Ground and Excited State Properties of Some New Highly Water Soluble N-Substituted Thiazine Dyes for Photogalvanic Applications

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Increasing remote cationic charge on the thiazine dye chromophore greatly suppresses ground state aggregation in water, increases the rate constants for intersystem crossing and quenching of the triplet state (T_1) by Fe^{II}, and the fraction of T_1 reduced by Fe^{II}, but does not affect the self-quenching of T_1 by the ground state.

The photoreduction[1] of thiazine dyes such as thionine (**1**) and methylene blue (**2**) by iron(II) is of interest in the development of more efficient photogalvanic[2,3] cells. The solubilities of (**1**) and (**2**) in water are however far too low for photogalvanic applications. Moreover at concentrations > *ca.* 10^{-5} mol dm^{-3} in water they form photochemically inert ground state aggregates.[2,4] Surprisingly there have been few systematic efforts[5] to develop better dyes for photogalvanic systems. We now report the synthesis of highly water soluble thiazine dyes (**3**), (**4**), and (**5**) with increasing cationic charge 1+, 2+, and 3+, respectively, in which formation of inert aggregates is increasingly suppressed. The increasing charge also facilitates intersystem crossing (i.s.c.) of the singlet states (S_1) and reduction of the protonated triplet states (T_1) by iron(II), but has no effect on self-quenching of T_1 by the ground state.

Phenothiazin-5-ium perbromide[6] (**6**) when treated with excess of a variety of secondary amines afforded a number of symmetrically substituted thiazine dyes including 3,7-bis-[di(2-hydroxyethyl)amino]phenothiazin-5-ium bromide (**3**) and 3,7-bis(4-methylpiperazin-1-yl)phenothiazin-5-ium bromide (**7**). Addition of one equivalent of 1-methylpiperazine to (**6**) gave (**8**), which on treatment with an excess of morpholine afforded asymmetrically substituted 3-(4-methylpiperazin-1-yl)-7-morpholinophenothiazin-5-ium bromide (**9**). Methylation (MeI) of photolabile† (**9**) and (**7**) and ion

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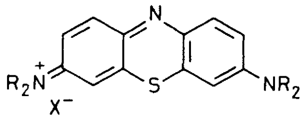
† The anomalously short singlet and triplet lifetimes of these tertiary amino substituted dyes suggest that the photoexcited chromophore may oxidise the side chain. It is well known that photoexcited (**2**) oxidises tertiary amines (R. H. Kayser and R. H. Young, *Photochem. Photobiol.*, 1976, **24**, 395).

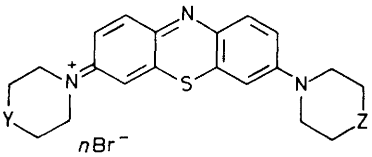
Table 1. Properties of the protonated triplet states of (3), (4), and (5) in dilute (0.005 M) sulphuric acid.

Dye	pK_T[a]	τ_T (μs)	$10^{-7}k_Q$[b]	$10^{-7}k_E$[c]	f_R	$10^{-8}k_{SQ}$[c]	$10^{-6}k_{Br}$[b]
(3)	7.7	5.1	1.8	1.2	0.7	1.3	2.2
(4)	5.2	5.3	4.6	4.6	1.0	3.9	2.8
(5)	4.5	8.2	21	19	0.9	1.5	5.3

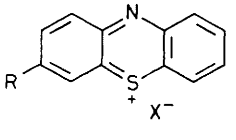
[a] Estimated precisions, ±0.1 units for (3); ±0.2 units for (4) and (5). [b] mol dm^{-3} s^{-1}: 2σ is typically $\leqslant 10\%$ of each k_Q or k_{Br} value. [c] mol dm^{-3} s^{-1}: 2σ is typically $\leqslant 20\%$ of each k_E or k_{SQ} value.



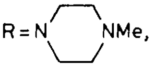
(1); R = H, X = Cl
(2); R = Me, X = Cl
(3); R = $[CH_2]_2OH$, X = Br



(4); Y = O, Z = $\overset{+}{N}Me_2$, n = 2
(5); Y = Z = $\overset{+}{N}Me_2$, n = 3
(7); Y = Z = NMe, n = 1
(9); Y = O, Z = NMe, n = 1



(6); R = H, X = Br_3

(8); R = 

, X = Br

exchange of Br^- for I^- using Br_2 in dimethyl sulphoxide afforded 3-(4,4-dimethyl-1-piperazinio)-7-morpholinophenothiazin-5-ium dibromide (4), and 3,7-bis(4,4-dimethyl-1-piperazinio)phenothiazin-5-ium tribromide, (5) respectively. All the dyes were purified by repetitive recrystallization to constant ϵ in their u.v.–visible spectra and each showed a single spot by t.l.c. on cellulose or neutral alumina. Their structures were confirmed by the similarity of their u.v.–visible spectra‡ to that of (2), ^{13}C n.m.r. spectra, and satisfactory elemental analyses.

The hydroxyalkyl substituted dye (3) was found to be miscible with water and solubilities of (4) and (5) exceeded 0.1 mol dm^{-3}, the 'ideal' concentration[3] for a dye with ϵ *ca.* 10^5 mol^{-1} dm^3 cm^{-1} in a photogalvanic system. Monocationic (3) is almost completely aggregated at 0.1 mol dm^{-3} despite being water miscible. Addition of organic solvents only partly suppressed aggregation. Aqueous solutions of both (4) and (5) at 0.1 mol dm^{-3} gave visible spectra indicating considerable aggregation of (4) and some aggregation of (5). However the spectra of (5) at 10^{-2} mol dm^{-3} in water and at 0.1 mol dm^{-3} in 25% dimethyl formamide or acetonitrile in H_2O were almost identical to those run at 10^{-5} mol dm^{-3} under the same conditions. Thus, in these last solvent mixtures (5) has close to ideal ground state properties for photogalvanic applications.

We have also investigated the excited state properties of (3), (4), and (5) and their photoreduction by Fe^{II}. Laser flash photolysis at varying pH using the 640 nm output of a Nd:YAG laser-pumped Rhodamine dye laser with pulse duration *ca.* 10 ns (< *ca.* 100 mJ/pulse) led to transients assigned to the protonated (T_1) and unprotonated triplet states. In dilute H_2SO_4 (0.005 to 0.05 M) absorption spectra and lifetimes, τ_T, of T_1 (Table 1) were similar to those reported[7] for the protonated triplet state of (2). By recording transient spectra as a function of pH, apparent pK_T values for each T_1 were obtained (Table 1). Extinction coefficients of 11 400 ± 1000, 11 100 ± 1000, and 11 100 ± 700 mol^{-1} dm^3 cm^{-1} at 370, 380, and 375 nm, were determined for T_1 of (3), (4), and (5) respectively, by total ground state depletion using laser pulse energies > *ca.* 20 mJ/pulse. At low pulse energies (< *ca.* 2 mJ/pulse) T_1 yields were linear with pulse energy and i.s.c. quantum yields, $\Phi_{i.s.c.}$ of 0.5, 0.25, and 0.7 were obtained for (3), (4), and (5), respectively, relative to $\Phi_{i.s.c.} = 0.52$ reported[8] for (2). The *ca.* 30 ps, 532 nm output of a frequency doubled, mode-locked Nd:YAG laser with streak camera detection was used to obtain fluorescence lifetimes, τ_F, of 313 ± 10, 111 ± 16, and 224 ± 10 ps for S_1 of (3), (4), and (5), respectively, in dilute (0.005 to 0.05 M) sulphuric acid. Rate constants, $k_{i.s.c.}$, for i.s.c. of 1.6×10^9, 2.2×10^9, and 2.9×10^9 s^{-1} for (3), (4), and (5), respectively, were calculated from the relationship $\Phi_{i.s.c.} = k_{i.s.c.}\tau_F$.

All three dyes underwent dark-reversible photobleaching by visible light in aqueous solution in the presence of Fe^{II}. At the concentration of Fe^{II} used ($< 10^{-2}$ mol dm^{-3}) fluorescence from short-lived S_1 is not quenched and reduction therefore must occur from T_1. Thus in the presence of Fe^{II} or with increasing dye concentrations τ_T decreased. Rate constants k_Q and k_{SQ} (Table 1) for quenching of T_1 by Fe^{II} and self quenching of T_1 by ground state dye, respectively, were obtained from the $[Fe^{II}]$ and [dye] dependence of τ_T. In the presence of Fe^{II} new longer lived transients were observed with absorption spectra similar to those reported[1,9] for semi-reduced (2). These species decayed by a second order process (k *ca.* 2 to 5×10^9 mol^{-1} dm^3 s^{-1}) presumed to be disproportionation to the dye plus its two electron reduced leuco form. Other kinetic characteristics of these radicals will be discussed elsewhere. Rate constants, k_E, for electron transfer from Fe^{II} to T_1 were obtained using the relationship[10] $[R]^\circ/[T_1]^\circ = k_E[Fe^{II}]\tau_{TQ}$ where the yield of T_1 after the flash, $[T_1]^\circ$, and the semi-reduced dye yield, $[R]^\circ$, after T_1 decay, were obtained from the transient bleaching of dye ground state absorption, and τ_{TQ} is the lifetime of T_1 at a given [dye] and $[Fe^{II}]$. Linear plots of $[R]^\circ/[T_1]^\circ$ *vs.* $[Fe^{II}]\tau_{TQ}$ afforded k_E (Table 1). The fractions of R which escape the encounter of T_1 and Fe^{II} are $f_R = k_E/k_Q$.

The small but significant increase in $k_{i.s.c.}$ for (3), (4), and

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‡ Visible absorption maxima, λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1}), in water (pH 7) were, for (3), 662 (92 600); (4), 648 (72 000); and (5), 638 (91 000). Remote point charge effects presumably shift λ_{max} for (4) and (5) progressivly to the blue. This phenomenon will be discussed elsewhere.

(**5**) is difficult to rationalize. Static quenching of S_1 by bromide ions, Br^-, with heavy atom enhancement of i.s.c. is one possible explanation although even for the tribromide (**5**) the $[Br^-]$ never exceeded 2×10^{-5} mol dm^{-3} and extensive ion-pairing seems unlikely in H_2O. The remote charges blue shift λ_{max} for (**4**) and (**5**) to 648 and 638 nm, respectively, from 662 nm for (**3**). Unless there is an identical effect on T_1 then the $S_1 - T_1$ energy gaps must change thus altering $k_{i.s.c.}$. A more dramatic effect is the low $\Phi_{i.s.c.}$ and τ_F for (**4**), both presumably due to enhanced radiationless deactivation of S_1 in less symmetrical (**4**).

The charge effects on k_Q and k_E are more easily explained. Charge repulsion between $Fe(H_2O)_6^{2+}$ and T_1 cannot be important since T_1 of (**5**) reacts the fastest (Table 1). There is probably an increase in the ground state reduction potential in the series (**3**), (**4**), and (**5**) due to increased positive charge. There may also be an increase in T_1 energy that parallels the small blue shifts in absorption maxima for this series. Either or both of these two factors would ensure that the triplet states of (**4**) and (**5**) are more reducible than T_1 of (**3**).

It is also noteworthy that whereas increasing the charge on (**3**), (**4**), and (**5**) suppresses ground state aggregation it has no systematic effect on self quenching of T_1. The rate constants, k_{Br} (Table 1), for bromide ion quenching of T_1, are too low for this process to be responsible for self-quenching of T_1. We suggest that the differential ground and excited state (T_1) effects reflect different geometries for aggregation and self quenching. It is generally accepted that the former involves co-operative stacking of dye molecules face to face.[11] This process will be inhibited by the repulsion of the bulky charged piperazinyl groups on (**4**) and (**5**). Self quenching of T_1 is however a different process in which partial electron transfer has been demonstrated[12] for (**2**). We suggest it involves approach of orbitals localized on N or S of the ground state to the plane of T_1. In this perpendicular geometry the charged piperazinyl groups do not come as close to one another and consequently have little effect on k_{SQ}.

From the point of view of photogalvanic cell development ideal ground state properties have been achieved for (**5**) and it is gratifying that k_Q increases in the series (**3**) < (**4**) < (**5**) and that f_R = *ca.* 1.0 for (**5**). However the constancy of non-productive self-quenching rates with increasing charge is disappointing. Preliminary results indicate that the back reaction of leuco forms of (**3**), (**4**), and (**5**) with Fe^{III} is too fast for this series to be useful except in very thin path length cells. Synthetic and mechanistic studies are underway designed to overcome this problem.

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