

## Fluorescent Signalling Crown Ethers; 'Switching On' of Fluorescence by Alkali Metal Ion Recognition and Binding *in situ*

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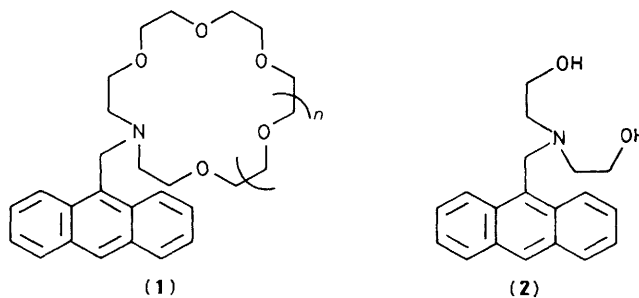
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Sodium and potassium ions enhance the fluorescence quantum yield of the *N*-(9-anthrylmethyl)monoaza crown ethers (**1**) in methanol by factors of up to forty-seven while all other electronic spectral parameters remain unaltered.

We report herein the largest useful perturbation to date of an optical property of an organic reagent in a hydroxylic solvent, caused by biologically important alkali metal ions.<sup>1</sup> This leads the way to quantitative remote signalling of the presence of these ions in microenvironments.‡ *N*-(9-Anthrylmethyl)monoaza-18-crown-6 (**1**;  $n = 1$ ) and the corresponding 15-crown-5 analogue (**1**;  $n = 0$ ), along with *N*-(9-anthrylmethyl)diethanolamine (**2**), are very weakly fluorescent in methanol solution in the presence of benzyltrimethylammonium hydroxide as a proton scavenger (Table 1). Addition of sodium or potassium, but not lithium, ions results in an enhancement of the fluorescence quantum yield ( $\phi_F$ ) of (**1**), but not of (**2**), by factors of  $\leq 47$ ; all other observable absorption and emission (steady state) spectral parameters remain unaffected. The enhancement factors are limited by the finite  $\phi_F$  value of 'metal free' (**1**) presumably caused by trace alkali metal ion contamination from glassware.<sup>4</sup> The

large enhancements observed justify the use of the phrase 'switching on.' Compound (**1**) is designed so that the anthracene fluorescence, which is efficiently quenched by electron transfer from the lone pair of nitrogen,<sup>5,6</sup> is recovered on incorporating alkali metal cations into the monoaza crown ether.

The  $\beta$  values (Table 1) are in reasonable agreement with those available for the parent macrocycles<sup>7</sup> indicating that the large anthracene moiety does not block the faces of the macrocycles in (**1**). The  $\phi_{F \max}$  values present a new parameter for alkali metal ion-macrocycle recognition and may be rationalized in terms of (a) the distance from the ion



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‡ Emission methods based on solvent extraction (ref. 2), non-hydroxylic solvents (ref. 3), and flames are unsuitable for monitoring ion concentrations in dynamic or living systems.

Table 1.<sup>a</sup>

	'Metal-free'	Na <sup>+</sup>		K <sup>+</sup>		H <sup>+</sup>
	$\phi_F$	$\log \beta$	$\phi_{F \max}$	$\log \beta$	$\phi_{F \max}$	$\phi_{F \max}$
(1; $n = 1$ ) <sup>b</sup>	0.003	3.10	0.053	4.40	0.14	0.38
(1; $n = 0$ ) <sup>b</sup>	0.009	2.30	0.057	2.45	0.019	0.32
(2) <sup>b</sup>	0.002	—	0.002	—	0.002	0.41

<sup>a</sup>  $10^{-5}$  M (1) or (2) [= (L)] in aerated methanol at 29 °C with  $10^{-3}$  M benzyltrimethylammonium hydroxide and  $0-10^{-1}$  M alkali metal acetate [= (M<sup>+</sup>)], except when protons are under study, in which case  $10^{-2}$  M HCl was the only additive. Li<sup>+</sup> gave no measurable  $\phi_F$  enhancement ( $\Delta\phi_F < 0.002$ ). Absorption and fluorescence spectral parameters (except  $\phi_F$ ) are virtually identical for (1), (2) [with or without (M<sup>+</sup>)], and 9-methylanthracene. However, the spectra of protonated (1) and (2) show subtle differences, cf. ref. 6. Fluorescence intensity ( $I_F$ ) measured with  $\lambda_{exc.}$  (0,1 band maximum) =  $368 \pm 2$  and  $\lambda_{em.}$  (0,1 band maximum) =  $414 \pm 2$ .  $\phi_{F \max}$ . Values calculated by comparison of corrected  $I_{F \max, \text{limit}}$  vs. photon energy spectra with that of 9,10-diphenylanthracene in deaerated methanol ( $\phi_F = 0.84$ , J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley, London, 1970, p. 128). The  $I_F$ -(M<sup>+</sup>) data were analysed according to  $[I_F/(I_{F \max, \text{limit}} - I_F)] = [\beta(M^+) - (L) (I_F/I_{F \max, \text{limit}})]$  to yield the binding constants ( $\beta$ ). The equation is derived by combining (a) the mass action expression for the metal ion-ligand equilibrium, (b) the separate conservation equations for metal ion species and ligand species, and (c) the fluorimetric proportionality between  $I_F$  and the fluor concentration (C. A. Parker, *Adv. Photochem.*, 1964, 2, 305).  
<sup>b</sup> Prepared from 9-chloromethylanthracene (F. H. C. Stewart, *Aust. J. Chem.*, 1960, 13, 478) and monoaza-18-crown-6 or 15-crown-5 (H. Maeda, Y. Nakatsuji, and M. Okahara, *J. Chem. Soc., Chem. Commun.*, 1981, 471), or diethanolamine according to a procedure adapted from A. H. Beckett and J. Walker, *Tetrahedron*, 1963, 19, 545. The spectral data were as expected.

centre to the nitrogen lone pair and (b) the degree of solvation of the ion which reduces its effective charge. Spin-orbit coupling<sup>8</sup> should be small for complexes of (1) with sodium ( $Z$

= 11) or potassium ( $Z = 19$ ) ions. We are attempting to improve the recognition by (1) of sodium or potassium ions in relation to protons.<sup>6</sup>

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