A small supramolecular system which emulates the unidirectional, path-selective photoinduced electron transfer (PET) of the bacterial photosynthetic reaction centre (PRC)

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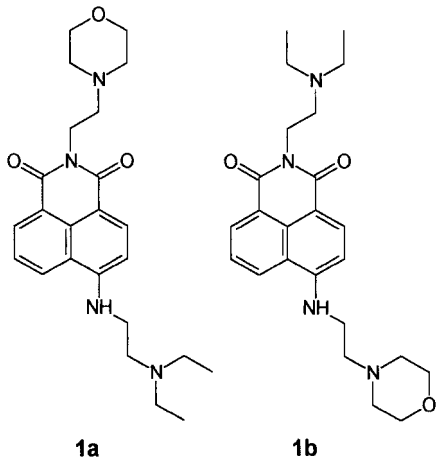
The singlet excited state of the 4-aminonaphthalimide fluorophore in 1a and 1b directs electron transfer from intramolecular but external amine groups along only one of two available paths.

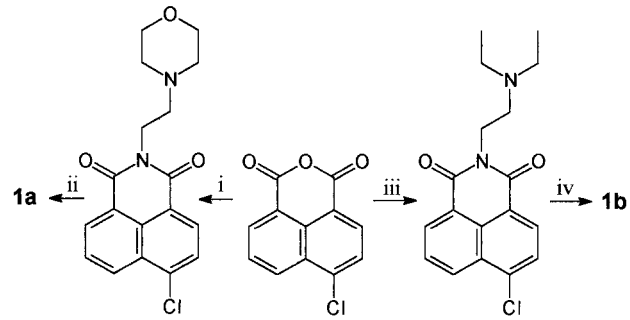
The availability of high-resolution X-ray structural information concerning the engines of photosynthesis, such as the bacterial reaction centres[1] and the antenna complexes,[2] challenges chemists to emulate their functions.[3] One of the most enigmatic aspects of PRC function is the unidirectional, path-selective electron transfer from the photoexcited porphyrin special pair to a quinone moiety along the L-branch rather than the symmetry-related M-branch. The path-selectivity in the PRC was established by picosecond transient absorption signatures which distinguished between the nearly identical bacterichlorophyll stations along the two possible electron paths.[4] In the present instance, we use pH-dependent steady-state fluorescence spectroscopy to distinguish between the two possible PET paths in a small supramolecular system[5] by means of the acid–base characteristics of two rather similar amine PET donors. As an additional point of interest, unidirectionality is much sought after in several research areas of photoscience and molecular electronics.[6] We now provide a simple basis for unidirectionality in PET processes.

Many aminoalkyl substituted fluorophores show weak fluorescence in basic solution owing to rapid PET from the amine unit to the fluorophore. Protonation of the amine arrests this PET process and causes a sharp fluorescence recovery.[7] We use the fluorescent 4-aminonaphthalimide chromophore[8] as the core of our system **1** since its photogenerated molecular-scale



1a **1b**

electric field can be used to control electron transfer rates.[9] Two nearly identical PET paths are provided for the fluorophore to choose from, in the form of two dialkylaminoethyl sidechains only differing in their dialkyl substituents. Such a choice of PET paths is also available to the porphyrin special pair in the PRC. The thermodynamic driving force for PET is equal in **1a** and **1b** for any given amine receptor. **1a** and **1b** are isomers which differ only in the placement of one oxygen and two hydrogen atoms at the termini. So the major difference between **1a** and **1b** regarding PET is the relative orientation of the photogenerated electric field of the 4-aminonaphthalimide excited state towards a given amine receptor. Supramolecular systems composed of a fluorophore flanked by two dissimilar receptors are also useful as selective sensors[10] and as AND logic gates.[11] Synthesis of **1a** and **1b**† is easily achieved in two steps (Scheme 1) starting from commercially available materials.



Scheme 1 *Reagents* i, 2-(morpholino)ethylamine, PhMe; ii, 2-(diethylamino)ethylamine; iii, 2-(diethylamino)ethylamine, PhMe; iv, 2-(morpholino)ethylamine.

The electronic absorption and fluorescence emission spectra of **1a** and **1b** are measured as a function of pH. The absorption spectra show variations across some pH ranges. These absorbance (A) changes are analyzed according to eqn. (1)[12] and the pK_a values obtained are given in Table 1. The variations in fluorescence emission spectra are largely confined to changes in the quantum yield (ϕ_{Flu}). These are plotted in Fig. 1 and analyzed according to eqn. (2).[13]

Table 1 Optical and acid–base parameters of **1a** and **1b**[a]

	1a	**1b**
$\lambda_{Abs\ pH\ =\ 3.0}$/nm (log ε)[b]	432 (4.19)	433 (4.21)
$\lambda_{Abs\ pH\ =\ 7.0}$/nm (log ε)[b]	432 (4.19)	452 (4.23)
$\lambda_{Abs\ pH\ =\ 10.8}$/nm (log ε)[b]	450 (4.20)	452 (4.23)
$\lambda_{Isosbestic}$	439	437
pK_a (morpholinoethyl)[c]	—[d]	5.8
pK_a (diethylaminoethyl)[c]	8.6	—[d]
λ_{Flu}/nm[e]	526	524
$\phi_{Flu\ pH\ =\ 3.0}$	0.53	0.52
$\phi_{Flu\ pH\ =\ 7.0}$	0.66	0.062
$\phi_{Flu\ pH\ =\ 10.8}$	0.030	0.070
$FE_{pH\ =\ 3.0/pH\ =\ 7.0}$[f]	0.81	8.4
$FE_{pH\ =\ 7.0/pH\ =\ 10.8}$[f]	21	0.83
pK_a' (morpholinoethyl)[g]	5.8	5.7
pK_a' (diethylaminoethyl)[g]	8.7	9.1

[a] 10^{-5} M **1a** or **1b** in aerated H_2O–MeOH (1 : 1, v/v). Fluorescence emission spectra are obtained by excitation at the isosbestic wavelength. [b] Extinction coefficient ε in units of dm^3 mol^{-1} cm^{-1}. [c] *via* Absorbance measurements. [d] Absorbance change is not large enough to permit analysis according to eqn. (1). [e] Value changes little with pH. [f] Fluorescence enhancement factor due to protonation in the specified pH range. [g] *via* Fluorescence measurements.

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

$$\log[(\phi_{Flu\,max} - \phi_{Flu})/(\phi_{Flu} - \phi_{Flu\,min})] = pH - pK_a' \quad (2)$$

Considering **1a**, we find there is only one clear sigmoidal step corresponding to proton-triggered fluorescence recovery as expected of a PET system. The fluorescence is enhanced by an order of magnitude. The corresponding pK_a' value (8.7) clearly belongs to the strongly basic diethylaminoethyl unit attached to the 4-amino position. There is a smaller sigmoidal step corresponding to weak fluorescence quenching due to protonation. This is due to the formation of an intramolecular hydrogen bond between the protonated amine and the imide carbonyl oxygen.[14] The corresponding pK_a' value (5.8) can be easily assigned to the morpholinoethyl unit attached to the imide position. We note that the two dialkylamino groups are held far enough apart by the rigid chromophore in **1a** (and **1b**) to prevent mutual perturbation of pK_a values.

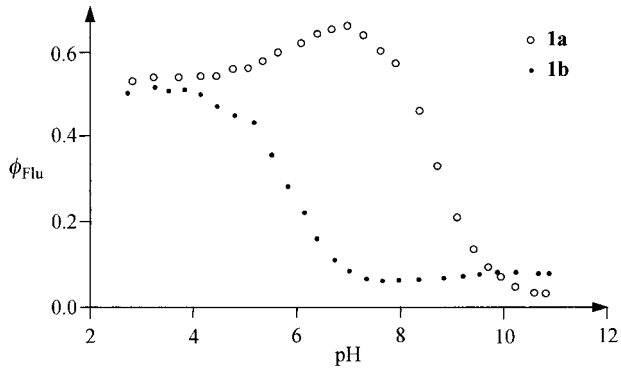


Fig. 1 Fluorescence quantum yields of **1a** and **1b** as a function of pH.

System **1b** shows the fluorescent PET switch behaviour with emission enhancement due to protonation of the morpholinoethyl unit connected to the 4-amino position. The dominant sigmoidal step has pK_a' = 5.7. The minor sigmoidal step has pK_a' = 9.1 which can be associated with the diethylaminoethyl group on the imide position. The slight fluorescence quenching seen upon protonation is again due to the intramolecular hydrogen bonding discussed above for **1a**.

The above analysis shows that in each case the electron transfer originates from the dialkylamino unit attached to the 4-amino position irrespective of the difference in PET driving force for the two alkylamino moieties. In the case of **1b** it is particularly remarkable that the PET path of apparently smaller PET driving force is selected by the supramolecular system. The morpholino unit is clearly a poorer PET donor than the diethylamino group when used in conjunction with porphyrin fluorophores for instance.[15] The PET path selection by the supramolecular system shows the remarkable marshalling efficiency of the excited state dipole of the 4-aminonaphthalimide fluorophore.[9] Unidirectional PET (but not path selectivity) has also been arranged with the ground state dipole of α-helical oligopeptides.[16] Taken together, these results demonstrate the capability of local electric fields to direct electron traffic. It is interesting that local electric fields due to the protein matrix of the PRC are among the possible causes advanced for the path-selectivity of PET.[17]

In conclusion, the simple technique of pH-dependent fluorescence is combined with the carefully designed, but structurally simple supramolecular systems **1a** and **1b** in order to emulate the one-way electron transfer seen within the PRC.

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Notes and references

† **1a**: Found: C, 68.2; H, 7.4; N, 13.1. $C_{24}H_{32}N_4O_3$ requires: C, 67.9; H, 7.6; N, 13.2%. ^{1}H NMR δ 1.09 (t, 6H, CH_3CH$_2$N), 2.63 (t, 4H, NCH_2CH$_2$O), 2.68 (q, 4H, CH$_3$CH_2N), 2.71 (t, 2H, CH_2NCH$_2$CH$_2$O), 2.90 (t, 2H, NCH_2CH$_2$NH), 3.41 (t, 2H, NCH$_2$CH_2NH), 3.71 (t, 4H, NCH$_2$CH_2O), 4.39 (t, 2H, CH_2CH$_2$NCH$_2$CH$_2$O), 6.53 (br s, 1H, NH), 6.67–8.61 (m, 5H, ArH); *m/z*(%) 425 (M^+, 14), 312(63), 100(52), 86(100); **1b**; Found: C, 68.2; H, 7.8; N, 13.3. $C_{24}H_{32}N_4O_3$ requires: C, 67.9; H, 7.6; N, 13.2%. ^{1}H NMR δ 1.13 (t, 6H, CH_3CH$_2$N), 2.58 (t, 4H, NCH_2CH$_2$O), 2.69 (q, 4H, CH$_3$CH_2N), 2.72 (t, 2H, NCH_2CH$_2$NH), 2.84 (t, 2H, CH$_3$CH$_2$NCH_2), 3.44 (t, 2H, NCH$_2$CH_2NH), 3.79 (t, 4H, NCH$_2$CH_2O), 4.29 (br t, 2H, CH_2CH$_2$NCH$_2$CH$_3$), 6.29 (br s, 1H, NH), 6.66–8.60 (m, 5H, ArH); *m.z*(%) 425 (M^+, 13), 326(17), 100(77), 86(100).

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