Proton controlled intramolecular photoinduced electron transfer (PET) in podand linked squaraine–aniline dyads†

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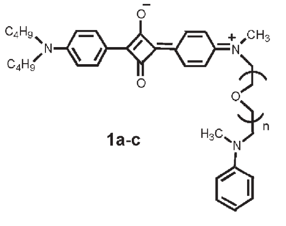
Proton controlled intramolecular PET from an aniline moiety to a squaraine chromophore, attached to podand chains is reported, which to our knowledge is the first example where a squaraine dye is involved as an electron acceptor in an intramolecular PET process, and has implication in the design of PET based sensors.

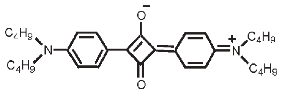
PET is a fascinating phenomenon for chemists and biologists due to its key role in photosynthetic systems[1] and in the design of artificial molecular switches and devices.[2] Upon excitation of a fluorophore, an electron of the HOMO is promoted to the LUMO, which enables transfer of an electron from the donor to the fluorophore, causing fluorescence quenching of the latter, which can be controlled with the aid of external stimuli. This idea has been cleverly exploited by de Silva and coworkers to design a variety of PET based chemosensors[3] and molecular logic gates.[4] Among different organic dye based fluorophores, squaraine dyes are known for their wide applications in material science[5] and in the design of low band gap polymers[6] and chemosensors[7,8] due to their intense absorption and emission properties, which are sensitive to their surrounding medium. From the view point of PET, there are a few reports describing electron transfer from a squaraine moiety to electron deficient systems.[9,10] However, the electron accepting property of squaraines is rather unknown. Herein we report an intramolecular PET in a podand tethered squaraine–aniline dyad where electron transfer takes place from an aniline moiety (donor) to a squaraine moiety (acceptor).

The photophysical properties of compounds **1a–c**, **2** and **3** are shown in Table 1.‡



1a-c

n = 1, 2, 4



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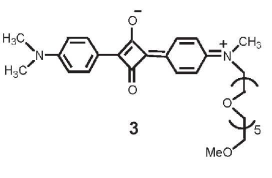

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They showed a sharp absorption around 636 nm and emission around 665 nm. However, the quantum yields (Φ_f) of **1a–c** were low when compared to those of **2** and **3**. Interestingly, the quantum yields of emission and the corresponding excited state lifetimes of **1a–c** are found to increase as the podand chain length increased from *n* 1 to 4. We speculated that the observed photophysical properties of **1a–c** could be the result of a possible intramolecular PET from the aniline moiety to the squaraine moiety. Redox potentials of *N*,*N*-dimethylaniline (0.53 V) and the squaraine dye **2** (−1.28 V) in acetonitrile revealed a favorable free energy for PET between the two when tethered to a flexible chain. The free energy of the electron transfer (ΔG_{el}) from the singlet excited states of the donor to the acceptor was calculated using the Rehm–Weller equation and was found to be −0.17 eV in acetonitrile. To confirm the role of electron transfer in the fluorescence quenching process, we carried out titration studies using trifluoroacetic acid (TFA) against **1a–c** and **2**. The initial addition of TFA to **1a–c** did not significantly affect the absorption spectrum. However, addition of TFA in higher concentrations induced significant changes in the absorption spectrum. The 636 nm band decreases in intensity, and new bands appeared at shorter wavelengths. Interestingly, initial additions showed an increase in the fluorescence emission properties of **1a–c** though the absorption spectra remain unchanged. Titration of TFA against **1a** showed an increase in the fluorescence intensity ($\Phi_f = 0.06$) and reached a maximum value ($\Phi_f = 0.1$) which started decreasing on further addition of TFA (Fig. 1). The initial enhancement in fluorescence is attributed to the protonation of the aniline group, which prevents the possible electron transfer to the squaraine dye. Further addition of TFA results in the protonation of the oxygen anions of the central cyclobutene ring and then on the anilinic nitrogen atom of the squaraine dye which disrupts the conjugation of the molecule resulting in the quenching of the emission.

While **1a–c** showed increase in emission during the initial addition of TFA, **2** and **3** showed a continuous decrease in emission (ESI†). Excited state fluorescence decay profiles of **2** showed a single exponential decay with a lifetime of 555 ps

Table 1 Photophysical properties[a] of **1a–c**, **2** and **3**

Compound	λ_{abs}/nm	λ_{em}/nm	Φ_f[b]	τ/ps
1a	636	665	0.06	200
1b	636	665	0.08	275
1c	636	666	0.09	299
1a + 0.95 mM TFA	637	664	0.1	365
1a + 5 mM TFA	658, 551, 520	661	—	—
2	636	664	0.15	555
3	631	658	0.2	560

[a] Average of three measurements. [b] Fluorescence quantum yields are calculated using 4,4-[bis(*N*,*N*-dimethylamino)phenyl]squaraine dye as standard ($\Phi_f = 0.7$ in $CHCl_3$), error *ca.* ±5%. $\lambda_{ex} = 590$ nm.

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† Electronic supplementary information (ESI) available: Change in absorption and emission spectra of **1**, **2** and **3** with TFA. Change in absorption spectrum of **2** with DMA. See http://www.rsc.org/suppdata/cc/b4/b412913j/

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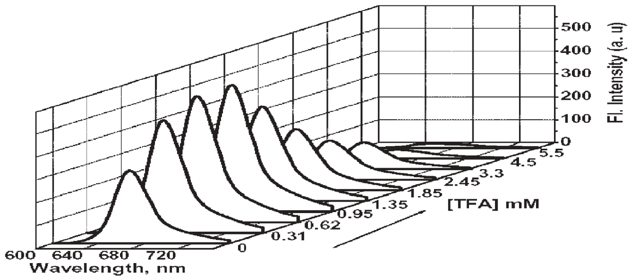

Fig. 1 Change in fluorescence intensity of **1a** (5.53 μM) with the gradual addition of TFA from 0 to 5 mM

whereas **1a** had a lifetime of 200 ps (Fig. 2). Partial protonation of **1a** with TFA gave a biexponential decay with a lifetime of 365 ps (55%) and 200 ps (45%). The fluorescence decay of the fully protonated **1a** followed a single exponential decay with a lifetime of 365 ps. The protonation induced increase in the lifetime of **1a** is an indication of the decrease in the electron transfer efficiency from the aniline moiety. Interestingly, **1b** and **1c** showed lifetimes of 275 and 299 ps respectively, which revealed a distance dependent PET. The calculated rates of electron transfer for **1a**, **1b** and **1c** are 3.2×10^9 s^{-1}, 1.83×10^9 s^{-1} and 1.54×10^9 s^{-1}, respectively.

PET between squaraine and aniline moieties is confirmed by the quenching of the fluorescence of the later upon addition of *N*,*N*-dimethylaniline (DMA). Addition of DMA to a solution of **2** (5.3×10^{-6} M) did not show any considerable change in the absorption spectrum, whereas strong quenching of the fluorescence could be observed (Fig. 3). On the basis of the fluorescence titration data, the calculated bimolecular Stern–Volmer quenching rate constant for **2** was found to be 8.41×10^9 M^{-1} s^{-1}. The observed high fluorescence quenching rate constants and the favorable change in free energy ($\Delta G = -0.17$ eV in acetonitrile) indicate that DMA moiety is capable of donating electrons to the squaraine moiety. Thus the observed low fluorescence quantum yields of **1a–c** and the protonation induced enhancement in the emission are justified by the intramolecular PET from the tethered aniline to the squaraine moiety.

In summary, we have demonstrated a proton switchable intramolecular PET from an aniline moiety to a tethered squaraine dye which is supported by the absorption, emission and lifetime changes of **1a** upon titration with TFA. Detailed photophysical studies and the design of squaraine based PET sensors are underway.

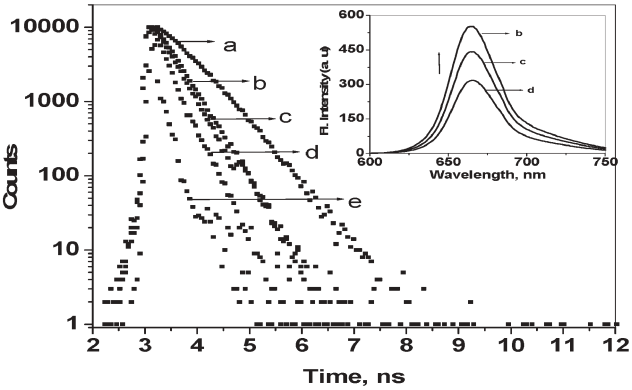

Fig. 2 Fluorescence decay profiles of (a) **2** (5.38 μM), (b) **1a** (5.53 μM) with 0.96 mM TFA, (c) **1a** (5.53 μM) with 0.48 mM TFA, (d) **1a** (5.53 μM), (e) lamp profile. Inset shows the corresponding variation in fluorescence intensity of **1a**.

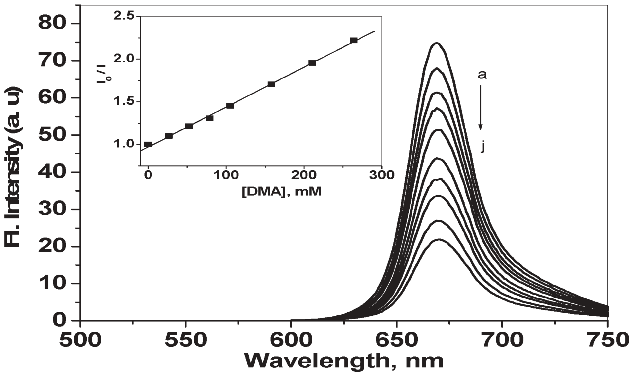

Fig. 3 Effect of DMA on the fluorescence emission spectra of **2** (5.3 μM) in acetonitrile. [DMA] (a) 0, (b) 26.38, (c) 52.76, (d) 79.14, (e) 105.5, (f) 158.28, (g) 211.04, (h) 263.38, (i) 369.32 and (j) 474.84 mM. Inset shows the Stern–Volmer plot for the quenching of **2** with DMA. $\lambda_{ex} = 580$ nm.

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Notes and references

‡ The synthesis and characterization of **1a** are reported in ref. 8. Characterization data of **1b** and **1c** are given here. **1b**: Yield 34%; FT IR (KBr): *v* 1582, 1387, 1348, 1268, 1169, 1108, 1030, 785 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.96–1.01 (t, 6H, $-CH_3$), 1.25–1.38 (m, 8H, $-CH_2$), 2.95 (s, 3H, $-NCH_3$), 3.15 (s, 3H, $-NCH_3$), 3.43–3.67 (m, 16H, $-NCH_2$ and $-OCH_2$), 6.65–6.9 (m, 7H, aromatic), 7.18–7.23 (t, 2H, aromatic), 8.34–8.38 (dd, 4H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.81, 20.18, 29.6, 38.86, 39.6, 51.1, 52.2, 52.4, 68.7, 69.1, 70.64, 112.12, 112.2, 112.33, 116.4, 119.8, 122.1, 129.4, 132.6, 133.8, 153.7, 153.9, 183.4 ppm. **1c**: Yield 35%; FT IR (KBr): *v* 1584, 1387, 1346, 1175, 1134, 1118, 1031 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.96–1.01 (t, 6H, $-CH_3$), 1.25–1.43 (m, 8H, $-CH_2$), 2.96 (s, 3H, $-NCH_3$), 3.18 (s, 3H, $-NCH_3$), 3.35–3.7 (m, 24H, $-NCH_2$ and $-OCH_2$), 6.65–6.78 (m, 7H, aromatic), 7.18–7.23 (t, 2H, aromatic), 8.34–8.38 (dd, 4H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.84, 20.2, 29.6, 29.67, 38.86, 39.62, 51.1, 52.3, 52.4, 68.51, 68.56, 70.6, 70.63, 70.85, 112.1, 112.3, 112.38, 116.2, 119.43, 120.02, 129.13, 132.8, 133.56, 153.75, 154, 183.4 ppm.

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