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ORIGINAL ARTICLE

Physicochemical and Critical Micelle Concentration (CMC) of Cationic (CATB) and Anionic (SDS) Surfactants with Environmentally Benign Blue Emitting TTQC Dye

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Abstract 4-(3,4,5-trimethoxyphenyl)-8-methoxy-2-oxo-1,2, 5,6 tetrahydrobenzo[h]quinoline-3-carbonitrile (TTQC) dye has synthesized by one-pot multicomponent reactions (MCRs) of 3,4,5-trimethoxybenzaldehyd, ethyl cyanoacetate, 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one and ammonium acetate under microwave irradiation. The structures of the synthesized compound was established by spectroscopic (FT-IR, ^{1}H-NMR, ^{13}C-NMR, EI-MS) and elemental analyses. In addition, spectroscopic and physicochemical parameters, including electronic absorption, excitation coefficient, Stokes shift, oscillator strength, transition dipole moment and fluorescence quantum yield were investigated in order to explore the analytical potential of synthesized compound. TTQC dye undergoes solubilization in different micelles and may be used as a probe to determine the critical micelle concentration (CMC) of CTAB and SDS.

Keywords Quinoline · Stokes shift · Oscillator strength · Fluorescence quantum yield · CMC

Introduction

Quinoline is six - member heterocyclic ring consisting of five carbon atoms and one nitrogen within the ring. It has two endocyclic double bond and is basic in nature [1]. Quinoline and their derivatives are of considerable interest as they possess a wide range of biological properties such as antibacterial anti cancer, anti inflammatory, anti-protozoal [2]. Its use as intermediate for the formation of various bi-cyclic heterocyclic compounds such as pyrazolo-quinolines [3], thiazolo-quinoline [4], pyrrolo-quinoline etc. [5]. Due to the presence of nitrogen and one carbonyl group in one ring the quinoline also use in the field of inorganic chemistry it can easily coordinate with transition metal series such as Ni, Cu. Co, Zn, Ru, Pt, Pd etc. [6]. Microwave has been employed in different kind of organic synthesis and has become popular for constructing new heterocycles [7]. Synthesis is easy, effective, economical and eco-friendly and is believed to be a step towards green chemistry. Under the framework of, "Green Chemistry" we have developed an environmentally benign approach for the synthesis of quinoline. Multi-component reactions (MCRs), by virtue of their flexibility to rapidly assemble three or more reactants and convert them into higher molecular weight compounds in one-pot [8], have become very popular in the discovery of biologically active novel compounds due to their experimental simplicity, atom economy and high product yields [9]. Quinoline framework containing donor acceptor long bi bond conjugates system typical ICT (Intermolecular Charge Transfer) compounds [10], are known as a kind of fluorescent brightening agents because they have strong blue [11] fluorescence in solution. Its fluorescence spectrum exhibits a large red shift with an increase in the polarity of solvents. It has a hole transport tendency [12]. An intramolecular conjugated charge transfer process has been reported to exist in it in the excited state. due to this reason its use in the field of martial science such as nonlinear optical properties, photonic materials, devices, optical limiting, electrochemical sensing, light-emitting devices, langmuir film, and solar cell materials. Because of these numerous applications of quinoline

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derivatives, we are reporting here the synthesis of novel doror acceptor long pi-bond conjugation quinoline based chromophore 4- (3, 4, 5-trimethoxyphenyl) -8-methoxy-2-oxo-1,2,5,6 tetrahydrobenzo [h] quinoline-3-carbonitrile (TTQC) by the multi-component reactions (MCRs) under microwave irradiation and physicochemical studies such as electronic absorption, molar absorptivity, oscillator strength, dipole moment fluorescence quantum yield are also determine. Critical micelle concentration (CMC) of CTAB and SDS are also calculated.

Experimental

4-(3,4,5-trimethoxyphenyl)-8-methoxy-2-oxo-1, 2, 5, 6-tetrahydrobenzo [h] quinoline - 3 - carbonitrile (TTQC)

A one-pot mixture of the 3,4,5-trimethoxybenzaldehyd (0.0056 mol), 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one (1 g, 0.0056 mol), ethyl cyanoacetate (1.1 g, 10 mmol) and ammonium acetate (2.99 g, 0.045 mol) in anhydrous ethanol (15 mL) in a beaker (100 mL) and the reaction mixture was heated inside a microwave oven for 5 min. (at 210 Watts, i.e., 30 % microwave power). Progress of reaction was monitored by TLC. After completion of the reaction and cooling, the product was obtained and recrystallization from methanol and chloroform [13].

Yellow solid: Yield: 92 %; m.p. 390 °C; EI-MS *m/z* (rel. int. %): 421 (78) [M+1]$^{+}$; IR (KBr) v_{max} cm^{-1}: 3254 (NH), 2932 (C-H), 2228 (CN), 1622 (C=O), 1554 (C=C), 1256 (N=C); ^{1}H NMR (600 MXz CDCl$_3$) (δ/ppm): 8.33 (s, NH), 7.28 (s, 1H, CHAr), 7.03 (d, 1H, CHAr, J=1.8 Hz), 6.031 (d, 1H, CHAr, J=1.8 Hz), 6.93 (s, 1H, CHAr), 6.81 (s, 1H, CHAr), 3.93 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 2.54–2.51 (m, 2H, CH$_2$cyclo, H-6, 2H), 2.37–2.33 (m, 2H, CH$_2$cyclo, H-5, 2H); ^{13}CNMR (CDCl$_3$) δ: 168.56 (pyridine C), 162.78 (C=O), 158.67, 155.00, 150.00, 144.84, 146.27, 141.72, 127.28, 123.66, 122.19 (Ar-C), 120.07 (CN), 116.09, 115.30, 28.59 (C-6), 28.23 (C-5) Anal. calc.for C$_{24}$H$_{22}$N$_2$O$_5$: C, 68.89, H, 5.30, N, 6.69. Found: C, 68.85, H, 5.27, N, 6.65.

Result and Discussion

Chemistry

TTQC was prepared by microwave irradiation Scheme 1. The purified product was characterized by the FT-IR, ^{1}H-NMR, ^{13}C-NMR and EI MS spectra. The IR spectrum of TTQC dye shows the characteristic band at 3254 cm^{-1} due to presence of -NH group and at 1622 cm^{-1} attributed to the C=O group. IR spectra shows sharp peek at 1256 cm^{-1} due

presence of C=N stretch which conforms the formation of TTQC dye. The ^{1}H-NMR spectra of all the TTQC dye measured at room temperature shows one singlet at 8.33 ppm for the NH. The appearance of multiplets at δ 6.81–7.28 was due to aromatic protons and two multiplets at δ 2.54–2.51 and 2.37–2.33 ppm corresponding to the benzylic protons (C6-*H* and C5-*H* respectively). Moreover, ^{13}C-NMR spectra showed signals in the range of δ 158.67– 122.19 ppm due to aryl carbon and at δ 168.56 ppm due to pyridine Carbon. Finally characteristic peaks were observed in the mass spectra of TTQC. The mass spectrum of TTQC dye shows a molecular ion peak (M$^{+\cdot}$) m/z 421.

Spectral Behavior of TTQC

The normalized absorption spectra of TTQC dye in various non-polar, polar aprotic and protic solvents. Absorption and emission spectra of 1×10^{-5} mol dm^{-3} TTQC dye in various non-polar, polar aprotic and protic solvents were studied (Figs. 1 and 2). Calculated physicochemical parameters obtained from steady state absorption and fluorescence spectra are tabulated in Table 1. As seen in Fig. 1 polarity of solvent has effected on the absorption maxima. TTQC dye is red –shifts with decreasing the solvent polarity (shifted 8 nm on going from DMSO to CCl$_4$) indicating the ground of dye is more polar than the excited state. These features indicate a strongly allowed n-π* transition [14].

Determination of Oscillator Strength and Transition Dipole Moment

The solvatochromic behaviour in TTQC dye allows one to determine the difference in the dipole moment between the excited singlet and the ground state (Δμ=μ$_e$ − μ$_g$). This difference can be obtained using the simplified Lippert- Mataga equation as follows [14, 15]:

$$\Delta\overline{\nu}_{st} = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3}\Delta f + Const. \tag{1}$$

$$\Delta f = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \tag{2}$$

where $\Delta\overline{\nu}_{st}$ is the Stokes–shift, which increases with increasing the solvent polarity pointing to stronger stabilization of the excited state in polar solvents, *h* denotes Planck's constant, *c* refers to the speed of light in vacuum and *a* is the Onsager cavity radius. Parameters *D* and *n*, in Eq. 2, correspond to the dielectric constant and refractive index of the solvent, respectively. The Onsager cavity radius was chosen to be 4.2 Å because this value is comparable to the radius of a typical

Scheme 1 Synthesis of TTQC dye
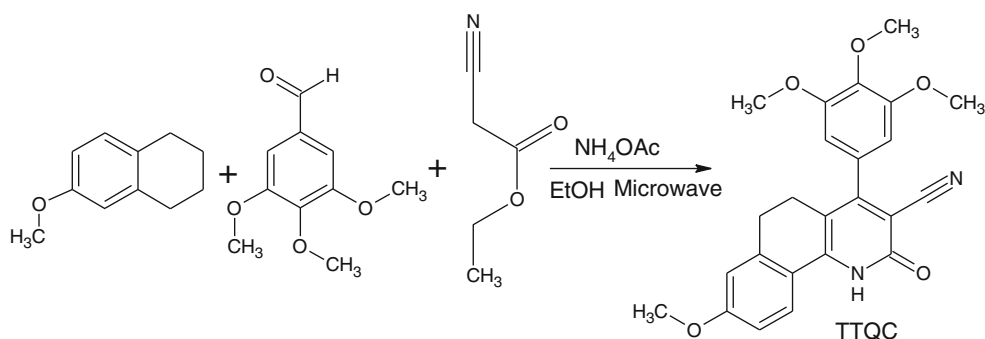
aromatic fluorophore. Stokes shifts ($\Delta\overline{\nu}_{ss}$) of TTQC dye in different solvents were calculated, as shown in Table 1, using the following the equation:

$$\Delta\overline{\nu}_{ss} = \overline{\nu}_{ab} - \overline{\nu}_{em} \tag{3}$$

where $\overline{\nu}_{ab}$ and $\overline{\nu}_{em}$ denote the wavenumbers of absorption and emission maxima (cm^{-1}), respectively The changes in dipole moment ($\Delta\mu$) between the excited singlet and ground state were calculated as 3.96 debye for TTQC dye. Positive value of dye indicates that the singlet exaited is more polar than the ground state.

The effective number of electrons transition from the ground to excited state is usually described by the oscillator strength, which provides the absorption area in the electronic spectrum. The oscillator strength, f, can be calculated using the following equation:

$$f = 4.32 \times 10^{-9} \int \varepsilon\left(\overline{\nu}\right) d\overline{\nu} \tag{4}$$

where ε is the extinction coefficient (Lmol^{-1} cm^{-1}), and $\overline{\nu}$ represents the numerical value of wavenumber (cm^{-1}). Oscillator strength values of TTQC dye in different solvents are reported in Table 1. In addition, the transition dipole

moment (μ) for TTQC from ground to excited state in Debye was estimated in different solvents using the following relation [16]:

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} \times E_{max}} \tag{5}$$

where E_{max} is the maximum energy of absorption in cm^{-1}

Fluorescence Polarity Study of TTQC Dye

The emission spectra of the 1×10^{-5} M of TTQC dye were measured in various polar aportic and polar protic solvents and shown in Fig. 2. Their spectral data are also collected in Table 1. The emission spectra of TTQC dye consist of one broad band in different solvents. This band can be assigned to S$_1$-S$_0$ electronic transition. Both dye gives the same behavior i.e., dyes show red shift with decreasing solvent polarity. TTQC dye shifted 11 nm on going from MeOH to THF indicating the involvement of photoinduced intramolecular charge transfer (ICT) in the singlet ground state than in excited state.
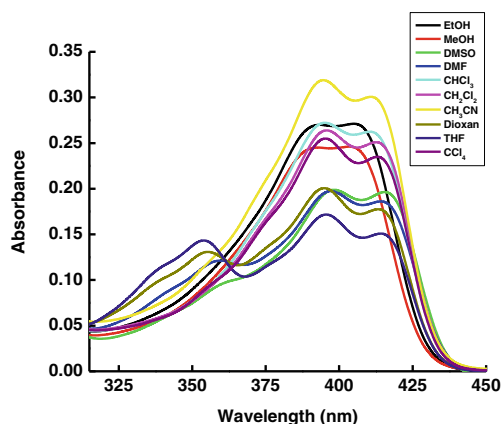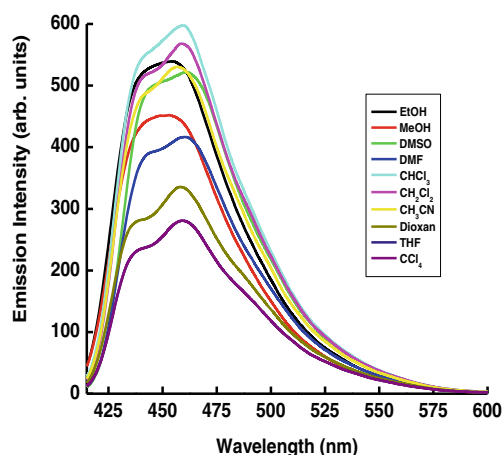

Fig. 1 Electronic absorption spectra of 1×10^{-5} mol dm^{-3} of TTQC dye in different solvents

Fig. 2 Emission spectra of 1×10^{-5} mol dm^{-3} of TTQC dye in different solvents

Table 1 Spectral data of TTQC dye in different solvents

Solvent	Δf	E_T^N	E_T (30) dye	λ_{ab}(nm)	λ_{em}(nm)	ε M^{-1}cm^{-1}	f	μ_{12} Debye	$\Delta \bar{\nu}$ (cm^{-1})	Φ_f
DMSO	0.266	1.23	70.76	404	459	18,510	0.21	4.32	2966	0.40
EtOH	0.305	1.22	70.42	406	458	26,710	0.29	5.06	2796	0.28
MeOH	0.308	1.23	70.59	405	452	24,320	0.24	4.62	2568	0.26
DMF	0.263	1.22	70.42	406	457	17,980	0.19	4.11	2749	0.33
CHCl$_3$	0.217	1.23	70.59	405	462	25,670	0.31	5.17	3046	0.33
CH$_2$Cl$_2$	0.255	1.21	70.07	408	462	24,380	0.27	4.91	2864	0.30
Acetonitrile	0.274	1.19	69.56	411	463	29,320	0.32	5.27	2732	0.25
Dioxan	0.148	1.18	69.22	413	464	17,180	0.18	3.98	2662	0.28
THF	0.208	1.16	68.39	418	469	14,600	0.15	3.65	2602	0.18
CCl$_4$	–	1.19	69.39	412	463	22,620	0.24	4.58	2673	0.17

The empirical Dimroth polarity parameter, E_T (30) and E_T^N of TTQC dye was also calculated according to the following equation [17].
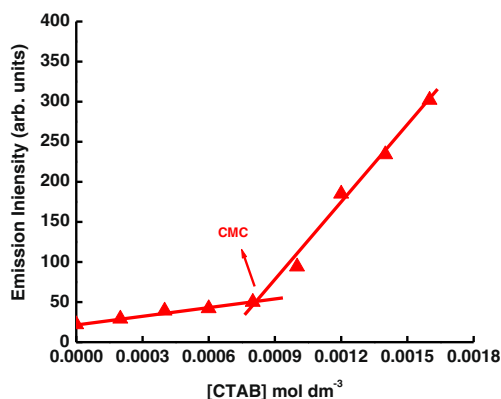
$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4} \qquad (6)$$

$$E_T(solvent) = \frac{28591}{\lambda_{max}} \qquad (7)$$

where λ_{max} corresponds to the peak wavelength (nm) in the red region of the intramolecular charge transfer absorption of all compounds.

The fluorescence quantum yield (φ_f) was measured using the optically diluted solution to avoid reabsorption effect (absorbance at excition wave relative method with solution of 9, 10-diphenylanthralene (DPA) in DMSO as reference standard [18]. The following relation has applied to calculate the fluorescence quantum yield:

$$\phi_f(s) = \varphi_f(r) \frac{F_{(s)} \left\{ 1 - \exp\left(-A_{ref} \ln 10\right) \right\} \times n^2 s}{F_{(ref)} \left\{ 1 - \exp\left(-A_s \ln 10\right) \right\} \times n^2 r} \qquad (8)$$

Flurescence quantum yield of TTQC dye in different solvent are also listed Table 1.

Effect of Surfactant on Emission Spectrum of TTQC Dye

The emission spectrum of 1×10^{-5} mol dm^{-3} of TTQC dye was also measured in sodium dodecyl sulphate (SDS) cationic micelle and ethyltrimethyl ammonium bromide (CTAB) anionic micelle. As shown in Figs. 3 and 4 the emission intensity of TTQC dye increases with increasing concentration of the CTAB surfactant and the emission intensity decreases of TTQC dye with increasing concentration of the SDS surfactant An abrupt change in fluorescence intensity was observed at surfactant concentrations of 5.9×10^{-3}, 9.1×10^{-4} for TTQC (Figs. 3 and 4) which are very close to the critical micelle concentration of SDS, CTAB [19]. Thus TTQC dye can be employed as a probe to determine the CMC of surfactants. It is well known that aromatic molecules are generally solubilized in the palisade layer of micelles [20].

Fig. 3 Plot of I_f versus concentration of CTAB for TTQC dye
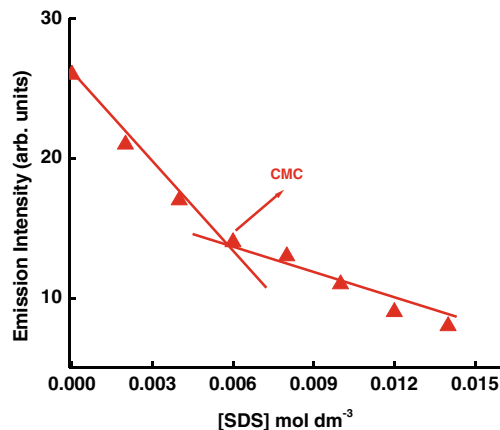
Fig. 4 Plot of I_f versus concentration of SDS for TTQC dye

Conclusion

TTQC dye has synthesized by one-pot multicomponent reactions (MCRs) of 3,4,5-trimethoxybenzaldehyd, ethyl cyanoacetate, 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one and ammonium acetate under microwave irradiation. Physicochemical studies of the dye including singlet absorption, extinction coefficient, Stokes shift, oscillator strength, dipole moment and florescence quantum yield were investigated on the basis of the polarity of solvent. The absorption spectra of TTQC dye exhibit an intramolecular charge transfer band; which showed a solavotochromism in different solvents. The emission spectra of the dyes also reveal the intramolecular charge transfer band character. These findings confirm that there is a significant electron transfer between the donating moiety and the accepting fragment through the π conjugated. A fluorescence enhancement of (TTQC) dye with CTAB was noticed, while a fluorescence quenching of (TTQC) dye with SDS was observed under the same experimental and instrumental conditions abrupt change in fluorescence intensity at CMC of micelle.

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