

Luminescence and Charge Transfer. Part 2.¹ Aminomethyl Anthracene Derivatives as Fluorescent PET (Photoinduced Electron Transfer) Sensors for Protons

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The importance of the modular structure 'fluor-spacer-amine' is pointed out for the design of fluorescent molecular sensors for pH according to the principle of photoinduced electron transfer (PET). Anthracen-9-yl methylamines (**24**) and some azacrown ether analogues (**15** and **23**) are examined in this context. They show pH-dependent fluorescence quantum yields describable by eqn. (5) while all other electronic spectral parameters remain essentially pH-invariant. The range of pK_a values of these sensors are understandable in terms of macrocyclic effects and the transmission of electric fields across the anthracene short axis. Phase-shift fluorometric determination of the fluorescence lifetimes of these sensors allows the calculation of the rate constant of PET in their proton-free form to be 10^{10} – 10^{11} s⁻¹, with the diamines **23** and **24b** exhibiting the faster rates.

The idea of photon-driven, coupled redox reactions has been widely employed in organic/inorganic photochemistry and in solar energy conversion for at least two decades. Several good reviews^{2,3} and two multi-volume works^{4,5} are available on this subject. In contrast, this principle has received little exploitation in the growing field of chemical and biological sensors.⁶ In this series we hope to demonstrate the wide scope and the special features of luminescent PET (photoinduced electron transfer) sensors. This paper focuses on fluorescent sensors for protons, *i.e.* fluorescent pH indicators and on aminomethyl anthracenes in particular.

Photoinduced electron transfer to aromatic hydrocarbons from aliphatic/aromatic amines has long been known to result in the fluorescence quenching of the former.⁷ The PET rate, which is considerably faster than the radiative rate of fluorescence in favourable cases, is a function of the thermodynamic driving force ΔG_{ET} [given in eqn. (i) in eV].^{4,5}

$$\Delta G_{ET} = -E_S - E_{red.fluor} + E_{ox.amine} - e^2/\epsilon r \quad (i)$$

E_S , $E_{red.fluor}$ and $E_{ox.amine}$ are the singlet energy (in eV) and reduction potential of the fluor and oxidation potential of the amine (in V), respectively. The typical situation is illustrated with a molecular orbital energy diagram (Fig. 1) and allows a rapid PET. It is clear that a suitable increase of $E_{ox.amine}$ (*i.e.* a lowering of the highest occupied orbital energy of the amine) will suppress the electron transfer (Fig. 2). This can be achieved by protonation of the amine lone electron pair. Indeed, it is known⁸ that protonation of some functionalities can alter electron transfer rates by a factor of 10^8 . Thus, fluorescence becomes the predominant deactivation channel for the excited state, *i.e.* a retrieval of quenched fluorescence is seen upon protonation. Intramolecular versions of the above can have very high quenching efficiencies while not significantly altering the energetics.⁹ The conditions under which such high quenching efficiencies are attained *via* intramolecular electron transfer has been delineated.¹⁰ Thus, in the unprotonated state, near-zero fluorescence quantum yields are achievable, and

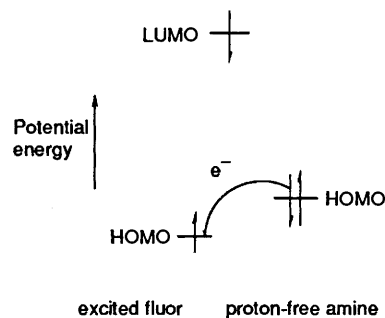


Fig. 1 Molecular orbital energy diagram to illustrate the thermodynamic situation which can permit rapid photo-induced electron transfer from an amine to a suitable fluorophore

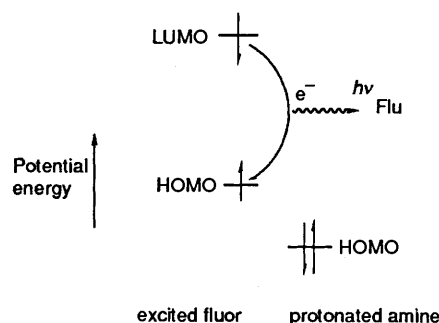


Fig. 2 Molecular orbital energy diagram to illustrate the thermodynamic situation which suppresses photo-induced electron transfer from the protonated amine to the fluorophore

'switching on/off' of fluorescence therefore becomes possible with these 'fluor-spacer-amine' assemblies. Such controllable 'on/off' characteristics of an optical phenomenon is of immediate relevance for the design of not only molecular sensors but also molecular digital devices for electronics and ionics.¹¹

Selinger¹² and Shizuka¹³ were among the first to apply their experience of exciplex/PET phenomena to develop fluorescent pH sensors 1–3, based on aromatic hydrocarbons. These broke the monopoly of photoinduced proton transfer as the basis of fluorescent pH indicators¹⁴ which had existed for three centuries.¹⁵ These latter indicators are invariably heteroatom-containing π -electron systems.¹⁴ Subsequent examples of fluorescent PET pH sensors 4–6^{16–19} also show the linking of polycyclic aromatic hydrocarbons to amines. The sensors 7–9 are earlier cases (see also 10) where protonation-caused fluorescence were noted.²⁰ However, the scope of fluorescent PET pH sensors is wide enough to include heterocyclic π -electron systems as in 11.^{21,22} With hindsight we can recognise the 'fluor-spacer-amine' structure in the classical fluorescent pH indicator quinine 12. Its second, and less spectacular, fluorescence-pH transition appears to be yet another example of fluorescent PET pH sensor action.²³ Anaesthetic 13 is also closely related.^{24,25} Furthermore, several sensors for alkali or alkaline-earth metal cations based on PET, 14–17,^{26,27} also show proton-induced fluorescence enhancement. Though interpreted differently by its authors, 18 also possesses the structural features expected of a fluorescent PET sensor for pH.²⁸ A PET mechanism is likely in view of the known quenching of fluorescence of even electron-rich coumarins by tertiary amines.²⁹ However, PET in many 'fluor-spacer-amine' systems has yet to be unequivocally demonstrated by the observation of the resulting transient radical ion-pairs even though such evidence is available for several cases with polycyclic aromatic hydrocarbons as fluors.³⁰ The proton-responsible fluorescence of 19–22 is closely connected to the present study even though the fluor and amine are formally conjugated.³¹ This is because of the deconjugation caused by significant twisting about the biaryl carbon-carbon bond. In these instances we therefore have a virtual spacer between the fluor and amine moieties. These systems are best described according to the TICT (twisted intramolecular charge transfer) model of excited states.³² The end result is an unconjugated radical ion pair, which is also attained in the PET systems. A related situation is found during the enhancement of luminescence by protons and other ions *via* MLCT (metal to ligand charge transfer)–LLCT (ligand to ligand charge transfer) state energy inversion.³³ Another variant of the PET sensor principle has inspired the development of fluorescent reagents for free radicals.³⁴ Chemiluminescence and electron transfer are also interwoven in the chemically induced electron exchange luminescence (CIEEL) mechanism.³⁵ Although electron transfer lies at the heart of this paper we conclude this paragraph by noting another quite different origin of protonation-induced fluorescence enhancement by the removal of a $n\pi^*$ – $\pi\pi^*$ state intersystem crossing.³⁶ In this paper we present new data on sensors 15a, 15b and 23 and their non-macrocylic analogues 24a and 24b to consolidate previous work on 6a–e.¹⁸

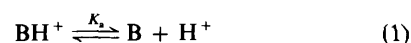
Results and Discussion

The fluorescent pH sensing ability and acid dissociation constants (pK_a values) have already been presented for some alkylaminomethyl anthracenes (6a–e).⁸ Now we consider some crown ether analogues 15 and 23 along with their associated non-macrocylic model compounds 24. Some key rate constants pertaining to these sensors are also revealed by means of time-resolved studies. These molecules have also found use for the fluorescent sensing of alkali- and alkane diammonium ions.^{27,37} All the sensors 15, 23 and 24 are easily prepared by nucleophilic substitution reactions on mono or bis(chloro or bromomethyl)anthracene³⁸ with the appropriate amine.³⁹

The fluorescence intensity-pH profiles (Fig. 3) were built up

by means of fluorescence titrations of 15, 23 and 24 in H₂O–CH₃OH (4:1, v/v). These profiles can be evaluated according to eqn. (5) which is easily derived as follows.

Consider the equilibrium between the protonated and unprotonated forms of the sensor with the fraction of the latter being α ;



Then the fluorescence intensity (I_F) would be $I_{F_{\max}}$ when $\alpha = 0$ but would be $I_{F_{\min}}$ when $\alpha = 1$. $I_{F_{\max}}$ is proportional to the fluorescence quantum yield of BH^+ (ϕ_{FBH^+})⁴⁰ and $I_{F_{\min}}$ is proportional to ϕ_{FB} with the same proportionality constant since all the other electronic spectral parameters of PET sensors with alternant aromatic hydrocarbon⁴¹ fluorophores remain essentially invariant with pH.¹⁸ Indeed, the absorption spectra of 15, 23 and 24 are essentially unchanged with pH and the same is true for the shape and wavelengths of the emission spectra. Under these favourable conditions, eqn. (2) can be written.

$$I_F = \alpha I_{F_{\min}} + (1 - \alpha) I_{F_{\max}} \quad (2)$$

From the mass action expression, we obtain eqn. (3),

$$\text{pH} = \text{p}K_a + \log[(\text{B})/(\text{BH}^+)] \quad (3)$$

which is, eqn. (4),

$$\text{pH} = \text{p}K + \log[\alpha/(1 - \alpha)] \quad (4)$$

Combining eqns. (2) and (4) we obtain eqn. (5):

$$\log[(I_{F_{\max}} - I_F)/(I_F - I_{F_{\min}})] = \text{pH} - \text{p}K_a \quad (5)$$

Data analysis *via* the linear least-squares method according to eqn. (5) has favourable features in that it involves no instrumental parameters and yields a check on normal behaviour *via* its gradient of unity. Other approaches⁴² to the analysis of I_F -pH profiles are useful in situations where $I_{F_{\max}}$ is either seriously perturbed (*e.g.* due to ionic strength effects) or unattainable (*e.g.* due to solubility difficulties). Ionic strength effects on $I_{F_{\max}}$ will be minimal for 15, 23 and 24 with anthracene-like fluors (and others based on alternant aromatic hydrocarbons)⁴¹ which involve no charge separation upon excitation. However, high concentrations of ions can cause quenching effects by other mechanisms.¹⁸ Other fluors with internal charge-transfer excited states,⁴³ which are also permissible within the PET sensor format,⁴⁴ could in principle involve varying degrees of ionic strength effects. These must be evaluated on an individual basis for the sensor and the ion concentration necessary for attainment of $I_{F_{\max}}$.

The fluorescence quantum yields $\phi_{F_{\max}}$ and $\phi_{F_{\min}}$ and the lifetime τ can be expressed in terms of the primary rate constants k_F , k_D and k_{PET} according to eqns. (6)–(8).

$$\phi_{F_{\max}} = \phi_{\text{FBM}^*} = k_F/(k_F + k_D) \quad (6)$$

$$\tau = \tau_{\text{BH}^*} = 1/(k_F + k_D) \quad (7)$$

$$\phi_{F_{\min}} = \phi_{\text{FB}} = k_F/(k_F + k_D + k_{\text{PET}}) \quad (8)$$

The implicit assumptions are that (a) the radiative rate constant k_F and the general non-radiative rate constant k_D are unaltered upon protonation of the sensors²² and (b) the PET rate constant is negligible, *i.e.* $< 10^6 \text{ s}^{-1}$ in the protonated sensors. Assumption (a) is justifiable because the hydrocarbon fluorophore is spatially separated from the amine unit.

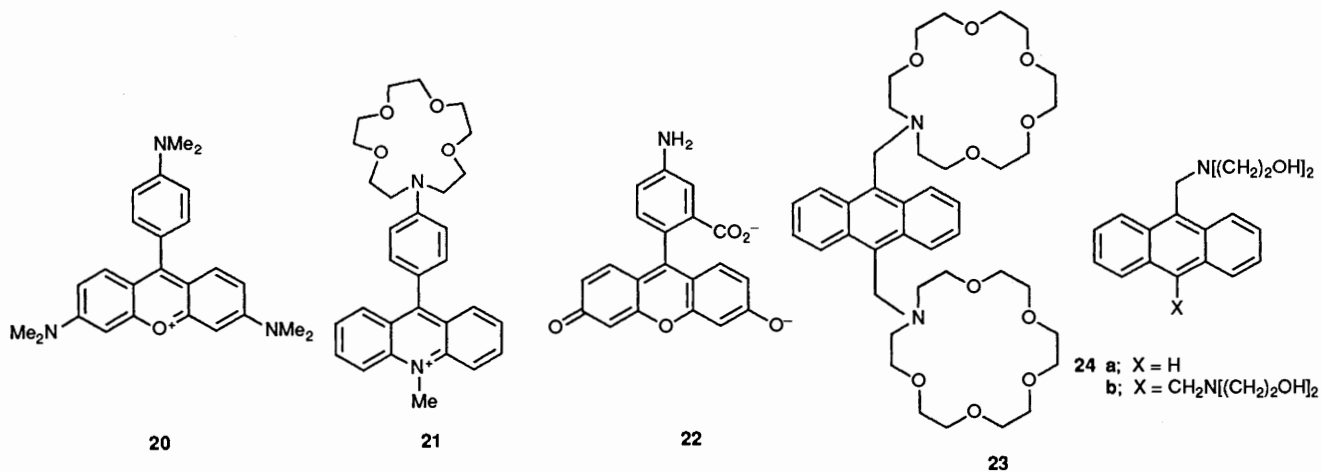
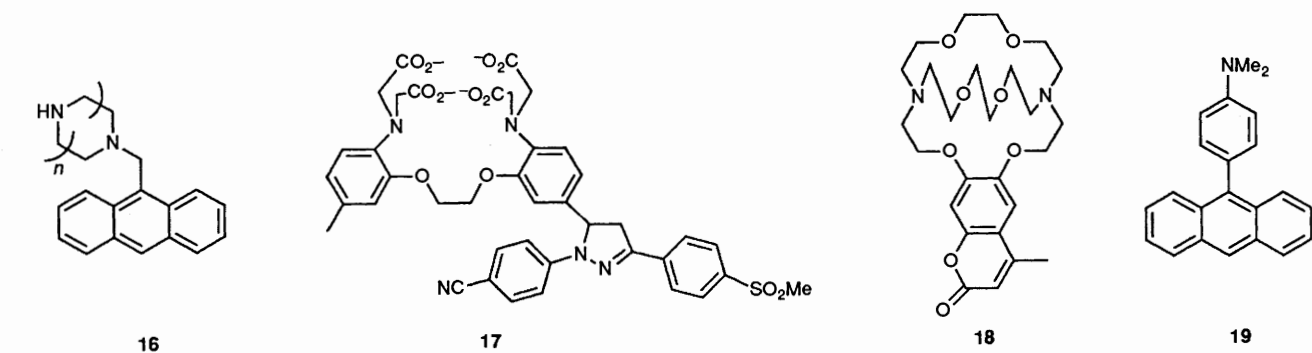
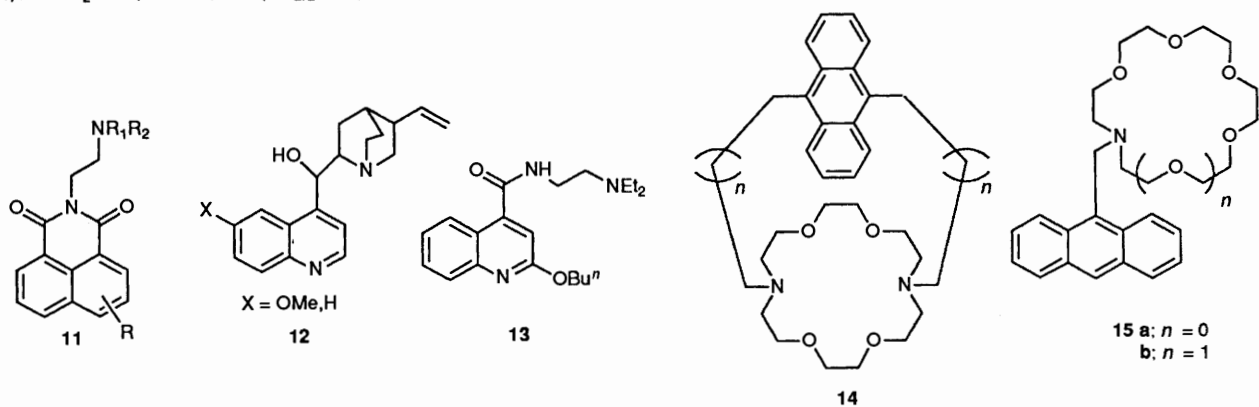
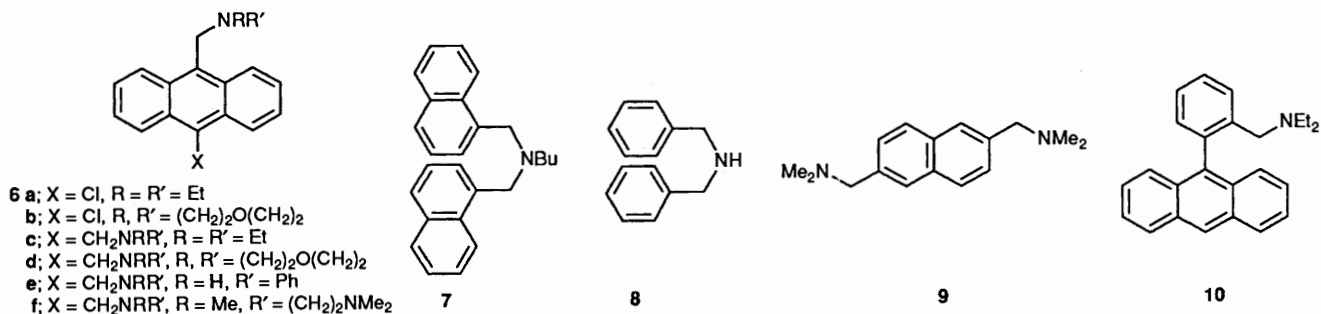
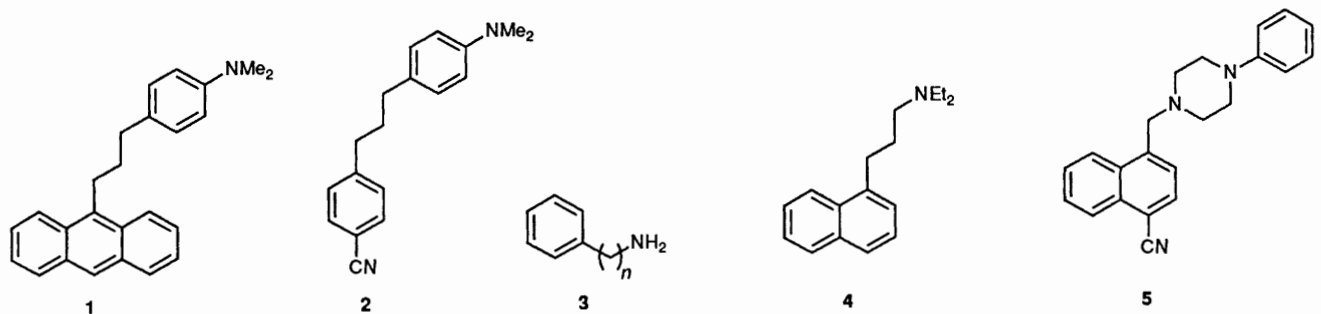


Table 1 Parameters for fluorescent sensors **15**, **23** and **24**^a

Sensor	pK _a	<i>m</i>	φ _{Fmax} ^b	φ _{Fmin} ^b	τ ^c / ns	k _F / 10 ⁻⁷ s ⁻¹	k _D / 10 ⁻⁷ s ⁻¹	k _{PET} / 10 ⁻¹⁰ s ⁻¹
23 ^d	7.1 ^e	0.98	0.64	0.0005	11.9	5.4	3	11
24b ^d	5.9 ^e	1.00	0.66	0.0005	11.8	5.6	3	11
15b ^f	8.5 ^g	1.00	0.51	0.0025	7.2	7.1	7	2.8
15a ^f	8.1 ^g	0.98	0.48	0.0024	7.3	6.6	7	2.7
24a ^f	7.2 ^g	0.92	0.41	0.0020	7.2	5.7	7	2.8

^a 10⁻⁶ mol dm⁻³ sensors in an aerated H₂O-CH₃OH (4:1, v/v) solution except for quantum yield, and lifetime determinations where the solutions were deaerated by argon bubbling. Fluorescence pH titrations⁴⁸ were conducted with excitation and emission at the (0, 1) vibrational bands of the appropriate spectra. pK_a and *m* values obtained with linear least-squares analysis according to eqn. (5) which is well fit to the data. Average correlation coefficient (no. of points) = 0.9984 (12). ^b Limiting fluorescence quantum yields at low pH (φ_{Fmax}) and high pH (φ_{Fmin}) measured by comparison with anthracene in ethanol.⁵⁷ Correction has been made for the refractive index of the solvent. ^c Measured in solution (pH 3.0) by phase fluorometry.⁵⁸ For comparison, the corresponding values for 9,10-dimethylanthracene and 9-methylanthracene in deaerated CH₃OH are found to be 14.1 and 4.8 ns, respectively. ^d λ_{max,abs}/nm (ε_{max})(CH₃OH); 356 nm (7600 dm³ mol⁻¹ cm⁻¹), 375 (13 000) and 396 (12 000). λ_{max,flu}/nm [H₂O-CH₃OH (4:1, v/v)]; 405, 427 and 451 nm (excited at 375). Wavelengths and extinction coefficients are identical within 2 nm and 10%, respectively, for **23** and **24b**. ^e pK_{a1} value for these dibasic compounds. The pK_{a2} value is not measurable *via* pH dependent fluorescence since both the mono-protonated and unprotonated forms of the sensor have near-zero fluorescence quantum yields. Both these forms possess at least one lone electron pair on nitrogen which causes a PET process. ^f λ_{max,abs}/nm (ε_{max})(CH₃OH) 347 (5200), 366 (9800) and 386 (9800). λ_{max,flu}/nm [H₂O-CH₃OH (4:1, v/v)]; 398, 420 and 444 nm (excited at 366). Wavelengths and extinction coefficients are identical within 2 nm and 10%, respectively, for **15a**, **15b** and **24a**. **15b**, **15a** and **24a** have pK_a values of 7.8, 7.6 and 6.5, respectively, in H₂O-CH₃OH (1:1, v/v) solution.

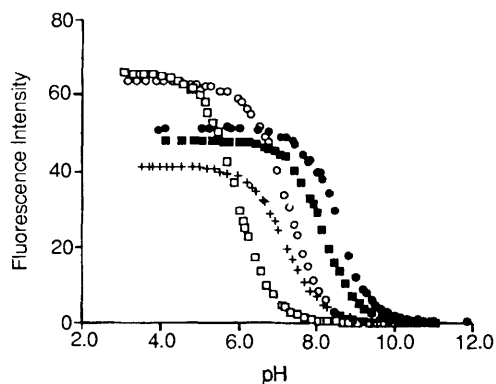


Fig. 3 Fluorescence intensity-pH profiles for sensors **23** (○), **24b** (□), **15b** (●), **15a** (■) and **24a** (+) in H₂O-CH₃OH (4:1, v/v) solution. The maximum fluorescence intensities of the various data sets have been scaled to their respective fluorescence quantum yields.

Assumption (b) relies on the large endergonicity for PET from the ammonium ion to the anthracene unit.

The pK_a values resulting from an analysis with eqn. (5) are gathered in Table 1, along with the other sensor parameters. It is notable that the linear fit to eqn. (5) is very good and the gradients (*m*) are in agreement with the theoretical value of unity. The 9,10-disubstituted sensors **23** and **24b** have distinctly higher φ_{Fmax} values than their 9-monosubstituted counterparts. 9,10-Dimethylanthracene and 9-methylanthracene also display such a difference.⁴⁵ On the other hand, the φ_{Fmin} values for **23** and **24b** are smaller by a factor of 4-5 than those for **15** and **24a**, even though all these values are tending to zero. The presence of two quenching amine sites leads to a higher electron transfer rate in these former cases.⁴⁶ This is quantitatively confirmed by the k_{PET} values given in Table 1. Overall, the extremely large¹⁹ fluorescence 'on-off' switching factors of 200-1300 are useful from the viewpoint of molecular sensing and signalling devices.¹¹ These large switching factors are caused by the suppression of fast PET rates (k_{PET} ~ 10¹⁰-10¹¹ s⁻¹). In contrast, **11** shows k_{PET} ~ 10⁹ s⁻¹ in keeping with the lower proton-induced φ_F enhancements. Interestingly, the relatively large φ_{Fmin} value of **11** allows the determination of the fluorescence lifetimes in both the protonated and unprotonated states.²²

Compounds **23** and **24b**, which possess two basic sites, display pK_a values which are less by *ca.* 1.3 pH units than those

of their 9-monosubstituted counterparts. These pK_a values are in fact the pK_{a1} values for the first dissociation of the doubly-protonated bis(aminomethyl)anthracenes. This difference must be due to the requirement of a second protonation, which is somewhat more difficult than the first, due to transmission of electric fields across the anthracene short axis. Both basic sites need to be protonated in order to 'switch on' the fluorescence of **23** and **24b**. Our previous deduction that the groups separated by the 9,10-dimethylanthracene moiety behave independently was caused by the fortuitous similarity of the electronic substituent effects of chloro and protonated dialkylamino-methyl groups employed in that study.¹⁸ The crown ether derivatives **23** and **15** possess significantly higher pK_a values than the electronically similar but non-crown amines **24**. Extra stabilization of the hydronium ion by hydrogen bonding with some of the crown ether oxygen atoms⁴⁷ is responsible for this pK_a increase of *ca.* 1.1 pH units. The higher basicity of **15b** as compared to **15a** reflects the optimal complementarity of the aza-18-crown-6 moiety with the hydronium ion which has C_{3v} symmetry.

An important feature of these PET sensors with alternant aromatic hydrocarbon fluors is that the pK_a values obtained fluorometrically are essentially identical with that obtained by ground state methods such as solubility-pH profiles¹⁸ or potentiometry.^{13,25} Electronic absorption spectral measurements do not permit evaluation of pK_a values since the former are essentially independent of pH. It is notable that such direct determination of thermodynamically valid information *via* excited state experiments is made possible since the proton-binding amine module is not electronically excited. This sets fluorescent PET pH sensors apart from common fluorescent pH indicators¹⁴ at the level of physical organic chemistry.⁴⁸

The pK_a values reported in Table 1 and ref. 18 are distinctly lower than those of the 'parent' amines⁴⁹ and have several causes.

(a) The use of H₂O-CH₃OH (4:1, v/v) instead of neat water (which was necessary for adequate solubility of the sensors); (b) steric hindrance by the bulky fluor module to the solvation of the protonated amine moiety;⁵⁰ (c) electron withdrawal of the sp² hybridized carbon atoms in the aromatic fluor, and (d) electron withdrawal (in the appropriate cases) by chloro or protonated dialkylamino methyl groups across the anthracene short axis.

As noted in the introduction, the modular structure 'fluor-spacer-amine' of the fluorescent PET pH sensors is a notable

aspect of their design. Other examples of modular construction are available in the design of (a) lanthanide probes with sensitized luminescence⁵¹ and (b) fluorescent reagents selective for protein thiols.⁵² Modularity implies preservation of 'parent' properties in the assembled sensor and this has been found to varying degrees in several instances.^{18,44} This allows the molecular designer a degree of quantitative prediction of the optical and proton-binding properties before the sensor itself has been synthesized. A substantial flexibility of design also arises, with a rather wide variation of fluor structure being apparent in 1–24, which permits selection of input and output wavelengths, Stokes shifts, maximum quantum yields and excited state lifetimes. Variation of the amine proton receptor results in sensors with different pH indicating ranges¹⁸ (Table 1). Other functionalities besides amines can serve as proton receptors in fluorescent PET sensors such as carboxylate,⁴⁴ but these are outside the scope of the present account. Several spacers have been employed thus far, but the methylene spacer group serves admirably in the present instance and several others. From a design viewpoint, proximal (but non-adjacent) modules are preferred due to the known exponential distance dependence of PET processes.⁵³ Also, a single methylene unit would be more rigid than oligomethylene groups with regard to folding. Furthermore, benzylic groups permit easy interconversion of functionalities and are therefore convenient for synthesis. However, we must note the failure of benzylic carbon centres to serve as insulating links in several other research areas, e.g. ionization potentials⁵⁴ and hydrophobicities.⁵⁵ It is interesting that the foundation of our present work is the violation of the spacer function of the benzylic methylene group by the PET process, whereas most other relevant processes are confined to either one of the terminal modules.

The present sensors were adequately photostable under the steady state fluorimetric conditions employed, though they were less so during phase fluorometry which requires longer exposures. The rapidity of thermal back electron transfer³ following the PET act must be responsible for this photostability. It is interesting that the practical utility of luminescent PET sensors relies on the rapidity of thermal back electron transfer, whereas the success of photo-electrochemical solar energy conversion schemes requires its suppression.³

Experimental

Steady state fluorimetry was conducted with Aminco-Bowman, Perkin-Elmer LS-5B and SLM 48000 instruments with phase fluorometry being carried out on the latter instrument. Supporting electronic absorption spectroscopy employed Perkin-Elmer lambda 9 and SLM DW-2000 instruments. The various experimental conditions are given as appropriate footnotes to Table 1. The details concerning the synthesis and characterization of the various sensors are given below. Light petroleum refers to the fraction boiling at 60–80 °C.

1,4,7,10,13-Pentaoxa-16-(anthracen-9-ylmethyl)-16-monoaza-cyclooctadecane (**15b**). 9-Chloromethylantracene (5.0 g) was dissolved in the minimum volume of hot toluene. Monoaza-18-crown-6⁵⁶ (6.3 g) and potassium carbonate (3.3 g) were added and the mixture was refluxed for 24 h. The solution was filtered while hot. After being cooled, the filtrate was extracted with 4 mol dm⁻³ hydrochloric acid. The acid extract was neutralized with potassium carbonate and extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and evaporated to give a yellow solid. Crystallization from ethanol gave **15b** as yellow rods (7.0 g, 65%), m.p. 93 °C (Found: C, 71.1; H, 7.7; N, 2.8. C₂₇H₃₅N₆O requires C, 71.5; H, 7.8; N, 3.1%; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.88 (t, 4 H, NCH₂CH₂O), 3.54–3.69 (m, 20 H, OCH₂CH₂O and OCH₂CH₂N), 4.58 (s, 2 H,

ArCH₂) and 7.42–8.57 (m, 9 H, Ar); m/z (%): 453 (M⁺, 43), 218 (5), 206 (22), 191 (100) and 178 (12).

The other sensors were prepared via analogous procedures and their characterization follows.

1,4,7,10-Tetraoxa-13-(anthracen-9-ylmethyl)-13-monoazacyclo-pentadecane (**15a**). Yellow rods (68% yield) crystallized from ethanol, m.p. 71 °C (Found: C, 73.0; H, 7.8; N, 3.7. C₂₅H₃₁NO₄ requires C, 73.3; H, 7.6; N, 3.4%; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.87 (t, 4 H, NCH₂CH₂O), 3.51–3.60 (m, 16 H, OCH₂CH₂O and OCH₂CH₂N), 4.53 (s, 2 H, ArCH₂) and 7.36–8.51 (m, 9 H, Ar); m/z (%): 409 (M⁺, 45), 218 (38), 204 (25) and 191 (100).

9,10-Bis(1,4,7,10,13-Pentaoxa-16-monoazacyclooctadecan-16-ylmethyl)anthracene (**23**). Yellow rods (48% yield) crystallized from ethyl acetate–light petroleum (1:1), m.p. 92–95 °C (Found: C, 66.1; H, 8.3; N, 3.7. C₄₀H₆₀N₂O₁₀ requires C, 65.9; H, 8.3; N, 3.7%; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.90 (t, 8 H, NCH₂CH₂O), 3.58–3.67 (m, 40 H, OCH₂CH₂O and OCH₂CH₂N), 4.60 (s, 4 H, ArCH₂) and 7.47–8.61 (m, 8 H, Ar); m/z (%): 728 (M⁺, 10), 466 (100), 262 (45), 218 (15), 205 (62), 191 (73) and 178 (6).

N-(Anthracen-9-ylmethyl)bis(2-hydroxyethyl)amine (**24a**). Yellow rods (62% yield) crystallized from ethyl acetate–light petroleum (1:1), m.p. 112 °C (Found: C, 76.9; H, 7.3; N, 4.5. C₁₉H₂₁NO₂ requires C, 77.3; H, 7.2; N, 4.7%; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.60 (s, 2 H, OH), 2.71 (t, 4 H, NCH₂CH₂O), 3.43 (t, 4 H, NCH₂CH₂O), 4.88 (s, 2 H, ArCH₂) and 7.49–8.52 (m, 9 H, Ar); m/z (%): 295 (M⁺, 5), 264 (12) and 191 (100).

9,10-Bis[bis(2-hydroxyethyl)aminomethyl]anthracene (**24b**). Yellow crystalline powder (40% yield) crystallized from ethyl acetate–light petroleum (1:1), m.p. 167 °C (Found: C, 69.8; H, 7.5; N, 6.7. C₂₄H₃₂N₂O₄ requires C, 69.9; H, 7.8; N, 6.8%; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.65 (s, 4 H, OH), 2.78 (t, 8 H, NCH₂CH₂O), 3.43 (t, 8 H, NCH₂CH₂O), 4.74 (s, 4 H, ArCH₂) and 7.53–8.53 (m, 8 H, Ar); m/z (%): 412 (M⁺, 0.2), 381 (0.6), 264 (15), 221 (10), 205 (15) and 191 (100).

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