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Solvatochromism of tricycloquinazoline based disk-shaped liquid crystal: A potential molecular probe for fluorescence imaging

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Abstract

Tricycloquinazoline (TCQ) based discotic liquid crystals (DLCs) were found to be fluorescent in nature. Such molecules can be employed for the fluorescence imaging of the another DLC. Therefore, it is essential to study systematically the photophysical properties of such molecules. In this article, we report the effect of solvents on the photophysical properties of DLC molecule possessing central TCQ core covalently linked with 6 ethelenoxy side chains (TCQDL molecule). The solutions of the TCQDL are prepared in organic solvents of different polarity. The solutions are scanned using ultraviolet - visible (UV-VIS) and fluorescence spectrophotometers. The excited state dipole moment of the TCQDL molecule is estimated from the data. The ground state dipole moment of TCQDL molecule is calculated using Gaussian 03. We observed that TCQDL molecule can be used as fluorophore and used to image other non-fluorescent DLC system. The epifluorescence imaging of the Langmuir monolayer of the pure TCQDL molecules at the air-water interface showed good contrast in the image for identifying surface phases even in the absence of additive fluorescent probe molecules.

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I. INTRODUCTION

The optical imaging of liquid crystals (LCs) provide vital physical insight related to molecular organization and the phase transitions [1, 2]. Various microscopy techniques like near-field scanning optical, fluorescence, fluorescence confocal polarizing, two photon and third harmonic generation microscopy have been employed for such studies [3–12]. In all these microscopy techniques, the LC systems have been doped with some fluorescent probe molecules. Incorporation of additives may lead to either phase separation or complex formation with the host molecules and thereby may alter the physical properties of the mixed system. So, it is preferable to employ some fluorescent probe with liquid crystalline nature which can be doped into a similar LC host. Several LC molecules with intrinsic fluorescence nature have been synthesized and are reported in literature [13–18].

Solvatochromism is one of the tools for quantifying the fluorescence response of dye molecules [19]. Several dye doped LC systems have been studied through solvatochromism [20–22]. In all such reported systems, LCs are doped with some dye molecules. The doping of dye molecules may give rise to impurity in LC system therefore, it is worth to study the solvatochromic behavior of pure LC molecules exhibiting intrinsic fluorescence behavior. Such studies will provide valuable information for LC imaging and display applications. To our best of knowledge, there are no such studies on pure LC molecules. Disoctic liquid crystals (DLCs) possessing tricycloquinazoline (TCQ) core have been reported to be fluorescent in nature [23, 24]. We believe that such DLC molecule can be potentially used as molecular probe for fluorescence imaging. Therefore, a systematic photophysical studies of such molecules are essential. In this paper, for the first time we report solvatochromic studies on a DLC molecule possessing TCQ core with 6 ethelenoxy side chains (TCQDL molecule) without the aid of any dye. Later, we employed TCQDL molecules as fluorescent probe for optical imaging of structurally similar another DLC system composed of hexa-alkoxy triphenylene (HAT5) molecules. The fluorescence microscope images reveal the potential of TCQDL molecules as a probe to study the optical properties of another DLC system. Epifluorescence microscopy technique can be used to visualize Langmuir monolayer at the air-water interface [25]. So, we further extended our studies by performing epifluorescence imaging of the Langmuir monolayer of pure TCQDL molecules at the air-water interface. We found reasonable contrast in the epifluorescence images necessary for identifying phases in the Langmuir monolayer of the TCQDL molecules.

We recorded ultraviolet-visible (UV-VIS) and fluorescence spectra for the TCQDL molecule in various solvents. The solvatochromic shifts were estimated. The ground state and excited state dipole moment of TCQDL molecule were determined using Lippert's [26], Bakhshiev's [27] and Kawski-Chamma-Viallet's [28, 29] equations. Using density functional theory (DFT) approach, the ground state dipole moment of the TCQDL molecule was computed employing Gaussian 03 programme package. Calculations were performed to find the parameters like angular difference between the ground and excited state dipole moments, oscillator strength, transition dipole moment and relative quantum yields of the TCQDL molecules in various solvents.

II. MATERIALS AND METHODS

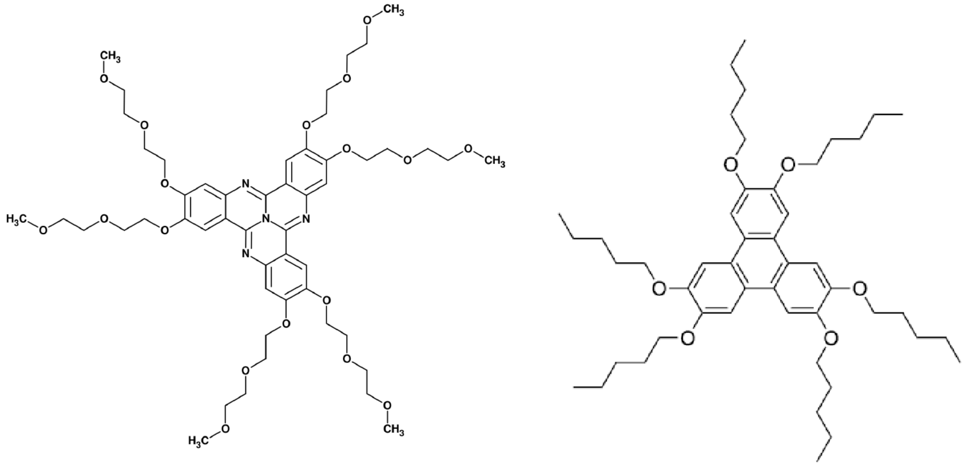
A. Materials

TCQDL and hexa-alkoxy triphenylene (HAT5) molecules (Figure 1) were synthesized as reported earlier [30–34]. TCQDL exhibits a hexagonal columnar phase (Col_h) between 77 and 233 °C [30–32]. Upon cooling from the isotropic phase, it displays classical texture of columnar mesophase as presented in Reference [30]. This compound has been well studied for its conducting and electrochemical properties [30, 31]. HAT5 was prepared following our previously reported method [33, 34]. Its phase behavior was in perfect agreement with the reported data [33, 34].

Spectroscopic grade chloroform, ethanol, acetone, dimethylformamide, acetonitrile, dimethylsulfide, methanol, toluene, benzene, butanol, carbontetrachloride, cyclohexane, dichloromethane, diethylether, tetrahydrofuran were used as procured from Sigma Aldrich and Merck. Optical quality quartz plate was used for fluorescence imaging of LC system of HAT5 molecules doped with TCQDL.

B. Experimental methods

The solutions of TCQDL were prepared in various solvents at a fixed solute concentration of 0.25 mM. The UV-VIS spectra were collected using a spectrometer from Jasco (V570). The luminescence spectra were recorded using a spectrofluorimeter (Shimadzu, RF-5301PC)



(a) (b)

FIG. 1. Chemical structure of (a) TCQDL and (b) hexalkoxytriphenylene (HAT5) molecules.

at an excitation wavelength of 390 *nm*. For fluorescence imaging of the HAT5 system, chloroform solutions of the mixtures of HAT5 doped with 1, 5 and 10 mole percent of TCQDL were spread on to the quartz plates. The solvent was allowed to evaporate for 60 minutes. The samples prepared were imaged using a fluorescence microscope (BX43 Olympus) in the transmission mode at a temperature of $\sim 20\ ^\circ C$. The Langmuir monolayer of TCQDL molecules were formed at air-water interface [35] and was observed under an epifluorescence microscope (Leitz Metallux 3). The images were captured using an intensified charge coupled device camera (Cairn Research). All the experiments were carried out at room temperature ($\sim$ 20°C).

C. Computational methods

First principles electronic structure investigation was done on TCQDL molecule using Gaussian 03 program package. The geometry optimization of TCQDL molecule (Figure 2) was carried out within DFT framework. This was followed with the evaluation of vibrational frequency analysis at the B3LYP level of theory. Ground state dipole moment of TCQDL was calculated by exchange correlation functional as hybrid B3LYP with full electron 6-311 G basis set [36–38].

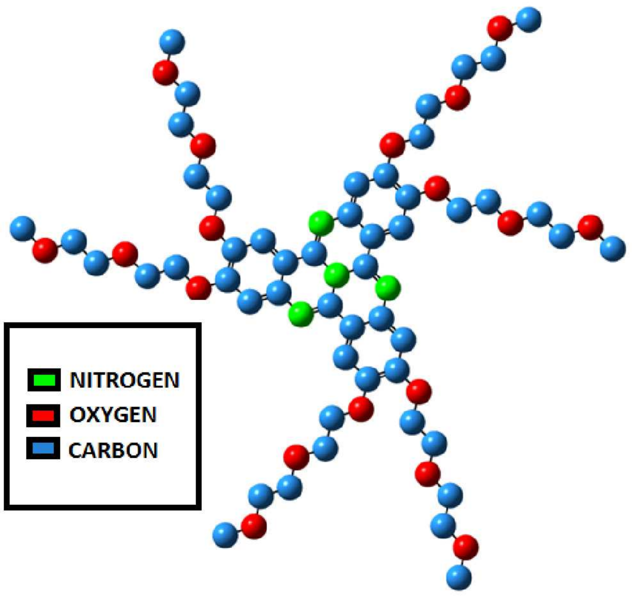


FIG. 2. Ball and stick model of TCQDL molecule

D. Theoretical methods

The ground state and the excited state dipole moment values of TCQDL molecule were estimated using the following equations.

Lippert's Equation :

$$v_a - v_f = mF(k,n) + C \tag{1}$$

Bakshiev's Equation :

$$v_a - v_f = m_1 F_1(k,n) + C \tag{2}$$

Kawski-Chamma-Viallet's Equation :

$$(v_a + v_f)/2 = -m_2 F_2(k,n) + C \tag{3}$$

Here v_a and v_f are the absorption and luminescence wavenumbers respectively, and C is a constant. The difference between v_a and v_f is Stokes shift. F(k,n), F_1(k,n) and F_2(k,n) are Lippert's, Bakshiev's and Kawski-Chamma-Viallet's polarity functions given by equations 4, 5 and 6 in terms of dielectric constant (k) and refractive index (n) of the solvents used.

Lippert's polarity function :

$$F(k,n) = \frac{k-1}{2k+1} - \frac{n^2-1}{2n^2+1} \tag{4}$$

Bakshiev's polarity function :

$$F_1(k,n) = \frac{2n^2+1}{n^2+2}\left(\frac{k-1}{k+2} - \frac{n^2-1}{n^2+2})\right) \tag{5}$$

Kawski-Chamma-Viallet's polarity function :

$$F_2(k,n) = \frac{2n^2+1}{2(n^2+2)}\left(\frac{k-1}{k+2} - \frac{n^2-1}{n^2+2}\right) + \frac{3n^4-1}{2(n^2-1)^2} \tag{6}$$

Slopes m and m_1 are estimated from the plots between F(k,n), $F_1(k,n)$ versus Stokes shift respectively. The slope m_2 is estimated from the plot of $F_2(k,n)$ vs. arithmetic mean of absorption and fluorescence wavenumber [26–29]. The values of slopes m, m_1 and m_2 can be further related to the ground state dipole moment (p_g), excited state dipole moment (p_e), Onsager radius cavity (a), Planck constant (h) and speed of light in vacuum (c) given by following equations:-

$$m = \frac{2(p_e - p_g)^2}{hca^3} \tag{7}$$

$$m_1 = \frac{2(p_e - p_g)^2}{hca^3} \tag{8}$$

$$m_2 = \frac{2({p_e}^2 - {p_g}^2)}{hca^3} \tag{9}$$

These equations are based on the Onsagers reaction field theory, which assumes that the fluorophore is a point dipole residing in the center of a spherical cavity in a homogeneous and isotropic dielectric with relative permittivity (k). The cavity radius chosen for our study is the radius of the TCQ core (=0.5 nm) of TCQDL molecule [23, 39].

Further the ground state and excited state dipole moments can also be calculated using the following equations:

$$p_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}} \tag{10}$$

$$p_e = \frac{m_2 + m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{\frac{1}{2}} \tag{11}$$

From equations (10) and (11) we get :

$$p_e = \frac{|m_2 + m_1|}{|m_2 - m_1|}p_g \tag{12}$$

Generally excited state dipole moment and ground state dipole moment are not parallel to each other. So, the angular separation (ϕ) between them is estimated by the following relation [40, 41]

$$\cos\phi = \frac{1}{2p_g p_e}[({p_g}^2 + {p_e}^2) - \frac{m_1}{m_2}({p_e}^2 - {p_g}^2)] \qquad (13)$$

Further from the fluorescence spectra, relative quantum yield, oscillator strength and transition dipole moment of the TCQDL molecule are estimated. In the fluorescence spectra, maximum intensity was observed in case of TCQDL molecule in dichloromethane. So, relative quantum yield ($\frac{\phi_1}{\phi_2}$) can be calculated from the quantum yield of TCQDL molecule in various solvents (ϕ_1) with respect to TCQDL molecule in dichloromethane (ϕ_2) using the following equation [42]:-

$$\frac{\phi_1}{\phi_2} = \frac{\left(1 - 10^{-A_2^*}\right) n_1^2 \alpha_1}{\left(1 - 10^{-A_1^*}\right) n_2^2 \alpha_2} \qquad (14)$$

where subscript 1 refers to the various solutions of the TCQDL molecule and subscript 2 refers to the reference solution. A* is the absorbance at 390 nm which is the excitation wavelength. Here, α is the area under the fluorescence curve for TCQDL in a particular solvent and n is the refractive index of different solvents used.

The oscillator strength (f) of TCQDL molecule in various solvents is computed using the following equation [43]:

$$f = 4.32 \times 10^{-9} \epsilon_{max} \nu_{1/2} \qquad (15)$$

The transition dipole moment of the TCQDL molecule is obtained using the approximated equation below [44]:

$$\mu = 0.0958 \left[\epsilon_{max} \times \frac{\nu_{1/2}}{\nu_{max}}\right] \qquad (16)$$

where ϵ_{max} is the molar absorbance at the maximum, ν_{max} is wavenumber for maximum absorption and $\nu_{1/2}$ is band width at half maxima.

III. RESULTS AND DISCUSSION

The absorption and the corresponding fluorescence spectra for TCQDL molecules in different solvents are shown in Figure 3. Values of absorption and fluorescence maxima wavenumbers were calculated from the spectra. The UV-VIS spectroscopic measurements

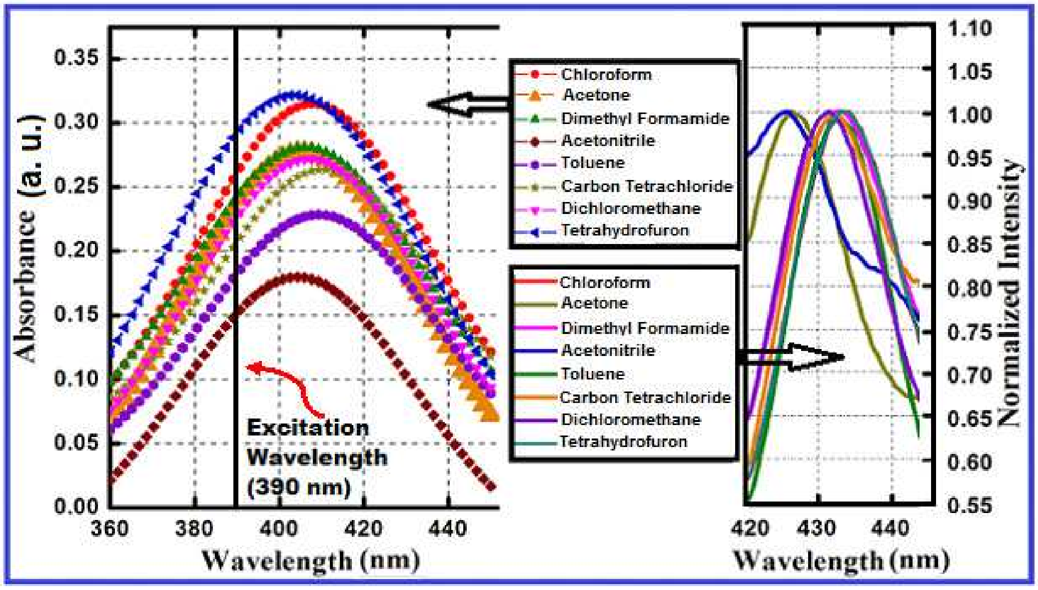


FIG. 3. The UV-VIS (left side) and fluorescence (right side) spectra of TCQDL molecules in various solvents.

show average absorption maxima at 402 nm. The luminescence spectra were recorded at an excitation wavelength of 390 nm.

Figure 3 shows that the solvent-induced shift of the emission spectrum is higher than the shift in the absorption spectrum. The shift observed in spectral band arises from the large reaction field which a solute molecule experiences due to the polarization of the surrounding solvent molecules [45]. This is due to the larger excited-state permanent dipole moment of TCQDL molecule when compared to its ground state. The shifts observed are dependent on the nature of solvent (polar or non-polar) and dielectric constant. Since in the present case, the excited state of a molecule is much different from its ground state, it may be more or less depending upon the transition involved. The ground state dipole moment may slightly change from solvent to solvent, but the excited state may be much different. Thus it is expected that little changes in absorption, while large change in the fluorescence spectrum with change in solvent.

Table I shows the absorption wavenumbers (v_a), emission wavenumbers (v_f), Stokes shift (v_f - v_a) and arithmetic mean of emission and absorption wavenumbers ((v_f+v_a)/2) of TCQDL molecule in different solvents. Stokes shift is an indicator about the change from ground state to excited state structure of TCQDL molecule. They can be attributed to

TABLE I. Spectral data: emission wavenumbers (v_f), absorption wavenumbers (v_a), Stokes shift (v_f - v_a) and arithmetic mean of Stokes shift ((v_f + v_a)/2)

Solvents used	v_f (cm^{-1})	v_a (cm^{-1})	v_f - v_a (cm^{-1})	(v_f + v_a)/**2** (cm^{-1})
Chloroform	23073.37	24517.01	1443.64	23795.19
Acetone	23397.29	24738.39	1341.11	24067.84
Acetonitrile	23408.24	24738.39	1330.15	24073.32
Dimethylformamide	23105.36	24738.39	1633.03	23921.88
Toluene	23126.73	24517.01	1390.28	23821.87
Dichloromethane	23126.73	24517.01	1390.28	23821.87
Carbontetrachloride	23141.18	24517.01	1375.83	23829.1
Tetrahydrofuran	22786.31	24738.39	1952.08	23762.35

factors such as dipole-dipole interaction between solvent and solute, change in the nature of emitting state induced by solvent and specific solvent-solute interactions such as hydrogen bonding [46]. They also define change in energies of levels of a solute due to change in the solvent medium. Emission states arise out of energy of more relaxed excited states and hence are more informative than absorption spectra. The parameters found using these shifts are vital for describing the intramolecular charge transfer in molecular excited states [47–51] and inter-molecular charge transfer in excited complex [52, 53].

TABLE II. Dielectric constants (k), refractive indices (n) of the solvents, Lippert ($F(k,n)$), Bakhshiev ($F_1(k,n)$), Kawski-Chamma-Viallet ($F_2(k,n)$) solvent polarity function

Solvents used	k	n	$F(k,n)$	$F_1(k,n)$	$F_2(k,n)$
Chloroform	4.81	1.442	0.147	0.371	0.487
Acetone	21.09	1.359	0.289	0.791	0.641
Acetonitrile	36.64	1.344	0.312	0.863	0.665
Dimethylformamide	36.7	1.431	0.274	0.835	0.709
Toluene	2.38	1.497	0.012	0.033	0.351
Dichloromethane	8.93	1.424	0.218	0.589	0.582
Carbon tetrachloride	2.24	1.459	0.014	0.015	0.318
Tetrahydrofuran	7.58	1.407	0.209	0.549	0.551

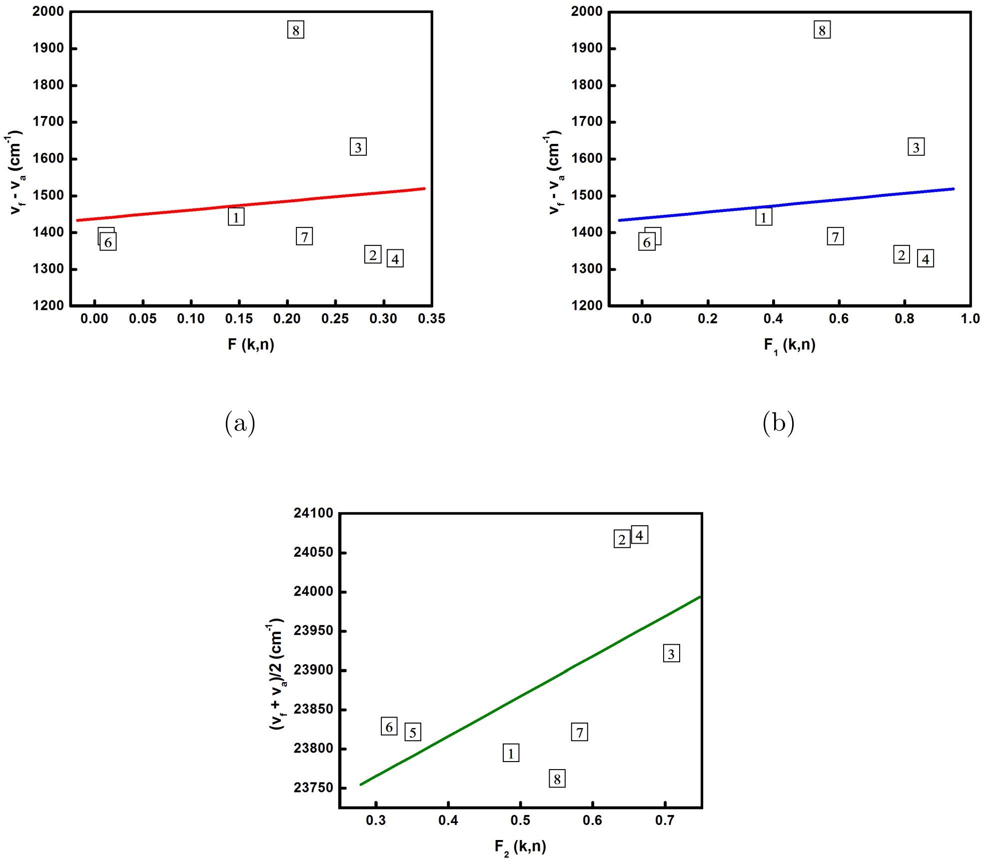
In the present study, non-polar (k<5), borderline polar aprotic (k ranges from 5-20) and polar aprotic solvents (k>20) were employed. We observed bathochromic shift (red shift) from ground to excited state of TCQDL in solvents of different polarity. Due to the efficiency of vibrational relaxation, there is loss of energy before fluorescent emission. This loss of energy results from several dynamic processes, including dissipation of vibrational energy, reorientation of the solvent molecules around the excited state dipole, redistribution of electrons in the solvent molecules as a result of the altered dipole moment of the excited fluorophore, and fluorophore-solvent interactions (such as hydrogen bonding). The shifts observed for the TCQDL molecule in various solvents indicate that the transition involved is from a π-bonding orbital to an antibonding (π^*) orbital ($\pi \rightarrow \pi^*$ transition) and lowest lying state of TCQDL molecule is $\pi \rightarrow \pi^*$.

Using equations (4)-(6), Lippert's, Bakshiev's and Kawski-Chamma-Viallet's polarity function for various solvents (Table II) are calculated. The k and n values were taken from the literature [29]. In Figure 4, the plot (a) shows Stokes shift versus $F(k,n)$; (b) shows Stokes shift versus $F_1(k,n)$; and (c) shows arithmetic mean of emission and absorption wavenumbers versus $F_2(k,n)$ of TCQDL molecule in various solvents. The linear dependence of spectral shifts on polarity functions (Figure 4) shows positive slopes.

TABLE III. Estimated values of ground state dipole moment (p_g) and excited state dipole moment (p_e).

Calculations	p_g **(D)**	p_e **(D)**	p_e / p_g	ϕ
Estimated	2.56	3.59	1.40	0°
Gaussian'03	3.20			
Lippert's Theory		4.28		
Bakshhiev's Theory		3.85		
Kawski-Chamma-Vallet's Theory		3.85		

From Figure 4, slopes m, m_1 and m_2 were estimated to be 239.2, 84.8 and 509.3 cm^{-1} respectively. Using equation 10, the ground state dipole moment (p_g) value of TCQDL molecule was found to be 2.56 D. The excited dipole moment (p_e) of the TCQDL molecule was found to be 3.59 D (Table III). The higher value of excited state dipole moment compared to that of ground state of the TCQDL might be due to an increase in charge separation in



(a) (b)

(c)

FIG. 4. The plot (a) is Stokes shift versus Lippert polarity function(F(k, n)), (b) is Stokes shift versus Bakshiev polarity function($F_1(k, n)$) and (c) is arithmetic mean of emission/absorption wavenumbers versus Kawski Chamma Vallet polarity function($F_2(k, n)$) of TCQDL in various solvents: (1) Chloroform, (2) Acetone, (3) Acetonitrile, (4) Dimethyl formamide, (5) Toluene, (6) Dichloromethane, (7) Carbon tetrachloride, (8) Tetrahydrofuran. (——Linear fit)

the excited state. The change in the excited state dipole moment with reference to ground state dipole moment (δp) i.e p_e - p_g and the ratio of excited state to ground state dipole moments ($\frac{p_e}{p_g}$) of the TCQDL molecule was found to be 1.03 D and 1.40, respectively. It can be seen that the p_e value obtained for TCQDL molecule by Lippert method is large as compared to values obtained by all other methods (Table III). It is due to the fact that this method does not take into account the polarizability of the solute. It is observed that the shift of emission peak with change in solvent polarity are more pronounced than the shift of absorption peak, indicating $p_e > p_g$; i.e. the dipole moment of the molecules increase on excitation. Therefore, the excited state of TCQDL is more polar than the ground state.

Using Gaussian 03, the ground state dipole moment value of the TCQDL molecule was computed and it was found to be 3.2 D. The difference in the estimated and computed values of dipole moment is due to the fact that the molecule is considered as an isolated system (as in gas phase) during computation, whereas the experimentally obtained values are in solution phase, where the solvent (matrix) introduces strong perturbation. Further it is evident from Table III that the changes in the dipole moments of the TCQDL molecule on electronic excitation is rather small. This suggests that the emission of the TCQDL molecule originates from a state, which although more polar than ground state, is probably a locally excited intramolecular charge transfer (ICT) state. Charge transfer accompanying excitation to lowest excited singlet state usually results in the excited molecule having a greater dipole moment than the ground state [54]. Usually while estimation of these parameters, it is generally assumed that excited state dipole moment is almost parallel with the ground state [55–58]. Accordingly using equation 13, we found no angular separation between the excited and ground state dipole moment of the TCQDL molecule (i.e. 0 °). Hence, the dipole moments in both the states were found to be collinear.

TABLE IV. Absorbance (A), Absorbance at excitation wavelength (A*), Polarity (P), Relative Quantum Yield (ϕ_1/ϕ_2)

Solvents used	**A**	**A*(390 nm)**	**P**	ϕ_1/ϕ_2
Chloroform	0.27	0.22	4.1	0.2
Acetone	0.26	0.22	5.1	0.1
Acetonitrile	0.21	0.18	5.8	0.014
Dimethylformamide	0.24	0.2	6.4	0.084
Toluene	0.21	0.16	2.4	0.754
Dichloromethane	0.25	0.21	3.1	1
Carbontetrachloride	0.22	0.17	1.6	0.29

The polarity of a solvent generally influences the fluorescence-emission spectra of fluorophores. Changes in quantum yields and shifts in spectra are valuable parameters of fluorophore sensitivity to the solvent polarity. Quantum yield is the ratio of total number of emitted photons to the total number of photons absorbed. The sensitivity of fluorophores to solvent polarity has practical applications in the field of physical biochemistry. When fluorophores are bound to proteins, nucleic acids, membranes, or macromolecules, in general, the fluorescence-emission spectra change. These changes can be employed to detect binding sites on macromolecules or to determine the polarity of binding sites [59].

The estimated values of relative quantum yield of TCQDL in various solvents is shown in Table IV. The estimated values indicated maximum quantum yield for TCQDL in toluene with respect to TCQDL in dichloromethane and minimum quantum yield for TCQDL in acetonitrile with respect to TCQDL in dichloromethane. The hydrogen-bonded solvents generally show a greater red shift than those which do not form hydrogen bond. Hence, larger quantum yields are observed in solvents with no hydrogen bonding. The estimated relative quantum yield value of TCQDL in acetonitrile is very low which could be due to emissionless deactivation processes during the transition from the excited state to ground state.

TABLE V. Molar absorbance (ϵ), band shift at half maxima (Δv_a), oscillator strength (f), transition dipole moment (μ_t)

Solvents used	ϵ **max**	Δv_a (cm^{-1})	f	μ_t(**D**)
Chloroform	864	144508.7	0.539	6.84
Acetone	832	152671.8	0.548	6.86
Dimethylformamide	672	152671.8	0.443	6.17
Acetonitrile	768	137362.6	0.455	6.26
Toluene	672	152671.8	0.443	6.2
Carbontetrachloride	800	137362.6	0.474	6.41
Dichloromethane	704	144508.7	0.439	6.17
Tetrahydrofuran	896	144508.7	0.559	6.93

Oscillator strength (f), a measure of the integrated intensity of the charge transfer complex and transition dipole moment (μ_t) of TCQDL molecules in various solvents, is listed in Table V. The values of the oscillator strength indicate a strong interaction between the donor-acceptor pair with relative high probability transitions in TCQDL molecule. The maximum oscillator strength of the TCQDL molecule was found out to be in tetrahydrofuran.

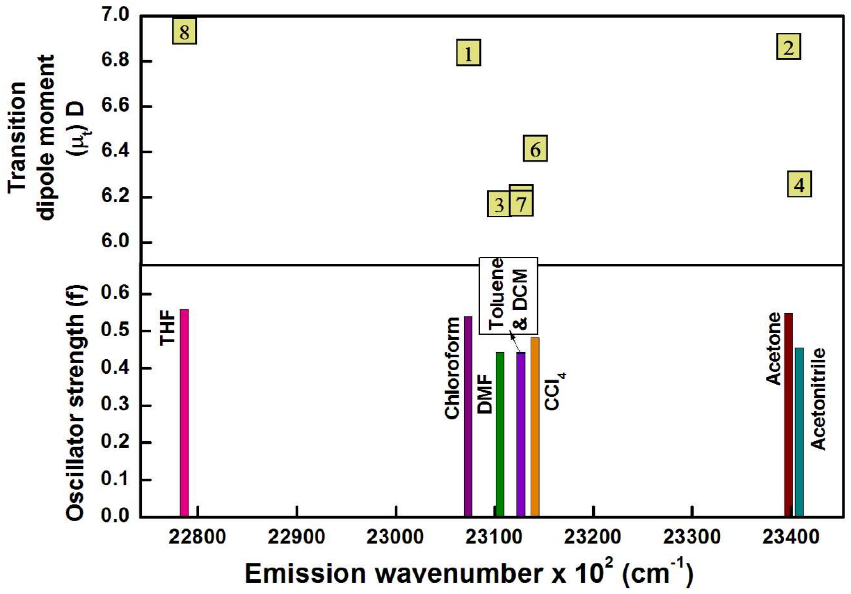
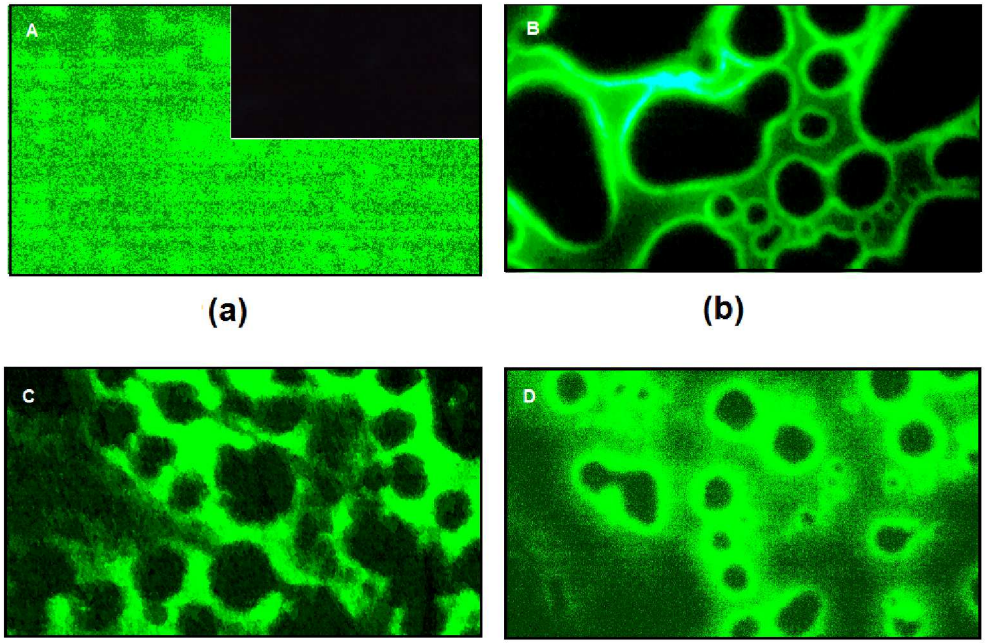


FIG. 5. The plot shows variation of transition dipole moment (Top) and oscillator strength (Below) as the function of emission wavenumber for TCQDL molecules in various solvents: (1) chloroform, (2) acetone, (3) dimethyl formamide, (4) acetonitrile, (5) toluene, (6) carbon tetrachloride,(7) dichloromethane, (8) tetrahydrofuran.

The transition dipole moment of TCQDL molecule in various solvents from absorption data is listed in Table V. They are based on the assumption of complete transfer of one unit charge in the transition. It is reasonable to assume that this represents a maximum in the amount of charge that might be separated, and therefore a minimum length for the charge separation [44, 60]. The estimated values ranged from 6.17-6.93 D. The transition dipole moment values for TCQDL in dimethylformamide and dichloromethane was found to be same (Figure 5).

In our study, we found the solvatochromic shifts without the aid of any inorganic or organic dye. This is an indicator that the TCQDL molecule can act as a fluorophore, hence does not require any dye to aid solvatochromism. In order to employ TCQDL molecules for fluorescence imaging, we doped another DLC system of HAT5 molecule with 1, 5 and 10 mole percent of TCQDL molecule. The fluorescence image of pure TCQDL molecule reveals bright green uniform region (Figure 6a). However the fluorescence image of pure HAT5 shows complete dark region indicating no signature of fluorescence (inset in (Figure 6a) The image corresponding to 1 % of TCQDL in HAT5 (Figure 6b) shows bright green texture and



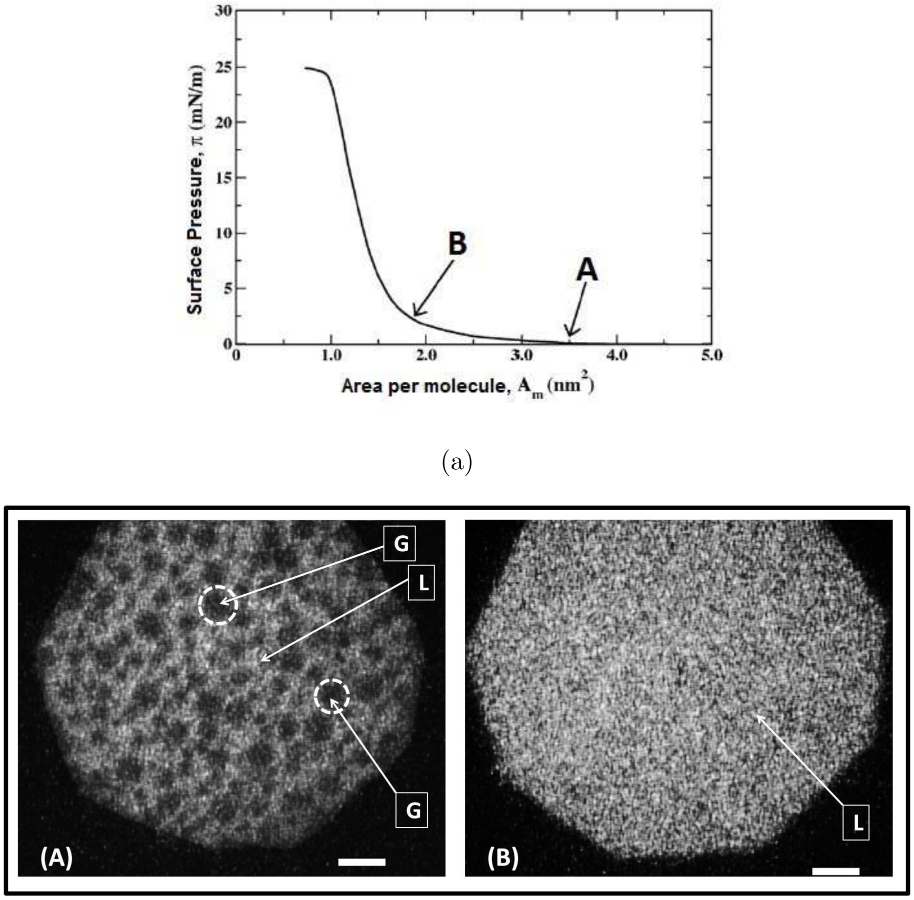
(a) (b)

(c) (d)

FIG. 6. The fluorescence microscopy images of (a) TCQDL molecule (Bright green region) (Inset shows fluorescence microscopy image of HAT5 molecules (Dark region)) and HAT5 system doped with (b) 1 % (c) 5 % (d) 10 % of TCQDL molecule.

dark regions. As both the TCQDL and HAT5 exhibit Col_h mesophase, they are well miscible in all proportions. The dark regions in the Figures 6(c)-(d) are voids. The brightness of the green region increases with the increase in the concentration of TCQDL in HAT5 (Figure 6c and Figure 6d). This indicates that even with 1 mole percent of TCQDL in HAT5, the imaging of a LC system can be obtained.

In order to observe the Langmuir monolayer of TCQDL molecules at the air-water interface, we have carried out the epifluorescence microscopy [25] without the aid of any fluorophore. The epifluorescence images were captured at the points A and B as indicated in the isotherm of the TCQDL monolayer (Figure 7a) and they are shown in Figure 7b. Both the figures show bright region indicating the fluorescent feature of the TCQDL molecules. Figure 7b(A) shows bright region and darks regions. The bright region is due to the liquid like phase of the TCQDL molecules whereas the dark regions indicate the gas phase. On compression the dark region disappears leading to a uniform bright region. This indicates



(a)

(b)

FIG. 7. (a) Surface pressure – area per molecule isotherm of Langmuir monolayer of TCQDL molecule at air-water interface. The arrows on the isotherm indicate the position at which the epifluorescence images were captured. (b) The epifluorescence images of LM of TCQDL captured at A and B as indicated in the isotherm. Figure A shows gas -liquid like coexistence phase and Figure B shows liquid like phase. The dark and bright regions representing gas and liquid like phases are labeled as G and L, respectively. The outer dark polygon is due to aperture diaphragm of the microscope. The scale bar is 500 μm in length.

that on compression of the monolayer, the gas phase disappears and a uniform liquid-like phase appears (Figure 7b(B)). Such observation further confirms that TCQDL molecules can be employed for various fluorescence studies.

IV. CONCLUSION

The effect of various solvents of different polarity on photophysical properties of TCQDL molecule was studied. We observed red shift in the emission spectra with increase in polarity of the solvent. The Stokes shift, Lippert's, Bakshiev's, and Kawski-Chamma-Viallet's polarity function were estimated from the experimental data. We found the ground and excited state dipole moment value of the molecule to be 2.56 D and 3.59 D respectively. Computationally, the ground state dipole moment value was calculated using Gaussian 03 package and it was found to be 3.20 D.

Our study indicates that TCQDL molecule can be employed as a fluorophore for imaging another non-fluorescent DLC. It will be interesting to study the photophysical properties of such molecules in a confined geometry formed by different mesophases of LCs. The potential of TCQ based LC can be used for imaging using confocal and two-photon microscopy.

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