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SOLVATOCHROMIC BEHAVIOUR OF DONOR-ACCEPTOR SUBSTITUTED 1,2-DIPHENYLETHENES IN ORGANIC SOLVENTS, REVERSE MICELLES AND POLYMER MATRIX

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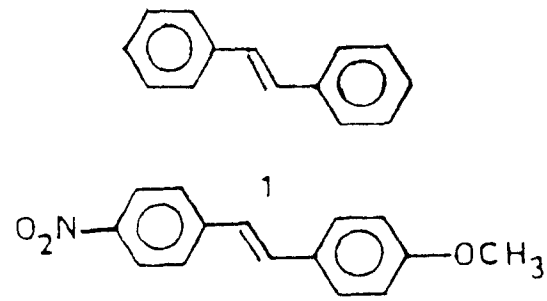
Abstract – Absorption and fluorescence studies of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene in homogeneous solvents, polymer matrix and normal and reverse micelles showing strong solvatochromic fluorescent emission properties with quasi-planar intramolecular charge transfer characteristics in the electronically excited singlet state are discussed.

INTRODUCTION

Diphenylpolyenes [$C_6H_5(CH{=}CH)_nC_6H_5$] have been the subject of extensive photochemical, photophysical, theoretical and spectroscopic investigations in recent years.[1-5] These molecules serve as models of retinylidene polyenes that are related to Vitamin A and the opsin family of protiens.[6-8] These are also important as photoprobes for investigating the microenvironment of self-organised assemblies.[9-10]

1,2-Diphenylethene (1, n = 1) is both the simplest member of the diphenylpolyene series and is also the most extensively studied. A comprehensive review of the photochemistry of 1,2-diphenylethene (1) is available in literature.[4,11] In order to better understand the nature of polyene excited states, the effects of substituents and solvents on the emission of certain diphenylethenes bearing electron donating and electron withdrawing substituents have been studied.[10,12-14] The excited state properties of diphenylpolyenes are governed by the shape of the lowest excited state potential surface. The lowest excited state of *trans* -1,2-diphenylethene (1) is of B_u^+ symmetry and the second excited state surface is of A_g symmetry with $^1B_u^*$- ^1A_g energy gap of *ca* 8065 cm^{-1}. The excited singlet state behavior of *trans*-1,2-diphenylethene (1) is governed by two processes. Its fluorescence from S_1 (B_u symmetry) competes effectively with the activated twisting of the C=C into a perpendicular geometry. This perpendicular state decays within *ca.* 5 ps to an energy maximum on the ground state potential surface.[15] From there, an exothermic 90° rotation gives either the *cis* or the *trans* isomer. A small barrier to forming the twisted perpendicular state has been attributed to a crossing of the $^1B_u^*$ surface and the second excited state $^1A_g^*$ surface as the molecule rotates out of its planar conformation.[16]

The nature of the $^1A_g^-$ and $^1B_u^+$ excited states has important consequences for diphenylpolyene photochemistry and photophysics. Solvent polarities, polarizabilities and substituents can change the relative positions of the $^1A_g^*$ and $^1B_u^*$ states. This not only alters the fluores-cence properties but can also change the shape of the S_1 potential surface influencing the isomerization dynamics.



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In addition to the above-mentioned photophysical studies, the excited state properties of diphenylpolyenes have also been used to characterize the microenvironments of the organized assemblies of micelles and vesicles.[9] These studies also help in better understanding of the nature of solubilization sites provided by such microheterogeneous media, which in turn leads to the development of a better comprehension of the ability of these media to modify or control reactivity.[10]

This work aims at investigating the effect of media on the fluorescence properties of donor-acceptor substituted diphenylethenes *viz.* (*E*)-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene (2). In view of a rather limited research work on the fluorescence characteristics of such diphenylpolyenes in organized assemblies and polymer matrices, a systematic study in micelles and polymer matrix appeared desirable to us.

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MATERIALS AND METHODS

GC measurements were performed on Shimadzu GC-9A instrument. Proton NMR spectra were recorded on Varian 300 MHz NMR spectrometer. Infrared spectra were obtained on Perkin Elmer 625 spectrophotometer. Uv-vis data were obtained on a Hitachi U-2000 spectrophotometer. Steady state fluorescence and fluorescence polarization measurements were performed on DM1B Spex Fluorolog spectrofluorimeter equipped with 1935B polarization unit. All the fluorescence spectra were recorded using the 370 nm excitation wavelength. Fluorescence quantum yields were determined by using the fluorescence of quinine sulphate as a standard after correction. All the solvents used for uv-vis and fluorescence studies were of uv grade and were flushed with dry and pure nitrogen before use. Double distilled and deionised water was used for micelle preparations.

p-Nitrotoluene was from M/S S.D. Fine Chem. Ltd. India and its purity was checked by GC (R_t = 1.25 min. under isothermal conditions at 210°C, C-R4A chromatopac, 500-17). Liquid bromine was obtained from E-Merck and triethyl phosphite was from Fluka. All other chemicals and solvents were obtained from SRL, India. Solvents used for crystallization were distilled before use. Freshly distilled DMF was used for the reaction. All the surfactants used for micelle preparations were obtained from Fluka. Polyvinyl alcohol (PVA, 80%, average molecular weight 60,000 at 25°C) was a gift from Indian Petrochemicals Ltd. Baroda, India.

(*E*)-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene (2) was synthesized stereoselectively by using a modified Wittig-Horner process,[17] wherein phosphonate anion of p-NO_2-C_6H_4-$CH_2PO(OEt)_2$ was allowed to react with *p*-methoxybenzaldehyde in presence of NaOMe/DMF. Compound 2 was obtained in 20% yield and it showed the following physicochemical characteristics : mp. 134- 135°C ; ^{1}HNMR ($CDCl_3$, 300 MHz) δ 3.85 (3H, s, -OMe), 6.93 (2H, d, J = 7 Hz, -ArH, *ortho* to -OMe), 7.01 (1H, d, J = 16 Hz, = CH near *para* -OMeAr), 7.22 (1H, d, J = 16 Hz, = CH near *para*-NO_2Ar), 7.50 (2H, d, J = 7 Hz, -ArH, *meta* to -OMe), 7.60 (2H, d, J = 7 Hz, -ArH, *meta* to -NO_2), 8.21 (2H, d, J = 7 Hz, -ArH, *ortho* to -NO_2); IR (nujol, cm^{-1}) 1600 (ν -CH = CH), 1340, 1250.

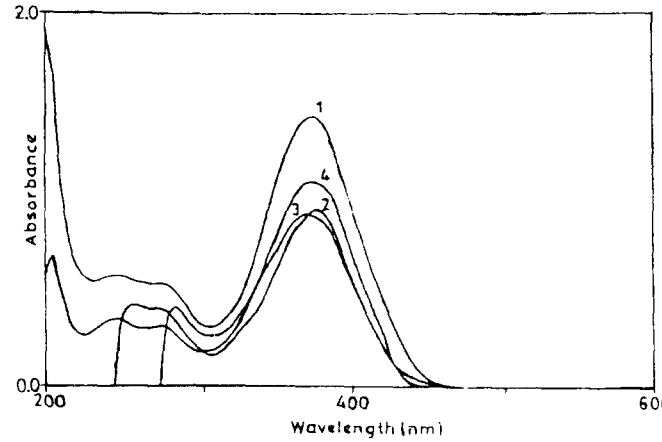

Figure 1. Absorption spectra of 2 (1×10^{-5} *M*, 25°C) in solvents of increasing polarity; (1) Acetonitrile, (2) Methanol, (3) THF and (4) Benzene

RESULTS AND DISCUSSION

Absorption and fluorescence studies in homogeneous media

Absorption spectra (Fig. 1) of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitirophenyl) ethene (2) were recorded in different solvents of increasing polarity and the data are presented in Table 1. As evident from the data, the absorption maxima do not change by increasing the polarity of the solvent. Excitation and fluorescence emission spectra of 2 were also measured in different solvents of increasing polarity and are shown in Figs. 2 and 3 respectively. The corresponding excitation and fluorescence maxima, the quantum yeilds of fluorescence, Stoke's shift and full width at half maximum (fwhm) data for 2 are summarized in Table 2. The excitation spectral band shifts towards red with the increasing concentration (10^{-3}-10^{-4} *M*) of 2 in all the solvents studied. The fluorescence spectra are insensitive to the increasing concentration of 2 and the fluorescence maxima are the same for different excitation wavelengths. However, decrease in fluorescence intensity at higher concentration (10^{-3} *M* and above) of 2 is observed which may be due to

Table 1. Absorption spectral data of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene (2.1×10^{-5} *M*) in homogeneous media at 25°C.

Medium	Dielectric constant	Absorption maxima(nm) λ_{max}	Molar extinction coefficient $dm^3\ mol^{-1}\ cm^{-1}$	fwhm(abs) cm^{-1}	Radiative lifetime τ_r (10^{-9}sec)
CCl_4	2.24	361.5	5222	5303	0.15
Benzene	2.30	373.5	12000	6655	0.16
THF	7.60	375.4	2900	5340	0.18
Methanol	32.60	370.0	15000	5912	0.20
Acetonitrile	37.50	369.5	12000	5546	0.19
PVA		386.0		3625	

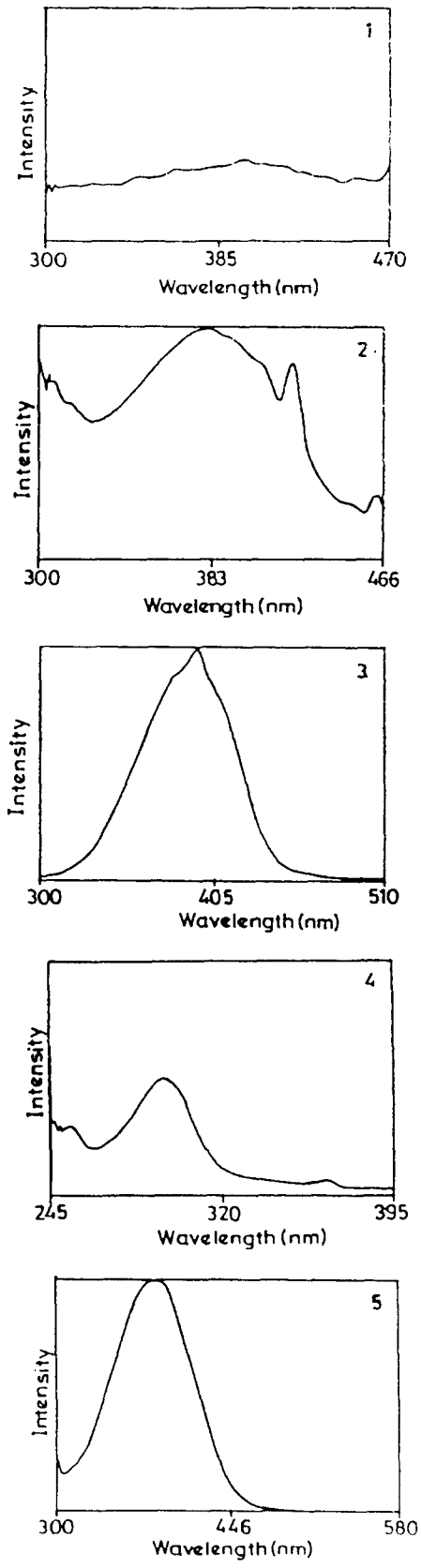

Figure 2. Excitation spectra of 2 (1×10^{-5} *M*, 25°C) in solvents of increasing polarity; (1) CCl_4, (2) Benzene, (3) THF, (4) Methanol and (5) Acetonitrile.

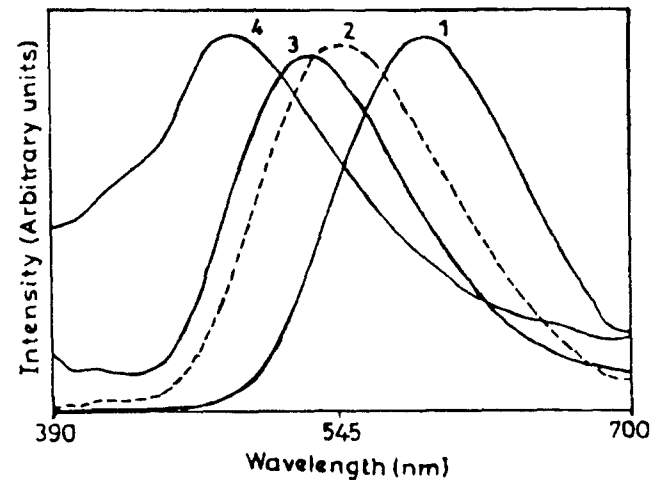

Figure 3. Fluorescence spectra of 2 (1×10^{-5} *M*, 25°C) in solvents of increasing polarity; (1) Acetonitrile, (2) THF, (3) PVA and (4) Benzene.

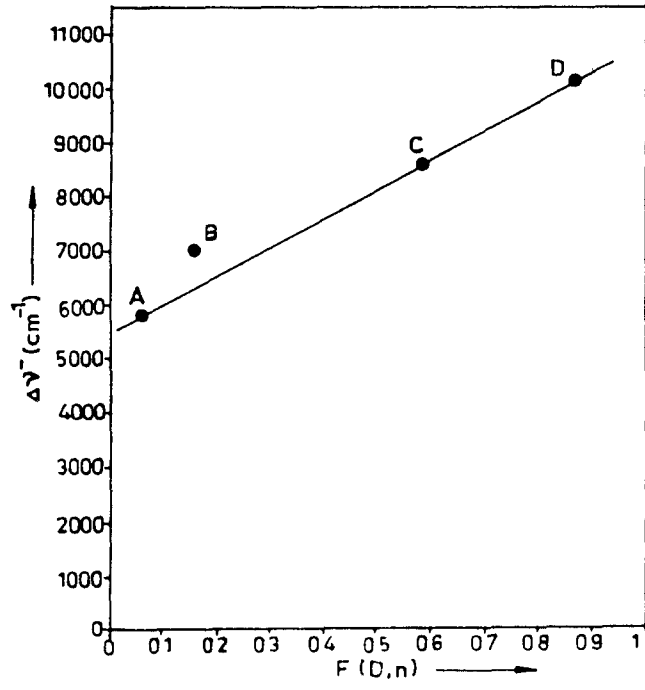

Figure 4. Lippert-Mataga plot of 2 (1×10^{-5} *M*, 25°C) in solvents of increasing polarity; (1) CCl_4, (2) Benzene, (3) THF and (4) Acetonitrile.

concentration quenching of fluorescence. The fluorescence spectra in different solvents were found to be quite sensitive to the increasing solvent polarity in the form of a marked red shift of the fluorescence band. Also, the solvent polarity dependent red shift in the fluorescence band is accompanied by increase in Stoke's shift. The red shift in the fluorescence maxima in solvents of increasing polarity indicates the large dipole moment in the excited state. The large dipole moment can cause solvent reorientation with the more polar

Table 2 . Excitation and fluorescence data of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene (2.1×10^{-5} *M*) in homogeneous media at 25°C.

Medium	Excitation maxima(nm) λ_{max}	Emission maxima(nm) λ_{max}	Quantum yield[a]	Stokes shift cm^{-1}	fwhm(flu) cm^{-1}
CCl_4	397.0	487.0	0.002	7136	7244
Benzene	382.0	487.5	0.002	6260	5174
THF	395.5	552.0	0.05	8515	4193
Methanol	377.0	586.0	0.003	9962	3750
Acetonitrile	379.5	593.0	0.065	10200	3598
PVA	397.0	532.0		6412	4335

a = ± 0.001

solvent stabilizing the excited state more effectively, thereby producing a large Stoke's shift. As is known, the effect of solvent on the absorption spectrum is dependent on the energy levels of the equilibrium ground state and the Franck-Condon excited state, whereas that of the emission depends on the energy levels of the equilibrium excited state and the Franck-Condon ground state. Using Lippert-Mataga plot,[13,18] as shown in Fig. 4, dipole moments of excited and ground state of 2 were determined to be 18.05 D (μ_e) and 8.00 D (μ_g) with $\Delta\mu$ of 10.05 D. These fluorescence data and rather high μ_e values indicate towards charge transfer phenomenon in the excited state of 2.

The theoretical or natural radiative lifetimes were calculated from the well known Strickler and Berg relation[19]

$$\tau_r = \frac{3.47 \times 10^8}{n_2(\bar{\nu}_{max})_2} \times \frac{g_m}{g_n} \times \left(\int \epsilon \, d\bar{\nu} \right)^{-1}$$

where g_m and g_n are the multiplicities of the excited and ground states and the ratio (g_m/g_n) is unity for the singlet-singlet transition, $\int \epsilon \, d\bar{\nu}$ is the area under the curve of molecular extinction coefficient plotted against wavenumber, $\bar{\nu}_{max}$ is the wavenumber of the maximum of the absorption band and n is the refractive index of the solvent. The τ_r values determined from the above equation are given in Table 1.

The geometry of the ground and excited singlet state is understood from the full width at half maximum (fwhm) values of the absorption and fluorescence spectra. The fwhm values for both absorption and fluorescence spectra are given in Table 1 and Table 2 respectively. In general, the fwhm of the fluorescence bands are less than that of the fwhm values of absorption bands in most of the solvents studied except in carbon tetrachloride, indicating towards the planar geometry of the relaxed excited singlet state.

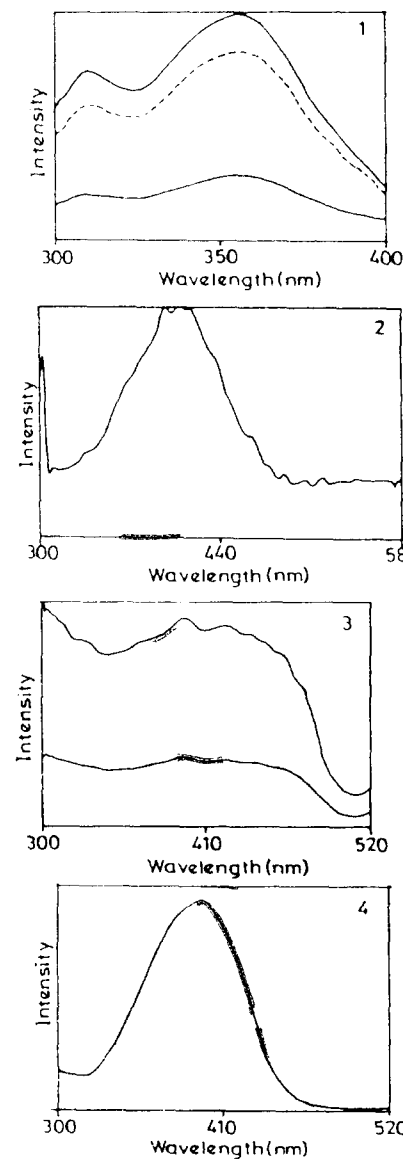

Figure 5. Excitation spectra of 2 in micellar solutions : (1) AOT/ *n*-heptane of different water pool (ω = 0, 5, 10 and 15) sizes. (2) CTAB (9.2×10^{-2} *M*), (3) SDS (8.1×10^{-2} *M*) and (4) Triton-X-100 (3×10^{-2} *M*).

Table 3 . Absorption spectral data of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene (2) in microheterogeneous media at 25°C.

Medium	Absorption maxima(nm) λ_{max}	fwhm(cm^{-1})
AOT/*n*-heptane[a]		
ω^b = 0	352.2	9146.9
ω = 5	352.2	9146.9
ω = 10	352.2	9146.9
ω = 15	352.2	9146.9
aq. CTAB[c]	380.5	25348.6
aq. SDS[d]	380.0	25000.0
aq. Triton-x-100[e]	377.5	9416.6

[M] 2 : a : 1×10^{-2} *M*; c : 9.2×10^{-4} *M*; d : 8.1×10^{-3} *M*; e : 3×10^{-4} *M*; b : [H_2O, M]/ [AOT, M].

Table 4. Excitation and fluorescence data of *E*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl) ethene[a] (2) in microheterogeneous media at 25°C.

Medium	Excitation maxima(nm) λ_{max}	Emission maxima(nm) λ_{max}	fwhm(cm^{-1}) (flu)	stoke's shift(cm^{-1})
AOT/*n*-heptane				
ω = 0	356.0	509.0		
ω = 5	356.0	509.5	3666.0	4469.0
ω = 10	356.0	509.5		
ω = 15	356.0	509.5		
aq. CTAB	408.5	606.0	3588.3	10511.8
aq. SDS	396.0	481.0	3606.0	5525.2
aq. Triton-x-100	394.5	546.0	4114.0	8175.1

Concentrations of 2 as given in Table 3.

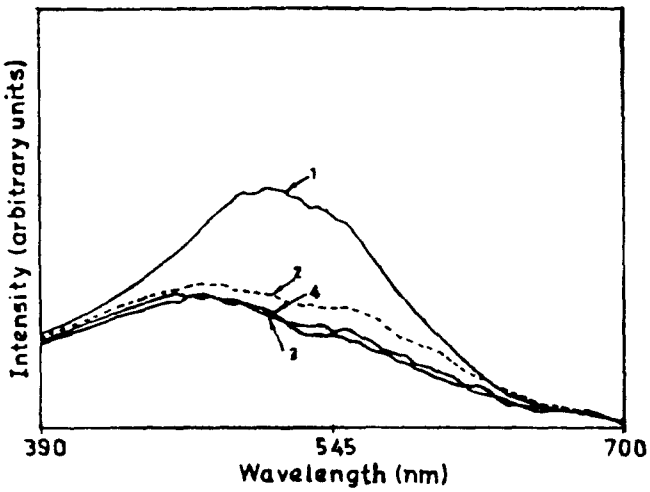

Figure 6. Fluorescence spectra of 2 in reverse micelle: (AOT / *n*-heptane, 25°C) of different water pool (ω) sizes (1) ω = 0, (2) ω = 5, (3) ω = 10, (4) ω = 15.

Absorption and fluorescence studies in reverse micelles of sodium bis (2-ethylhexyl) sulfosuccinate (AOT)

Absorption studies were carried out in *AOT/n*- heptane reverse micelles of different water pool sizes (*i.e.*, ω = 0, 5, 10, 15) and the data are presented in Table 3. The absorption maxima obtained in the reverse micelles are blue shifted as compared to the absorption maxima in the homogeneous media indicating towards the nonpolar nature of the solubilization site. However, the absorption maxima were observed to be unaffected by the varied water pool sizes.

Excitation and fluorescence emission spectra of 2 in *AOT/n* -heptane reverse micelles of different water pool sizes (ω = 0, 5, 10, 15) were studied and the spectra are shown in Fig. 5 and 6 respectively while the corresponding data are presented in Table 4. It is observed that the excitation maxima is unaffected by the water pool size of the micelles. However, as evidenced by decrease in fluorescence intensity, the emission spectra in reverse micelles (*i.e.,AOT/n* -heptane) are sensitive to the micellar water pool size. It is also observed that the fluorescence maxima obtained in the reverse micelles are blue shifted as compared to the fluorescence maxima obtained in the homogeneous media of organic solvents. This indicates towards the stabilization the fluoroprobe in or near water pool of the reverse micelles.

Absorption and fluorescence studies in micelles of N-cetyl-N,N,N-trimethylammonium bromide (CTAB), sodium dodecyl sulfonate (SDS) and Triton X-100

Absorption properties of 2 were studied in CTAB, SDS and Triton-X-100 micelles and the spectra are shown in Fig. 7. The absorption spectral data are given in Table 3. The absorption maxima obtained in these micelles were almost the same and are independent of the concentration of the micelles in 10^{-6} *M* - 10^{-2} *M* range. However, the absorption maxima obtained in the normal micelles are red shifted as compared to the

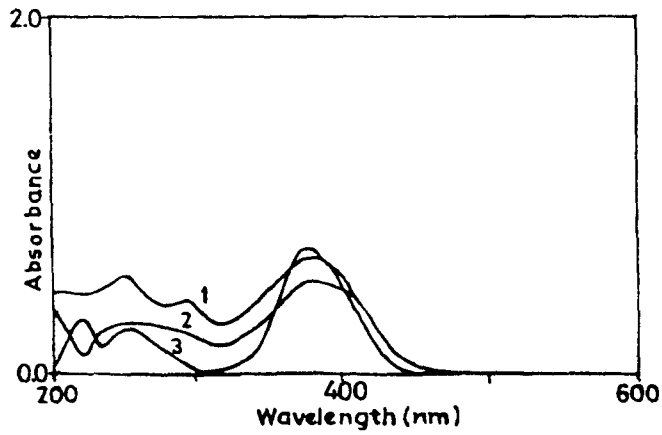

Figure 7. Absorption spectra of 2 in normal micelles : (1) Triton-X-100 (3×10^{-2} *M*), (2) CTAB (9.2×10^{-2} *M*), (3) SDS (8.1×10^{-2} *M*).

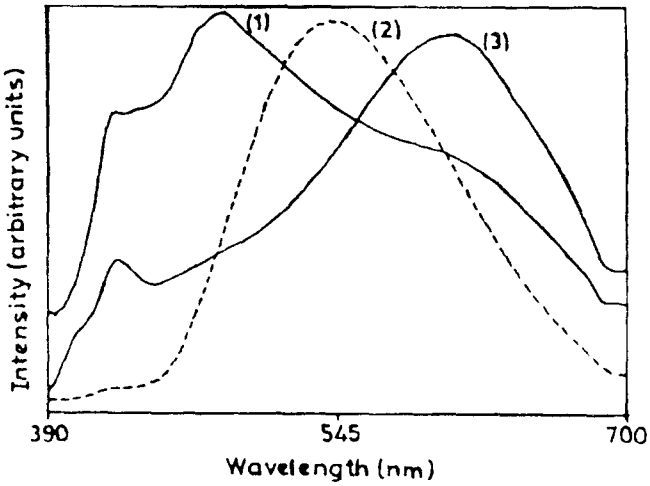

Figure 8. Fluorescence spectra of 2 in normal micelles : (1) SDS (8.1×10^{-2} *M*), (2) Triton-X-100 (3×10^{-2} *M*) and (3) CTAB (9.2×10^{-2} *M*).

absorption maxima observed in the reverse micelles and in homogeneous organic solvents. The absorption maximum of a solution of 2 in water-methanol mixture (10 : 1 v/v) showed absorption band similar to the one obtained in micelles.

The excitation and fluorescence spectra of 2 in aqueous CTAB, SDS, Triton-X-100 micelles are shown in Figs. 5 and 8 respectively, and the corresponding data are summarized in Table 4. CTAB micelles cause a red shift in the fluorescence maxima of 2 at different concentration of the micelles while SDS micelles cause a blue shift in the same concentration range. However, the Triton-X-100 micelles did not affect the fluorescence maxima of 2. Similar to the observations made in homogeneous media, the fluorescence fwhm values of 2 were found to be lesser than the absorption fwhm values (Tables 3 and 4). It is interesting to note that while excitation spectrum of 2 does not change significantly in the micelles, the fluorescence spectra are influenced significantly by the cationic and anionic micelles. This indicates that there is a significant change in the geometry of the excited state when molecule comes to S_1 for fluorescence in the ionic micellar media. Also unusually large fwhm values for absorption were seen in the anionic and cationic micelles which may be due to some specific bonding of the chromophore in the ionic micelles.

Absorption and fluorescence studies in polyvinyl alcohol (PVA) polymer matrix

The absorption and the fluorescence excitation maxima of 2 in PVA (Tables 1 and 2 and Fig. 9a) are red-shifted as compared to that in homogeneous solvents of high polarity. This indicates the stabilization of the π, π^* excited states in the constrained and relatively polar environment of the polymer matrix. However, the fluorescence emission maximum as shown in Fig. 9b is blue-shifted as compared to that in highly

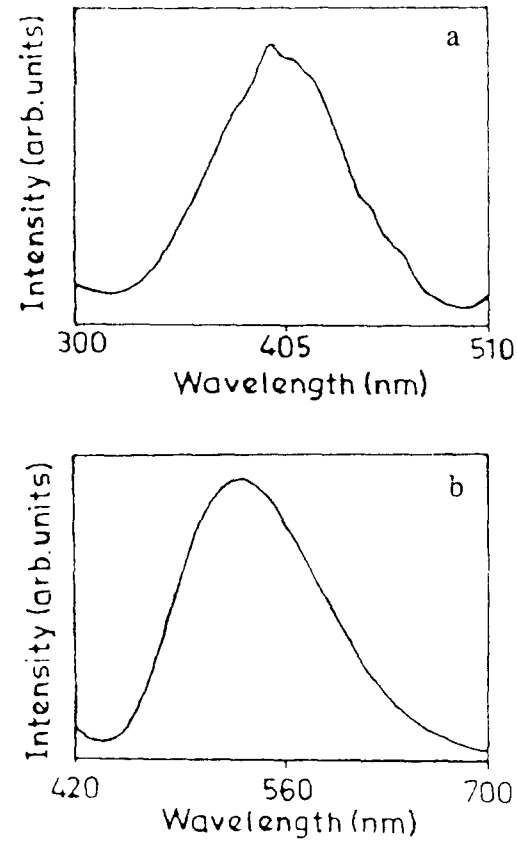

Figure 9. (a) Excitation spectra of 2 in polyvinyl alcohol (PVA) at 25°C. (b) Fluorescence spectra of 2 in PVA at 25°C.

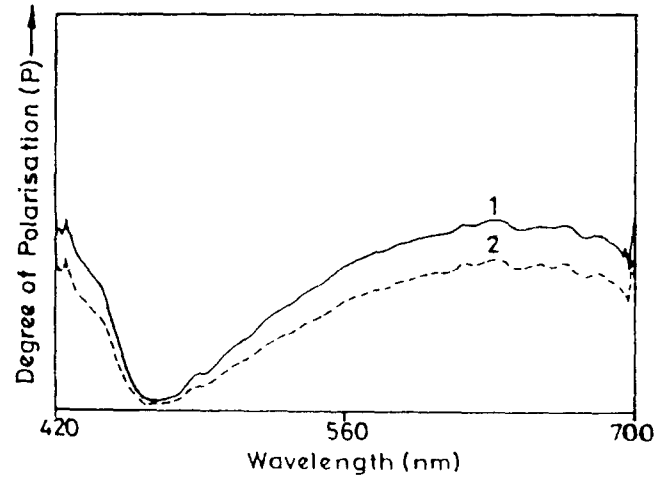

Figure 10. Fluorescence polarization spectra of 2 in PVA at 25°C. (1) Degree of polarization (P), and (2) Anisotropy (r).

polar homogeneous solvents. These excitation and fluorescence data indicate towards change in the geometry of the chromo- and fluoro- phore in the excited state(s). In contrast to the earlier observed higher fwhm absorption values and lower fluorescence fwhm values for 2 in solution states, lower fwhm absorption values and higher fluorescence fwhm values were observed for 2 in PVA

matrix. This shows that polymer-intercallated 2 adopts a relatively non-planar geometry in its excited state. The increased non-planarity of electronically excited 2 in the polymer may be due to restricted environment of polymer matrix. The abundant presence of polar hydroxyl groups in PVA may provide stabilization to the polar excited state.

Fluorescence polarization spectrum (Fig. 10) of 2 in solution (THF, 25 °C) and in condensed state of the PVA matrix showed positive anisotropy (r) and degree of polarization (P) value in the region of charge transfer emission. This further indicate that charge transfer emission is polarised parallel to the molecular long axis. These observations indicate towards the possibility of the involvement of intramolecular quasi-planar twisted charge transfer phenomenon in the photoprocesses of 2.

Thus, fluorescence properties of donor-acceptor substituted compounds in diphenylpolyene series are influenced by microenvironment of heterogeneous and constrained media. It is found that such media can provide microenvironment wherein the dipolar electronically excited singlet states of diphenylpolyenes can be stabilized. The present studies provide evidence towards the involvement of polarized excited states in the photoprocesses of linearly conjugated polyenes containing carbon, carbon double bonds.

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