Arenedicarboximide Building Blocks for Fluorescent Photoinduced Electron Transfer pH Sensors Applicable with Different Media and Communication Wavelengths

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Abstract: *N*-(aminoalkyl)-4-chloronaphthalene-1,8-dicarboximides **1**, *N*-(aminoalkyl)-4-acetamidonaphthalene-1,8-dicarboximides **3** and *N,N′*-bis(aminoalkyl)-perylene-3,4:9,10-tetracarboxydiimides **4** show good fluorescent off–on switching in aqueous alcoholic solution with protons as required for fluorescent PET sensor design. The excitation wavelengths lie in the ultraviolet ($\lambda_{max} = 345$ and 351 nm) for **1** and **3** and in the blue-green ($\lambda_{max} = 528$, 492 and 461 nm) for **4**; the emission wavelengths lie in the violet ($\lambda_{max} = 408$ nm) for **1**, in the blue ($\lambda_{max} = 474$ nm) for **3** and in the yellow-orange ($\lambda_{max} = 543$ and 583 nm) for **4**. Compound **4b** shows substantial fluorescence enhancement with protons when immobilized in a poly(vinylchloride) matrix, provided that 2-nitrophenyl-octyl ether plasticizer and potassium tetrakis(4-chlorophenyl)borate additive are present to prevent dye crystallization and to facilitate proton diffusion into the membrane, respectively.

Keywords: fluorescence · membranes · photoinduced electron transfer · pH sensors · sensors

Introduction

Fluorescence is a powerful sensing technique when expressed through molecular[1] or macroscopic devices.[2] The former offers access to small spaces down to the nanometer domain[3] and allows real-time visualization in micron-scale fields of importance in biology.[4] The latter offers robust and reusable optode systems for monitoring larger scale targets encountered in medical,[5] chemical[6] and environmental[7] science. While several principles are available for the design of fluorescent sensors,[8] photoinduced electron transfer (PET) is particularly valuable in this regard.[9] Briefly, the principle is to bias the competition between PET and fluorescence in a fluorophore–spacer–receptor system. This bias is achieved by allowing the receptor to bind to the chosen analyte. Thus, the presence of the analyte is signalled by a switching on of fluorescence. Fluorescent PET sensors possess the feature of modularity[1c,10] which potentially allows the combination of various fluorophores of different colours with a given receptor provided that certain criteria for PET are met. Here we present a rare instance where a whole family of sensors is constructed from a single simple reaction type involving commercially available materials[11]—arenedicarboxyanhydrides and *ω*-*N*,*N*-dialkylaminoalkylamines. This sensor family possesses amine receptors for protons and several arenedicarboximide fluorophores addressable at different wavelengths. The pH-sensing behaviour of this family is examined in fluid solution and, importantly, in polymer membrane matrices. The latter media are crucial for the application of fluorescent PET sensors as optode macro devices. Fluorophore–spacer–receptor systems have not previously been incorporated into optode macro devices, though an orthogonal fluorophore–receptor system[1c] has been so used recently.[12] The nature of the membrane material and additives are found to be critical determinants of sensor performance.

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Results and Discussion

The design of systems **1a**,**b**, **2**, **3**, **4a**–**c** involved the following considerations. PET processes occur readily between naphthalene and amines in intra[13]- and intermolecular[14] contexts. Naphthalene-1,8-dicarboximide is also a good PET acceptor from amines.[15] Amines cease to be PET donors when they

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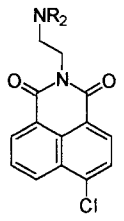
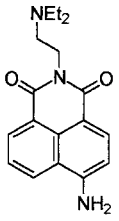
are protonated. The molecular orbital description of fluorescent PET sensing[9a] suggests that the HOMO of the fluorophore must lie lower in energy than the receptor HOMO.



1a; R = Et
1b; R,R = $(CH_2)_2O(CH_2)_2$



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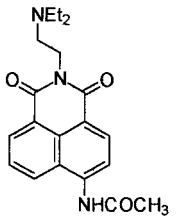

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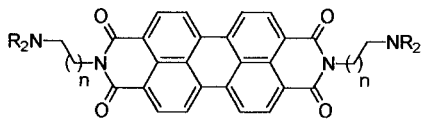

4a; R = H, n = 1
4b; R = Et, n = 1
4c; R = Et, n = 2

Therefore it is very probable that the HOMO of 4-chloronaphthalene-1,8-dicarboximide will lie even lower than that of naphthalene and naphthalene-1,8-dicarboximide, that is, **1a** and **b** should be effective PET sensors for pH.

While the redox potentials of 4-chloronaphthalene-1,8-dicarboximide are not available, estimates can be made from available values for naphthalene-1,8-dicarboximide itself. Samanta and Saroja find that the thermodynamic driving force for PET (ΔG_{PET}) from triethylamine to naphthalene-1,8-dicarboximide is -1.5 eV,[15] according to the Weller equation.[16] Systems analogous to **2** are known to be capable of acting as fluorescent PET sensors provided that the amine receptor is attached by a spacer to the 4-amino position rather than the imide nitrogen since kinetic barriers to PET arise in the latter case.[17] Thus **2** is expected to show little PET sensing activity. In fact, this expectation has been borne out in a previous study by Yuan and Brown.[18] On the other hand, PET thermodynamics are likely to be more favourable in the case of **3** due to the attenuation of the electron-releasing character of the 4-amino group. The origin of the kinetic barrier in **2** also disappears in **3** since the strongly push–pull internal charge transfer (ICT) fluorophore is not present.[17] Perylene-3,4:9,10-tetracarboxydiimides are good electron acceptors[19, 20] and the prognosis for the fluorescent PET sensing activity of **4b** and **c** is favourable. For instance, we can apply Weller's Equation (1)[16] to the case of **4b** and **c**.

$$\Delta G_{PET} = -E_{S\cdot Fluorophore} - E_{red\cdot Fluorophore} + E_{ox\cdot Receptor} - e^2/\varepsilon r \quad (1)$$

The singlet energy of the perylene-3,4:9,10-tetracarboxydiimide fluorophore ($E_{S\cdot Fluorophore}$) can be estimated as 2.3 eV from the value for the *N,N'*-bis(2′,5′-*tert*-butylphenyl) derivative.[19, 21] The same model compound provides an estimate for the reduction potential of the fluorophore ($E_{red\cdot Fluorophore}$) as -0.7 V (vs SCE).[20] The oxidation potential of the receptor ($E_{ox\cdot Receptor}$) can be approximated by the value for triethylamine as $+1.0$ V.[22] The radical ion pairing term ($e^2/\varepsilon r$) is $+0.1$ V.[23] The thermodynamic driving force for PET (ΔG_{PET}) in **4b** and **c** is therefore -0.7 eV. Since primary amines are weak PET donors compared to their tertiary counterparts,[24, 25] the sensing performance of **4a** is likely to be poorer than that of **4b** and **c**. We included some preliminary results concerning the sensing ability of **4a–c** in a 1992 review.[1c] Petkov and coworkers have also noted the proton-induced switching on of the fluorescence of **4b** and **c** in 1994.[26]

Compounds **4a**,[27] **4b**,[28, 26] and **4c**[26] are known from previous studies, none of which examined their detailed pH-sensing behaviour. Compounds **1a** and **b**, **2** and **4a–c** were synthesized according to one-step procedures; **3** was prepared from **2** by acetylation. These general procedures are available in the literature because 4-aminonaphthalene-1,8-dicarboximides and perylene-3,4:9,10-tetracarboxydiimides have been useful compounds in areas other than sensing. 4-Chloronaphthalene-1,8-dicarboximides frequently serve as synthetic precursors of their 4-amino counterparts.[24] 4-Aminonaphthalene-1,8-dicarboximides have found use as antitumour agents,[29] fluorescent cell markers and stains,[30] laser dyes,[31] solar collectors,[24] fluorescent flaw detectors[32] and models for PET processes.[17, 33, 34] Perylene-3,4:9,10-tetracarboxydiimides have been used as laser dyes,[35] solar collectors[32] and reprographic media,[36, 37] especially when good photostability is sought.[38–40]

The absorption spectra of **1a** and **b** are independent of pH in all respects, as required of an ideal fluorescent PET sensor for protons. The relevant parameters are collected in Table 1. The 4-chloronaphthalene-1,8-dicarboximide fluorophore is essentially devoid of ICT character in the (Franck–Condon or thexi) excited state. The situation for **3** is similar. Even though the 4-aminonaphthalene-1,8-dicarboximide fluorophore possesses considerable ICT character,[41, 17] the extensive delocalization of the negative charge over the arenedicarboximide group reduces any interaction across the spacer with the protonated amine receptor to very low levels[17] in the case of **2**. The absorption spectra of **4a–c** do not show any pH-dependent band shifts, since the perylene-3,4:9,10-tetracarboxydiimide fluorophore does not give rise to ICT excited states.[19–21] However, in the case of **4b** and **c**, there are significant pH-dependent changes in band height (Figure 1) which suggest reversible aggregation processes at alkaline pH values. Analysis of these absorbance (A) changes according to Equation (2)[42] gives the pK_a values listed in Table 1.

$$\log[(A_{max} - A)/(A - A_{min})] = pH - pK_a \quad (2)$$

Only one pK_a value is found experimentally for these diamines since the two amines are widely separated and hence their pK_a values should only differ by the statistical value of 0.3.[43] The pK_a values of 9.5 and 10.1 for **4b** and **4c** are in the range expected for the tertiary amine receptor with an electron-withdrawing imide some distance away. Compound

Table 1. Optical and protonation properties of systems **1a**,**b**, **2**, **3**, **4a**–**c**.[a]

Property	**1a**[b]	**1b**[b]	**2**	**3**	**4a**	**4b**	**4c**
$\lambda_{max\cdot Abs}$ (nm)	346	345	434	351	527, 492, 457	529, 494, 463	528, 492, 461
log ε_{max} ($M^{-1}cm^{-1}$)	4.2	4.2	4.1[c]	4.5	4.8,[d] 4.6, 4.2	4.9, 4.8, 4.6	5.0, 4.8, 4.4
pK_a	–[e]	–[e]	9.7	9.8	–[e]	9.5, 4.2	10.1
$\lambda_{max\cdot Flu}$ (nm)	408	407	548	474	542, 582	543, 582	543, 582
FE	56	25	0.8	10	2.6	11	46
pK_a'	9.8	6.0	10.0	10.0	9.9	9.7, 4.6	9.9

[a] MeOH/H_2O (1:4, *v*/*v*) was used as solvent for **1**–**3** but the less soluble **4a--c** were examined in EtOH/H_2O (1:1, *v*/*v*), with NaCl (0.1M) for ionic strength control unless noted otherwise. All the λ_{max} values in both absorption and emission are essentially independent of pH, except in the case of $\lambda_{max\cdot Flu}$ value of **2**, which has a small hypsochromic shift of 6 nm in basic solution, and the $\lambda_{max\cdot Abs}$ value of **3**, which shows a small bathochromic shift of 6 nm in basic solution. The fluorescence emission of **1a** and **b** is so low in basic solution that a $\lambda_{max.Flu}$ value could not be determined. Fluorescence experiments are performed with excitation at wavelengths where there is no pH dependence of absorbance. [b] Model fluorophore **1c** has the following parameters: $\lambda_{max\cdot Abs} = 341$ nm, $\lambda_{max\cdot Flu} = 410$ nm. [c] In EtOH, from ref. [18]. [d] In HCO_2H, from ref. [27]. [e] Absorbance changes are too small to permit reliable determination of pK_a value.

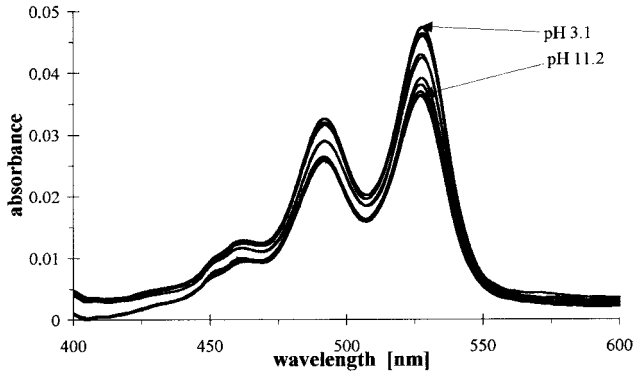

Figure 1. pH dependence of the absorption of **4b**.

4c yields the higher value owing to the longer trimethylene spacer. For comparison, 1-amino-2-diethylaminoethane and 1-amino-3-diethylaminopropane have pK_a values (for the monoprotonated species) of 9.9 and 10.6 respectively.[44] The lower pK_a value of 4.2 detected for **4b** is probably characteristic of the aggregate.

As Figure 2 shows, the fluorescence emission spectra of **1a** and **3** are smoothly pH-dependent with proton-induced fluorescence enhancements (FE) of 1–2 orders of magnitude. Thus the PET sensor design is justified. The preservation of the emission band position and shape across the pH range is typical.[1c, 9a] The smaller proton-induced FE value of **1b** compared with **1a** is a result of the slower PET rate arising from the morpholino nitrogen centre of higher oxidation potential than diethylamino nitrogen.[45] The pH dependence of fluorescence intensity can be analyzed with Equation (3)[1c, 9a] giving the pK_a' values listed in Table 1. The

$$\log[(I_{Fmax} - I_F)/(I_F - I_{Fmin})] = pH - pK_a' \quad (3)$$

pK_a' values are so designated in order to distinguish them as fluorimetrically determined quantities unlike the pK_a values obtained absorptiometrically.[11] Since the receptor units of these supramolecular systems remain in the ground state in these studies, the pK_a' values are different from pK_a^* values commonly discussed in the fluorescence literature concerning electronically excited receptors.[46] Therefore the present pK_a' values remain in line with expectations of ground-state physical organic chemistry.[47]

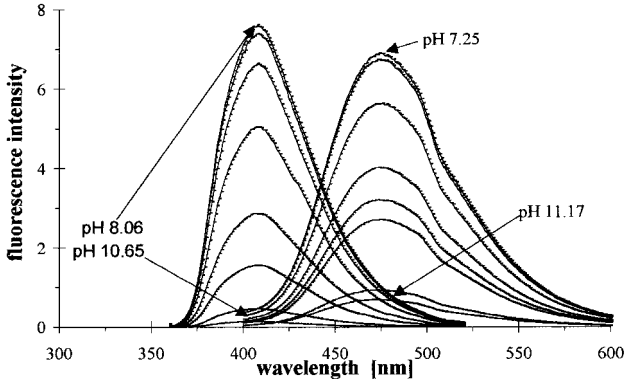

Figure 2. pH dependence of fluorescence emission spectra of 10^{-5} mol L of **1a** (left) and **3** (right) in MeOH/H_2O (1:4, *v*/*v*). The pH values are, in order of decreasing intensity, 8.06, 9.03, 9.55, 9.81, 9.93, 10.03, 10.32 and 10.65 for **1a** and 7.25, 9.61, 9.83, 9.97, 10.08, 10.17, 10.62 and 11.17 for **3**. The excitation wavelengths are 355 nm for **1a** and 320 nm for **3**.

System **2** shows a small pH dependence of fluorescence in the direction opposite to that expected of a PET off–on sensor for protons. The kinetic barrier to PET that can arise in the excited state of 4-aminonaphthalene-1,8-dicarboximide[17] has been pointed out earlier. The lack of PET sensing ability of **2** has been reported previously by Yuan and Brown.[18] The small amount of proton-induced fluorescence quenching in **2** is due to intramolecular hydrogen bonding of the protonated amine receptor to a carbonyl group of the fluorophore in its ICT excited state.[17, 48] The pK_a' value (10.0) corresponding to this behaviour is virtually identical to the pK_a' values observed for similar diethylamino sidechains in **1a** and **3**. The fluorescence of **2** undergoes strong and irreversible quenching in alkaline media (pH > 11) due to hydrolysis.

The pH-dependent fluorescence properties of **4a**–**c** were eagerly awaited because of the long communication wavelengths exhibited by these molecules. Long-wavelength excitation reduces problems of autofluorescence and scattering during fluorescent sensing within many biological and industrial matrices.[49] Furthermore, the prospect of employing blue-light-emitting diodes for visible excitation bodes well for the construction of macro devices. While porphyrin–tin(IV)[50] and tris(bipyridyl)ruthenium(II)[51] systems have been used for pH sensing with visible excitation, the former requires excitation at the more intense Soret band at 423 nm ($\varepsilon =$

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$8.4 \times 10^5\,M^{-1}cm^{-1}$) rather than the weak Q band at 577 nm ($\varepsilon = 1.4 \times 10^4\,M^{-1}cm^{-1}$). The latter systems are best excited at 473 nm ($\varepsilon = 6.8 \times 10^3\,M^{-1}cm^{-1}$).

The attraction of **4a–c** is that they potentially allow wavelengths up to 528 nm with ε values of up to $8.0 \times 10^4\,M^{-1}cm^{-1}$.[26] In the event, the fluorescence of **4a** and **c** is conveniently excitable at the isosbestic points of 470 nm and that of **4b** at 452 nm. The longer wavelength of 528 nm can also be used with suitable correction for absorbance changes if so desired. The fluorescence emission spectra of **4a–c** are smoothly dependent on pH. An example (for **4b**) is presented in Figure 3. The main pH dependence of fluorescence

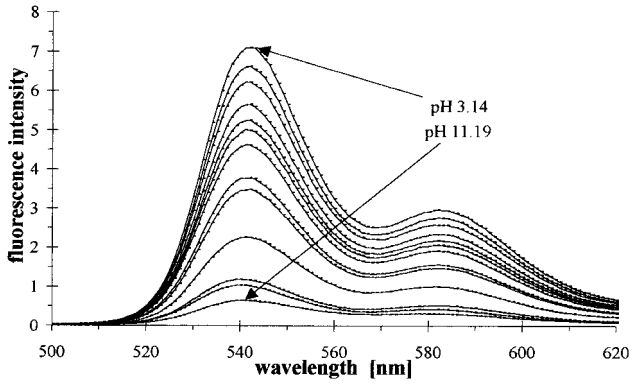

Figure 3. Fluorescence spectra of compound **4b**, excited at 452 nm, in an EtOH/H_2O mixture (1:1, *v*/*v*). The pH values are, in order of decreasing intensity, 3.10, 4.31, 4.45, 4.67, 4.85, 5.15, 7.45, 9.45, 9.63, 9.85, 10.10, 10.19 and 11.19.

intensity gives rise to pK_a' values of 9.7–9.9 after analysis with Equation (3). As noted under the discussion of pH-dependent absorption spectra, only one pK_a' value will emerge from such measurements on these diamines. Of course, the fluorescence will only be switched on when both of the amine receptors are protonated.[43] These pK_a' values for **4b** and **c** are in close agreement with the corresponding pK_a values obtained from the pH-dependent absorption spectra discussed above. This has been found to be the case in PET pH sensors irrespective of the fluorophore type.[52] The pK_a' value of **4a** also lies in the expected range. The proton-induced FE values are over an order of magnitude greater for **4b** and **c** as expected for well-behaved PET sensors.

The observation that the highest FE value in this set is seen for **4c** in spite of its longest spacer suggests that the trimethylene unit is undergoing folding in these aggregation-prone molecules. Folding of trimethylene chains brings terminal groups closer together than in dimethylene chains, as found in the classical Hirayama rule for intramolecular excimer formation.[53] The FE values decrease upon increasing the spacer length from di- to trimethylene in more soluble PET sensors where such folding is less likely.[52] Further evidence for the aggregation tendency is the observation of a second step with $pK_a' = 4.6$ in the fluorescence intensity/pH profile of **4b**. This second step was also detected by pH-dependent absorption spectroscopy as noted above. Such aggregation effects can be minimized by working with very dilute solutions of these sensor molecules. Their detectability remains high owing to their high extinction coefficients and their high fluorescence quantum yields. Case **4a** has a noticeably lower, but still useful, FE value than its relatives **4b**,**c**. Primary amines are much less oxidizable than their tertiary amine counterparts[22] and hence the probability of PET in the unprotonated form of **4a** is significantly less. Recent examples of this phenomenon are found in 9-aminomethylanthracenes[25] and 3-(2′-aminoethyl)amino benzimidazo[2,1-a]benz[*de*]isoquinolin-7-ones.[52]

Figure 4 displays the fluorescence emission spectra of **4b** embedded in a poly(vinylchloride) (PVC) matrix with 2-nitrophenyloctyl ether (NPOE) plasticizer and potassium

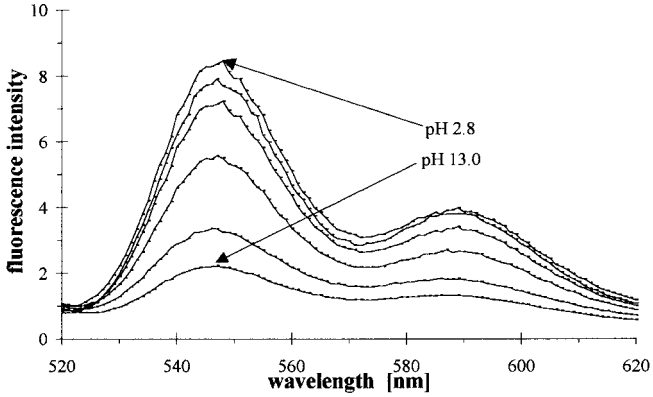

Figure 4. Excitation and emission spectra of **4b** in a plasticized PVC membrane. Emission spectra, excited at 497 nm, were acquired at pH values (in order of decreasing intensity) of 2.8, 7.0, 10.0, 11.08, 12.0 and 13.0.

tetrakis(4-chlorophenyl)borate (PTCB) additive as a function of pH of the contacting solution. The spectral positions and shape are in reasonable agreement with the aqueous alcohol data in figure 3. The temporal response (< 100 s) is seen in Figure 5. Analysis of the information in Figure 4 according to

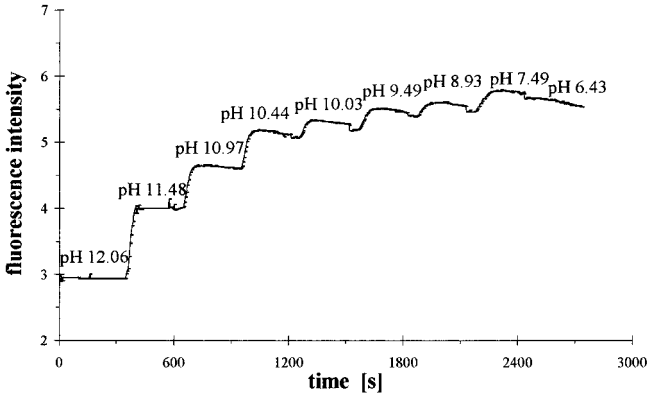

Figure 5. Response time and relative signal change of membrane **4b** containing PTCB additive.

Equation (3) gives a pK_a' value of 11.6, which is considerably larger than the corresponding value found in aqueous alcoholic solution. This is to be expected since the membrane exerts a substantial matrix effect on protonation equilibria.[3, 54] Compound **4c**, under similar conditions, yields a pK_a' value of 11.9. The proton-induced FE values are also

reduced from the values seen in aqueous alcoholic solution. Values of 4.0 and 3.5 are found for membrane-embedded **4b** and **4c**, respectively. Both inter-[16] and intramolecular[55] PET are known to be retarded in less polar media. More viscous media have the same effect.[56, 57] Nevertheless, the pH response of these visibly excitable optode macro devices are clearly large enough to be useful. An additional positive feature is that there is no evidence of any aggregation of the dyes within the membrane under these conditions.

The essential role of the PTCB additive is again underlined by the fact that pH-dependent emission spectra of **4b** or **4c** cannot be observed in its absence. The NPOE plasticizer also proved to be irreplaceable, in spite of its undesirable yellow colour, since the use of the colourless 2-cyanophenyloctyl ether (CPOE) derivative resulted in leaching of the dye or its crystallization. Attempts to replace the PVC membrane with a hydrogel led to small pH responses or none at all.

Compounds **1a** and **2** leach rapidly (ca. 5 min) from PVC/NPOE membranes when contacted with aqueous pH buffer solutions. The addition of lipophilic borate salts such as PTCB stabilizes against dye leaching.[58] It also improves selectivity and response by aiding attainment of electroneutrality by ion exchange. Optical sensory macro devices require such mass transfer to establish equilibrium between the analyte phase and the membrane matrix.[59] The short communication wavelengths of **2** lead to a poor fluorescence signal against the fluorescence background from the membrane support. The relatively high fluorescence quantum yield of **1a** produces a measurable signal above the background in spite of the short wave excitation required. However, the pH-responsive fluorescence intensity change is small (ca. 10%) and in the opposite direction to that seen in aqueous alcoholic solution. The fluorescence signal from **1a** embedded in the membrane is largely unaltered by pH changes. The effects due to the lower polarity and higher viscosity of membrane media discussed in the previous paragraph are obviously of major consequence here. The small (ca. 10%) quenching effect corresponding to a pK_a' value of 10.1 seen in less basic solution can be assigned to ion-pairing of the tetrakis(4-chlorophenyl)borate anion with the protonated **1a**.

Conclusion

The aminoalkyl arenecarboximides are shown to be a versatile family of fluorescent PET pH sensor molecules with the advantages of one-step synthesis, the availability of a range of appropriate starting materials and the accessibility of communication wavelengths spanning the rainbow. When incorporated in plasticized polymer membranes containing lipophilic borate salts, the longer wavelength members show promise as optode macro devices for pH monitoring.

Experimental Section

UV-visible absorption spectra were recorded on Perkin–Elmer Lambda 9 and Hitachi U-3000 spectrophotometers. Fluorescence emission and excitation spectra were obtained with Perkin–Elmer LS-5B and Aminco Bowman Series 2 instruments. The general conditions are given in Table 1. General Electric QE300 and Bruker AC250 nuclear magnetic resonance spectrometers and VG MS902 and Varian MAT 311A mass spectrometers were also employed for data gathering. The recommended corrections[60] were applied to the measured pH values[61] in aqueous alcoholic solutions. The conditions used for the spectroscopic studies in aqueous alcoholic solution are given in the footnotes to Table 1.

The polymer membranes required for optode macro devices were prepared in several stages. Dye–polymer–plasticizer–additive cocktails consisting of dye in PVC polymer–NPOE plasticizer–PTCB lipophilic borate additive were formulated in THF with a PVC/THF ratio of 13.5 mg mL^{-1}. The solute composition was PVC (34.5%)–NPOE (63.2%)–PTCB (1.7%) (*w*/*w*). The dye content was determined by its solubility in the plasticizer at saturation. 100 μL of the dye–polymer–THF cocktail was dropped onto a dust-free polyester support of 125 μm thickness and 25 mm diameter (Goodfellow Cambridge LS146585). The membranes were conditioned by exposure to a THF-saturated atmosphere for 4 hours followed by further exposure to ambient air for another hour. Final conditioning was accomplished by placing the membrane in a flow-through fluorescence cell and pumping 0.1M NaCl solution until a constant fluorescence signal was obtained. The fluorescence signal was recorded from a front-face configuration.

***N*-(2′-Diethylaminoethyl)-4-chloronaphthalene-1,8-dicarboximide (1a)**: *N,N*-diethylaminoethylamine (1.45 g, 12.5 mmol) was added to a suspension of 4-chloronaphthalene-1,8-dicarboximide (2.91 g, 12.5 mmol) in toluene (30 mL). The mixture was then refluxed for 4 hours, after which the solvent was evaporated under vacuum. The residue was then dissolved in hydrochloric acid (1.0M), washed with dichloromethane, basified with sodium carbonate (1.0M) and extracted with dichloromethane. The solvent was evaporated under vacuum and the product crystallized from ethanol. Yield 60%. M.p. 104°C; MS: *m*/*z* (%) = 332 (1%) [M^+(Cl^{37})], 330 (4%) [M^+(Cl^{35})]; $C_{18}H_{19}N_2O_2Cl$ (332): calcd C 65.35, H 5.79, N 8.47, Cl 10.72; found C 65.01, H 5.46, N 8.19, Cl 10.57; ^{1}H NMR ($CDCl_3$): δ = 8.65 (d, 1H, 7-Ar*H*), 8.59 (d, 1H, 2-Ar*H*), 8.50 (d, 1H, 5-Ar*H*), 7.83 (m, 2H, 3,6-Ar*H*), 4.28 (t, 2H, OCNCH_2), 2.78 (t, 2H, CH_2N(CH_2)$_2$), 2.63 (q, 4H, N(CH_2)$_2$), 1.07 (t, 6H, CH_3).

***N*-(2′-Morpholinoethyl)-4-chloronaphthalene-1,8-dicarboximide (1b)**: Obtained from 4-(2′-aminoethyl)morpholine according to the procedure for **1a**. The product was crystallized from ethanol. Yield 45%. M.p. 158°C; MS: *m*/*z* (%) = 346 (1%) [M^+(Cl^{37})], 344 (3%) [M^+(Cl^{35})]; $C_{18}H_{17}N_2O_3Cl$ (346): calcd C 62.70, H 4.97, N 8.12; found C 62.23, H 4.73, N 7.88; ^{1}H NMR ($CDCl_3$): δ = 8.65 (d, 1H, 7-Ar*H*), 8.59 (d, 1H, 2-Ar*H*), 8.50 (d, 1H, 5-Ar*H*), 7.83 (m, 2H, 3,6-Ar*H*), 4.35 (t, 2H, OCNCH_2), 3.65 (t, 4H, (CH_2)$_2$O), 2.72 (t, 2H, CH_2N(CH_2)$_2$), 2.57 (t, 4H, N(CH_2)$_2$).

***N*-*n*-Butyl-4-chloronaphthalene-1,8-dicarboximide (1c)**: Obtained from *n*-butylamine according to the procedure for **1a**. The product was crystallized from glacial acetic acid. Yield 60%. M.p. 180°C; MS: *m*/*z* (%) = 289 (1%) [M^+(Cl^{37})], 287 (4%) [M^+(Cl^{35})]; $C_{16}H_{14}NO_2Cl$ (287.0713): found 287.0801; ^{1}H NMR ($(CD_3)_2SO$): δ = 8.59 (m, 2H, 2,7-Ar*H*), 8.39 (d, 1H, 5-Ar*H*), 7.96 (m, 2H, 3,6-Ar*H*), 4.05 (t, 2H, NCH_2), 1.57 (dd, 2H, N CH_2CH_2), 1.30 (m, 2H, C$H_2$$CH_3$), 0.89 (t, 3H, C$H_3$).

***N*-(2′-Diethylaminoethyl)-4-acetamidonaphthalene-1,8-dicarboximide (3)**: *N*-(2′-diethylaminoethyl)-4-aminonaphthalene-1,8-dicarboximide (**2**; 1.0 g, 3.2 mmol), acetic anhydride (5 mL) and glacial acetic acid (10 mL) were refluxed with magnetic stirring for 45 minutes. The product crystallized on cooling and was recrystallized from glacial acetic acid. Yield 70%. M.p. 135°C; $C_{20}H_{23}N_3O_3$ (353.33): calcd C 67.97, H 6.56, N 11.89; found C 67.76, H 6.28, N 11.72; ^{1}H NMR (CD_3OH): δ = 7.8–8.7 (m, 5H, Ar*H*), 4.5 (t, 2H, OCNCH_2), 3.4 (m, 6H, NCH_2), 2.3 (s, 3H, CH_3CO), 1.4 (t, 6H, CH_3).

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