Effects of Liquid Crystal Environment on the Spectroscopic and Photophysical Properties of Well-Known Reacting Systems 2,3-Dimethylindole (DMI) and 9-Cyanoanthracene (9CNA)

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Electrochemical and steady-state and time-resolved spectroscopic studies on a disubstituted indole, 2,3-dimethylindole (DMI), and well-known electron acceptor 9-cyanoanthracene (9CNA) in liquid crystal (LC) 4-(n- pentyl)-4′-cyanobiphenyl (5CB) environment demonstrate entirely different spectroscopic and photophysical behaviors from those observed earlier by our research group with the same reacting systems in isotropic media n-heptane and acetonitrile (ACN). From the UV−vis absorption spectral measurements of the donor DMI in the presence of the acceptor 9CNA in liquid crystal medium (in 5CB) in various temperatures above the nematic−isotropic phase transition from 308 to 313 K (pseudo-ordered domain), it was observed that the lower energy lying absorption band of DMI situates in a longer wavelength region than the corresponding band observed in isotropic medium n-heptane or ACN. The possibility of the photochromic effect is discussed. In this band, the degree of mixing of the two closely spaced electronic states ^1L_a (S_2) and ^1L_b (S_1) of DMI was very prominent in the ordered LC environment (5CB) whereas in isotropic medium the dominant contribution for the formation of the lower energy band system primarily originates from the ^1L_b (S_1) state, as evidenced from the steady-state polarization measurements. Both steady-state fluorescence quenching and time-resolved fluorescence studies clearly demonstrate in favor of the presence of only the static mode in LC environment. The situation differs in isotropic media where the dynamic process possesses the key role in the quenching mechanism. Expectedly, the transient absorption measurements by the nanosecond laser flash photolysis technique show a lack of formation of transient ionic species in the pseudo-ordered domain of 5CB. On the contrary, in isotropic solvents n-heptane and ACN, the transient absorption spectra measured by the same nanosecond laser flash photolysis technique exhibit the broad band of 9CNA radical anion at around 560 nm ($9CNA^-$) and the band of neutral radical of DMI at 540 nm. It is inferred that the charge-separation reactions occurring within the present intermolecular systems could be stopped significantly by changing the nature of the environment from the isotropic to the LC's pseudo-ordered domain which situates closely above the nematic (N)−isotropic (I) phase transition temperature. From the steady-state and time-resolved investigations, it is revealed that, due to the hysteresis phenomenon, the nematic phase properties persist over a wide temperature range well within pseudo-ordered domain to some extent into the isotropic phases. The investigations with the different donor−acceptor inter- and intramolecular systems in 5CB and some other LC's environment are underway.

1. Introduction

In recent years, great attention has been devoted to the study of intermolecular photoinduced electron transfer (PET) and photophysical properties of different molecules in different anisotropic environments due to their wide applications in electronics devices and photosynthesis and in the areas of solar energy conversion and optical signal processing.[1−4] An excellent anisotropic medium is a liquid crystalline medium, both below and a few degrees (K) above the nematic−isotropic temperature range.[5−8] Both physical and chemical properties of many compounds have been drastically changed when the observations proceed from isotropic to anisotropic environments. Both theory and experiments have shown that the domain effect persists at temperatures several degrees above the nematic (N)−isotropic (I) phase transition temperature of nematic liquid crystals.[9−11] Spectroscopic measurements conducted on these heated liquid crystal samples assumed to have the pseudodomain or partially ordered medium a few degrees above the N−I phase transition temperature. The liquid crystal 5CB displays a nematic liquid crystal phase at room temperature, and its N−I phase transition occurs at 35 °C. The pseudo-ordered domain of liquid crystals provides an intriguing environment to study PET. This order provides a way of controlling electron-transfer rates and also provides insights into the mechanisms of electron-transfer reactions.[9,12−14] Studies of electron-transfer reactions in LCs provide a conceptual bridge between experimental results obtained in isotropic solvents and those obtained in more ordered environment such as surfaces, monolayers, macromolecular ensembles, and crystals. In all of these cases, the "solvent" has an ordered structure that could have a critical impact on electron transfer (ET) processes. An understanding of how molecular order affects charge transfer or ET processes has importance in developing technologies based on this process.

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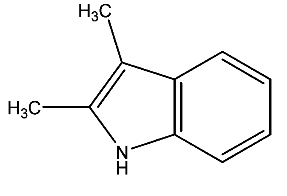
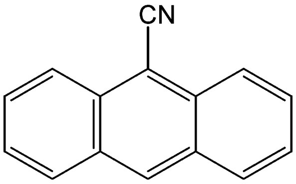


DMI



9CNA

Figure 1. Molecular structures of DMI and 9CNA.

In the present investigation, systematic studies were made on 2,3-dimethylindole (DMI) and 9-cyanoanthracene (9CNA) (Figure 1) in liquid crystal 5CB environment by using electrochemical and steady-state and time-resolved spectroscopic (fluorescence lifetime by time correlated single photon counting and transient absorption spectra with the help of nanosecond laser flash photolysis) techniques. The results are described in this paper, and the data obtained from the present investigation at temperatures above the nematic to isotropic (N−I) phase transition of the liquid crystal 5CB, i.e., within small pseudo-short-range ordered domain, have been compared with those obtained with the same reacting systems in the environment of isotropic solvents[15] of varying polarity, e.g., n-heptane (NH) and acetonitrile (ACN).

2. Experimental Section

2.1. Materials. All the samples of DMI and 9CNA (97% pure), supplied by Aldrich, were purified by vacuum sublimation. The solvent used here is liquid crystal 4-(n-pentyl)-4′-cyanobiphenyl (5CB).

2.2. Steady-State Spectroscopic Apparatus and Time Resolved Fluorescence. At the ambient temperature (296 K), steady-state electronic absorption spectra of solutions (10^{-5} to 10^{-6} mol dm^{-3}) of the samples in 5CB were recorded by using 2 mm path length rectangular quartz cells by means of an absorption spectrophotometer (Shimadzu UV−vis 2401PC). A long cylindrical quartz tubing of 2 mm diameter was used for the spectroscopic study of the samples in the liquid crystal environment. A 6 wt % nylon solution was made in concentrated formic acid; this solution was poured into some of the shorter tubes; and, after $^2/_3$ min, the cylindrical tubes were emptied, then baked in the oven at 120 °C for 1 h, and then slowly cooled down. A uniform velvet paper was then rolled and inserted into the tube so that the thin nylon layers inside the tubes were scratched. In this way, the tubes have been prepared for the measurement of steady-state fluorescence emission spectra using the F-4500 fluorescence spectrophotometer (Hitachi). The surface of the tubes could influence LC molecules up to a certain distance. Consequently, the LC molecules became aligned along the axis of the cylinder; i.e., the preferred direction of the director **n** was parallel to the axis of the cylinder. After that, the cylinders were used as a sample holder for the spectroscopic study. Polarized spectra were measured with the UV−vis polarizer. For fluorescence lifetime measurements, the samples (DMI, 9CNA, and the different mixtures of DMI and 9CNA wherein a fixed concentration of the latter and varying concentrations of the former were used) were excited at 380 nm using a picosecond diode (IBH Nanoled-07). The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). The time correlated single photon counting (TCSPC) setup consists of an ortec 9327 CFD and a Tennelec TC 863 TAC. The data are collected with a PCA3 card (Oxford) as a multichannel analyzer. The typical fwhm of the system response is about 80 ps. The channel width is 12 ps/channel. The fluorescence decays were deconvoluted using IBH DAS6 software.

The degree of polarization (P) was measured with the help of UV−vis polarizer accessories including a UV linear dichoric polarizer, with wavelength range 230−770 nm, purchased from Oriel Instruments. The observed degree of polarization (P) values were obtained from the following relation:[16,17]

$$P = [I_{EE} - (I_{BE}/I_{BB})I_{EB}]/[I_{EE} + (I_{BE}/I_{BB})I_{EB}] \qquad (1)$$

Here, I_{EE} and I_{EB} are the intensities of parallel and perpendicular polarized emission with vertically polarized excitation, and I_{BB} and I_{BE} are the intensities of horizontally and vertically polarized emission when excited with horizontally polarized light. I_{BE}/I_{BB} defines the instrumental correction factor G (polarization characteristic of the photometric system). This correction is made for any change in the sensitivity of the emission channel for the vertically and horizontally polarized components.

2.3. Laser Flash Photolysis. The experiments were carried out in a conventional laser flash photolysis (LFP) setup (laser kinetic spectrometer, Applied Photophysics). In the present LFP studies, the third harmonic (355 nm) of a Nd:YAG (DCR-11, Spectra Physics) laser as a pump source, and a 250 W pulsed xenon lamp as the monitoring source, have been used.

2.4. Electrochemical Measurements. Electrochemical measurements were made to determine the redox potentials of the reactants by using the PAR model VersaStat II electrochemistry system. Three electrode systems including Ag/AgCl as reference electrode were used in the measurements. The voltage sweep rate was 100 mV/s. Tetraethylammonium perchlorate (TEAP) in ACN (∼0.1 M) was used as a supporting electrolyte. Electrochemical measurements were carried out under Ar atmosphere.

3. Results and Discussion

3.1 Study on Spectroscopic Properties. *3.1.1. Steady State Measurements.* The optical UV−vis absorption spectra of the donor DMI in the presence of the acceptor 9CNA were measured (Figure 2) in a liquid crystal medium (in 5CB) at various temperatures above the N−I phase transition from 308 to 313 K. The N−I phase transition of 5CB is around 35 °C (308 K). From Landau−deGennes theory, the molecular correlation length $\xi(T)$ is given by the following relationship:

$$\xi(T) = \xi_0\left[\frac{T^*}{T - T^*}\right]^{1/2} \qquad (2)$$

where ξ_0 is a molecular length and T^* is temperature just below the N−I phase transition. This shows that the molecular correlation length of approximately 20 exists just above the N−I phase transition and gradually decreases to three molecular lengths at 343 K. Recent work by Sinks and Wasielewski[6] and earlier observations made by Deeg and co-workers[8] on nematic LCs have shown that even at temperatures above the nematic to isotropic phase transition, a small short-range ordered domain exists. This existence of a small ordered pseudodomain above the N−I temperature (up to 30−40 °C above the phase

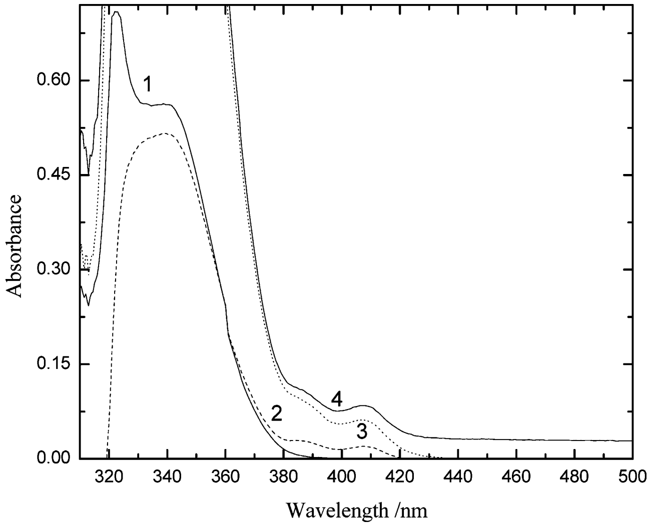


Figure 2. UV−vis absorption spectra of (1) DMI (conc ∼ 4.26×10^{-6} mol dm^{-3}), (2) 9CNA (conc ∼ 8.86×10^{-5} mol dm^{-3}), (3) mixture of DMI (conc ∼ 7.1×10^{-6} mol dm^{-3}) and 9CNA (conc ∼ 8.86×10^{-5} mol dm^{-3}), (4) mixture of DMI (conc ∼ 1.14×10^{-5} mol dm^{-3}) and 9CNA (conc ∼ 8.86×10^{-5} mol dm^{-3}) at the ambient temperature in 5CB.

transition) begins to affect the dynamics of the liquid crystal and consequently the charge-transfer properties and other photophysical and photochemical properties of the observing compounds.

The donor compound DMI exhibits the lower energy band system in the region 320−390 nm in the small ordered pseudodomain of the LC medium whereas it was observed before[15] that in the various isotropic media like nonpolar n-heptane (NH) and polar acetonitrile (ACN) the lower energy absorption band of DMI resides in the region 250−325 nm. Thus, in the LC environment of 5CB, the lower-lying absorption band of DMI undergoes a large red shift. Due to this unusual observation, the experiment was repeated several times, and each time highly purified samples were used. The similar large absorption shift in the red region of DMI was found in the pseudo-ordered domain of 5CB nematic liquid crystal. The exact mechanism of this phenomenon is not very clear at the present stage of investigations. However, as a plausible interpretation, it could be stated that DMI being dissolved in 5CB liquid crystal may show a photochromic effect under irradiation by UV light as similar or more large absorption red shifts were found in the cases of some indolylfulgides[18] when the mixture of this and the nematic liquid crystal are irradiated by visible light. Janicki and Schuster[19] reported a large red shift of the absorption spectra of some fulgides when irradiated with UV light in a photochemically inert liquid crystal. They attributed this phenomenon as a photochromic effect of fulguide molecules. As a similar large red shift of the lower energy band system of DMI was also observed well within the region of the nematic phase, i.e., at temperatures lower than the temperature 308 K (N−I phase transition temperature of 5CB), it appears that the small pseudo-ordered domain corresponds to cybotactic groups maintaining the nematic character similar to the situations observed earlier by Levanon et al.[20] for a tetraphenylporphyrin (free base) system.

The absorption spectrum of DMI looks very similar to the corresponding bands of methylindoles,[21] and the lower energy electronic absorption band envelope should be due to the overlapping of two closely lying electronic transitions $^1L_b \leftarrow {}^1A$ (solvent insensitive) and $^1L_a \leftarrow {}^1A$. However, to assign the nature of absorption bands unambiguously, steady-state polarization measurements were carried out. The results obtained from the polarization experiments have been described in the following section.

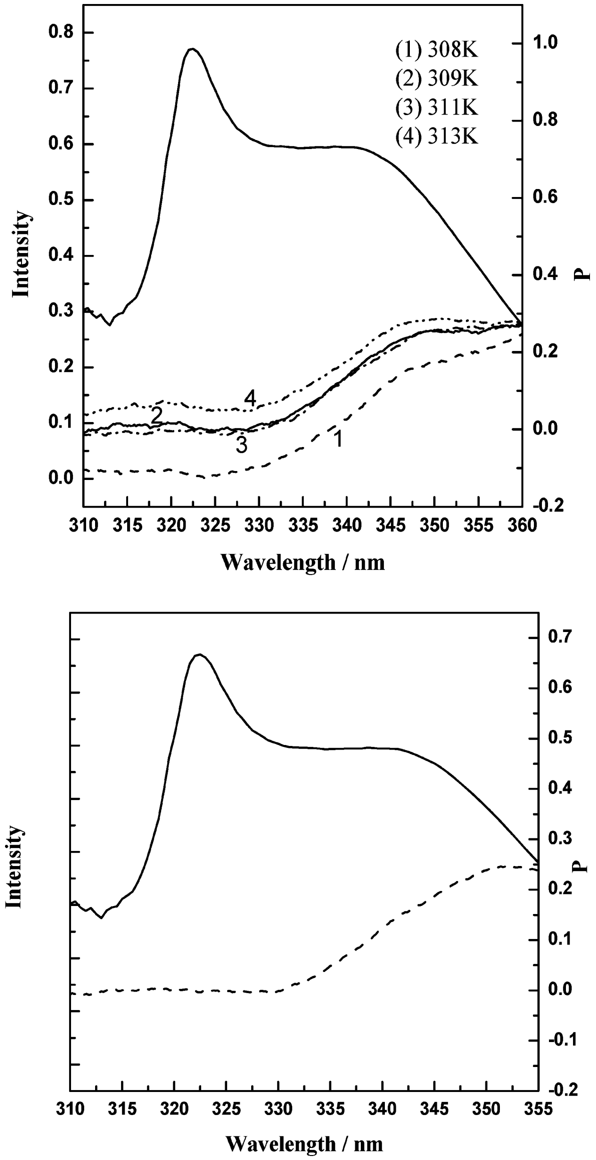


Figure 3. (a) The upper solid line represents the fluorescence excitation spectra of DMI in 5CB, and the broken line shows the excitation polarization spectra (λ_{em}= 392 nm) at (1) 308 K, (2) 309 K, (3) 311 K, and (4) 313 K in the unscratched cell. (b) The lower solid line represents the fluorescence excitation spectra of DMI in 5CB, and the broken line shows the excitation polarization spectra (λ_{em} = 392 nm) in the scratched cell.

3.1.2. Polarized Fluorescence Excitation Spectra. In LC medium, the fluorescence emission of DMI, produced by exciting the lower energy absorption band at either 325 or 340 nm, exhibits a maximum at the energy position 392 nm. However, with the variation of the temperature from 313 to 308 K, the peak position of the emission remains unaltered. In the present investigation, the polarized fluorescence excitation spectra (Figure 3) were measured for the DMI within a temperature range from 308 K (35 °C) to 313 K (40 °C). From Figure 3a, it is found that the fluorescence excitation polarization spectra, measured by monitoring at the fluorescence maximum 392 nm, exhibits a negative P value (∼ −0.10) at temperature 308 K at absorption band maximum around 325 nm and clearly a positive P value (∼ +0.2) at the longer wavelength side of the (0, 0) band position around 345 nm. This observation demonstrates that in case of the absorption spectra of DMI the nature of the transition involved in the band maximum differs from that of the (0, 0) band. The band around 340 nm has been assigned to mostly ^1L_b and the band at 325 nm to ^1L_a. The fluorescence emission of the compound should originate primarily from the lower ^1L_b state. From the observed both positive and negative values of P along the lower energy absorption band from (0, 0) to the band maximum, it is revealed that the overlapping of the ^1L_a and ^1L_b states is responsible for the observed low energy absorption band ranging between 320 and 365 nm showing the contribution of the ^1L_b state to be much more prominent ($P \sim +0.2$) at the (0, 0) band position. The negative value of P ($P \sim -0.10$) indicates the dominancy of the ^1L_a state in the region of band maximum.

In an earlier observation,[15] the polarization studies on DMI in a purely isotropic medium had been carried out. The value of the degree of polarization, P (~0.23), of fluorescence excitation spectra around the band maximum (~281 nm) was found to be a little less than the P value (0.28) near the (0, 0) band (^1L_b) position around 291 nm. Thus, throughout the lower energy band system of DMI, observed in the isotropic medium, the ^1L_b band predominates and a small contribution of ^1L_a is apparent at the region of band maximum which causes a little lowering of the P value. Further, in LC medium, the changes of the degree of polarization P also have been measured with the variation of the temperature from 308 to 313 K. In this temperature domain, the LC medium can be treated as a short range ordered medium (Figure 3a). The observation clearly shows that as the temperature increases, i.e., as the isotropic character of LC increases (pseudodomain decreases), in the overlapping of the lowest lying energy states, the contribution of ^1L_b becomes gradually larger, as evidenced from the increase of P values from the negative to the positive side, in the region of the band maxima, whereas the corresponding value remains more or less same positive in the (0, 0) region. From the above experimental findings, it appears that, in the isotropic medium, the low energy band consists of mainly the ^1L_b band and a small overlap exists with ^1L_a in the band maximum region, whereas, in the pseudodomain of 5CB, the ^1L_b band has a tendency to shift to the lower energy (red) region making the ^1L_a band in the band maximum position more visible and free from considerable overlap with the other closely lying state, ^1L_b. The observed negative value of P in the band maximum region (Figure 3a) demonstrates this fact.

The polarization excitation spectra of DMI, dissolved in 5CB, had also been studied within the scratched cell at 309 K which is well above the N−I phase transition temperature. The homogeneous alignment of the LC director of 5CB along the rubbing direction within the cell was verified using crossed polarizers. However, in this case, also the emission spectrum shows no significant change in polarization characteristics compared to the observations made with the unscratched cell (Figure 3b).

From the theoretical considerations made by using time-dependent density functional theory (TD-DFT), it appears that the transition moment of the lowest excited-state of DMI is polarized along the long axis of DMI.[22] This is actually what we observed from the steady-state measurements: the emission mostly originates from the lowest lying ^1L_b level.

The dichoric ratio (from a polarized excitation spectra) is defined as the ratio of the intensities of parallel and perpendicular polarized emission (I_{EE}/I_{EB}, see the Experimental Section). The measured dichoric ratios of the lowest energy absorption of DMI in all cells are high, within the range 1.6−1.9, at various temperatures. Such a high dichoric ratio indicates that the long axis of DMI is aligned reasonably well along the LC director of 5CB.[15,23,24] Similar dichoric ratios were observed within the scratched and unscratched cells. This indicates clearly that, due to the pseudodomain structure of the LC medium, which appeared closely above the N−I phase transition temperature, most of the molecules dissolved in 5CB are oriented in a particular direction. This orientation of the particular molecules within the LC medium affects the various photophysical and photochemical behaviors, some of which, what we observed from the present investigations, have been discussed above.

From the UV−vis spectrum (Figure 2) it is apparent that the acceptor 9CNA of concentration $\sim 8.86 \times 10^{-5}$ mol dm^{-3} possesses a well-resolved band system in the 5CB medium in the energy region 380−420 nm. On the other hand, the donor DMI was found to be transparent within the regime 390−420 nm even when its concentration is increased from 10^{-6} to 10^{-5} mol dm^{-3}. When we observe the absorption spectra of the mixture of the donor DMI and the acceptor 9CNA, keeping the concentration of 9CNA fixed at 8.86×10^{-5} mol dm^{-3} and using the varying DMI concentrations (10^{-6} to 10^{-5} mol dm^{-3}), clearly the formation of an additional band in the region 400−420 nm is apparent from the considerable enhancement of the lower energy absorption band system of 9CNA.

It indicates that this enhancement is due to the summation of the 9CNA band and the newly developed band possibly due to formation of a ground state complex between DMI and 9CNA. It is to be mentioned here that, in an isotropic environment, e.g., n-heptane or ACN, the situation was different from the observations made in the present investigation using LC medium. In isotropic media, the UV−vis absorption spectra of the mixture of the donor DMI and the acceptor 9CNA appear to be just a superposition of the corresponding spectra of the individual reacting systems. The true nature of the complex formed in the ground state from the interaction between DMI and 9CNA in LC medium is not very clear at the present stage of investigation. However, from the present data it could be inferred that the formation of the ground state complex is only favored in the pseudo-ordered domain of LC medium, but in purely isotropic media (such as ACN, n-heptane, ethanol) no such band was found to develop.

3.2. Search for the Possibility of Occurrences of Electron-Transfer Processes within DMI and 9CNA.

3.2.1. Fluorescence Emission Spectra in 5CB. The fluorescence intensity of 9CNA (excited at 400 nm) strongly quenches regularly over the whole band envelope in the presence of donor molecule DMI at various temperatures ranging from 308 to 313 K (Figure 4). Because at 400 nm DMI is transparent, the inner-filter effect could not be responsible for the observed quenching phenomena. However, it is observed that the quenching of fluorescence emission of 9CNA in the presence of the quencher DMI does not obey the simple Stern−Volmer (SV) relation:[25−27]

$$f_0/f = 1 + K_{SV}[Q] \tag{3}$$

where K_{SV} ($=k_q\tau_0$) is the SV constant, k_q is the bimolecular dynamic quenching rate constant, and τ_0 corresponds to the fluorescence lifetime of the fluorescer 9CNA in the absence of a quencher DMI. f_0 and f denote the relative integrated fluorescence emission intensities of the fluorescer without and with the quencher concentration $[Q]$, respectively. It is apparent from Figure 5 that SV plots are curved upward at all temperatures observed from 308 K (35 °C) to 313 K (40 °C). Like our present experimental findings, the positive deviation from

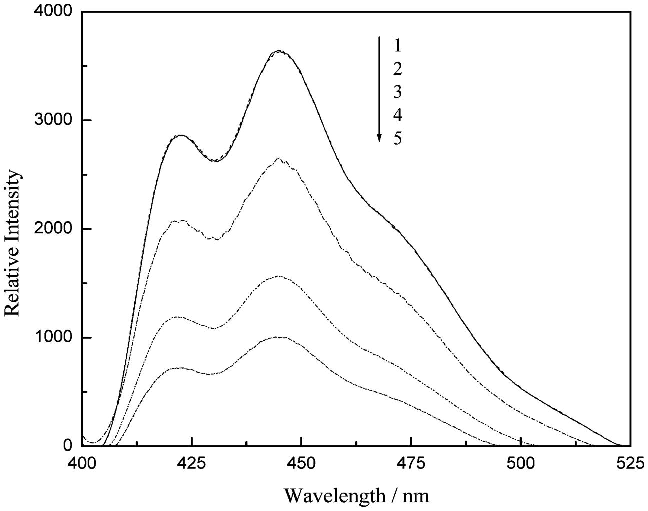


Figure 4. Fluorescence emission spectra of 9CNA in 5CB (conc ~ 8.86×10^{-5} mol dm^{-3}) ($\lambda_{ex} = 386$ nm) in the presence of DMI of concentration (mol dm^{-3}) in (1) 0, (2) 1.42×10^{-6}, (3) 2.84×10^{-6}, (4) 4.26×10^{-6}, and (5) 5.68×10^{-6} in the unscratched cell at 313 K.

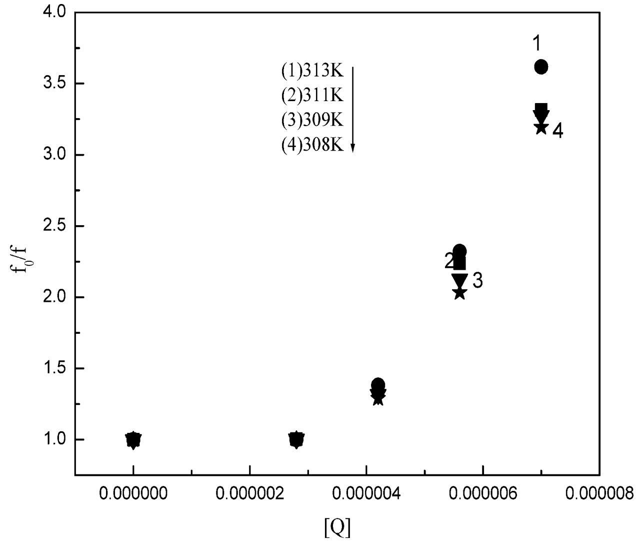


Figure 5. Stern−Volmer (SV) plot from steady-state fluorescence emission intensity measurements in the case of singlet (S_1) excitation of 9CNA in the presence of DMI in 5CB liquid crystal environment at (1) 313 K, (2) 311 K, (3) 309 K, and (4) 308 K.

the linearity of the SV plot was observed earlier in several cases of quenching studies.[28−31] By monitoring the 425 nm wavelength, the fluorescence lifetimes of the fluorescer 9CNA were measured both without and in presence of the various concentrations of the quencher DMI. The fluorescence lifetimes of unquenched 9CNA ($\tau_0 \sim 13.6$) and the quenched one ($\tau \sim 13.5$) were found to be nearly (within the experimental error) the same. Thus, the steady-state coupled with time-resolved fluorescence quenching measurements indicates that the quenching should be static type quenching. The fluorescence lifetime measurements have been made at different temperatures and are presented in Table 1. The formation of a ground state complex, as proposed in section 3.1.2, appears to be further confirmed from lifetime measurements. However, the possibility of the concurrent occurrences of dynamic processes (photoinduced electron transfer, excitational energy transfer), if any, along with the static mode has been tested using the modified SV relation (eq 4)[21]

$$[(f_0 - f)/f]/[Q] = (K_{SV} + K_0) + K_{SV}K_0[Q] \qquad (4)$$

TABLE 1: Fluorescence Lifetime Data of 9CNA and Mixture of Both 9CNA and DMI at Different Temperatures and at the Different Concentrations of DMI in the Liquid Crystal (5CB) (The Measurements within Pseudo-Ordered Domain Were Made with the Degassed Samples)

T^a (°C)	system	conc (mol dm^{-3})	τ_0 (ns)
35 (308 K)	9CNA^a + 5CB	8.86×10^{-5}	13.5
40 (313 K)	9CNA^a + 5CB	8.86×10^{-5}	13.7
35 (308 K)	9CNA^a + DMI + 5CB	conc of DMI ~ 7.1×10^{-6} conc of 9CNA ~ 8.86 10^{-5}	13.6
40 (313 K)	9CNA^a + DMI + 5CB	conc of DMI ~ 7.1×10^{-6} conc of 9CNA ~ 8.86×10^{-5}	13.5
35 (308 K)	9CNA^a + DMI + 5CB	conc of DMI ~ 1.14 10^{-5}	13.8
40 (313 K)		conc of 9CNA ~ 8.86×10^{-5}	13.7

[a] The electronic excited singlet state.

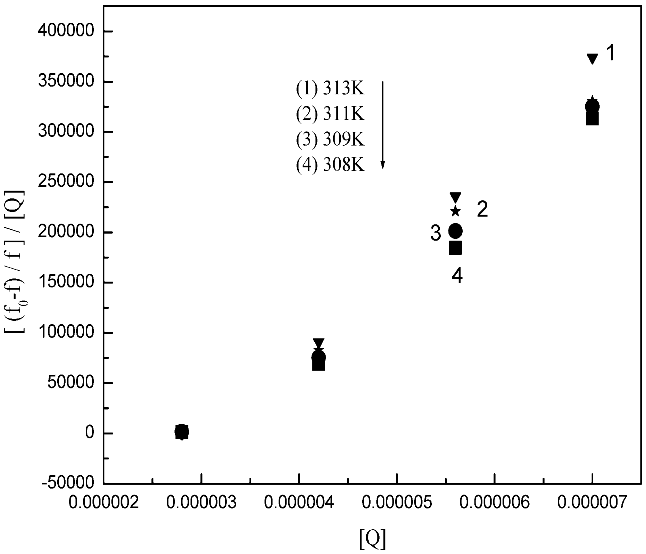


Figure 6. Modified Stern−Volmer (SV) plot from steady-state fluorescence emission intensity measurements in the case of singlet (S_1) excitation of 9CNA in the presence of DMI in 5CB liquid crystal environment at (1) 313 K, (2) 311 K, (3) 309 K, and (4) 308 K.

within the temperature range 308−313 K. From the linearity of the curve, shown in Figure 6, collisional (K_{SV}) and static (K_0) parts were estimated. The negligible contribution of the dynamic part (~0) along with the observation of a constant lifetime of the fluorescer 9CNA with and without quencher in the LC medium (from the time-resolved experiments) infers that the static mode possesses the dominant role in quenching phenomena occurring within the present intermolecular donor−acceptor systems. The nature of the ground complex formed, whether it is charge-transfer type, is not clear from the present study. But from the computations of the ΔG_{CS} value (vide infra), a large positive magnitude indicates in favor of the slim possibility of the charge-transfer nature of the ground state complex.

3.2.2. Electrochemical Studies. The free energy (ΔG_{CS}) for charge separation is estimated using the Weller expression based on dielectric continuum model of the solvent:[32,33]

$$\Delta G_{CS} = E_{1/2}^{OX}(D/D^+) - E_{1/2}^{RED}(A^-/A) - E_S - \frac{e^2}{\epsilon_S r_{DA}} + e^2\left(\frac{1}{2r_D} + \frac{1}{2r_A}\right)\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_{SP}}\right) \qquad (5)$$

where $E_{1/2}^{OX}$ (D/D$^+$) is the half-wave oxidation potential of DMI and $E_{1/2}^{RED}$ (A$^-$/A) represents the half-wave reduction potential of 9CNA in ACN. E_S is the lowest excited singlet state of 9CNA, e is the elementary charge, ϵ_S is the static dielectric constant of the spectroscopic solvent, and r_{DA} is the ion pair distance; r_{DA} was calculated from the energy minimized ground state structure of 9CNA−DMI. ϵ_S value of LC medium (5CB) was computed from the method of L. Sinks et al.[34] and was found to be ∼10.5 for 5CB. r_D and r_A are the ionic radii of the electron donor and acceptor molecules, respectively; ϵ_{SP} is the static dielectric constant of ACN. A positive value of +0.24 eV for ΔG_{CS}, obtained from eq 5, indicates endergonicity, i.e., a slim possibility, from the thermodynamic point of view, of the occurrence of photoinduced electron-transfer reactions between the donor DMI and the acceptor 9CNA in LC environment. The situation is completely different for isotropic solvent. The Gibbs free energy of ET reactions from the well-known Rehm−Weller relation[35−38] is −0.99 eV. This value of Gibbs free energy suggests the dominant involvement of a photoinduced ET process[39] in the quenching mechanism of the donor−acceptor system DMI and 9CNA in isotropic solvents. The electrochemical results support our propositions made from the steady-state and time-resolved spectroscopic investigations that primarily the static process is involved in the quenching phenomenon occurring in the pseudo-ordered domain of the LC (5CB), whereas in isotropic media NH ($\epsilon_s \sim 2$) or ACN ($\epsilon_s \sim 37.5$) we observed[15] that the dynamic process plays the key role. From the observed value of ΔG_{CS} (~ -0.99 eV) in ACN medium, it is apparent from the thermodynamic point of view the PET process should occur in the intermediate region (0.4 eV $< -\Delta G_{CS} <$ 2.0 eV).[39]

The estimated bimolecular fluorescence quenching rate constants, k_q's, both in ACN and NH, are found to be nearly equal to the diffusion-controlled limit.[15] This observation is in accord with our expectation as Kikuchi proposed[39] that ET reactions in the intermediate region occur through diffusion-assisted mechanisms, if no other nonradiative processes are involved.

3.2.3. Transient Absorption Measurements. Using the third harmonic (∼355 nm) output of the Nd:YAG laser system, the transient absorption spectra of the mixture of DMI and 9CNA were measured in LC (5CB) environment. The temperature of the cell containing the sample was kept at 309 K (within the pseudo-ordered domain). No noticeable absorption bands of transient ions are observed. This observation was in accord with our expectation as electrochemical measurements and steady- state investigations clearly indicate the lack of occurrence of dynamic processes. Time-resolved fluorescence measurements demonstrate in favor of static quenching in LC medium.

On the contrary, in isotropic solvents n-heptane and ACN, the transient absorption spectra measured by nanosecond laser flash photolysis technique exhibit[15] the broad band at around 560 nm of 9CNA radical anion ($9CNA^-$)[40,41] and at 540 nm for the neutral radical of the donor DMI.[42,43]

To examine whether the PET process (dynamic quenching) could reappear in the deep of the isotropic phase of 5CB (≫313 K), the transient absorption spectra of the mixture of DMI and 9CNA are measured in 5CB liquid crystal environment at the temperature 320 K. However, no transient ions could be found even at this temperature which is well within the isotropic phases. Though the exact mechanism of this observation is not very clear at the present stage of investigation, but following the propositions made earlier by Levanon et al.,[20] it could be inferred that, due to the hysteresis phenomenon, the nematic phase properties persist over a wide temperature range well within the pseudo-ordered domain to some extent into the isotropic phases.

It is to be pointed out here that, in NH and ACN media, the transient absorption spectra of the mixture of DMI and 9CNA also exhibit a photoexcited 9CNA triplet apart from the radical ions of the two reacting species. From the analysis of the spectra, it is revealed that the formation of the triplet results from the charge recombination of the radical cations and anions, because with an increase of delay, the absorption band of the triplet state enhances at the expense of the corresponding transient bands of radical ions. A similar observation of the production of a photoexcited triplet in the case of a typical metalloporphyrin was also made earlier by Levanon[44] using a nanosecond laser flash photolysis technique but in the LC environment cyanohexylbiphenyl (6CB). From the experimental evidence, he suggested that this triplet is produced by a back electron-transfer process within the triplet radical pair. As no experimental observations of the presence of a radical ion pair was made, it was inferred that the energy states attributed to the radical pairs should reside above that triplet level. In the present investigations made in the 5CB liquid crystal environment, a lack of formation of charge-separated species, e.g., cations or anions, should possibly be responsible for the absence of a transient triplet, the formation of which in isotropic media NH or ACN resulted from the recombination of the radical ions. Further investigations, using both inter- and intramolecular donor−acceptor systems in 5CB and other LC environments, are underway.

4. Concluding Remarks

Though highly exergonic photoinduced electron-transfer reactions were apparent within the electron donor DMI and well-known acceptor 9CNA in isotropic media NH and highly polar ACN, the pseudo-ordered domain above the N−I phase transition temperature (up to 35−40 °C above the phase transition) of the liquid crystal 5CB begins to affect the dynamics of the liquid crystal and consequently the charge transfer and other photophysical and photochemical properties of the present donor and acceptor systems. It is inferred from the present experimental findings that the pseudodomain of 5CB acts as an inhibitor of the production of charge-separated species from the present intermolecular electron donor and acceptor reacting systems. From the steady-state and time-resolved investigations, it is revealed that, due to the hysteresis phenomenon, the nematic phase properties persist over a wide temperature range well within a pseudo-ordered domain to some extent into the isotropic phases. Further investigations, using both inter- and intramolecular donor−acceptor systems in 5CB and other LC environments, are underway.

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