Luminescence and Charge Transfer. Part 3.[1] The Use of Chromophores with ICT (Internal Charge Transfer) Excited States in the Construction of Fluorescent PET (Photoinduced Electron Transfer) pH Sensors and Related Absorption pH Sensors with Aminoalkyl Side Chains

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7-Methoxycoumarin, 3-aminobenzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one and 4-nitroaniline derivatives, useful as chromatographic derivatizing agents, dyes and solvent polarity indicators respectively, are easily transformed into optical pH sensors **3a–c**, **4a–c** and **5a–c** respectively by attachment of a proximal, non-adjacent amine moiety. The availability of ICT (internal charge transfer) excited singlet states in each of these sensor families leads to protonation-induced wavelength shifts of their electronic absorption spectra. A similar phenomenon is observed in those fluorescence emission spectra where the proton-free form of the sensor is weakly emissive due to the sluggishness of the designed PET (photoinduced electron transfer) process. Except for these differences, sensors **3a–c** and **4a–c** show the expected pH dependence of fluorescence quantum yields, thus extending the scope of the fluorescent PET pH sensor design logic to electronic push–pull fluorophores besides aromatic hydrocarbons.

In Part 2 of this series, aminomethylanthracene derivatives were demonstrated to be useful fluorescent PET sensors for protons. These were based on the 'Fluorophore–Spacer–Receptor' format (**1**) which has been extensively used for the construction of fluorescent sensors for various chemical species.[2–4] In several

1

2

cases it has been demonstrated that the spacer plays a crucial role by spatially isolating the terminal functional units in all respects except for a long-range photoinduced electron transfer (PET) process,[5] which is responsible for the species-switchable fluorescence. In these instances, a large number of important sensor parameters are quantitatively predictable.[6] Also, the species-binding equilibria are apparently quantitatively identical in the excited and ground states of the sensors.[3,4,6,7] We now present the first fluorescent PET sensor families composed of all-organic systems where the isolation role of the spacer is overcome by an additional long-range electrostatic force. We also demonstrate that the same force in 'Chromophore–Spacer–Receptor' systems (**2**) can result in absorption pH sensor action. The common logical feature in all three sensor families is the optical generation of an internal charge transfer (ICT) excited state[8] which is proximal but non-adjacent to an electrically chargeable atomic centre. ICT excited states are commonly found in heterocyclic and aromatic hydrocarbon derivatives with electronic push–pull systems and they optically express themselves with red shifted absorption and emission spectra relative to purely hydrocarbon systems of similar chromophore size. We show that such chromophores can be a valuable resource for fluorescent PET sensor designers, even though simple aromatic hydrocarbons continue to feature strongly in the design of fluorescent sensors of various types.[6d,9–14] Thus, in this part of the series, the emphasis is on the co-occurrence of two types of charge transfer processes within a given family of luminescent molecules.

Results and Discussion

4-Bromomethyl-7-methoxycoumarin (Br-mmc) is a commercially available reagent for derivatizing carboxylic acids prior to chromatographic (HPLC) analysis with fluorescence detection.[15] Br-mmc is easily converted to **3a–c** by treatment with the appropriate amine. The extreme convenience of the synthesis is a special attraction of this sensor family. Compounds **3a–c** display pH-sensitive fluorescence quantum yields (Φ_F) with essentially 'on–off' action (Table 1). An example is presented in Fig. 1 for sensor **3a**. However, the emission spectral shapes and positions are pH invariant due to the essential non-emissivity of the unprotonated forms of **3a–c**. This is as expected for fluorescent PET sensors based on format **1**.[1,2] Given the appropriate thermodynamic driving force, rapid PET is expected to cause fluorescence quenching of **3a–c** only when unprotonated. This has been observed in a 6,7-dimethoxycoumarin-diamine system **6** during its use as a sensor for potassium ions.[16] Even 7-aminocoumarins are known to undergo such processes intermolecularly with tertiary amines.[17] However, unlike previous fluorescent PET sensors,[1] **3a–c** show a significant pH dependence in their absorption spectra. The proton induced bathochromic shift is rationalized as being due to the electrostatic stabilization of the 7-methoxycoumarin excited singlet state, which has ICT character due to the methoxy donor and the heterocycle acceptor,[18] by the ammonium group proximal but non-adjacent to the heterocycle. The corresponding stabilization energies are 9, 13 and 11 kJ mol^{-1} for **3a**, **b** and **c** respectively. The ICT nature of related 7-aminocoumarin excited singlet states have received experimental verification.[19] The lack of such absorption spectral shifts in previous fluorescent PET pH sensors with ICT fluorophores such as 1,3-diaryl-2-pyrazolin-5-ylbenzoic acids **7** can be ascribed to the remote and delocalized nature of the carboxylate anion.[6b] Another fluorescent PET sensor family of aminoethylnaphthalimide derivatives **8** with demonstrable ICT character[20] shows a strong pH dependence in their fluorescent quantum yields but not in their absorption spectra.[20] The latter observation can be rationalized in terms of the solvation and

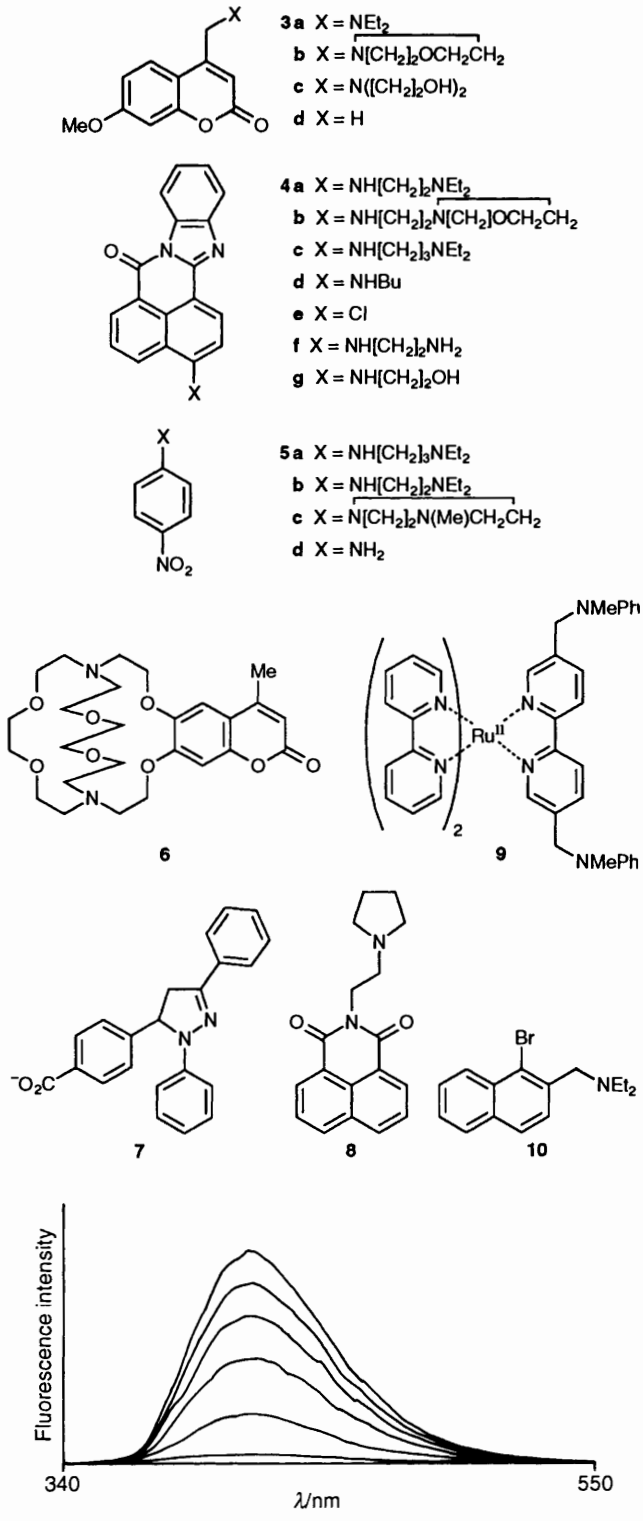

Fig. 1 Family of uncorrected fluorescence emission spectra excited at 328 nm for a 10^{-5} mol dm^{-3} solution of **3a** in MeOH–H_2O (1:4, v/v) with pH values (in order of decreasing intensity) of 2.6, 6.3, 6.7, 7.1, 7.6 and 8.6

delocalization of the photogenerated negative charge density within the imide moiety in the ICT excited state. On the other hand, it has been reported very recently that luminescent metal complexes with MLCT (metal to ligand charge transfer) excited states display coupling effects with external charges.[4] Upon diprotonation, the luminescent pH sensor **9** and relatives (which are designed according to PET principles) do show a red shift of their absorption onsets though their absorption spectral maxima move in the opposite direction. The behaviour of the absorption onsets agree with the stabilizing interaction expected between the protonated aminomethyl group and the photocreated negative charge density in the substituted bipyridyl moiety in the MLCT excited state.

Analysis of the pH dependent absorption spectra and the fluorescence quantum yields according to eqns. (1)[21] and (2)[1]

$$\log[(A_{max} - A)/(A - A_{min})] = \mp pH \pm pK_a \quad (1)$$

$$\log[(\Phi_{Fmax} - \Phi_F)/(\Phi_F - \Phi_{Fmin})] = pH - pK_a' \quad (2)$$

$$pK_a(S_1) - pK_a(S_0) = (hc/2.3\,RT)\{[1/\lambda_{abs}(base)] - [1/\lambda_{abs}(acid)]\} \quad (3)$$

respectively gives rise to pK_a values for **3a–c** measured in their ground (S_0) and excited (S_1) states, respectively (Table 1). However we see that these two values are identical within experimental error. While this equality has several experimental precedents in fluorescent PET sensor research,[3,4,6b–d,7,22] the present case requires analysis in the light of the following question; why are the protonation properties of the receptor unaffected by the excitation status of the fluorophore (S_0 or S_1), whereas the converse disturbance of the excited fluorophore by the protonation status of the receptor is clearly seen in the pH dependent absorption spectra? The thermodynamically expected $pK_a(S_1)$ values for **3a**, **b** and **c** would have been 8.6, 6.8 and 6.6 respectively, if the bathochromism in acid solution were translated into ΔpK_a values by employing the Forster–Weller eqn. (3).[23] This apparent breakdown of microscopic reversibility is probably caused by the kinetic limitation to the attainment of a new protonation equilibrium during the short lifetime of the excited singlet state,[24] *i.e.*, the excited state measurement reflects the ground state equilibrium. Such kinetic limitations are known in protonation equilibria of fluorescent pH sensors, even with integrated fluorophore and receptor moieties.[23] In contrast, protonation equilibria can be fully re-established during the lifetime of triplet excited states. Phosphorescent PET pH sensor **10** when included in β-cyclodextrin[25] shows a considerable difference between $pK_a(S_0)$ and $pK_a(T_1)$ values even though the ICT character in the triplet excited state of the bromonaphthalene phosphor is not expected to be large. Compound **3d** serves as a suitable quantitative model for several optical parameters of **3a–c**, except for those in acid solution due to the proton induced bathochromism. It is notable that the fluorescence spectra of **3a–c** are only observed at substantially longer wavelengths than that of **3d**. The 'parent' tertiary amines are not accurate models for the protonation properties of **3a–c** (as judged by the corresponding pairs of pK_a values in Table 1) due to the electronic and steric perturbation of the amine/ammonium moiety by the proximal heterocycle across the methylene spacer.

The points presented so far receive additional thrust when 3-aminobenzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one derivatives are adapted and co-opted into sensory roles. The parent fluorophore has seen use as a dye for flaw detection in solids[26] and in solar energy collectors.[27] It possesses an electronic push–pull system created by the 6-amino donor and the electron accepting heteroatom array. In this connection, it has also been the subject of photophysical studies as part of a 4-amino-1,8-naphthalimide family where the ICT nature of the excited state of the latter was demonstrated *via* solvent effects.[28,20] We were attracted to this fluorophore because of its communication wavelengths in the visible region and the ready adaptability of its synthesis to allow the grafting of 'Spacer–Receptor' assemblies as required in **4a–c**. Treatment of 3-chlorobenzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one **4e**[27] with the appropriate diamine directly results in the desired sensors. Another

Table 1 Electronic absorption and fluorescence parameters for **3**, **4** and **5**[a]

Parameter	**3a**[b]	**3b**[b]	**3c**[b]	**4a**[c]	**4b**[c]	**4c**[c]	**5a**[d]	**5b**[d]	**5c**[d]
λ_{abs}(acid)/nm	332	331	333	440	440	451	398	384	377
log ε(acid)	4.11	4.11	4.17	4.47	4.32	4.34	4.24	4.28	4
λ_{abs}(base)/nm	324	320	323	452	453	454	405	405	.16
log ε (base)	4.12	4.14	4.18	4.47	4.31	4.34	4.26	4.30	400
λ_{isos}[e]/nm	328	326	328	441	442	—[f]	398	388	4
pK_a[e]	7.1[g]	4.5[g]	4.7[g]	8.7[h]	5.9[h]	—[i]	9.6[j]	8.8[j]	.17
λ_{Flu}[k]/nm	415	415	414	503	502	513			385
					(518)[l]	(521)[l]			7.2[j]
Φ_{Fmax}(acid)[m]	0.37	0.35	0.34	0.77	0.74	0.68			
Φ_{Fmin}(base)[m]	0.010	0.011	0.011	0.008	0.056	0.11			
FE[n]	37	32	31	100	13	6			
pK_a'[o]	7.1[g]	4.3[g]	4.7[g]	8.5[h]	5.8[h]	9.2[h]			

[a] Sensors (10^{-5} mol dm^{-3}) and model compounds in aerated MeOH–H_2O (1:4, v/v) with phosphate pH buffers. The possibility of coumarin ring hydrolysis[43] was considered, but no such problems were encountered with **3a–d** under our conditions (pH range 2–10), as is the case for the families **4a–d** (pH range 4–11) and **5a–d** (pH range 3–12). pH Dependent fluorescence measurements were carried out with excitation at isosbestic wavelengths. [b] The model compound **3d** has pH invariant spectra; λ_{abs} = 319 nm, log ε = 4.20 (ε in all cases is in units of dm^3 mol^{-1} cm^{-1}), λ_{Flu} = 380 nm (corrected), Φ_F = 0.36. [c] The model compound **4d** has pH invariant spectra; λ_{abs} = 452 nm, log ε = 4.06, λ_{Flu} = 522 nm (corrected), Φ_F = 0.31. The relatively low Φ_F value may be due to aggregation effects originating in the solubility difficulties experienced with this compound. [d] The model compound **5d** has pH invariant absorption spectra; λ_{abs} = 378 nm, log ε = 4.11. Compounds **4a–d** showed no fluorescence under our conditions. [e] These values are obtained by analysing the pH dependence of absorbance (A) values at appropriate wavelengths according to the eqn. (1). Either set of signs on the right hand side of eqn. (1) can be valid, depending on the analytical wavelength chosen. Isosbestic points (λ_{isos}) are observed in all cases except for **4c** where the spectral changes are too small to allow such an assignment. The fit of experimental points to the equation is good [average least squares correlation coefficient (r) = 0.995, average number of points (n) = 10]. The average experimental gradient = 1.00, standard deviation = 0.09 for the eight cases. [f] No clear isosbestic point due to the small spectral shift upon protonation. [g] The parent N-methylamines corresponding to **3a**, **b** and **c** have pK_a values (in H_2O) of 10.3, 7.4 and 8.6 respectively.[44] [h] The closest parent amines corresponding to **4a**, **b** and **c** for which data are available have pK_a values (in H_2O) of 9.9 (*N,N*-diethyl-*N'*-methyl-1,2-diaminoethane), 7.4 (*N*-methylmorpholine) and 10.6 (*N,N*-diethyl-1,3-diaminopropane) respectively.[44] [i] Indeterminable in this manner due to the small spectral shift upon protonation. [j] The closest parent amines corresponding to **5a**, **b** and **c** for which data are available have pK_a values (in H_2O) of 10.6 (*N,N*-diethyl-1,3-diaminopropane), 9.9 (*N,N*-diethyl-*N'*-methyl-1,2-diaminoethane) and 9.7 (piperazine) respectively.[44] [k] Obtained from fluorescence spectra which have been corrected for wavelength dependence of response of the photon detection system using quinine bisulfate.[45] [l] Fluorescence emission maximum in the 'switched off' form of the sensor in basic solution. [m] 4-acetoxymethyl-7-methoxycoumarin [Φ_F = 0.44 in neutral MeOH–H_2O (1:9, v/v)[15b]] is used as a secondary standard for sensors **3a–c** and Rhodamine B(Φ_F = 0.65 in EtOH[46]) is employed for the same purpose with regard to sensors **4a–c**. In the latter case, comparison of corrected spectra are necessary owing to the different spectral shape of the secondary standard with regard to the sensor family **4a–c**. [n] Fluorescence enhancement factor = Φ_{Fmax}(acid)/Φ_{Fmin}(base). [o] These values are obtained by analysing the pH dependence of fluorescence quantum yield (Φ_F) values according to eqn. (2). The use of this equation is facilitated by the proportionality of Φ_F to fluorescence intensities[47] due to the pH invariance of spectral shape and position in most cases. In the cases of **4b** and **c**, small wavelength shifts are observed as a function of pH. Hence corrected spectral areas need to be employed during the use of eqn. (2). The fit of experimental points to the equation is good (r = 0.996, n = 9). The average experimental gradient = 0.99, standard deviation = 0.01 for the six cases.

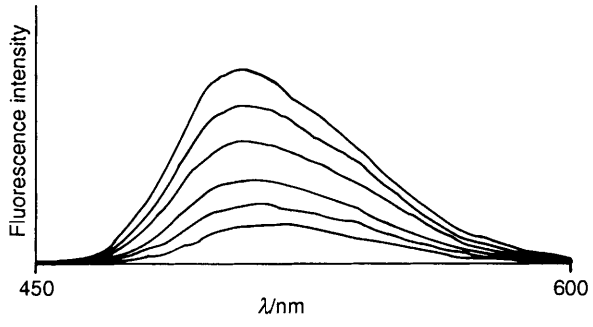

Fig. 2 Family of uncorrected fluorescence emission spectra excited at 452 nm for a 10^{-5} mol dm^{-3} solution of **4c** in MeOH–H_2O (1:4, v/v) with pH values (in order of decreasing intensity) of 6.3, 8.8, 9.1, 9.7, 10.0 and 11.2

reason for examining the sensor family **4a–c** was the previously reported observation[27] that the aminoethyl derivative **4f** had a significantly lower fluorescence quantum yield than its hydroxyethyl counterpart **4g**. On the suspicion that PET processes were responsible for this experimental fact, we reasoned that alkyl disubstitution on the terminal amino unit in **4f** would lower its oxidation potential[29] and thus permit far stronger 'switching off' of fluorescence with the option of a 'switched on' fluorescent state upon protonation. All the members of the sensor family **4a–c** showed the expected sensory behaviour, but with varying degrees of efficiency which are understandable in terms of their structural features (Table 1). It must be noted that the experiments with **4a–d** discussed here are conducted in the pH range of 4–11. More acidic solutions result in protonation of the imidazole nitrogen in the excited singlet state causing losses in fluorescence with even ground state protonation beginning to occur below pH 3. Fig. 2 details the fluorescent pH sensory behaviour of the least efficient, but still very useful, member **4c**. For a given thermodynamic driving force and type of spacer (if any) the rates of PET processes depend exponentially on the distance of separation of the donor and acceptor components.[30] Thus it is not surprising that **4c** possesses the longest spacer. Reduction of the spacer length by a single methylene unit to yield **4a** results in the improvement of the proton-induced fluorescence switching action by a factor of *ca.* 16. Comparison of the sensory behaviour of **4b** with that of **4a** shows the detrimental effect of reduced thermodynamic driving force for PET (ΔG_{PET})[31] due to the increased oxidation potential of the morpholino moiety relative to the diethylamino unit which is expected on the basis of substituent effects on amine oxidation.[29] Interestingly, no such influence of the amino receptor moiety was found within the 7-methoxycoumarin family **3a–c**. One reason for this difference could arise from the fact that the spacer length is shorter by one methylene unit for **3a** and **b**, as compared to **4a** and **b**, which leads to faster PET processes. Another reason could also be that the ΔG_{PET} values are substantially negative for unprotonated forms of all the members of the sensor family **3a–c** whereas the corresponding value must be more finely balanced in the cases of **4a–c**. Unfortunately, the current unavailability of reduction

potentials of the two fluorophores concerned prevents us from testing this deduction by application of the Weller eqn. (4).[32] However a rough estimate can be made for **3a** as follows. The reduction potentials of 7-diethylamino-4-methylcoumarin and unsubstituted coumarin are reported as -2.2 [19b] and -1.4 V [33] (*vs.* SCE) respectively. The corresponding value for **3d** ($E_{red.fluorophore}$) can then be obtained as -1.7 V assuming that the 7-substituent controls the reduction potentials according to a linear free energy relationship.[34] The oxidation potential for triethylamine, the model receptor for **3a** is 1.1 V.[35] The singlet energy of the model fluorophore **3d** ($E_{S.fluorophore}$) can be calculated as 3.6 eV from the average of the energies of the spectral maxima in absorption and emission. The attractive potential between the radical ion pair $-e^2/\varepsilon r$ is approximately -0.1 eV.[36] Application of these values into eqn. (4) yields ΔG_{PET} as -0.9 eV or -87 kJ mol^{-1} which is a substantially negative value. Interestingly, the magnitude of ΔG_{PET} is significantly lower in a diethylamino substituted tetraphenylporphyrin–tin(IV) derivative ($\Delta G_{PET} = -0.5$ eV) where the counterpart with the morpholino unit is found to be much less efficient for fluorescent PET sensor action.[3]

$$\Delta G_{PET} = -E_{S.fluorophore} - E_{red.fluorophore} + E_{ox.receptor} - e^2/\varepsilon r \quad (4)$$

From Fig. 2, it is also worth noting the small but significant shift of the fluorescence emission spectrum of **4c** to longer wavelengths as the pH value of its environment is increased. This contrast with the family **3a–c** (Fig. 1) has its roots in the significant emissivity ($\Phi_{Fmin} = 0.11$) of **4c** in its unprotonated form due to the sluggish PET process discussed above. It is gratifying to find that these fluorescence spectral maxima for **4b** and **c** in basic solution are very close to the limiting value displayed by the model compound **4d**. The proton-induced blue shift in **4c** and **b** can be understood as being caused by the electrostatic destabilization of the thermally equilibriated ICT excited singlet state at the 6-amino donor terminal by the pendant protonated amino receptor which is three or two methylene groups away. As might be expected, this blue shift is larger for **4b** *vis-a-vis* **4c** due to the short spacer in **4b**. These observations support the proton-induced (absorption) hypsochromic shifts seen more generally within this sensor family with the qualification that the absorption spectral effects refer to Franck–Condon ICT excited singlet states. The proton-induced hypsochromism is a minimum in **4c** where the spacer length is a maximum. The destabilization energies corresponding to the hypsochromic shifts seen in **4a**, **b** and **c** are 7, 8 and 2 kJ mol^{-1} respectively. The energies are noticeably smaller than those observed for **3a–c** and are at least partly a reflection of the shorter spacer present in **3a–c**. We close this paragraph by noting that similar proton-induced blue shifts in fluorescence spectra, but of larger magnitude, are commonly seen in fluorescent pH sensors based on the very different concept of photoinduced proton transfer.[23a]

As in the case of **3a–c**, the sensor family **4a–c** shows essentially the same pK_a values whether they are interrogated in the ground or excited singlet states. A kinetic limitation to the attainment of a new protonation equilibrium at the receptor which is spaced from the excited fluorophore is the probable cause, judging by the 6.9 ns lifetime of the excited singlet state of **4d** in ethanol solution.[28] A wide range of pK_a values (4.4–9.2) are attained in this study of **3a–c** and **4a–c** even though it was restricted to sensors with amine building blocks which were commercially available. The maximum pK_a value found in the present study is 9.2 measured for **4c** which is to be compared with the value of 10.2 for 3-phenylpropylamine which is the largest yet encountered among fluorescent PET sensors for pH.[7a]

The system **2** was examined as a simpler version of **1** since it is free of any complications due to fluorescence. However, some nitroaniline derivatives are fluorescent and in fact serve as fluorescence standards for the correction of spectrofluorimeter response as a function of observation wavelength.[37] Chromophores with ICT excited states such as 4-nitroanilines are known to interact with neighbouring solvent electric dipoles which result in solvatochromism.[38] A similar outcome should therefore be attainable by electrically charging a proximal neutral group, *i.e.* by protonation of a neighbouring, but non-adjacent amine unit in **5a–c**. These are easily prepared from 4-fluoronitrobenzene by nucleophilic aromatic substitution with the appropriate amines. As expected, hypsochromism is observed in **5a–c** upon protonation and is due to destabilization of the ICT excited state resulting from the amine donor and the nitro acceptor by the proximal ammonium group. The magnitude of the hypsochromism in **5a–c** is controlled by the length and the connectivity of the spacer unit(s). The double connection of the chromophore and the receptor units with dimethylene spacers in **5c** leads to a particularly large spectral shift. The destabilization energies are 5, 16 and 18 kJ mol^{-1} for **5a**, **b** and **c** respectively. These energies are quite large compared to those encountered with **3a–c** in spite of the longer spacer units employed in **5a–c**, attesting to the relatively large dipole created in the Franck–Condon excited singlet ICT state of the 4-nitroaniline chromophore. The pK_a values (Table 1) are similarly understandable at least approximately when the appropriate model compounds are used for comparison. The absorption pH sensor family (**5a–c**) is interesting because it differs conceptually from the many hundreds of pH indicators accumulated over several centuries that operate mainly by protonation/deprotonation of a group which is an integral part of the chromophore.[39]

Besides their usefulness as sensors, systems **1** and **2** and their examples **3a–c**, **4a–c** and **5a–c** can serve as prototypes from two other general viewpoints. Because **1** and **2** optically respond to the arrival of a (positive) electric charge at a defined site, such systems may be employed for the optical tracking of the movement of charged components within supramolecular assemblies.[40] Also, **1** and **2** contain an electroneutral optical reporter moiety separate from, but in the neighbourhood of, the reaction site. So the optical reporter substitutes for a part of the cybotactic region of the reaction site and is in a position to signal intimate details of the reaction. The present cases **3a–c**, **4a–c** and **5a–c** contain one of the most elementary of reaction sites, that of a protonation equilibrium and the protonation status of the reaction site (and its attendant solvation status) is signalled optically by the reporter.

In summary, *trans*-spacer electrostatic interactions can result in pH controlled wavelength shifts of obsorption and fluorescence spectra in 'Chromophore–Spacer–Receptor' systems. Thus, fluorescent PET pH sensors can be endowed with additional absorption-based sensory channels if push–pull heterocyclic fluorophores are employed.

Experimental

Electronic absorption and fluorescence spectroscopy was carried out with Perkin-Elmer lambda-9 and LS-5B instruments, respectively. The experimental conditions are given as appropriate footnotes to Table 1. The synthesis and characterization of the various sensors are detailed below.

4-Diethylaminomethyl-7-methoxycoumarin (**3a**).—4-Bromomethyl-7-methoxycoumarin (1.5 g), diethylamine (0.5 g), potassium carbonate (5.0 g) and dry dichloromethane (40 cm^3) were stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate was evaporated. The resulting mass was

dissolved in diethyl ether and saturated with hydrogen chloride. The precipitate obtained was dissolved in water and saturated aq. sodium tetrafluoroborate was added. The resulting salt **3a**·HBF_4 was crystallized from diethyl ether–methanol as pale yellow crystals (0.3 g, 20% yield) m.p. 150 °C [Found (free base): M, 261.1372. $C_{15}H_{19}NO_3$ requires *M*, 261.1365]; δ_H([$^2H_6$]DMSO) 9.43 (br s, 1 H, N^+H), 7.87 (d, 1 H, 5-H), 7.04 (m, 2 H, 6,8-H), 6.56 (s, 1 H, 3-H), 4.57 (s, 2 H, $ArCH_2N$), 3.87 (s, 3 H, OCH_3), 3.26 (q, 4 H, NCH_2CH_3) and 1.24 (t, 6 H, NCH_2CH_3); *m*/*z* (%) (free base) 261 (M^+, 7), 247 (16), 246 (100), 191 (13) and 190 (94).

Sensors **3b** and **c** were prepared *via* analogous procedures except that the free bases were directly obtained as solids.

4-*Morpholinomethyl*-7-*methoxycoumarin* (**3b**).—Pale yellow crystals (52% yield) obtained from methanol, m.p. 134 °C (Found: C, 65.1; H, 6.1; N, 4.9. $C_{15}H_{17}NO_4$ requires C, 65.4; H, 6.2; N, 5.1%); δ_H($CDCl_3$) 7.74 (d, 1 H, 5-H), 6.85 (m, 2 H, 6,8-H), 6.37 (s, 1 H, 3-H), 3.87 [s, 3 H, OCH_3), 3.74 [t, 4 H, $(CH_2)_2O$], 3.59 (s, 2 H, $ArCH_2N$) and 2.52 [t, 4 H, $(CH_2)_2N$]; *m*/*z* (%) 275 (M^+, 9), 191 (12) and 190 (94).

2-[N,N-*Bis*(2-*hydroxyethyl*)*aminomethyl*]-7-*methoxycoumarin* (**3c**).—Nearly colourless crystals (50% yield) obtained from diethyl ether–dichloromethane–ethanol, m.p. 122 °C (Found: C, 61.1; H, 6.4; N, 4.6. $C_{15}H_{19}NO_5$ requires C, 61.4; H, 6.5; N, 4.8%); δ_H($CDCl_3$) 7.34 (d, 1 H, 5-H), 6.85 (m, 2 H, 6,8-H), 6.48 (s, 1 H, 3-H), 3.89 (m, 5 H, OCH_3, $ArCH_2N$), 3.70 [t, 4 H, $(CH_2CH_2OH)_2$] and 2.83 [t, 4 H, $(CH_2CH_2OH)_2$]; *m*/*z* (%) 293 (M^+, 3), 263 (18) and 262 (100).

3-*Diethylaminoethylaminobenzimidazo*[2,1-a]*benz*[de]*isoquinolin*-7-*one* (**4a**).—3-Chlorobenzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one[27] (3.2 g), diethylaminoethylamine (9.3 g), copper sulfate pentahydrate (0.4 g) and 2-methoxyethanol (100 cm^3) were refluxed for 6 h. The reaction mixture was poured into excess water and the precipitate was collected, dried and crystallized from chlorobenzene as orange-red crystals (2.8 g, 73% yield) m.p. 170 °C (Found: C, 74.6; H, 6.4; N, 14.3. $C_{24}H_{24}N_4O$ requires C, 75.0; H, 6.3; N, 14.6%); δ_H($CDCl_3$) 8.85–6.67 (m, 9 H, ArH), 3.35 (m, 2 H, $ArNCH_2$), 2.87 (t, 2 H, CH_2), 2.65 [q, 4 H, $N(CH_2)_2$], 1.09 (t, 6 H, CH_3) and NH (not observed); *m*/*z* (%) 384 (M^+, 2), 87 (7) and 86 (100).

Sensors **4b** and **c** and model compound **4d** were prepared *via* analogous procedures except that a preliminary purification step *via* acid extraction and rebasification was carried out before crystallization of **4b** and **c**.

3-*Morpholinoethylaminobenzimidazo*[2,1-a]*benz*[de]*isoquinolin*-7-*one* (**4b**).—Red crystals (76% yield) obtained from ethanol, m.p. 254–258 °C (Found: C, 72.0; H, 5.1; N, 14.0. $C_{24}H_{22}N_4O_2$ requires C, 72.3; H, 5.6; N, 14.1%); δ_H($CDCl_3$) 8.78–6.61 (m, 9 H, ArH), 6.35 (br s, 1 H, NH), 3.78 [t, 4 H, $(CH_2)_2O$], 3.30 (q, 2 H, $ArNCH_2$), 2.74 (t, 2 H, CH_2N) and 2.04 [t, 4 H, $N(CH_2)_2$]; *m*/*z* (%) 398 (M^+, 4), 101 (6) and 100 (100).

3-*Diethylaminopropylaminobenzimidazo*[2,1-a]*benz*[de]*isoquinolin*-7-*one* (**4c**).—Red crystals (51% yield) obtained from dichloromethane–hexane (1:1), m.p. 134–138 °C (Found: C, 75.2; H, 6.2; N, 14.0. $C_{25}H_{26}N_4O$ requires C, 75.4; H, 6.6; N, 14.1%); δ_H($CDCl_3$) 8.78–6.54 (m, 9 H, ArH), 3.41 (m, 2 H, $ArNCH_2$), 2.67 [m, 6 H, $CH_2N(CH_2)_2$], 1.89 (m, 2 H, $ArNCH_2CH_2$), 1.09 (m, 6 H, CH_3) and NH (not observed); *m*/*z* (%) 398 (M^+, 46), 306 (16), 305 (10), 304 (47), 298 (10), 100 (13), 86 (100) and 72 (27).

3-*Butylaminobenzimidazo*[2,1-a]*benz*[de]*isoquinolin*-7-*one* (**4d**).—Pale red crystals (56% yield) obtained from ethanol, m.p. 186–188 °C (Found: C, 76.7; H, 5.7; N, 12.3%. M, 341.1541. $C_{22}H_{19}N_3O$ requires C, 77.4; H, 5.6; N, 12.3%. *M*, 341.1528); δ_H($CDCl_3$) 8.65–6.51 (m, 9 H, ArH), 5.17 (br s, 1 H, NH), 3.13 (m, 2 H, $ArNCH_2$), 1.63 (m, 2 H, NCH_2CH_2), 1.48 (m, 2 H, CH_2CH_3) and 1.00 (t, 3 H, CH_3); *m*/*z* (%) 341 (M^+, 60), 306 (35), 305 (21), 304 (100), 299 (10) and 298 (48).

N,N-*Diethyl*-N′(4-*nitrophenyl*)-1,3-*diaminopropane* (**5a**).—4-Fluoronitrobenzene (10.0 g), 3-diethylaminopropylamine (13.0 cm^3), sodium acetate (10.0 g) and ethanol (70 cm^3) were refluxed for 1.5 h. The reaction mixture was filtered and the filtrate was evaporated. Water was added to the resulting mass and extracted with dichloromethane. The dichloromethane extract was dried (anhyd. magnesium sulfate) and evaporated. The residue was taken up in hydrochloric acid (2 mol dm^{-3}), washed with dichloromethane and basified with sodium hydroxide. The alkaline mixture was extracted with dichloromethane. After drying, the dichloromethane extract was evaporated. The residue was distilled under vacuum to give a yellow oil (6.3 g, 35%) b.p. 160 °C/0.5 mmHg (Found: C, 61.8; H, 8.1; N, 16.8. $C_{13}H_{21}N_3O_2$ requires C, 62.1; H, 8.4; N, 16.7%); δ_H($CDCl_3$) 8.04 (d, 2 H, 3′,5′-ArH), 6.99 (br s, 1 H, NH), 6.49 (d, 2 H, 2′,6′-ArH), 3.26 (m, 2 H, $ArNCH_2$), 2.54 [m, 6 H, $CH_2N(CH_2CH_3)_2$], 1.78 (m, 2 H, $ArNCH_2CH_2$) and 1.01 [t, 6 H, $N(CH_2CH_3)_2$]; *m*/*z* (%) 251 (M^+, 16), 178 (10) and 86 (100).

Sensors **5b** and **c**[41] were prepared *via* analogous procedures, except that **5c** was obtained as a solid.

N,N-*Diethyl*-N′-(4-*nitrophenyl*)-1,2-*diaminoethane* (**5b**).—Yellow oil (25% yield), b.p. 170 °C/0.5 mmHg (Found: C, 60.7; H, 8.0; N, 17.9. $C_{12}H_{19}N_3O_2$ requires C, 60.7; H, 8.1; N, 17.7%); δ_H($CDCl_3$) 8.06 (d, 2 H, 3′,5′-ArH), 6.51 (d, 2 H, 2′,6′-ArH), 5.37 (br s, 1 H, NH), 3.17 (m, 2 H, $ArNCH_2$), 2.69 (t, 2 H, $ArNCH_2CH_2$), 2.52 [q, 4 H, $N(CH_2CH_3)_2$] and 1.00 [t, 6 H, $N(CH_2CH_3)_2$]; *m*/*z* (%) 237 (M^+, 3), 87 (6) and 86 (100).

N-*Methyl*-N′-(4-*nitrophenyl*)*piperazine* (**5c**).—Bright yellow crystals (63% yield) obtained from ethanol, m.p. 92–93 °C (lit.,[42] 103–104 °C) (Found: C, 59.6; H, 6.8; N, 19.0. $C_{11}H_{15}N_3O_2$ requires C, 59.7; H, 6.8; N, 19.0%); δ_H($CDCl_3$) 8.09 (d, 2 H, 3′,5′-ArH), 6.80 (d, 2 H, 2′,6′-ArH), 3.43 [t, 4 H, $ArNCH_2CH_2)_2N$], 2.54 (t, 4 H, $ArN(CH_2CH_2)_2N$] and 2.35 (s, 3 H, NCH_3); *m*/*z* (%) 221 (M^+, 100) and 220 (14).

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