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A Fluorescent Photoinduced Electron Transfer Sensor for Cations with an Off-On-Off Proton Switch†

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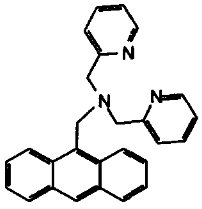
Abstract: A photoinduced electron transfer cation sensor which can function as an off-on-off fluorescence switch for protons and an off-on fluorescence switch for zinc (II) ions is described. © 1997 Elsevier Science Ltd.

The design of fluorescent chemosensors is an aspect of supramolecular chemistry which has developed rapidly during the past decade.[1] Many of these fluorescent sensors involve photoinduced electron transfer (PET) as the key principle in the signalling process and are designed for s-block ions and protons. In addition, a small number of sensors capable of binding transition metal ions which operate on both principles, photoinduced electron transfer as well as energy transfer, have been developed.[2] The signalling process of these sensors involve the generation (off-on switching) or quenching (on-off switching) of fluorescence due to cation binding. We wish to report the synthesis of 9-anthrylmethyl-bis(2-picolyl)amine (**1**),[3] and its $ZnCl_2$ complex (**2**),[4,5] as a part of our research on novel fluorescent PET sensors for protons and post transition metal ions. The sensor **1**, designed to function as an off-on-off switch for protons, and an off-on fluorescent switch for post transition metal ions, is a more sophisticated molecular photoionic device than most of the current fluorescent PET sensors.



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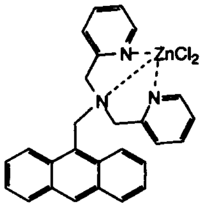

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† In memory of Professor Paul G. Gassman

The most important and unique feature of sensor **1** is its fluorescence intensity (I_f) vs pH profile (Figure 1) which shows a dual fluorescence switch. This capability is achieved by the incorporation of two different proton receptors (the tertiary amine and the pyridyl group) which function as independent PET switches at different pH values. The three species responsible for the off-on-off positions of this proton modulated fluorescence switch with decreasing pH are **1**, **1•H$^+$**, and **1•2H$^+$** respectively (Figure 2).

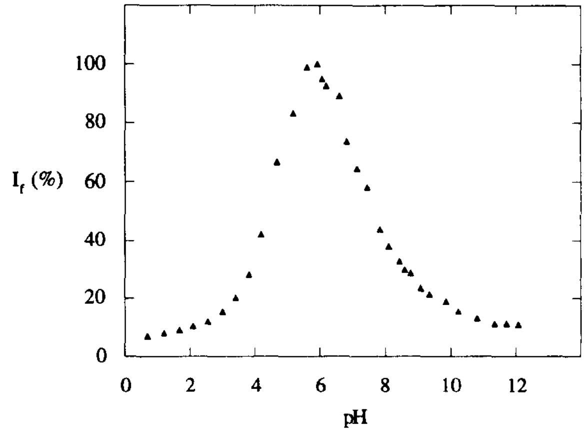
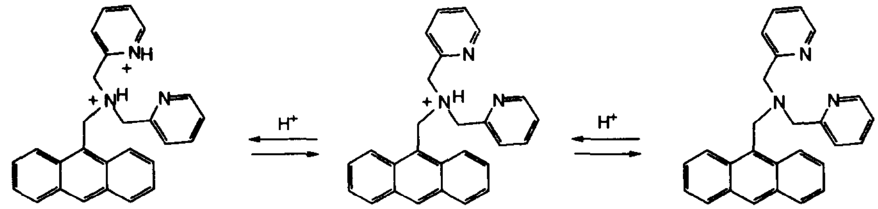


Figure 1. pH dependence of the fluorescence intensity (I_f) of the sensor **1** in methanol/water(1:1) (λ_{ex} = 350, λ_{em} = 370 - 550 nm). pH adjusted by adding HCl or NaOH (fluorescence of **1** is not affected by Na$^+$).



1•2H$^+$
Non Fluorescent

1•H$^+$
Fluorescent

1
Non Fluorescent

Figure 2. Protonation pattern of **1**.

The fluorescence of **1** is quenched due to the thermodynamically favoured PET between the tertiary aliphatic nitrogen (tertiary amine) and the excited chromophore (*Anth). Increasing the oxidation potential of the tertiary amine due to protonation prevents this PET and regenerates the fluorescence of the chromophore.[1a,6] Therefore formation of **1•H$^+$** is accompanied by an increase of the fluorescence intensity which reaches a maximum at pH 6.0. Further decrease of pH protonates a pyridine ring of the receptor to form a pyridinium (pyH$^+$) group, leading to a significant change in its reduction potential (- 2.62 and - 1.25 V vs

SCE respectively).[7] A secondary PET process (*Anth to pyH$^+$) now becomes thermodynamically favorable [$\Delta G_{PET} = - E_{s.Anth} + E_{ox.Anth} - E_{red.pyH^+} = - 3.28 + 1.16 - (- 1.25) = - 0.87$ eV][8] and quenches the fluorescence of **1•2H$^+$** leading to the second off mode. The second PET process, although less common, has been observed in other sensors which contain pyridine rings as proton receptors.[8a] The pK$_a$ values for the protonation of the tertiary amine and the pyridine ring are 7.5 and 4.4 respectively.[9a,b]

The primary PET process of **1** (tertiary amine to *Anth) can also be prevented by binding zinc(II) ions within the bis-(2-picolyl)amine receptor. As expected,[2] the sensor-zinc(II) complex (**2**), shows a significant enhancement of fluorescence due to prevention of this PET process. The fluorescence quantum yield (compared with 9,10-diphenylanthracene)[10] of **1** [$\Phi_{f(1)}$] in acetonitrile is 0.01. Intensity of fluorescence of **1** increases with the chelation of zinc (II) and leads to the formation of a 1:1 complex (Figure 3) with a log K value of 5.3.[9a,c] The fluorescence quantum yield of **2** [$\Phi_{f(2)}$], in acetonitrile is 0.77 and the sensor shows a maximum fluorescence enhancement factor of 77 with chelation of zinc (II) ions.[11]

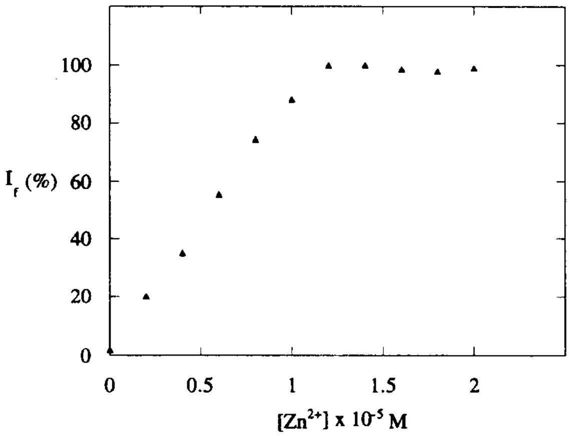


Figure 3. Fluorescence intensity (I_f) of **1** (1 x 10^{-5} M) vs zinc (II) ion concentration (0 - 2 x 10^{-5} M) in acetonitrile ($\lambda_{ex} = 350$, $\lambda_{em} = 370 - 550$ nm).

While single off-on or on-off fluorescent switches for protons are well documented, sensor **1** combines both these functions in a dual off-on-off fluorescent switch over 6 pH units.[12] Incorporation of two opposing PET switches in a single molecule as shown here, leads to systems with many potential applications as chemosensors and molecular photoionic devices. In summary, we have introduced a unique fluorescent PET sensor which functions as an off-on-off switch towards protons and as an off-on switch towards zinc(II)ions.

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