ORIGINAL ARTICLE



A Combined Experimental and Computational Investigation on Spectroscopic and Photophysical Properties of a Coumarinyl Chalcone

Abdullah G. Al-Sehemi^{1,2} · Mehboobali Pannipara² · Abul Kalam^{1,2} · Abdullah M. Asiri^{3,4}

Received: 6 January 2016 / Accepted: 9 May 2016 © Springer Science+Business Media New York 2016

Abstract Here, we synthesized a new coumarinyl chalcone derivative 3-[3-(3-Methyl-thiophen-2-yl)-acryloyl]-chromen-2-one (MTC) by simple and proficient method. A comprehensive study on the photophysics of a coumarinyl chalcone derivative having pi-conjugated potential chromophore system 3-[3-(3-Methyl-thiophen-2-yl)-acryloyl]-chromen-2-one (MTC) has been carried out spectroscopically. The electronic absorption and emission characteristic of MTC were studied in different protic and aprotic solvents using absorption and steady-state fluorescence techniques. The spectral behavior of this compound is found to be extremely sensitive to the polarity and hydrogen bonding nature of the solvent. The compound shows very strong solvent polarity dependent changes in their photophysical characteristics, namely, remarkable red shift in the emission spectra with increasing solvent polarity, change in Stokes shift, significant reduction in the fluorescence quantum yield; indicating that the fluorescence states of these compounds are of intramolecular charge transfer

Electronic supplementary material The online version of this article (doi:10.1007/s10895-016-1823-2) contains supplementary material, which is available to authorized users.

Abdullah G. Al-Sehemi agmasq@gmail.com

- ¹ Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia
- ² Research Center for Advanced Materials Science (RCAMS), King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia
- ³ Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
- ⁴ Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

(ICT) character. The solvent effect on the photophysical parameters such as singlet absorption, molar absorptivity, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of the compound has been investigated in detail. The difference between the excited and ground state dipole moments ($\Delta \mu$) were estimated from solvatochromic methods using Lippert–Mataga and Reichardt's correlations. The prepared compound was also studied by density functional theory (DFT) and time-dependent density functional theory (TDDFT). The results revealed that it could be easily reproduce by computational means.

Keywords Coumarin derivative \cdot Photophysics \cdot ICT \cdot Effect of solvent

Introduction

Coumarins and its derivatives are important class of compounds that possess multiple biological activities including disease prevention, growth modulation and antioxidant properties [1]. As these classes of compounds encompass a broad array of photophysical properties including high molar absorptivity, quantum yield, large Stokes shift, lifetime and ability to respond towards the immediate environment [2], it is widely used in synthesizing laser dyes, fluorescent whiteners and organic nonlinear optical materials [3]. The optical properties these compounds are strongly altered by the nature of substituent, substituted position in the coumarin ring and the surrounding media [4]. Since the photophysics and photochemistry of coumarin derivatives mainly rely on the effect of substitution on the ring, structurally modified coumarin based luminophores have become a subject of intense research in various aspects of science.

The dipole moments of a molecule offer an insight to their ground and excited state and give information about change in electronic distribution upon excitation. Hence, the knowledge of dipole moment is useful in designing non-linear optical materials [5], studying the nature of photochemical reactions [6], and calculation of molecular polarizability [7]. Though there are various methods used for experimental determination of dipole moment that include electric dichroism [8], microwave conductivity [9], Stark splitting [10] and thermochromic shift method [11], the use of these methods are limited because they are equipment sensitive and the studies have been restricted to relatively very simple molecules. The use of solvent shift method based on absorption and emission intensity is the most widely accepted method for the estimation of the dipole moments of a molecule [12]. Understanding solute-solvent interactions and measuring them quantitatively is an active area of research since the solvent affects the equilibria, absorptions, emissions and the mechanisms of reactions for many compounds.

Compounds containing electron donor and acceptor functionality in conjugation exhibit interesting optical and spectral properties due to intramolecular charge transfer (ICT) that can be exploited in various fields. The aim of the present work is to perform a detailed investigation on the spectral behaviors and photophysical properties of a donor–acceptor type coumarin derivative in different media by applying steady state spectroscopy and density functional theory (DFT) calculation.

Experimental

Materials and Methods

All solvents and chemicals used in this work were of spectroscopic grade obtained from Sigma Aldrich and used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and the infrared (IR) spectra were recorded on Shimadzu FT-IR 8400S infrared spectrophotometer using the KBr pellet technique. The NMR (¹H and ¹³C) spectra were recorded on a Bruker DPX-600 at 600 MHz and 150 MHz, respectively, using tetramethylsilane as the internal standard. The chemical shift values are recorded on δ scale and coupling constants (J) in Hertz; Splitting patterns were designated as follows: s: singlet; d: doublet; m: multiplet. UV-Vis electronic absorption spectra were recorded on a PG UV-vis double-beam spectrophotometer, and the steady-state fluorescence spectra were measured Varain Cary Eclipse spectrofluorophotometer using a rectangular quartz cell of dimensions $0.2 \text{ cm} \times 1 \text{ cm}$. The emission was monitored at right angle. The fluorescence quantum yield (ϕ_f) was measured using an optically diluted solution of quinine sulfate as reference according to Eq. (1):

$$\phi_u = \phi_s \times \frac{I_u}{I_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2} \tag{1}$$

where ϕ_u , ϕ_s are the fluorescence quantum yields of the unknown and standard, respectively, *I* is the integrated emission intensity; A is the absorbance at excitation wavelength, and *n* is the refractive index of the solvent. The subscript *u* and *s* refers to unknown and standard, respectively.

Procedure for the Synthesis of 3 – Acetyl Coumarin (2)

To a solution of salicylaldehyde (1 mg, 8.1 mmol) and ethylacetoacetate (1.06 mg, 8.1 mmol) in ethanol (20 ml), 0.3 mL of piperidine and 2–3 drops of glacial acetic acid were added. The mixture was refluxed for 4 h. After the completion of the reaction as identified by TLC, the reaction mixture was cooled to room temperature and 20 mL of ice cold water was added. The solid product was collected by filtration, dried and recrystallized from ethanol to give **2** (0.36 mg, 72 %) as yellow solid.

Yield 72 %, yellow solid, Melting point: 154 °C; IR (KBr, ν cm⁻¹): 1640 (CO), 1725 (CO), 1497, 1420, 1232, 792, 648; ¹H NMR (600 MHz, CDCl₃): δ 7.62 (m, 4H, Ar-H), 8.72 (s, 1H, Ar-H), 2.27 (s, 1H, -CH₃); ¹³C NMR (150 MHz, CDCl₃) δ 196.23, 150.96, 131.27, 165.07, 125.22, 123.90, 127.40, 149.45, 22.18, 124.03, 125.79.

Procedure for the Synthesis of 3-[3-(3-Methyl-thiophen-2-yl)-acryloyl]-chromen-2-one (MTC) (3)

To a solution of *3–Acetyl coumarin* (0.5 mg, 2.65 mmol) and 3-methyl-2-thiophenecarboxaldehyde (0.38 mg, 2.65 mmol) in ethanol (50 ml), 0.3 mL of piperidine and 2–3 drops of glacial acetic acid were added. The mixture was refluxed for 12 h. After the completion of the reaction as identified by TLC the solvent was removed under vacuum. The residue thus obtained was triturated with 10 mL of ethanol until the formation of fine precipitates. The precipitate was filtered off and recrystallized from methanol to give **3** (0.36 mg, 76 %) as pale yellow solid.

Yield 76 %, Pale yellow solid; Melting point: 176-178 °C; IR (KBr, $v \text{ cm}^{-1}$): 1640 (CO), 1725 (CO), 1497, 1420, 1232, 792, 648; ¹H NMR (600 MHz, CDCl₃): δ 7.72 (m, 4H, Ar-H), 8.02 (s, 1H, Ar-H), 5.32 (d, 1H, J = 15.4 Hz), 4.98 (d, 1H, J = 15.1 Hz) 2.27 (s, 1H, $-\text{CH}_3$), 7.02 (d, 1H, J = 8.0 Hz), 7.42 (d, 1H, J = 8.0 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 186.0, 196.2, 162.96, 160.27, 150.07, 126.22, 125.90, 121.40, 121.45, 127.18, 134.03, 135.79, 150.82, 132.63, 130.70, 132.07, 137.51, 15.58 (Scheme 1).



Scheme 1 Synthetic route of MTC

Results and Discussion

Absorption and Emission Spectra of MTC in Different Solvents

UV-vis absorption spectra of 1 x 10^{-5} mol L⁻¹ MTC recorded in solvents of different polarity show slight variation in the absorption maxima on going non polar solvents to polar protic solvents. Representative absorption spectra of MTC recorded in some selective solvents are depicted in Fig. 1 and the corresponding spectroscopic, optical band gap and photophysical properties are collected in Table 1. As seen in Fig. 1, the compound show narrow absorption band at ~375 nm on going from aprotic to protic solvents and hence, the absorption spectra and optical band gap are hardly solvent dependent while the high molar absorption coefficients indicates the π to π^* transition in all the solvents. On excitation at 365 nm, the emission spectrum show smooth correlation with increasing polarities of the solvents (Fig. 2; Table 1). A considerable red shift is observed in the emission spectrum from 445 to 471 nm on changing the solvent polarity from nonpolar to polar, whereas no such shift is observed in the absorption spectrum with varying solvent polarity, suggesting the involvement of photo induced intramolecular charge transfer (ICT) in the singlet excited state [13, 14]. Only one emission peak is observed for MTC in non-polar solvents but in polar solvents a red shifted emission band is observed in addition to the short wave length band. This kind of dual emission is characteristic of compounds containing electron donor and acceptor group



Fig. 1 Electronic absorption spectra of $1\times 10^{-5}\mbox{ mol }L^{-1}$ of MTC in different solvents

constituted of a conjugated π -electron system. The red shifted band in polar solvents arises from the charge transfer state and short wavelength emission band originate from a locally excited state (Fig. 2).

It is concluded that emission spectra is more sensitive to solvent polarity compared to absorption spectra, which indicates that photoinduced intramolecular charge transfer (ICT) occurs in the singlet excited state from the electron donating substituent group to the electron acceptor carbonyl group of chromophore. Moreover, stabilization of highly dipolar excited state in polar solvents confirm the presence of π - π * transitions in MTC. The intensity of the emission spectra of MTC was found to be highest in polar aprotic solvents and lowest in polar protic solvents due to solute-solvent interaction such as hydrogen bonding.

Estimation of Dipole Moments Using Solvatochromic Methods

The extent of charge distribution in a molecule used to elucidate a variety of physical and chemical properties. The change in dipole moment between the excited singlet state and ground state has been calculated using the method proposed by Lippert-Mataga (2, 3) [15, 16], which is based on the correlation of energy difference between the ground and excited states (Stokes' shift) with the solvent orientation polarizability (Δf).

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

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{3}$$

where $\Delta \overline{\nu}_{st}$ is the Stokes shift expressed in wave numbers (cm⁻¹), *h* is Planck's constant, *c* is the speed of light, *a* is the Onsager cavity radius, ε and *n* are the dielectric constant and refractive index of the solvent, respectively; μ_e and μ_g are the dipole moments in the excited and ground state, respectively, and Δf is the orientation polarizability of the solvent which measures both electron mobility and dipole moment of the solvent molecule. The Onsager cavity radii (*a*) from molecular volume of molecules is calculated by using Suppan's Eq. (4) [17]

$$a = \left(\frac{3M}{4\pi\delta N}\right)^{1/3} \tag{4}$$

Table 1 Spectral,	optical banc	1 gap (Eg) and phot	tophysical par	rameters of MT	C in different so	olvents							
Solvents	$\lambda_{abs}(nm)$	λ^*_{abs} (nm)	$\lambda_{\rm em}({\rm nm})$	$\Delta \overline{ u} (\mathrm{cm}^{-1})$	$\varepsilon~{\rm M}^{-1}~{ m cm}^{-1}$	Φ_f	f	<i>f</i> *	μ ₁₂ Debye	$E_{T}(30)$ K cal mol ⁻¹	$\Delta f(D,n)$	E_T^N	Eg (eV)
Toluene	375,310	415.9,352.12	448	4345	25,800	0.252	0.61	0.5819 0.2694	6.95	33.9	0.0132	0.099	2.95
Dioxane	375,310	411.5 351.58	446	4245	2600	0.28	0.63	0.5622 0.2691	7.08	36	0.021	0.164	3.0
THF	375,310	411.58,352.81	445	4195	28,200	0.26	0.96	0.6151 0.2188	8.73	37.4	0.210	0.210	3.0
Acetonitrile	365,310	409.01,353.13	447	5026	26,200	0.042	1.01	0.6261 0.1926	8.83	45.6	0.304	0.472	3.05
DMF	375,310	410.5,353.64	459	4880	24,600	0.038	1.07	$0.648\ 0.1969$	9.23	43.8	0.274	0.404	3.0
Dichloromethane	375,310	411.6,353.05	449	4395	27,300	0.25	1.14	0.6249 0.2153	9.50	40.7	0.218	0.309	2.95
Propanol	378,310	410.06,353.23	465	4950	23,100	0.032	0.60	0.6312 0.1996	6.95	49.2	0.274	0.570	2.8
Ethanol	375,310	409.51,353.15	471	5435	25,300	0.03	1.07	0.6273 0.1963	9.23	51.9	0.288	0.654	2.95
Methanol	378,310	408.76,353.02	465	4950	24,700	0.025	1.08	0.6212 0.1923	9.29	55.4	0.308	0.762	2.95



Fig. 2 Emission spectra of 1×10^{-5} mol L⁻¹ of MTC in different solvents ($\lambda_{ex} = 365$ nm)

where δ is the density of dye, M is the molecular weight of dye and N is Avogadro's number. From the slope of Stokes shift versus the orientation polarization (Δf) plot (Fig. 3), change in dipole moment calculated to be 5.17 D. Thus, the high value for dipole moment and the linear correlation of Lippert-Mataga plot further corroborates the occurrence of photoinduced intramolecular charge transfer.

In addition, the change in dipole moment $(\Delta \mu)$ between the excited singlet and ground state was also investigated using solvatochromic shift method [18, 19], making use of the dimensionless microscopic solvent polarity parameters E_T^N given by the Eq. (5)

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4} \tag{5}$$

where λ_{max} corresponds to the peak wavelength in the red region of the intramolecular charge transfer absorption of the betain dye. In this method, change in dipole moment is calculated by correlating the Stokes shift of the fluorophore to E_T^N (Fig. 4) according to Eq. (6).

$$\Delta \,\overline{\nu} = 11307.6 \left(\frac{\Delta \mu}{\Delta \mu_D}\right)^2 \left(\frac{a_D}{a}\right)^3 E_T^N + Const. \tag{6}$$



Fig. 3 Plot of ΔF versus Stokes shift (cm⁻¹)

 λ^*_{abs} (nm) and f^* are calculated values



Fig. 4 Plot of E_T^N versus Stokes shift (cm⁻¹)

 $\Delta\mu$ is the difference between the excited and ground state dipole moments of the probe molecule and $\Delta\mu_D$ is the change in the dipole moment of the betaine dye; *a* (taken as 4.35 Å) and a_D are the Onsager cavity radiia of the probe molecule and betaine molecule respectively. Since the values of a_D and μ_D are known (6.2 Å and 9 Debye, respectively) the change in dipole moment is calculated using Eq. (7),

$$\Delta \mu = \left[\frac{81m}{\left(6.2/a\right)^3 \times 11307.6}\right]^{1/2}$$
(7)

where, m is the slope of linear plot of E_T^N vs Stokes shift (Fig. 4) and the value for $\Delta \mu$ is found to be 2.16 D. The value of $\Delta \mu$ obtained by Lippert-Mataga's equation is greater than that obtained by dimensionless microscopic solvent polarity parameters E_T^N , because in Lippert's plot only the dipole-dipole interactions are considered and does not consider the polarizability of solute molecules.

The ground to excited state transition dipole moment (μ_{12}) in various solvents was calculated using Eq. (8) [20]:

$$\mu_{12}{}^2 = \frac{f}{4.72 \times 10^{-7} E_{\text{max}}} \tag{8}$$

where, Emax is the energy maximum absorption in cm⁻¹ and *f* is the oscillator strength which shows the number of electrons whose transition from ground to excited state gives the absorption area of the electronic spectrum. The experimental oscillator strength values were ascertained using Eq. (9) [21]

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

where, ε is the numerical value for molar decadic extinction coefficient measured in dm mol⁻¹ cm⁻¹ and $\overline{\nu}$ is the numerical value of the wave number measured in cm⁻¹. The values of *f* and μ_{12} are listed in Table 1 and indicate that the S_o \rightarrow S₁ transition is strongly allowed.



Fig. 5 Plot of $E_T(30)$ versus fluorescence quantum yield

Effect of Solvents on Fluorescence Quantum Yield

The knowledge of fluorescence quantum yield (ϕ_f) values gives an insight on the photophysical properties of an unknown fluorescent molecule. Fluorescence quantum yield of MTC was measured in solvents of different polarity. The fluorescence quantum yield has been correlated with E_T (30) of the solvent, where $E_T(30)$ is the solvent polarity parameter put forward by Reichardt [18], that deliberates interactions such as solvent polarizability and hydrogen bonding besides those of a specific nature. The fluorescence quantum yield (ϕ_f) of MTC is strongly affected by the polarity and hydrogen bonding ability of the solvents as shown in Table 1 and Fig. 5, where

Table 2The bond length (Å) of ground and excited states at B3LYP/6- $31G^*$ and TD-B3LYP/6- $31G^*$ level of theories

Bonds	Bond Length (Å)		Bonds	Bond Length (Å)	
	S ₀	S_1		S ₀	S ₁
C1-C2	1.4065	1.4032	C11-C12	1.3580	1.3862
C1-C6	1.3858	1.3880	C12-C13	1.4353	1.4045
C2-C3	1.3916	1.400	C13-C16	1.3927	1.4236
C3-C4	1.3950	1.3861	C13-S1	1.7640	1.7686
C4-C5	1.4071	1.4211	C17-C16	1.5045	1.4996
C4-O1	1.3638	1.3690	C16-C15	1.4276	1.4034
C5-C6	1.4115	1.4208	C15-C14	1.3680	1.3845
C5-C9	1.4271	1.4130	C14-S1	1.7294	1.7177
C8-C9	1.3677	1.4163	Solvents	Dipole	
C8-C10	1.5104	1.4203		S ₀	S_1
C7-C8	1.4669	1.4329	Acetonitrile	2.31	9.72
C7-O1	1.3920	1.3690	Dichloromethane	2.22	9.64
C7-O3	1.2159	1.2404	Propanol	2.29	9.78
C10-C11	1.4668	1.5046	Ethanol	2.30	9.77
C10-O2	1.2378	1.2532	Methanol	2.31	9.72
H6-O3	2.1498	2.6141			
H5-O2	2.3117	2.7596			





 φ_f values undergo very sharp decline on increasing the solvent polarity. This kind of change in the φ_f values with the solvent polarity strongly implies that there is a large structural change for the MTC following their photo excitation in the fluorescent state. The decrease in φ_f (positive solvatokinetic effect) with charge transfer character was explained by several mechanisms such as proximity effect and conformational changes [22]. The reduction of φ_f in highly protic alcoholic solvents is caused by the hydrogen bonding between solvent molecules and the carbonyl group of fluorophore due to enhanced radiationless processes.

Computational Details

Here, we used Gaussian 09 program to achieve all calculation for the synthesized molecule. The geometries, electronic and absorption spectra of synthesized molecule were executed by means of density functional theory (DFT) and time dependent density functional theory (TDDFT), respectively [23].

All calculations were executed by using 6-31G* basis set [24] and we used Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP) [25–27] for DFT. TDDFT



Fig. 7 The representations of the HOMO and LUMO orbital charge density of MTC at B3LYP/ 6-31G* level of theory and their energy

 Table 3
 Calculated global reactivity descriptors for MTC at B3LYP/6-31G(d,p) level

Sample	E _{HOMO}	E _{LUMO}	Eg	η	x	ω	S
MTC	-5.87	-2.54	3.33	1.665	4.205	5.309917417	0.3003003

approach is used for the calculation of the absorption spectra of molecule after the optimization which showed an efficient method [28, 29]. In last two decades, the polarizable continuum model (PCM) [30–32] has been appeared as the most actual tools to realize the effects of bulk solvents for both the ground- and excited-states. In this paper, the absorption spectra has been computed by using PCM-TDB3LYP/6-31G* level of theory.

The DFT method can be used to calculate reactivity descriptors like electronegativity (χ), hardness (η), electrophilicity (ω) and softness (S).

Mulliken electronegativity (χ) was calculated from the following equation:

$$\chi = (E_{HOMO} + E_{LUMO})/2$$

Hardness (η) was calculated from the following equation:

 $\eta = (E_{LUMO} - E_{HOMO})/2$

Electrophilicity (ω) was calculated from the following equation:

$$\omega = (E_{HOMO} + E_{LUMO}/2)^2/2r$$

Softness (S) was calculated from the following equation:

$$S = 1/2\eta$$

The B3LYP/6-31G* and TD-B3LYP/6-31G* level of theory have been applied to compute the ground state and excited state geometries, respectively. Their geometrical parameters are listed in Table 2 and labeling scheme is showed in Fig. 6. The results revealed that bond length increased from ground state to excited state in C4-C5, C7-O3, C8-C9, C10-C11, C10-O2, C11-C12, C13-C16 and C15-C14 as 0.014, 0.024, 0.048, 0.037, 0.015, 0.028, 0.030 and 0.016 Å, respectively. While bond length shortened from ground state to excited state in C5-C9, C7-C8, C8-C10, C7-O1, C12-C13, C16-C15 and C14-S1 as 0.014, 0.090, 0.034, 0.023, 0.030, 0.024 and 0.011 Å, respectively. The major change toward lengthening has been noticed for C8-C9, C10-C11, and C13-C16, i.e., 0.048, 0.037 A, and 0.030 ° A while shortening has been noticed for C14-S1, i.e., 0.011 A. There are also intramolecular hydrogen bonding between H5-O2 and H6-O3 and bond length increased from ground state to excited state i.e., 0.447 A, and 0.464 A, respectively.

From ground to excited state the dipole moment is also increased. The effect of change in dipole moment from ground to excited state studied by Godefroid et al. and determined that quantum phosphorescence efficiency decreased if change in dipole moment from S0 \rightarrow S1 (0.26 D/0.32 D) was lowly whereas quantum phosphorescence efficiency increased if change in dipole moment from S0 \rightarrow S1 (0.38 D/2.76 D) was huge. In our case, we calculated dipole moment in



Fig. 8 The computed absorption spectra of MTC in different solvents

different solvents and the S0 \rightarrow S1 dipole moment change is 7.41–7.49 D showing that this material would have good quantum phosphorescence efficiency (Table 2). The calculated dipoles are in good agreement with experimental observation.

Figure 7 shows the highest occupied molecular orbitals (HOMOs) energies (EHOMO), lowest unoccupied molecular orbitals (LUMOs) energies (ELUMO) and HOMO–LUMO energy gaps (E_{gap}). In the target molecule HOMOs are delocalized toward the right side of the schemes while the LUMOs are delocalized over the entire molecule. The HOMO-LUMO energy gap of this compound was calculated at the B3LYP/6-31G* level (Fig. 7) and orbital energy level analysis at the B3LYP/6-31G* level of theory. The kinetic strength of a molecule is determined by the resultant HOMO–LUMO energy gap (E_{gap}). The calculated energy gaps are in good agreement with the experimental values (Table 1).

The DFT method can be used to calculate reactivity descriptors like electronegativity (χ), hardness (η), electrophilicity (ω) and softness (S) at the B3LYP/6-31G (d,p) level of theory has been presented in Table 3. The value of chemical hardness is 1.665 eV. In terms of chemical hardness, if HOMO–LUMO energy gap of a molecule is large then it is hard. Conversely, if the HOMO–LUMO energy gap is small, it is soft. One can also relate molecular strength to hardness, which means that the molecule with smaller HOMO–LUMO energy gap is more reactive because it's very easy to add electron to LUMO and remove electron from LUMO.

The UV–Vis absorption spectra of MTC exhibit two band of absorption between 351–353 and 408–415 nm, depending on the solvent (Fig. 8 and Table 1). The results revealed that calculated value increase regularly with an increase in dielectric constant of the solvents. The calculated absorption spectra are in good agreement with experimental observation.

Conclusion

A novel coumarin derivative having pi-conjugated system has been synthesized and characterized by spectroscopic methods. Solvent polarity effect on the photophysical properties has been investigated in different protic and aprotic solvents and solvent mixtures and it is inferred from the absorption and emission spectra that emissive state of MTC has intramolecular charge transfer characteristics. Analysis dipole moment calculation using solvatochromic methods suggest that excited state of MTC is more polar than the ground state. The fluorescence quantum yield (ϕ_f) values undergo very sharp decrease on increasing the polarity of the solvent. The large change in the ϕ_f values with the solvent polarity has been attributed to the ICT mediated non-radiative de-excitation of the fluorescent ICT state of the dye to their ground state. The density functional theory (DFT) was used to compute ground state geometries of the molecule. The computed peak observed between 351–353 nm and 408–415 nm are very close to the experimental absorption wavelengths.

Acknowledgments Authors are thankful to Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha, Saudi Arabia for the support and facilities to carry out the research work.

References

- Lacy A, O'Kennedy R (2004) Studies on coumarins and coumarinrelated compounds to determine their therapeutic role in the treatment of cancer. Curr Pharm Des 10(30):3797–3811
- Gonçalves MS (2009) Fluorescent labeling of biomolecules with organic probes. Chem Rev 109:190–212
- Ye FF, Gao JR, Sheng WJ, Jia H (2008) One-pot synthesis of coumarin derivatives. Dyes Pigments 77:556–558
- Dhar S, Rana DK, Roy SS, Roy S, Bhattacharya S, Bhattacharya SC (2012) Effect of solvent environment on the photophysics of a newly synthesized bioactive 7-oxy(5-selenocyanato-pentyl)-2H-1benzopyran-2-one. J Lumin 132:957–964
- Chemla DS, Zyss J (1987) Non-linear optical properties of organic molecules and crystals. Academic Press, New York
- Kawski A (1994) Progress in photochemistry and photophysics. CRC Press, New York
- Haley LV, Hameka HF (1977) Calculation of molecular electric polarizabilities and dipole moments. II. The LiH molecule. Int J Quantum Chem 11:733–741
- Liptay W (1974) Dipole moments and polarizabilities of molecules in excited electronic states, Excited States, 1. Academic Press, Inc., New York
- Hass MP, Warman JM (1982) Photon-induced molecular charge separation studiedby nanosecond time-resolved microwave conductivity. Chem Phys 73:35–53
- Lombardi JR (1970) Correlation between structure and dipole moments in the excitedstates of substituted benzenes. J Am Chem Soc 92:1831–1833
- Kawski A, Kuklinski B, Bojarski P (2005) Dipole moment of aniline in the excited S1state from thermochromic effect on electronic spectra Chem. Phys Lett 41:5251–5255
- Pannipara M, Asiri AM, Alamry KA, Arshad MN, El-Daly SA (2015) Synthesis, spectral behaviour and photophysics of donor– acceptor kind of chalcones: excited state intramolecular charge transfer and fluorescence quenching studiesSpectrochim. Acta, Part A 136:1893–1902
- 13. Lakowicz JR (2006) Principle of fluorescence spectroscopy. Plenum Press, New York
- Birks JB (1970) Photo physics of aromatic molecules. Wiley-Interscience, New York
- Lippert E (1957) Spectroscopic determination of the dipole moment of aromatic compounds in the first excited singlet state. Z Elektrochem 61:962–975
- Mataga N, Kubota T (1970) Molecular interactions and electronic spectra. Marcel Dekker, Inc., New York
- Suppan P (1983) Excited-state dipole moments from absorption/ fluorescence solvatochromic ratios. Chem Phys Lett 94:272–275
- Reichardt C (1994) Solvatochromic dyes as solvent polarity indicators. Chem Rev 94(8):2319–2358
- RaviM ST, Samanta A, Radhakrishnan TP (1995) Excitedstate dipole moments of some coumarin dyes from a solvatochromic

method using the solvent polarity parameter, E_T^N . J Chem Soc Faraday Trans 91(17):2739–2742

- Coe BJ, Harris JA, Asselberghs I, Clays K, Olbrechts G, Persoons A, Hupp JT, Johnson RC, Coles SJ, HursthouseMB NK (2002) Quadratic nonlinear optical properties of N-aryl stilbazolium dyes. Adv Funct Mater 12:110–116
- 21. Gordon P, Gregory P (1987) Organic chemistry in colour. Chimia, Moskva
- 22. Shaikh M, Mohanty J, Singh PK, Bhasikuttan AC, Rajule RN, Satam VS, Bendre SR, Kanetkar VR, Pal H (2010) Contrasting solvent polarity effect on the photophysical properties of two newly synthesized aminostyryl dyes in the lower and in the higher solvent polarity regions. J Phys Chem A 114:4507
- 23 Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.1. Gaussian, Inc., Wallingford

- Sun J, Song J, Zhao Y, Liang WZ (2007) Real-time propagation of the reduced one-electron density matrix in atom-centered Gaussian orbitals: application to absorption spectra of silicon clusters. J Chem Phys 127:234107
- Becke AD (1993) Density-functional thermochemistry. III The role of exact exchange. J Chem Phys 98(7):5648–5652
- Miehlich B, Savin A, Stoll H, Preuss H (1989) Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr. Chem Phys Lett 157:200–206
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:785–789
- Zhang CR, Liang WZ, Chen HS, Chen YH, Wei ZQ, Wu YZ (2008) Theoretical studies on the geometrical and electronic structures of *N*methyle-3,4-fulleropyrrolidine. J Mol Struct (THEOCHEM) 862:98– 104
- Matthews D, Infelta P, Grätzel M (1996) Calculation of the photocurrent–potential characteristic for regenerative, sensitized semiconductor electrodes. Sol Energy Mater Sol Cells 44:119–155
- Tomasi J, Mennucci B, Cammi R (2005) Quantum mechanical continuum solvation models. Chem Rev 105:2999–3039
- Cossi M, Barone V (2001) Time-dependent density functional theory for molecules in liquid solutions. J Chem Phys 115:4708–4717
- Amovilli C, Barone V, Cammi R, Cancès E, Cossi M, Mennucci B, Pomelli CS, Tomasi J (1998) Recent advances in the description of solvent effects with the polarizable continuum model. Adv Quantum Chem 32:227–262