Free Rotor Styrylcyanine Chromogens

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Fluorescence spectra (maximum wavelength λ_F) and fluorescence quantum yields (ϕ_F) were measured for four structurally related styrylcyanine chromogens of the pyridinium and quinolinium type (1–4) in different solvents at ambient temperature and 77 K. The response of λ_F and ϕ_F values to changes in solvent polarity, solvent hydrogen bonding donor strength, viscosity and temperature was a sensitive function of chromogen structure. The sensitivities of the λ_F and ϕ_F values correlate with the degree of charge transfer character of the $S_{1,CT}$ state; Stokes shift of fluorescence was progressively decreased while ϕ_F value was enhanced as the CT character of $S_{1,CT}$ state increases. Moreover, a large edge-excitation red shift was observed in ethanol glass at 77 K. The dominant photophysical features for these dyes are discussed in terms of strong emission from an intramolecular CT state characterized by different solvation sites indicated by the observation of the excitation-wavelength dependent phenomenon in ethanol at 77 K and an important non-radiative decay channel involving rotation of the different parts of molecules leading to a more relaxed weakly fluorescent $S_{1,CT}$ created in fluid media. The viscosity dependence of fluorescence properties (a marked increase in ϕ_F was observed with increasing viscosity) suggests that these dyes can be useful reporters of microviscosity for different sites in various organized assemblies. Moreover, it was suggested that increasing H-bonding donor strength of the solvent activates a rotatory non-radiative decay channel probably by localizing charge densities and decreasing CT nature of the $S_{1,CT}$ state.

KEY WORDS: Fluorescence spectra and quantum yields; Styrylcyanine chromogens; Charge transfer.

INTRODUCTION

Recent years have witnessed an increasing interest in the photophysical relationship between fluorescence properties of free rotor chromogens of important modern applications and the molecular structure, solvent viscosity and temperature.[1-5]

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It has been previously shown that the energy and yield of fluorescence emission for a negatively solvatochromic styrylcyanine chromogen (1) of the electron donor–acceptor type, representing an important class of fluorescence probe dyes,[1,6,7] depend critically on solvent viscosity.[1,7] A model of nonradiative decay has been proposed.[1] This model employs a planar highly emissive intramolecular *CT* excited state ($S_{1,CT}$) capable of decay to a weakly fluorescent twisted *CT* state by radiationless isomerization process involving rotation of the different parts of the molecule; a hindered rotor effect. Intersystem crossing to the triplet states was considered inefficient. The viscosity dependence of photophysical properties suggested that this molecule can be a useful sensor of microviscosity for different sites in various organized assemblies.[1,7]

In continuation of our work we report in the present paper further studies on the fluorescence properties of four structurally related styrylcyanine chromogens (1–4) in three solvents; ethanol, CH_2Cl_2, and glycerol representing three different classes of solvents, namely hydrogen bonding donor, non-hydrogen bonding solvent and highly viscous solvent, respectively. The measurements are performed at
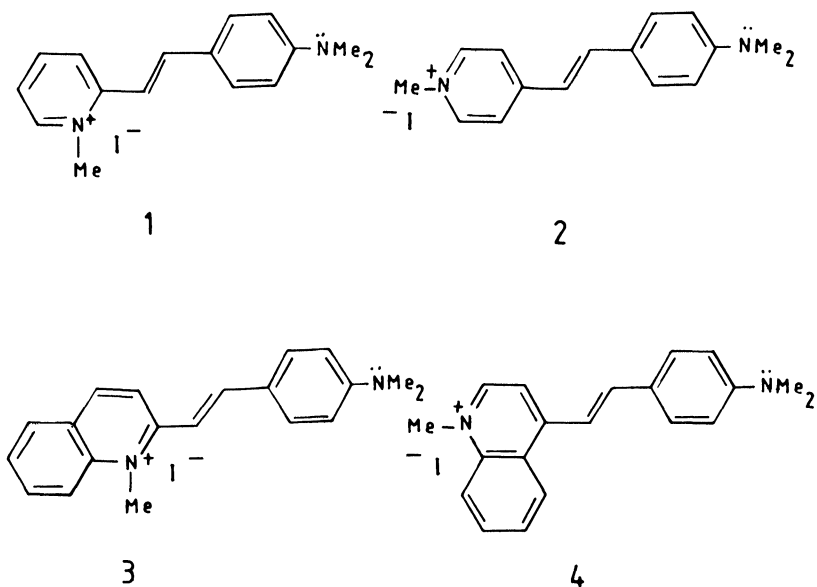
ambient temperature and 77 K. The results have a significant bearing on the structure requirements for engineering deactivation pathways of the $S_{1,CT}$. Moreover, the role of solvation-site heterogeneity[8] in the fluorescence spectra of compounds 1-4 in ethanol at 77 K, were examined.

EXPERIMENTAL

Styrylcyanine chromogens (1-4) were prepared by condensing the pyridinium and quinolinium salts, namely 1,2-dimethylpyridinium-, 1,4-dimethylpyridinium, 1,2-dimethylquinolinium- and 1,4-dimethyl-quinolinium iodides, respectively, with an excess amount of p-N,N-dimethylamino-benzaldehyde in the presence of piperidine as a basic catalyst. Their purities were checked by TLC on silica gel with methanol as an eluent.

Spectroscopic pure solvents were used for all measurements. Absorption spectral data were obtained on a SP-1800 Pye Unicam spectrophotometer. Fluorescence spectra were taken on a Shimadzu 510 spectrofluorimeter. Fluorescence quantum yields were determined by comparing with a fluorescein fluorescence standard ($\phi_F = 0.85$). Preliminary measurements showed that degassing of the chromogen solution has practically no effect on the ϕ_F value, a result which eliminates the possibility of bimolecular quenching by dissolved oxygen.

RESULTS AND DISCUSSION

Earlier work on styrylcyanine and merocyanine-like dye-stuffs suggested that the longest wavelength electronic transition in the visible spectra of these negative solvatochromic compounds is due to intramolecular CT ($S_0 \rightarrow S_1$) transition.[6,8,9] The spectra of the compounds under investigation exhibit a similar intramolecular CT transition characterized by a decreasing CT energy, E (CT), in the sequence $1 > 2 > 3 > 4$. This parameter has been used as a convenient gauge of the degree of CT in the first singlet excited state of $D - A$ class compounds.[10] This trend is further supported by diminution of half-band width, $\Delta \bar{\nu}_{1/2}$, and enhancement of molar absorptivity, ε_{max}, in the same sequence mentioned above. These observations indicate that

the electronic distribution within these molecules tends to symmetrize[6] (become less polar) in the order $1 > 2 > 3 > 4$ in their S_0 states so that optical excitation to the $S_{1,CT}$ state occurs with decreasing changes in their electronic distribution in the sequence $1 > 2 > 3 > 4$. In other words, optical pumping occurs with a decreasing degree of CT as the sequence above. The wavelength and quantum yield of fluorescence of chromogens (1-4) are sensitive to changes in solvent viscosity, temperature and excitation wavelength. Therefore, fluorescence spectra and quantum yield determinations were made in different media at room temperature and at 77 K (Table I).

At ambient temperature, changing the solvent from non-viscous ethanol to glycerol has the expected effect on the fluorescence properties. For a given dye molecule, the Stokes shift of fluorescence decreases, reflecting a decrease in geometry difference between ground state and the emitting state. Moreover, ϕ_F is enhanced markedly due to an increasing lifetime of the $S_{1,CT}$ state by increasing the contribution of the solvent-dependent viscosity barrier to a weakly fluorescent state.[1]

Interestingly, about three orders of magnitude increase in ϕ_F for dyes 1-4 in ethanol on going from ambient temperature (fluid medium) to 77 K (rigid medium) was observed. Furthermore, a pronounced decrease in Stokes shift was observed as the temperature is lowered to 77 K. Moreover, once the solution is made rigid, excitation-wavelength dependence was observed for dyes 1-4. The fluorescence spectra of a dilute solution ($\sim 10^{-6}$ M) of dye (4) in ethanol at 77 K as a function of excitation wavelength are shown in Figure 1. A large red shift in the range (800-1000) cm^{-1} for dyes 1-4 has been observed as the excitation wavelength is tuned from the absorption maximum to about 40 nm higher to the red edge of the absorption band. However, the fluorescence spectra of dilute solutions of dyes 1-4 at room temperature are excitation wavelength independent.

In order to explain these observations we refer to a qualitative excited state potential energy surface (Figure 1b) representing the solvent interaction with the flexible dye molecules that may assume different rotational conformation.[1,8] It is reasonable to assume a statistical distribution of the solute among different solvation sites.[8] In rigid ethanol at 77 K the lifetime of the various solvation sites is large compared to the excited state lifetime due to the existence of high solvent-dependent viscosity and torsional barriers, so that dissipation
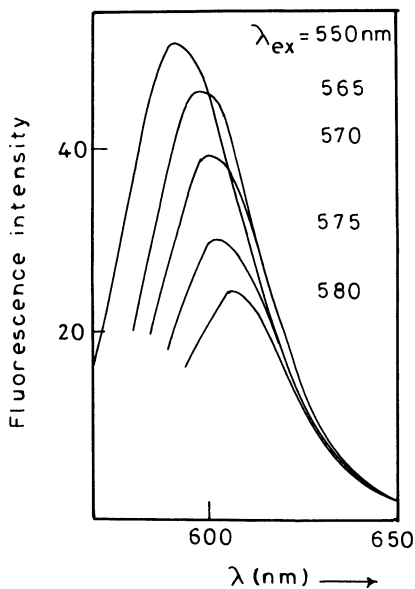
FIGURE 1a Excitation-wavelength-dependent fluorescence spectra of chromogen (4) in ethanol glass at 77 K (Red edge effect). Tuning λ_{exc} from the absorption maximum (550 nm) to the red edge of the absorption band results in a red shift of λ_F.
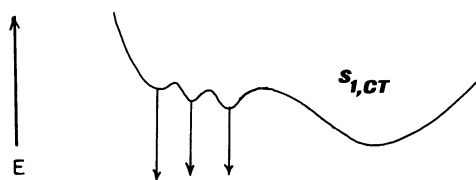
FIGURE 1b Postulated potential energy surface for different solvation sites in rigid medium.

of electronic energy by crossing these barriers is considerably prohibited. Excitation of the dye molecules in any specific site gives rise to a sudden strained Franck-Condon state leading to a fast solute-solvent relaxation to the equilibrium excited state of this specific site, from which strong emission originates. This accounts for the observed high ϕ_F and small Stokes shift[1] in the rigid medium.

TABLE I

Spectral and photophysical data of chromogens (1–4)

(A) In ethanol at RT

Chromogen	λ_A^a	$\Delta\tilde{\nu}_{1/2}^b$	$\varepsilon \times 10^{-3\,c}$	τ_0^d	λ_F^e	$\phi_F \times 10^3$	τ^f (PS)	$\Delta\tilde{\nu}^g$ A $-$ F	$K_F \times 10^{-11\,h}$
1	466	4160	33.0	5.54	560	1.2	06.65	3602	01.50
2	482	3800	43.0	4.98	580	0.8	03.98	3505	02.51
3	530	3760	47.0	5.65	592	0.4	02.26	1976	04.43
4	550	3600	48.0	6.13	614	0.1	00.61	1895	16.40

(B) In ethanol at 77 K

Chromogen	λ_A^a	$\Delta\tilde{\nu}_{1/2}^b$	$\varepsilon \times 10^{-3\,c}$	τ_0^d	λ_F^e	$\phi_F \times 10^3$	τ^f (NS)	$\Delta\tilde{\nu}^g$ A $-$ F	$K_F \times 10^{-8}$
1	466	4160	33.0	5.54	515	888	04.86	2042	02.06
2	482	3800	43.0	4.98	525	722	02.54	1698	03.94
3	530	3670	47.0	5.65	570	163	00.92	1324	10.87
4	550	3600	48.0	6.13	587	51	00.31	1146	32.26

(C) In dichloromethane at RT

	λ_A[a]	$\Delta\bar{\nu}_{1/2}$[b]	ε[c]	τ_0[d]	λ_F[e]		(PS)[f]		$K_F \times 10^{-11}$[h]
1	477	3990	32.2	6.20	550	6.0	37.20	2780	0.27
2	502	3170	36.7	7.58	560	3.0	22.70	2063	0.44
3	556	2890	61.0	6.14	608	0.6	03.68	1538	2.72
4	570	3050	45.0	8.29	620	0.3	02.50	1414	4.00

(D) In glycerol at RT

	λ_A[a]	$\Delta\bar{\nu}_{1/2}$[b]	ε[c]	τ_0[d]	λ_F[e]		(PS)[f]		$K_F \times 10^{-11}$[h]
1	466	3894	44.9	4.35	550	10.0	43.50	3277	0.22
2	486	3888	42.0	5.05	574	8.5	42.90	3154	0.23
3	525	3172	40.0	7.60	590	0.8	06.08	2098	1.64
4	542	3686	22.9	12.20	605	0.3	03.66	1921	2.73

[a] λ_A in nm.
[b] $\Delta\bar{\nu}_{1/2}$ in cm^{-1}.
[c] ε in l cm^{-1} mol^{-1}.
[d] $\tau_0 = 1/K_R = 3.5 \times 10^8 / \bar{\nu}_{max}^2 \cdot \varepsilon \Delta\bar{\nu}_{1/2}$ (in NS); K_R = radiative rate constant.
[e] λ_F in nm.
[f] $\tau = 1/(K_R + K_{IC}) = \tau_0 \cdot \phi_F$.
[g] $\Delta\bar{\nu}_{A-F}$ in cm^{-1}.
[h] K_F = rate constant of fluorescence decay (in S^{-1}).

In fluid ethanol the lifetime of the various solvation sites is short compared to the excited state lifetime and a dynamic equilibrium exists, leading to a weak emission from the most stable solvation site indicated by larger Stokes shift. Emission will occur at the same wavelength independent of the excitation wavelength.

The principal structure feature affecting photophysical properties noted here is the role of the electron-acceptor cationic heterocyclic groups in 1-4 which results in a systematic differential response to changes in solvent properties and temperature (Table I). The change in emission spectral properties of dyes 1-4 could be readily understood in terms of the degree of intramolecular CT which involves promotion of electronic charge from an orbital which is significantly weighted at the donor part of the molecule, particularly at the N,N-dimethylamino group.[6]

The greater CT character of the $S_{1,CT}$ state of (1) and (2) relative to (3) and (4) is associated with substantial alteration of the electron densities and bond orders[6] which results in pronounced different response to medium effects. As indicated by the spectral observations above mentioned, it could be concluded that, a larger contribution from the locally excited state of molecules (3) and (4) lowers the barrier to rotation which ensures that the excited state molecules travel faster to the most favourable geometry for nonradiative decay to the S_0 state.

Finally changing the solvent from a non-hydrogen bonding CH_2Cl_2 to ethanol (α-value $= 0.850$)[11] also activates extensive rotatory decay probably due to increasing specific H-bonding interaction with the $S_{1,CT}$ state in the sequence $1 < 2 < 3 < 4$. This accounts for the larger Stokes shift ($\Delta\bar{\mu}_{A-F}$) and smaller ϕ_F value in ethanol (Table I).

Similar to a previously found correlation[5] it has been found that, in a given medium the size of the Stokes shift of fluorescence ($\Delta\bar{\nu}_{A-F}$) is a measure of CT nature of the $S_{1,CT}$ state of dyes. The greater the CT nature of the $S_{1,CT}$ state, the smaller is the probability that rotational-viscosity barrier can be crossed.

The rate constants of internal conversion determined from the difference in decay rates in ethanol at room temperature and at 77 K are so close to K_f in value and increases as the degree of CT character decreases in the order 1-4 (Table 1, Section A). The results suggest that these molecules can be used as fluorescent indicators to study microscopic structural detail in organized assemblies.[7,12]

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