gate for protons and sodium ions,[4a] with an anthracene chromophore. During the design of this system, it occurred to us that the proton receptors for the 'off-on-off' switch, a tertiary amine and a pyridine, could be provided by anabasine, an alkaloid closely related to nicotine. System **1** was synthesized by the formylation of 4-(anthracen-9′-ylmethyl)-benzo-15-crown-5 ether at the 10′ position[4a] followed by reductive amination with anabasine,[6] and was characterized by NMR spectroscopy and high resolution mass spectrometry.

System **1** is designed to have no (or weak) PET between the chromophore and the receptors only when the tertiary amine is protonated in the presence of sodium ions bound within the benzo-crown ether, leading to the 'on' state of fluorescence. All other cation binding events, protonation of both nitrogens with or without sodium ions, sodium ion binding without protonation, and the absence of protons and sodium ions, allow for PET in system **1**, leading to the 'off' state of fluorescence.

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The fluorescence emission spectra of system **1** in the presence of sodium ions and/or protons, as well as in the absence of sodium ions and protons, is shown in Fig. 1. The five different species of cation bound system **1** and the cation free system **1** (blank) responsible for these spectra are shown in Fig. 2. Results of this study including the fluorescence quantum yields (Φ_F) of **1** in cation bound and free states are summarized in Table 1.

In the absence of protons the tertiary amine of **1** serves as a PET donor to the excited chromophore and quenches its emission.[3,4a] Although this PET process (PET-1) is inhibited due to protonation of the tertiary amine in **1-H$^+$**, the protonated aminomethyl moiety acts as an electron withdrawing group on the anthracene leading to a second PET (PET-2) from the benzo-crown to the excited chromophore.[4a] The addition of a second proton leading to **1-2H$^+$** generates a third PET (PET-3) process between the excited chromophore and the pyridinium moiety further suppressing the residual fluorescence of system **1**.[5a] All of these species, **1**, **1-H$^+$** and **1-2H$^+$**, represent fluorescence 'off' states of system **1** with Φ_F of 0.04, 0.04 and 0.02 respectively.

In the presence of sodium ions bound within the benzo-crown, and in the absence of any protons, the fluorescence of **1-Na$^+$** is quenched by the PET between the tertiary amine and the excited chromophore as mentioned above. However, protonation of the tertiary amine does not lead to a second PET process, since the benzo-crown is no longer a donor due to the presence of sodium ions.[4a] This makes **1-Na$^+$H$^+$** the only species without a PET process that competes with its emission leading to the fluorescence 'on' state. The addition of a second proton to this species initiates the third PET process between the excited chromophore and the pyridinium quenching the emission of **1-Na$^+$2H$^+$**. The three species, **1-Na$^+$**, **1-Na$^+$H$^+$** and **1-Na$^+$2H$^+$** represent fluorescence 'off', 'on' and 'off' states with Φ_F of 0.03, 0.54 and 0.03 respectively.

In mixed aqueous media (MeOH–H_2O, 1:1, v/v) the fluorescence signal of **1** does not show a significant change with

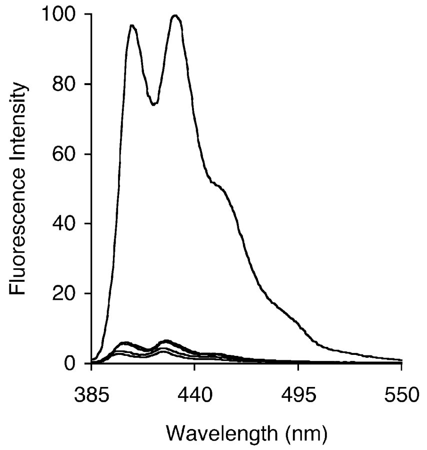

Fig. 1 Fluorescence emission spectra of **1-Na$^+$H$^+$** (highest intensity), **1**, **1-H$^+$**, **1-Na$^+$**, **1-Na$^+$2H$^+$** and **1-2H$^+$** (lowest intensity) in methanol (λ_{ex} = 377 nm).

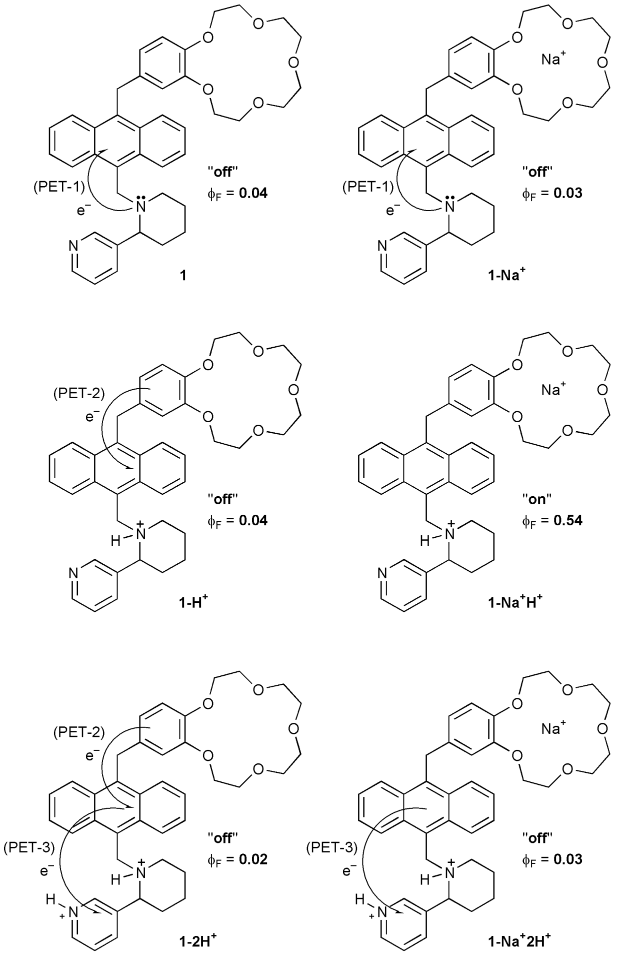

Fig. 2 Fluorescence 'off' and 'on' states of system **1** with PET processes that correspond to various cation binding events.

Table 1 Operating conditions for the fluorescent 'off-on-off' proton switch with the overriding 'enable-disable' sodium ion switch **1**[a]

			Fluorescence[c]	
	Proton input[b]	Sodium input[b]	Φ_F	Output
1	None[d]	None	0.04	Off
1-H$^+$	10^{-6} M	None	0.04	Off
1-2H$^+$	10^{-2} M	None	0.02	Off
1-Na$^+$	None[d]	10^{-2} M	0.03	Off
1-Na$^+$**H**$^+$	10^{-6} M	10^{-2} M	0.54[e]	On
1-Na$^+$**2H**$^+$	10^{-2} M	10^{-2} M	0.03	Off

[a] 10^{-6} M **1** in methanol excited at the isosbestic point (377 nm). λ_{em} = 385–550 nm. [b] H^+ and Na^+ inputs are provided as toluenesulfonate and methanesulfonate respectively. [c] Φ_F values are reported with reference to the primary standard 9,10-diphenylanthracene.[10] [d] In the presence of 10^{-3} M tetramethylammonium hydroxide as a proton scavenger. [e] Upper limit.

pH (adjusted with tetramethylammonium hydroxide and HCl). In the absence of sodium ions the Φ_F of **1** is 0.09, 0.1 and 0.04 at pH 11.66, 5.19 and 1.36 respectively. In the presence of sodium ions, **1** shows 'off-on-off' fluorescence modulation with Φ_F of 0.18, 0.26 and 0.13 at pH 11.44, 5.11 and 1.41 respectively. Although the fluorescence enhancement in MeOH–H_2O in the presence of sodium ions is not as large as in MeOH, the I_f (fluorescence intensity) *vs.* pH profile of **1** with sodium ions is consistent with the I_f *vs.* pH profile of our 'off-on-off' switch where PET-1 and PET-3 lead to fluorescence modulation with pH.[5a] Protonation of the tertiary amine of **1-Na**$^+$ (pK_a of 6.7) that generates the 'off-on' segment of the fluorescence switch and the protonation of the pyridine ring of **1-Na**$^+$**H**$^+$ (pK_a of 2.9) that generates the 'on-off' segment are well separated leading to a broad maximum (from pH 5.5 to 4.5) in the I_f *vs.* pH profile of **1-Na**$^+$.

In summary, the three PET processes utilized for signaling in system **1**, PET-1,[3a] PET-2[7] and PET-3,[8] are well documented as individual processes in first generation systems that act as 'off-on' or 'on-off' fluorescent switches with cation binding. All three processes are sufficiently exothermic to compete with and quench the emission of the chromophore, and can be inhibited or initiated by changing the oxidation/reduction potential of individual receptors with cation binding.[9] Second generation PET systems reported to date, have successfully combined two of these processes to achieve AND gate behaviour (PET-1 and PET-2),[4a,4d] and 'off-on-off' fluorescence switching (PET-1 and PET-3)[5] with cation binding. System **1**, described in this paper, is the first example of a third generation PET system that combines three PET processes to signal three cation binding events.

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