# Effect of microheterogeneous media on the fluorescence and fluorescence probe properties of donor–acceptor diarylbutadienes

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Diarylbutadienes, namely 1-(*para*-cyanophenyl)-4-phenylbuta-1*E*,3*E*-diene (**1**), 1-(*para*-methoxyphenyl)-4-phenylbuta-1*E*,3*E*-diene (**2**), 1-(*para*-cyanophenyl)-4-(*para*-methoxyphenyl)-buta-1*E*,3*E*-diene (**3**) have been prepared and investigated for their absorption and fluorescence properties in homogeneous media of organic solvents, dioxane–water binary mixtures and in the microheterogeneous media of sodium dodecyl sulfate, cetyl trimethyl ammonium bromide and Triton-X-100 micelles. The fluorescence behaviour in various media has been correlated in terms of empirical solvent parameters such as Dimroth $E_T(30)$ and Kamlet–Taft $\pi^*$ values, and Kirkwood functions. A Linear correlation between solvent polarity and fluorescence properties is observed. In ethanol–methanol (1 : 1, v/v) matrix at 77 K, a blue-shifted fluorescence maximum with enhanced fluorescence quantum yields is observed for dienes **2** and **3**. The singlet excited state of diene **3** is found to be highly polar in nature. The fluorescence peak intensity of dienes **1** and **2** and the fluorescence emission wavelength maximum ($\lambda_f$ max) of diene **3** undergo significant changes upon changing the concentration of surfactants. The fluorescence properties of these dienes have been further used to characterize the micelles in terms of their critical micelle concentration and micropolarity.

## Introduction

Fluorescence probes as sensors and reporters of microenvironments are of much current interest.[1] However, only a few mechanisms and sensing systems have been described. In this context, fluorescence from twisted intramolecular charge transfer (TICT) excited states appears interesting.[2] Since TICT emission intensity and peak positions are known to be greatly affected by solvent polarity and polarizability, compounds capable of exhibiting TICT fluorescence may be used as sensors, chromogenic indicators and reporters of microenvironments. The molecules in TICT excited states have relatively large dipole moments and consequently the TICT excited state is influenced by the electronic properties of substituents, and is stabilized in polar environments.

Recently, we have reported that suitably tailored donor–acceptor 1,4-diarylbutadienes can also exhibit TICT fluorescence[3] and the TICT emission so observed for nitro-substituted diarylbutadienes can be employed for characterizing the microenvironment of micelles.[4] These photophysical investigations provided valuable information about the excited state nature of α,ω-diphenylpolyenes[5] which have attracted a great deal of attention in recent years because of their relevance to linear retinylidene polyenes that are involved in biological sensory and energy transductions.[6] Further, these studies gave new directions for the development of α,ω-diphenylpolyene-based fluorescence probes as sensors and reporters of microenvironments of organized assemblies.

The excited state structure and dynamics of diphenylpolyenes are, however, not clearly known and the sensing applications are very limited. The known probe applications of diarylbutadienes are based on the environment polarity sensitiveness of the charge transfer fluorescence maximum of the probe dienes bearing a strong electron withdrawing group on one of their phenyl rings.[4] It has, however, been found that the dienes substituted with donor–acceptor groups such as methoxy or cyano do not exhibit large solvent polarity dependent changes in their fluorescence maximum, thereby limiting their use as sensors and reporters of the microenvironment of organized assemblies.

We have now observed that for monosubstituted dienes bearing either a donor (*e.g.* OMe) or an acceptor (*e.g.* CN) group on the phenyl ring, while the changing surfactant concentration does not significantly affect the probes' fluorescence emission wavelength maximum ($\lambda_f$ max), significant change in the fluorescence peak intensity of the probe diene occurs. Such concentration dependent changes in fluorescence intensity of disubstituted dienes bearing both a donor and an acceptor (*e.g.* OMe and CN) is not observed. However, for such substituted dienes, the fluorescence peak position (*i.e.* $\lambda_f$ max) changes with changing surfactant concentration. The $\lambda_f$ max, in the case of disubstituted diene, and the fluorescence peak intensity, in the case of monosubstituted dienes, could be utilized to probe the microenvironment of micelles.

Thus, in this work, diarylbutadienes, namely 1-(*para*-cyanophenyl)-4-phenylbuta-1*E*,3*E*-diene (**1**), 1-(*para*-methoxyphenyl)-4-phenylbuta-1*E*,3*E*-diene (**2**), 1-(*para*-cyanophenyl)-4-(*para*-methoxyphenyl)buta-1*E*,3*E*-diene (**3**) [Fig. 1] have been prepared and investigated for their absorption and fluorescence properties in homogeneous media of organic solvents, 1,4-dioxane–water binary mixtures and in the microheterogeneous media of sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB) and Triton-X-100 micelles. The fluorescence probe properties of these dienes have been used to characterize the micelles in terms of their critical micelle concentration (CMC) and micropolarity.

## Experimental

### Apparatus and general procedures

Melting points were recorded on Veego melting point apparatus using capillary methods and are uncorrected. IR spectra

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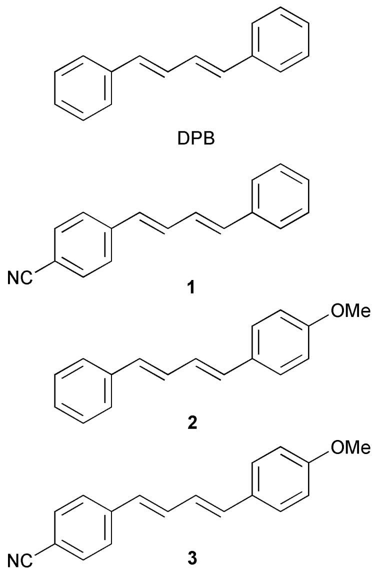

**Fig. 1** Structure of dienes **1**–**3**.

were measured on an Impact 400 Nicolet FTIR spectrophotometer in KBr discs. $^1$H NMR spectra in $CDCl_3$ were recorded on a 300 MHz FT NMR using $SiMe_4$ as internal standard. UV-vis measurements were done on Hitachi U-2000 or Shimadzu UV-260 spectrophotometers. Fluorescence measurements were performed on a Spex-fluorolog spectrofluorimeter equipped with accessories for low-temperature emission studies. Fluorescence measurements at low temperatures were made using ethanol–methanol (1 : 1 v/v) glass. Quantum yields of fluorescence ($\Phi_f$) were determined using quinine sulfate as standard.[7] For all the electronic spectroscopic studies (absorption, fluorescence excitation and emission), $1.0 \times 10^{-5}$ M solutions of the dienes were used. A Branson B-12 sonifier (450 W, 15 °C, 5 min) was used for sonification of the micellar solutions. All solutions of dienes were handled under protective red light conditions (10 W CEMA General Electric night lamp, red colour). Thin layer chromatographic (TLC) analyses were performed on silica gel plates using a 10% ethyl acetate–*n*-hexane (v/v) solvent system. Column chromatography was done on silica gel using a 5% ethyl acetate–*n*-hexane (v/v) mixture as eluting solvent. All solvents were dried and freshly distilled prior to their use.

### Reagents and synthesis procedure

The starting materials and reagents (cyanobenzyl bromide, benzyl bromide, triethyl phosphite, sodium methoxide *etc.* for synthesis of dienes **1**–**3**), 1,4-diphenylbutadiene (DPB), surfactants [cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and Triton-X-100 for micelle preparation], quinine sulfate [for determination of $\Phi_f$], $CDCl_3$ and $SiMe_4$ for NMR, and KBr for IR studies were from Aldrich Chem. Co. U.S.A. Solvents such as acetonitrile (MeCN), diethyl ether, dimethylformamide (DMF), dioxane, ethanol, ethyl acetate, *n*-heptane, *n*-hexane, methanol (MeOH) and tetrahydrofuran (THF), used in spectroscopic and other studies, were obtained from Spectrochem Pvt. Ltd., Mumbai. Petroleum ether (bp 60–80 °C) was from local suppliers. Deionized, double distilled water (Millipore) was used for preparing the micelle solutions. Chromatography grade silica gels were obtained from E. Merck (India) Ltd., Mumbai.

The dienes 1-(*para*-cyanophenyl)-4-phenylbuta-1*E*,3*E*-diene (**1**), 1-(*para*-methoxyphenyl)-4-phenylbuta-1*E*,3*E*-diene (**2**) and 1-(*para*-cyanophenyl)-4-(*para*-methoxyphenyl)-buta-1*E*, 3*E* diene (**3**) were synthesized from respective aldehydes and phosphonates by a generalized Emmons–Horner procedure.[8] Thus, **1** and **2** were obtained by the reaction of cinnamaldehyde with phosphonate esters, *p*-$NCC_6H_4CH_2PO(OEt)_2$ and *p*-$MeOC_6H_4CH_2PO(OEt)_2$ in the presence of sodium methoxide in DMF at ambient temperature. Similarly, the reaction of *para*-methoxycinnamaldehyde with the phosphonate *p*-$NCC_6H_4CH_2PO(OEt)_2$ afforded diene **3**. In a typical procedure, 0.01 mol phosphonate, 0.015 mol sodium methoxide and freshly distilled DMF were taken in a two-necked round-bottomed flask. The mixture was stirred for 10–15 min and a DMF solution of the appropriate aldehyde was added drop-wise under inert conditions. The stirring was continued until most of the aldehyde had reacted as indicated by TLC. After completion of the reaction, the reaction mixture was quenched with brine and the organic material was taken-up in diethyl ether. Usual work-up yielded a solid compound that was subjected to column chromatography to obtain the diene. Further purification of the diene was carried out by crystallization from petroleum ether (bp 60–80 °C) when yellowish needles of the dienes were obtained.

**1-(*para*-Cyanophenyl)-4-phenylbuta-1*E*,3*E*-diene (1).** This compound, obtained in 50% yield, showed physico-chemical data as described in literature[4] [mp 158–159 °C (lit.,[4] 158–159 °C)].

**1-(*para*-Methoxyphenyl)-4-phenylbuta-1*E*,3*E*-diene (2).** Yield 40%; mp 166–167 °C; UV-vis (THF): λmax, 340 nm, (ε, 65 909 $mol^{-1}$ $cm^{-1}$ l); $^1$H NMR ($CDCl_3$, 300 MHz): δ 3.80 (3H, s, methoxy protons), 6.62 (2H, d, $J = 14.83$ Hz, PhC*H*=CHCH=C*H*$C_6H_4$OMe), 6.83 (1H, dd, $J = 14.83/10.43$ Hz, *p*-$MeOC_6H_4$CH=C*H*), 6.94 (1H, dd, $J = 15.19/10.43$ Hz, *p*-PhCH=C*H*CH=), 7.21–7.35 (5H, m, phenyl protons), 6.87 (2H, dd of AB quartet, $J = 8.79/1.83$ Hz, *p*-methoxyphenyl protons), 7.38 (2H, dd of AB quartet, $J = 8.79/1.83$ Hz, *p*-methoxyphenyl protons).

**1-(*para*-Cyanophenyl)-4-(*para*-methoxyphenyl)-buta-1*E*,3*E*-diene (3).** Yield 40%; mp 173–174 °C; UV-vis (MeCN): λmax, 359 nm, (ε, 59 722 $mol^{-1}$ $cm^{-1}$ l); $^1$H NMR ($CDCl_3$, 300 MHz): δ 6.59 (1H, d, $J = 15.38$ Hz, *p*-$MeOC_6H_4$C*H*=CH), 6.71 (1H, d, $J = 15.38$ Hz, *p*-$NCC_6H_4$C*H*=CH), 6.82 (1H, dd, $J = 15.38/10.25$ Hz, *p*-$MeOC_6H_4$CH=C*H*), 7.03 (1H, dd, $J = 15.38/10.25$ Hz, *p*-$NCC_6H_4$CH=C*H*), 6.89 (2H, dd of AB quartet, $J = 8.79/1.83$ Hz, *p*-methoxyphenyl protons), 7.40 (2H, dd of AB quartet, $J = 8.79/1.83$ Hz, *p*-methoxyphenyl protons). 7.48 (2H, dd of AB quartet, $J = 8.42/1.83$ Hz, *p*-cyanophenyl protons), 7.59 (2H, dd of AB quartet, $J = 8.42/1.83$ Hz, *p*-cyanophenyl protons).

## Results and discussion

### Absorption and fluorescence studies in homogeneous media of organic solvents and microheterogeneous media of micelles and dioxane–water system

The absorption and fluorescence spectral data of dienes **1**–**3** in organic solvents of different polarity are given in Table 1. Representative fluorescence spectra in different media are shown in Fig. 2. As compared to the parent diphenylbutadiene (DPB), the substituted dienes exhibit red-shifted absorption λmax. The magnitude of shift varies with the substituents. In contrast to nitro-substituted diphenylbutadienes, solvent polarity does not significantly affect the absorption λmax of these dienes. Among the three substituted dienes, the disubstituted diene **3** exhibits the maximum red shift in the absorption λmax. The red-shift is attributed to the increased conjugation due to the presence of an additional substituent on the *para* position of the second aromatic ring.

As compared to the homogeneous media of organic solvents, the micellar environment does not cause significant change in the absorption spectra of these dienes (Table 2).

**Table 1** UV-vis absorption and fluorescence data of dienes **1**–**3** in homogenous media[a]

| Diene | Solvent | Maximal wavelength/nm Absorption | Emission | Excitation | $\Phi_f$ ($\pm$0.001) | Stokes' shift/ $cm^{-1}$ |
|---|---|---|---|---|---|---|
| **1** | *n*-Heptane | 344 | 406 | 344 | 0.003 | 4439 |
| | Dioxane | 347 | 407 | 345 | 0.007 | 4248 |
| | THF | 346 | 418 | 346 | 0.007 | 4978 |
| | DMF | 349 | 422 | 345 | 0.014 | 4956 |
| | MeCN | 344 | 421 | 344 | 0.003 | 5260 |
| | MeOH | 344 | 421 | 343 | 0.004 | 5480 |
| **2** | *n*-Heptane | 338 | 387 | 334 | 0.050 | 3833 |
| | Dioxane | 340 | 399 | 337 | 0.019 | 4349 |
| | THF | 341 | 418 | 337 | 0.009 | 5402 |
| | DMF | 342 | 419 | 337 | 0.009 | 5373 |
| | MeCN | 338 | 413 | 334 | 0.004 | 5372 |
| | MeOH | 337 | 413 | 333 | 0.004 | 5460 |
| **3** | *n*-Heptane | 354 | 399 | 362 | 0.008 | 3186 |
| | Dioxane | 356 | 431 | 364 | 0.006 | 4688 |
| | THF | 354 | 442 | 365 | 0.005 | 5624 |
| | DMF | 350 | 488 | 371 | 0.009 | 7441 |
| | MeCN | 353 | 484 | 362 | 0.003 | 7667 |
| | MeOH | 352 | 482 | 364 | 0.003 | 7662 |

[a] 1,4-Diphenylbutadiene (DPB): abs $\lambda_f$ max 335 nm, em $\lambda_{max}$ 375–378 nm (in *n*-heptane, dioxane, methanol and acetonitrile); $\Phi_f$ :0.222 (*n*-heptane), 0.052 (dioxane), 0.015 (methanol), 0.009 (acetonitrile).

Only a very moderate red shift in the absorption λmax of dienes **1** and **3** is observed. The absorption and fluorescence data for dienes **1**–**3** in various compositions of dioxane–water are presented in Table 3. The increasing amount of water in dioxane does not alter the absorption maximum of these dienes to any significant extent. Thus, in general, solvent polarity does not significantly affect the ground state of these dienes.

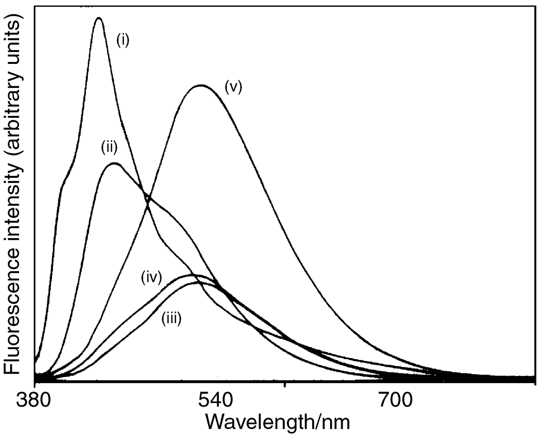

**Fig. 2** Fluorescence spectra of diene **3** in (i) *n*-heptane, (ii) dioxane, (iii) methanol, (iv) MeCN, (v) DMF.

In contrast to a rather moderate solvent polarity effect on the absorption spectra, significant solvent polarity effects are seen in the fluorescence behavior of these substituted dienes. In organic solvents and dioxane–water systems, as the polarity (relative permittivity, ε) of the media is increased, the $\lambda_f$ max undergoes a red shift. The maximum red shift is observed for the disubstituted diene **3**.

The dependence of Stokes' shift on the solvent polarity is correlated with solvent parameters like the Dimroth parameter, $E_T(30)$ [a plot of $E_T(30)$ of various solvents, as given in ref. 9, *vs.* Stokes' shift of dienes **1**–**3** in those solvents is given in Fig. 3][9] and Kamlet–Taft $\pi^*$ scale [a plot of $\pi^*$ values of various solvents, as given in ref. 10, *vs.* $\nu_f$ max of diene **1**–**3** in those solvents as given in Fig. 4].[10] It is observed that the Stokes' shift increases linearly with increase in solvent polarity. The dienes show reasonable correlation with solvent parameters $E_T(30)$ and $\pi^*$ with the following regression data: **1** [slope = 32.25, linear correlation ($r$) = 0.8441, number of data points ($N$) = 11], **2** (slope = 45.45, $r$ = 0.8366, $N$ = 11) and **3** (slope = 128.57, $r$ = 0.9139, $N$ = 11). The slope in case of diene **3** is the highest compared to other dienes.

**Table 2** UV-vis absorption and fluorescence data of dienes **1**–**3** and DPB in microheterogeneous media of micelles

| Diene | Media | Maximal wavelength/nm Absorption | Emission | Excitation | $\Phi_f$ ($\pm$0.001) | Stokes' shift/ $cm^{-1}$ |
|---|---|---|---|---|---|---|
| DPB | CTAB | 334 | 381 | 331 | 0.148 | 3694 |
| | SDS | 333 | 379 | 329 | 0.108 | 3645 |
| | Triton-X-100 | 334 | 381 | 331 | 0.166 | 3693 |
| **1** | CTAB | 350 | 421 | 346 | 0.012 | 4818 |
| | SDS | 350 | 421 | 346 | 0.007 | 4818 |
| | Triton-X-100 | 350 | 418 | 346 | 0.020 | 4647 |
| **2** | CTAB | 343 | 417 | 337 | 0.022 | 5173 |
| | SDS | 340 | 395 | 335 | 0.017 | 4095 |
| | Triton-X-100 | 343 | 399 | 338 | 0.042 | 4091 |
| **3** | CTAB | 365 | 483 | 361 | 0.013 | 6693 |
| | SDS | 361 | 484 | 358 | 0.008 | 7039 |
| | Triton-X-100 | 365 | 468 | 359 | 0.018 | 6029 |

**Table 3** UV-vis absorption and fluorescence data of dienes **1**–**3** in dioxane–water binary mixtures

| | **1** | | | | **2** | | | | **3** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % Water | $\lambda$ abs/ nm | $\lambda_f$ max/ nm | $\lambda$ ex/ nm | Stokes' shift/ $cm^{-1}$ | $\lambda$ abs/ nm | $\lambda_f$ max/ nm | $\lambda$ ex/ nm | Stokes' shift/ $cm^{-1}$ | $\lambda$ abs/ nm | $\lambda_f$ max/ nm | $\lambda$ ex/ nm | Stokes' shift/ $cm^{-1}$ |
| 0 | 347 | 407 | 347/362 | 4248 | 340 | 399 | 337 | 4349 | 353 | 431 | 356 | 5126 |
| 10 | 346 | 417 | 351/363 | 4920 | 338 | 417 | 337 | 5604 | 356 | 435 | 364 | 5101 |
| 20 | 347 | 419 | 363 | 4952 | 340 | 417 | 336 | 5430 | 355 | 451 | 363 | 5996 |
| 30 | 347 | 419 | 363 | 4952 | 340 | 417 | 336 | 5430 | 356 | 480 | 363 | 7256 |
| 40 | 346 | 421 | 363 | 4952 | 339 | 418 | 336 | 5575 | 356 | 485 | 364 | 7471 |
| 50 | 344 | 422 | 363 | 5373 | 339 | 418 | 335 | 5575 | 356 | 487 | 364 | 7556 |
| 60 | 344 | 422 | 362 | 5429 | 338 | 418 | 338 | 5662 | 354 | 492 | 364 | 7923 |

Similarly, when the Kamlet–Taft $\pi^*$ scale is plotted against $\nu_f$ max, a linear decrease is observed with increase in the value of $\pi^*$. The observed solvent correlations are as follows: **1** (slope $= -8.10 \times 10^{-5}$, $r = -0.8250$, $N = 6$), **2** (slope $= -1.42 \times 10^{-4}$, $r = -0.9052$, $N = 5$), **3** (slope $= -3.91 \times 10^{-5}$, $r = -0.9329$, $N = 5$) (Fig. 4). The Stokes' shifts of the dienes in DMF are excluded from the calculation of linear correlation $r$ in the plot of $E_T(30)$ *vs.* Stokes' shifts. The deviations from linearity in the case of aprotic solvents like DMF can be accounted for in terms of net stabilization of the diene in the excited state due to specific solute–solvent interactions. These quantitative analyses of solvent polarity parameters reveal that the solvated excited state of the dienes is more stabilized in polar medium than the ground state. Thus, the excited states of these dienes can be of a polar nature. The solvatochromic shift of these dienes were further analysed using the Lippert–Mataga[11] equation: $\nu_a - \nu_f = \{[2(\mu_e - \mu_g)^2/hca^3]F(D, n)\}$, where $\nu_a - \nu_f$ is the Stokes' shift, $\mu_e$ and $\mu_g$ are excited and ground state dipole moments respectively, $\mu_e - \mu_g = \Delta\mu$ (change in dipole moment), $h$ is Plancks' constant, $c$ is the velocity of light, $a$ is the Onsagers' radius, and $F(D, n) = \Delta f$ is the solvent polarity determining factor. $\Delta f = [(D - 1)/(2D + 1)] - [(n^2 - 1)/(2n^2 + 1)]$ where $D$ is the relative permittivity and $n$ is the refractive index of the solvent. The Onsager radius for these dienes was taken as 9 Å which is a known value for similar diphenybutadiene compounds namely 1-*para*-*N*,*N*-dimethylaminophenyl)-4-(*para*-nitrophenyl)-buta-1*E*,3*E*-diene.[12] For dienes **1**–**3**, the Lippert–Mataga plot of Stokes' shift *vs.* solvent parameter $\Delta f$ is shown in Fig. 5. The change in dipole moment ($\Delta\mu$) thus obtained for dienes **1**–**3** are as follows: $\Delta\mu$ in Debye:

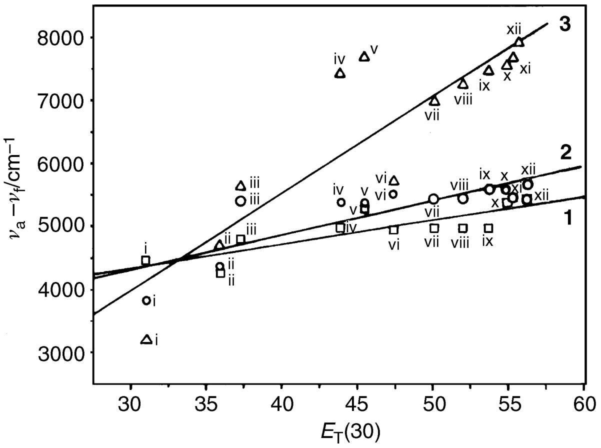

**Fig. 3** A plot of Dimroth empirical solvent parameter[9] $E_T(30)$ *vs.* Stokes' shifts of dienes **1**–**3** in: (i) *n*-heptane, (ii) dioxane, (iii) THF, (iv) DMF, (v) MeCN, (vi) 10% water in dioxane, (vii) 20% water in dioxane, (viii) 30% water in dioxane, (ix) 40% water in dioxane, (x) 50% water in dioxane, (xi) methanol, (xii) 60% water in dioxane.

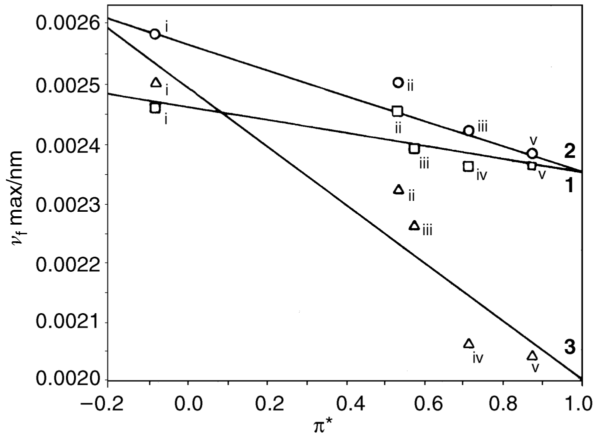

**Fig. 4** A plot of Kamlet–Taft $\pi^*$ scale[10] against $\nu_{f\,max}$ of dienes **1**–**3** in (i) *n*-heptane, (ii) dioxane, (iii) THF, (iv) MeCN, (v) DMF.

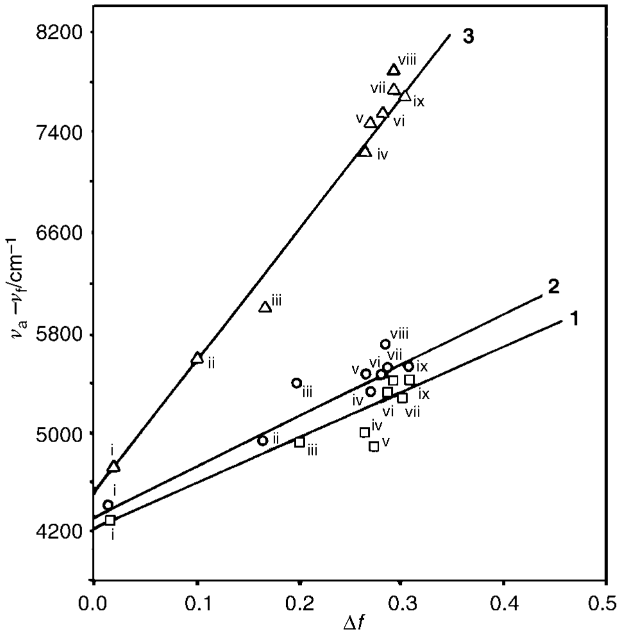

**Fig. 5** Lippert–Mataga[11] plots of solvent parameter $\Delta f$ *vs.* Stokes' shifts of dienes **1**–**3** in: (i) *n*-heptane, (ii) dioxane, (iii) THF, (iv) DMF, (v) MeCN, (vi) 10% water in dioxane, (vii) 20% water in dioxane, (viii) 30% water in dioxane, (ix) methanol.

**1**: 13.01, **2**: 13.60, **3**: 21.30. The Lippert–Mataga plot clearly demonstrates the solvent polarity sensitive fluorescence behaviour of these dienes. These dipole moment values point towards a polar nature for the singlet excited states of these dienes. A rather large change in dipole moment upon excitation of diene **3** indicates that its singlet excited state is certainly polar in nature. Based on changes in dipole moments excited state polarity has also been argued in other molecules.[3,4,13,14]

In micellar media, $\lambda_f$ max of the parent DPB is slightly red-shifted as compared to in organic solvents. Diene **1** shows a fluorescence peak at around 418–421 nm, similar to its fluorescence in polar solvents like methanol and acetonitrile. The fluorescence spectrum of diene **3** in micelles is significantly red-shifted as compared to that in non-polar *n*-heptane. However, the fluorescence maxima in micelles are similar to those in polar solvents like DME, MeCN and MeOH. As compared to in polar solvents, the fluorescence maximum of **3** is blue-shifted in Triton-X-100 micelles (Fig. 6). In general, as compared to the fluorescence of dienes **1**–**3** in non-polar *n*-heptane, in micellar media the fluorescence of these dienes is red-shifted; the maximum red shift is observed for diene **3**. A comparison of the $\lambda_f$ max of dienes **1**–**3** in polar organic solvent such as methanol with those in micelles reveals that the dienes experience relatively polar environment in the micelles.

The $\Phi_f$ of these dienes in organic solvents is generally very low. The fluorescence efficiency of dienes **2** and **3** is generally decreased in polar solvents. As compared to the unsubstituted parent DPB, the substituted dienes show relatively small $\Phi_f$. The $\Phi_f$ of these dienes is relatively higher in Triton-X-100 as compared to either SDS or CTAB. The fluorescence efficiency is lowest in SDS micelles for all four dienes (DPB and **1**–**3**). DPB shows relatively greater fluorescence efficiency in all the micelles. Thus, the presence of substituents as well as solvent polarity causes a decrease in $\Phi_f$ in donor–acceptor diarylbutadienes. The decrease in fluorescence efficiency as the substitution takes place suggests increased non-radiative transitions in the photoprocesses of diphenylbutadienes.

The Stokes' shift for diene **3** in polar homogeneous media of organic solvents such as DMF, acetonitrile and methanol is greater than that in micellar media. Among the three micelles studied, the smallest Stokes' shift is observed in neutral Triton-X-100. Thus, the ionic micelles of SDS and CTAB affect the fluorescence spectra most. This can be due to interactions between the micellar charges and the polar diene fluorophore. Thus, while diene **3** shows significant micelle-charge-dependent fluorescence peak shifts, dienes DPB, **1** and **2** do not show such marked changes in their fluorescence $\lambda_f$ max.

As compared to that in fluid solution at 298 K, the $\lambda_f$ max of dienes **1** and **3** gets blue-shifted in ethanol–methanol glass at 77 K (Table 4). Fig. 7 shows the fluorescence of dienes **2** and **3** at 77 K and at 298 K. However, the blue shift is more

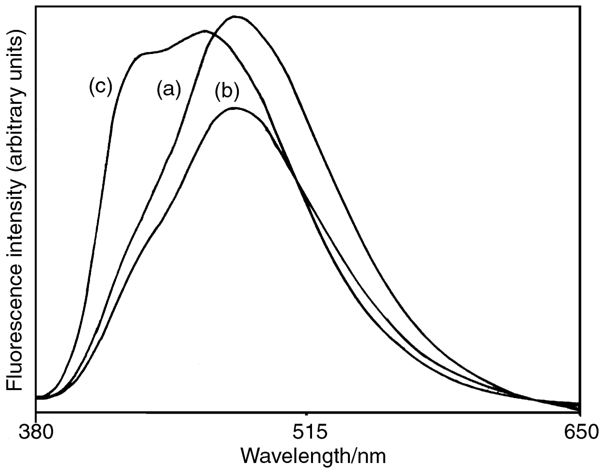

**Fig. 6** Fluorescence spectra of dienes **3** in micelles of (a) CTAB, (b) SDS and (c) Triton-X-100.

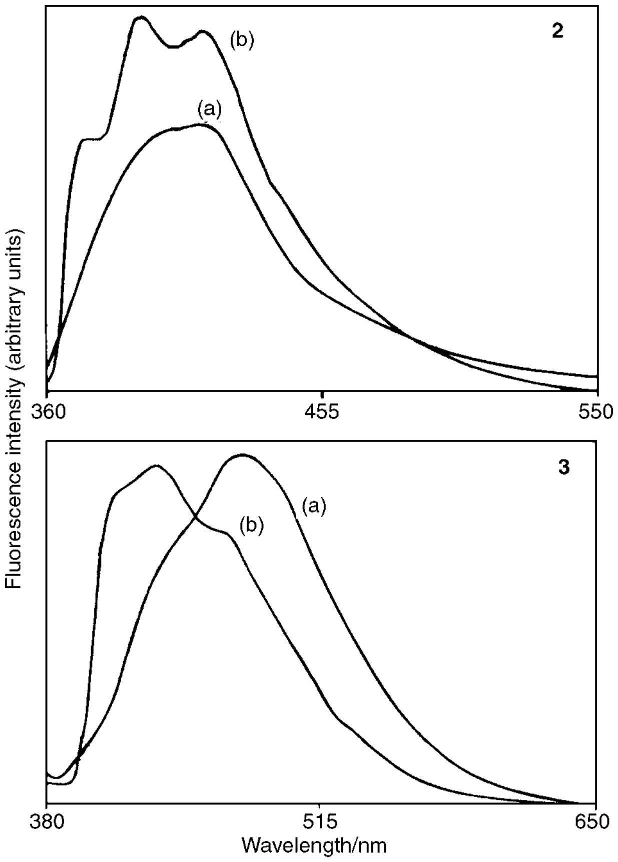

**Fig. 7** Fluorescence spectra of dienes **2** and **3** at 298 K (a) and 77 K (b).

**Table 4** Fluorescence emission and excitation data for dienes **1**–**3** and DPB at 298 K and at 77 K in 1 : 1 (v/v) ethanol–methanol matrix

| | 298 K | | | 77 K | | |
|---|---|---|---|---|---|---|
| Diene | $\lambda_f$ max Emission | $\lambda_f$ max Excitation | $\Phi_f$ $\pm 0.001$ | $\lambda_f$ max Emission | λmax Excitation | $\Phi_f$ $\pm 0.001$ |
| DPB | 375 | 335 | 0.018 | 379 | 334 | *ca.* 1.0 |
| **1** | 418 | 347 | 0.007 | 412 | 328 | 0.500 |
| **2** | 416 | 333 | 0.005 | 417 | 333 | 0.401 |
| **3** | 478 | 357 | 0.006 | 436 | 360 | 0.509 |

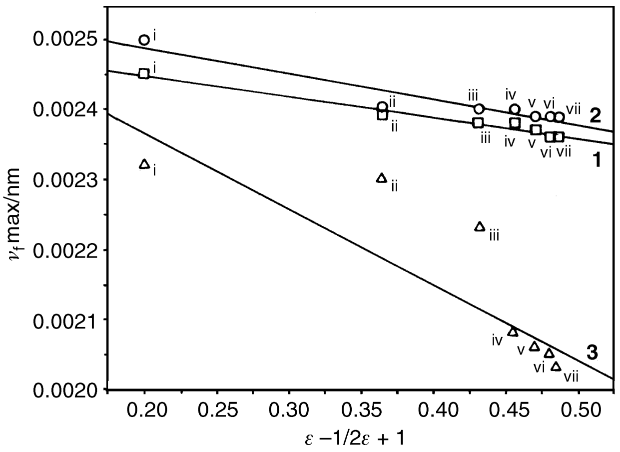

**Fig. 8** Variation of $\nu_f$ max of dienes **1**, **2** and **3** with Kirkwood function[18] ($\varepsilon - 1/2\varepsilon + 1$) for dioxane–water binary mixtures: (i) dioxane, (ii) 10% water, (iii) 20% water, (iv) 30% water, (v) 40% water, (vi) 50% water and (vii) 60% water in dioxane.

pronounced (42 nm) in diene **3** bearing the cyano as well as the methoxy group on the phenyl rings than in diene **1**, which has only the cyano group on one of its phenyl rings. The $\Phi_f$ dramatically increases for all the dienes at lower temperature in the glassy matrix. For the substituted dienes, however, $\Phi_f$ is far from unity though they are increased compared to $\Phi_f$ obtained at 298 K. This indicates that even at low temperatures the non-radiative transitions tend to decrease the fluorescence in substituted dienes. All the fluorescence spectra observed in rigid matrices are finely structured indicating the absence of the stabilizing effects of solvent polarity, molecular motions and related geometrical changes resulting in blue-shifted emissions and increased fluorescence quantum yields.

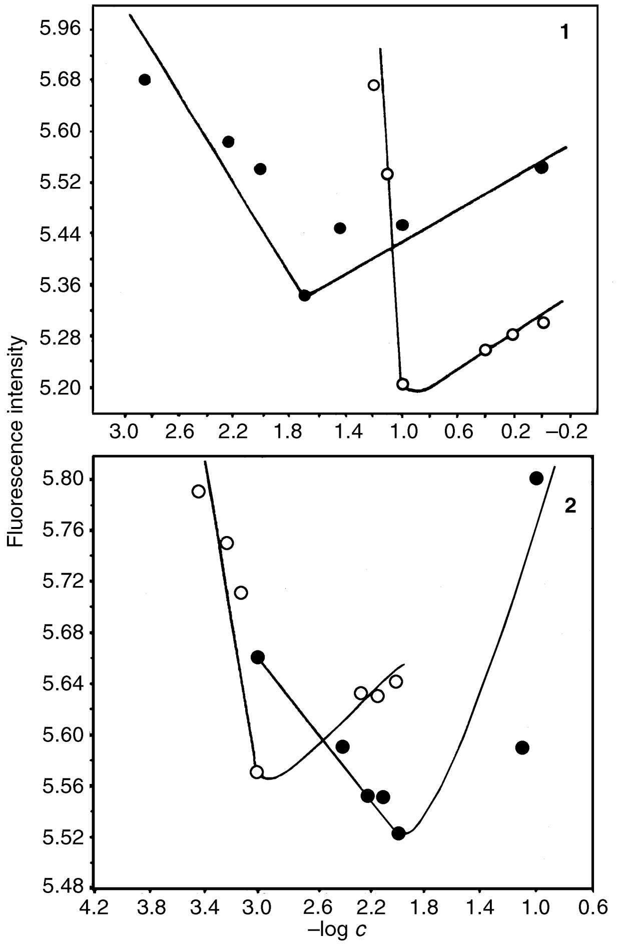

**Fig. 9** Variation of the fluorescence intensity of dienes **1** and **2** with surfactant concentration. CTAB (○), SDS (●).

All-*trans*-diphenylpolyenes belong to the $C_{2h}$ point group and their ground states are characterized by $A_g$ symmetry while the excited $\pi\pi^*$ states can have either $A_g^-$ or $B_u^+$ symmetry.[15] The $A_g$ excited state is covalent in nature and hence it is insensitive to solvent polarity. However, the $B_u$ excited state is ionic and it is expected to be stabilized in polar as well as polarizable environments. The excited state properties of these polyenes are governed by several factors including the order of the two low-lying excited state levels, their electronic energy gap and the inter-state mixing. The order of the two lowest-lying excited states of longer all-*trans*-diphenylpolyenes is relatively better understood. However, for 1,4-diphenylbutadiene, the energy gap between the two lowest excited states ($2A_g$ and $1B_u$) is rather small and their actual order is not clearly known. Given a rather small $2A_g$–$1B_u$ splitting, small changes in molecular structure or solvent orientation are expected to affect the relative ordering of the lowest lying excited states and hence the excited state properties of these dienes.

The present results indicate that the lowest excited state of these dienes is of $B_u$ character. The $B_u$ excited state, being ionic in nature, is stabilized by the polar electronic effects of the substituents and the polar solvents and hence the red shifts in the fluorescence. The magnitude and the trends in $\Phi_f$ are not very clear, however. Highly solvent dependent singlet–triplet mechanisms in donor–acceptor diarylethene compounds have been reported.[16] Whether the presence of donor–acceptor groups promotes intersystem crossing leading to the formation of triplets and hence diminished fluorescence in these dienes is not presently clear. The reduced and varying fluorescence efficiency can also be due to state switching. In non-polar solvents, the fluorescent excited state can be of $2A_g$ nature. Since the $2A_g^- \rightarrow A_g$ transition is symmetry forbidden, the resulting emission is weak.

## Micropolarity and CMC of SDS, CTAB and Triton-X-100 micelles as probed by donor–acceptor diarylbutadienes

Microheterogeneous media of surfactant assemblies are known to influence the excited state properties of linear polyenes.[17] Using the charge transfer fluorescence properties of the nitro-substituted dienes, we have recently reported the determination of the relative permittivity and CMC of micelles.[4] Because of the lack of strong charge transfer fluorescence in monosubstituted dienes **1** and **2**, we have used the changes in the fluorescence peak intensity of these dienes to determine the CMC and relative permittivity of the micelles incorporating the dienes. As reported earlier, the relative permittivity of micellar domains incorporating the dienes, was determined by first investigating the fluorescence characteristics of these dienes in dioxane–water binary mixtures.[4] Diene **3** shows a maximum increase of about 61 nm in $\lambda_f$ max as the percentage of water is increased to 60%. However, for a 60% water content dienes **1** and **2** show an increase of only about 15–19 nm (*cf.* Table 3).

Changing the composition of the binary solvent mixtures is expected to bring about changes in the electrostatic solute/solvent interactions that can be analyzed in terms of the Kirkwood function ($\varepsilon - 1/2\varepsilon + 1$)[18] relating relative permittivity ($\varepsilon$) of solvents. The Kirkwood correlation in terms of an electrostatic model is used to show that the energy associated with charge or dipole varies according to relative permittivity function. In order to describe such electrostatic solvent effects, we plotted fluorescence wavenumber ($\nu_f$ max) of dienes **1**–**3** *vs.* Kirkwood parameter ($\varepsilon - 1/2\varepsilon + 1$) and the results are shown in Fig. 8. In all three cases, a linear correlation is observed with the largest slope in case of diene **3** (slope $= -1.1 \times 10^{-2}$, $r = -0.9062$, $N = 7$) as compared to the dienes **1** (slope $= -3.46 \times 10^{-4}$, $r = -0.9499$, $N = 6$) and **2** (slope $= -3.8 \times 10^{-4}$, $r = -0.9830$, $N = 7$) indicating the more polar nature of its excited state.

Perusing the data of Fig. 8 and comparing the fluorescence of micelle-incorporated diene **3** with that of dioxane–water-incorporated diene **3,** it is inferred that the diene is located in the polar interfacial domain of the micelle especially for CTAB and SDS micelles. Since the fluorescence $\lambda_f$ max of diene **1** in micelles is similar to that observed in polar methanol, it is further believed that these dienes are also located in the interfacial region, while diene **2** occupies a hydrophobic site especially in SDS and Triton-X micelles.

For determining the CMC values, fluorescence intensities of the micelle-constituted dienes **1** and **2** were plotted against the varying concentration of the surfactants (CTAB and SDS) (Fig. 9). For diene **3**, a plot of changing $\lambda_f$ max *vs.* varying concentration of surfactant CTAB and SDS was made (Fig. 10). The CMC values calculated thus are given in Table 5. The CMC values so obtained are in fair agreement with the CMC values reported in the literature.[19] Since the critical concentration of micelles is also dependent on the stereo-electronic nature of the fluorophores, slight variation in the values of CMC are expected. Below the CMC, dienes **1** and **2** show structured fluorescence with a significant increase in intensity in the premicellar region. The increase in fluorescence intensity of dienes **1** and **2** corresponds to the formation of premicellar aggregates due to the interaction of monomeric surfactant with probe molecules.[20] The fluorescence intensity changes for monosubstituted dienes are predominant in ionic micelles, while in the micelles of Triton-X-100, the intensity changes observed do not show a regular trend. Thus, diphenylbutadienes bearing relatively weak donor–acceptor substituents can act as probes in ionic micelles.

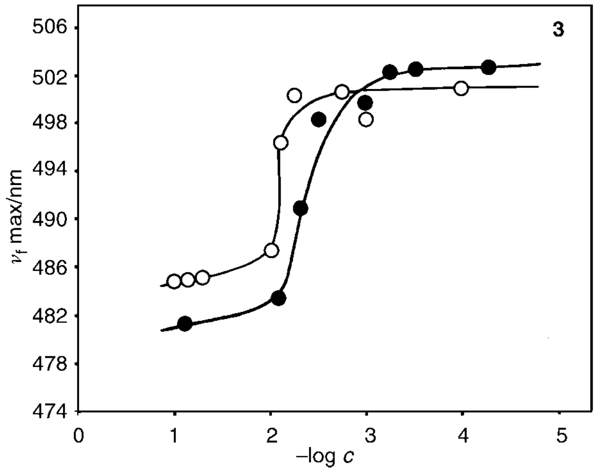

**Fig. 10** Variation of $\lambda_f$ max of diene **3** with surfactant concentration. CTAB (○), SDS (●).

**Table 5** Critical micelle concentration (CMC) of CTAB and SDS as determined using fluorescence of dienes **1**–**3** and DPB

| Diene | Surfactant | CMC[a]/ mol L$^{-1}$ | ε |
|---|---|---|---|
| DPB | CTAB | $1.10 \times 10^{-3}$ | |
| | SDS | $5.75 \times 10^{-3}$ | — |
| | Triton-X-100 | — | |
| 1 | CTAB | $3.60 \times 10^{-3}$ | 18.0 |
| | SDS | $1.80 \times 10^{-2}$ | 18.0 |
| | Triton-X-100 | — | 9.0 |
| 2 | CTAB | $3.00 \times 10^{-3}$ | 11.0 |
| | SDS | $2.10 \times 10^{-3}$ | 2.5 |
| | Triton-X-100 | — | 2.0 |
| 3 | CTAB | $1.9 \times 10^{-3}$ | 19.0 |
| | SDS | $6.3 \times 10^{-3}$ | 19.5 |
| | Triton-X-100 | — | 13.0 |

[a] Lit.,[19] CMC: CTAB, $9.4 \times 10^{-4}$; SDS, $8 \times 10^{-3}$; Triton-X-100, $2.4 \times 10^{-4}$.

## Conclusion

In conclusion it can be said that the present study has brought out hitherto unknown aspects of the excited state of donor–acceptor diarylbutadienes. The fluorescence of donor–acceptor 1,4-diarylbutadienes in polar solvents is from the polar $B_u$ excited state. The electronic effects of the substituents and the solvent polarity greatly influence the relative ordering of the two lowest-excited states of these dienes. It has also been found that the dienes bearing relatively weaker donor–acceptor groups do not exhibit dramatic solvent polarity based shifts in their $\lambda_f$ max. However, such dienes exhibit micellar charge dependent changes in their fluorescence intensity in the micellar environment. These fluorescence properties of the dienes can be utilized to investigate the microenvironment of ionic micelles and related organized assemblies. In terms of the development of charge on the fluorophore and consequent polarity in the excited state, this study brings out interesting features of the electronically excited state potential energy surface of linear polyenes. Besides, the results can be useful in developing newer molecular systems as environment polarity probes and all-optical ultrafast switching mechanisms.[2,21]

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