



Synthesis, spectroscopic properties, and DFT correlative studies of 3,3'- carbonyl biscoumarin derivatives

Shashikant Walki^a, G.H. Malimath^b, K.M. Mahadevan^{a,*}, Soniya Naik^c, Suraj M. Sutar^d, Hemantkumar Savanur^e, Lohit Naik^{b,*}

^a Department of Chemistry, Kuvempu University, P. G. Centre Kadur, Shivamoga, Karnataka, India

^b UG & PG Department of Physics, Karnatak Science College, Dharwad, Karnataka, India

^c Department of Chemistry, IIT Bombay, Powai, Mumbai 400076, India

^d Department of Chemistry, Karnatak Science College, Dharwad, Karnataka, India

^e Department of Studies and Research in Chemistry, P. C. Jabin Science College, Hubli, Karnatak 580021, India

ARTICLE INFO

Article history:

Received 26 February 2021

Revised 18 May 2021

Accepted 26 May 2021

Available online 30 May 2021

Keywords:

Carbonyl biscoumarin

Dipole moments

HOMO-LUMO

Solvatochromism

Chemical hardness

ABSTRACT

A facile and simple method for the synthesis of a library of 3,3'- Carbonyl biscoumarin derivatives via a one-pot chemical reaction is reported. The synthesized fluorescent dyes were purified and characterized by analytical methods. The IR, ¹H-NMR, and MS results confirmed the corresponding structure of the fluorescent dyes. The absorption and fluorescence spectra of fluorescent dyes were recorded in different solvents of varying polarity to understand the solvatochromic behaviour and dipole moments. Stoke's shift exhibits a redshift with an increase in solvent polarity for all molecules indicating a $\pi \rightarrow \pi^*$ transition. The ground state dipole moments of all fluorescent dyes are estimated theoretically from *ab initio* computations (integral equation formalism of polarizable continuum model) and experimentally from the solvatochromic method and the results are compared. Further, using solvatochromic correlations like Lippert's, Bakshshiev's, Kawski-Chamma-Viallet's, and solvent polarity parameter the excited state dipole moments are determined. Results show that the excited state dipole moments are higher than the ground state dipole moments which suggests that, all fluorescent dyes are more polar in the excited state. The HOMO-LUMO energy gaps computed from density functional theory and absorption threshold wavelengths are found to be in good agreement and also support intramolecular charge transfer (ICT). Using HOMO-LUMO energies, the chemical hardness (η) of the molecules is determined and the chemical stability is discussed. Further, using DFT molecular electrostatic potential (MESP) plots, the electrophilic site and nucleophilic site which are useful in photochemical reactions were identified. The preliminary observations and results suggest that the fluorescent dyes can be considered as potential candidates for fluorescent probes and construction of dye-sensitized solar cell in future

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

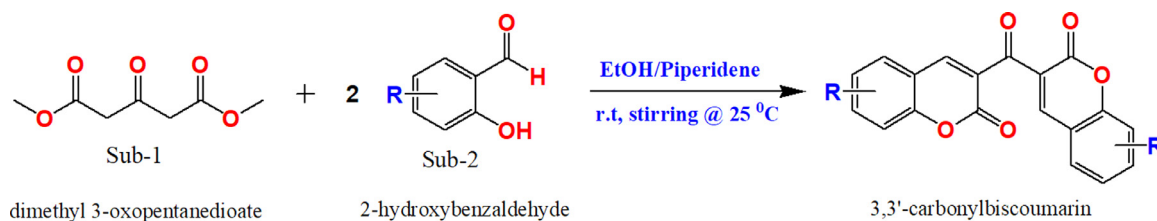
The well-known family of coumarin derivatives, called biscoumarin (dimeric coumarins) occupies an interesting position due to its interesting application in the optoelectronic and pharmaceutical industry [1–4]. These compounds occur naturally in a large number of plants and micro-organisms and it shows anti-fungal, anti-anthelmintic, anti-coagulants, analgesic, anti-tumor, anti-HIV, anti-apoptotic, and antioxidant activities [5–7]. Along with these properties biscoumarin derivatives are also the most widely used class of fluorescent dyes, highly efficient laser dyes [8–

9], their inclusion in zeolites could lead to artificial antenna systems [10], active material for organic light-emitting devices [11], dying stuff [12] and signaling units in fluorescent ion sensors [13]. These properties of biscoumarin dyes are influenced by the nature and position of substituents. Additionally, the way the two coumarin moieties are linked to each other, as well as the chemical nature of the bridge, play a determining role in the optical properties.

In recent decades, many researchers focused on the development of suitable synthetic methodologies for biscoumarin due to their different optoelectronic and biological applications. The novel method for the synthesis of biscoumarin derivatives is the Knoevenagel-Michael reaction. Because of the importance of biscoumarin essentially bis(4-hydroxycoumarin) in the mentioned fields, many catalysts in various conditions [14] have been intro-

* Corresponding author.

E-mail address: lohitresearch@gmail.com (L. Naik).



Scheme 1. Synthesis of 3, 3'- Carbonylbiscoumarin.

duced for the preparation of them such as o-benzenedisulfonimide, phospho sulfonic acid, [bmim]BF₄, cellulose sulfonic, SDS, [PSebim] [OTf], propane-1,2,3-triyl tris (hydrogen sulfate), boron-sulfuric acid Nanoparticles, [pyridine-SO₃H]Cl, W-doped ZnO nanocomposite, Bi (NO₃)₃·5H₂O, choline hydroxide, P4VPy-CuO-NPs sulfonated rice husk ash, silica-Bonded Npropylpiperazine sodium n-propionate, P4VPy-BuSO₃H X(AlCl₃), and 4-(dimethylamino) pyridine [15–32].

Although these methods suffer from harsh reaction conditions, some of them have relatively long reaction times, low yields, use of metals and toxic solvents. In view of the above, in these findings, we have synthesized a library of carbonyl biscoumarin derivatives using piperidine as the catalyst and studied the solvatochromic behavior and dipole moment using theoretical and experimental techniques.

2. Experimental

2.1. Material and methods

Chemicals and reagents used for the synthesis and analysis were procured from a commercial supplier, Sigma Aldrich, India. Analytical grade solvents were purchased from Loba chemie. Pvt Ltd., Mangalore. The Melting points of the synthesized compounds were determined by electrothermal apparatus in open capillaries in a Boetius-Mikroheiztisch. TLC was performed by using an aluminum foil fluorescent indicator from Merck KGaA (silica gel 60 F254, layer thickness 0.2 mm). ¹H-NMR spectrum was recorded using a Jeol with 100MHz operating frequency deuterated chloroform (CDCl₃) solvents. IR spectra were of the dyes recorded using Nicolet 5700 FT-IR instrument.

The absorption, fluorescence, and fluorescence lifetime measurements were measured using Carry-100, Hitachi F-7000, and ISS ChronoBH time-correlated single-photon counting spectrometer.

3. Result and discussions

3.1. Synthesis and characterization

In the present work, we described the expedite, cheaper and benign synthesis of some important fluorescent organic 3,3'- Carbonylbiscoumarin derivatives which seem to be very important and useful for dye-sensitized solar cells (DSSC) applications. To a mixture of dimethyl-1,3 acetone dicarboxylate (0.5g, 0.0287mol), the appropriate salicylaldehyde (0.54g, 0.00442, mole ratio 1:2), absolute ethanol (10-20 ml) and a catalytic amount of piperidine was added. The obtained clear solution was stirred at room temperature (25°C) for 12 hrs. After completion of the reaction (monitored by TLC) the solvent was evaporated under a vacuum. The crude product was washed with the diethyl ether and residue mass obtained was further recrystallized from acetic acid to get analytically pure yellow coloured 3,3'-Carbonylbiscoumarins (3a-h) in moderate to good yields. Their structural identities and purities were confirmed by ¹H-NMR, IR, and MS and were found to be in

good agreement with the proposed structures. The FT-IR, ¹H-NMR, and MS spectra are given in supplementary files. The schematic synthesis of 3,3'-Carbonylbiscoumarins are shown in Scheme 1 and its derivatives are listed in Table 1.

3.1.1. 3-(2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3a) [33,48]

White solid, mp: 247-249 °C (Lit. 251-252°C); IR (KBr, cm⁻¹): 1731, 1658, 1272, 1095. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 8.68 (s, 1H and 1' H), 7.97 (d, J= 7.60 Hz, 1H and 1' H), 7.76-7.80 (m, 1H and 1' H), 7.45-7.47 (m, 2H and 2' H). LC-MS: 319.0(M+1).

3.1.2. 7-(diethylamino)-3-(7-(diethylamino)-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3b) [12,33,34,48]

Yellow solid, mp: 208-209 °C (Lit. 214-217°C); IR (KBr, cm⁻¹): 1705, 1638, 1076, 1349. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 8.28 (s, 1H and 1' H), 7.60-7.64 (m, 1H and 1' H), 6.77- 6.80 (m, 1H and 1' H), 6.58 (s, 1H and 1' H), 3.48 (q, J= 6.80 Hz, 13.6Hz, 4H and 4' H), 1.14 (s, J= 14Hz, 6H and 6' H). LC-MS: 461.0 (M+1)

3.1.3. 6,8-dichloro-3-(6,8-dichloro-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3c) [33]

Red solid, mp: 245-246 °C (Lit. 246-248°C); IR (KBr, cm⁻¹) 1716, 1665, 1086, 1060. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 8.63 (s, 1H and 1' H), 8.24 (d, J= 3.2Hz, 1H and 1' H), 7.92-7.93 (m, 1H and 1' H), 7.51 (d, J= 12Hz, 1H and 1' H). LC-MS: 478.2 (M+2).

3.1.4. 8-ethoxy-3-(8-ethoxy-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3d) [33]

Light yellow solid, mp: 263-265 °C (Lit. 264-266°C); IR (KBr, cm⁻¹) 1731, 1658, 1272, 1095. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 8.64 (s, 1H and 1' H), 7.49(d, J= 6.80Hz, 1H and 1' H), 7.45(d, J= 8.40 Hz, 1H and 1' H), 7.37 (d, J= 16Hz, 1H and 1' H), 4.20 (q, J= 13.6Hz, 2H and 2' H), 1.41 (t, J= 13.6Hz, 3H and 3' H). LC-MS: 407.4(M+1).

3.1.5. 6-bromo-3-(6-bromo-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3e) [33]

White solid, mp: 316-318°C (Lit. 316-318); IR (KBr, cm⁻¹) 1740, 1679, 1088, 1028. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 3.38 (s, 1H and 1' H), 8.60 (s, 1H and 1' H), 8.05-8.16 (m, 1H and 1' H). LC-MS: 458.8 (M+2)

3.1.6. 7-hydroxy-3-(7-hydroxy-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3f) [33]

White solid, mp: 215-217°C (Lit. 216-218°C); IR (KBr, cm⁻¹) 3124, 1720, 1651, 1245. ¹H NMR (400MHz, DMSO-d₆, δ ppm): 11.10 (s, 1H and 1' H), 8.50 (s, 1H and 1' H), 7.78 (d, J=11.6Hz, 1H and 1' H) 6.86-6.89 (m, 1H and 1' H), 6.80 (d, J= 2.80Hz, 1H and 1' H). LC-MS: 351.4(M+1).

Table 1
list of derivatives of 3, 3'- Carbonylbiscoumarin.

Entry	Sub-2	Products	Time (in hrs)	% of Yield
3a			4	70
3b			5	75
3c			4	60
3d			5	75
3e			6	75
3f			4	66
3g			4	85
3h			5	88

3.1.7. 8-methoxy-3-(8-methoxy-2-oxo-2H-chromene-3-carbonyl)-2H-chromen-2-one (3g)

[33]

Light Yellow solid, mp: 260–262°C (Lit. 264–266°C); IR (KBr, cm^{-1}) 1776, 1665, 1275, 1086. ^1H NMR (400MHz, $\text{DMSO}-d_6$, δ ppm): 8.64 (s, 1H and 1' H), 7.46–7.52 (m, 2H and 2' H), 7.37–7.41 (m, 1H and 1' H), 3.93 (s, 3H and 3' H). LC-MS: 379.2 (M+1).

3.1.8. 2-(3-oxo-3H-benzo [f]chromene-2-carbonyl)-3H-benzo [f]chromen-3-one (3h) [12]

White solid, mp: >350 °C (Lit. >350 °C); IR (KBr, cm^{-1}) 1716, 1665, 1086. ^1H NMR (400MHz, $\text{DMSO}-d_6$, δ ppm): 9.4 (s, 1H and 1' H), 8.75 (d, $J = 7.6\text{Hz}$, 1H and 1' H), 8.38 (d, $J = 9.2\text{Hz}$, 1H and 1' H), 8.13 (d, $J = 8\text{Hz}$, 1H and 1' H), 7.81 (d, $J = 6.80\text{Hz}$, 1H and 1' H), 7.69–7.71 (m, 2H and 2' H). LC-MS: 419.2 (M+1)

3.2. Estimation of ground and excited-state dipole moments

The absorption and fluorescence spectra of fluorescent dyes (3a–3h) in toluene, ethyl acetate, tetrahydrofuran, dichloromethane, butanol, propane-2-ol, acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were recorded multiple numbers times to check the reproducibility of readings, to avoid any procedural mistakes and the verified spectra are shown in Figs. 1 and 2. The absorption maxima, emission maxima, Stoke's shift, and arithmetic mean of Stoke's shift values in different solvents for all molecules are tabulated in Tables S1–S8. The value of Stokes shift undergoes redshift with an increase in solvent polarity for all the molecules, which indicates $\pi \rightarrow \pi^*$ transition and also suggests that the dipole moments for all the molecules in the excited state may be higher than the ground state.

When a molecule is excited, the solvent dipoles can reorient or relax around the excited probe molecule and lowers the energy of the excited state. Further, as the solvent polarity increases, this effect becomes larger, which in turn, may result in the emission at lower energies or longer wavelengths. When the molecule is in the excited state, there will be a redistribution of the charges, which may lead to the change in the dipole moment. In the excited state, no more the fluorophore remains in equilibrium with its environment. As the molecule relaxes and attains equilibrium with the surrounding environment, some amount of energy is dissipated in the form of non-radiative energy and as a result, the fluorescence emission wavelength gets shifted. In addition to this, there may be specific interactions between the probe molecule and solvent like hydrogen bonding, formation of charge-transfer states, complex formation, etc., which may lead to large spectral shifts. Therefore, a systematic analysis of the solvent effect is useful to understand the effect of the environment and the various mechanisms of deexcitation and relaxation of an excited molecule in solution.

In this regard, the theories developed by various researchers in the field of estimation of ground and excited-state dipole moments through solvatochromic methods are used in the present study. Lippert [35] derived equations based on Onsager's reaction field theory for the determination of dipole moments considering fluorophore as a point dipole in a continuous medium of uniform dielectric constant. The excited-state dipole moments can also be estimated using Bakhshiev's [36] equations. Kawski [37] have developed a simple quantum mechanical second-order perturbation theory to explain absorption and fluorescence band shifts in different solvents of refractive index (n) and varying permittivity (ϵ_0) corresponding to the band position of a solute molecule

According to Lippert [35], the expression for Stoke's shift is

$$\bar{\nu}_a - \bar{\nu}_f = S F(\epsilon, n) + \text{const} \quad (1)$$

Table 1a

Some physical constants along with the calculated values of various polarity functions.

Solvent	ϵ	n	E_T^N	$F(\epsilon, n)$	$F_1(\epsilon, n)$	$F_2(\epsilon, n)$
Toluene	2.40	1.49	0.09	0.01	0.03	0.35
Ethyl Acetate	6.08	1.37	0.22	0.20	0.49	0.49
Tetrahydrofuran	7.58	1.40	0.20	0.21	0.55	0.55
Dichloromethane	8.90	1.42	0.30	0.21	0.58	0.58
Butanol	17.40	1.39	0.58	0.26	0.74	0.64
Propane-2-ol	20.18	1.37	0.61	0.27	0.78	0.64
Acetonitrile	36.64	1.34	0.46	0.30	0.86	0.66
DMF	38.25	1.43	0.38	0.27	0.83	0.71
DMSO	46.70	1.47	0.44	0.26	0.84	0.74

ϵ , n , E_T^N values are taken from the literature [39–41].

Where $F(\epsilon, n)$ is Lippert's polarity function and is given by,

$$F(\epsilon, n) = \left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \quad (2)$$

The expression for Stoke's shift according to Bakhshiev [36] is given by,

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F_1(\epsilon, n) + \text{const} \quad (3)$$

Where $F_1(\epsilon, n)$ is Bakhshiev's polarity function and is given by,

$$F_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (4)$$

According to Kawski-Chamma-Viallet's [37] equation,

$$\frac{1}{2}(\bar{\nu}_a + \bar{\nu}_f) = S_2 F_2(\epsilon, n) + \text{const} \quad (5)$$

Where $F_2(\epsilon, n)$ is Kawski-Chamma-Viallet's polarity function and is given by

$$F_2(\epsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] + \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (6)$$

Here $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima in wave numbers respectively and other terms have their usual meaning.

The dielectric constants, refractive indices, solvent polarity parameter, and the calculated values of various polarity functions like $F(\epsilon, n)$, $F_1(\epsilon, n)$, and $F_2(\epsilon, n)$ are given in Table 1a.

From Eqs. (1), (3) and (5), it follows that $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F(\epsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$ and $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(\epsilon, n)$ plots should be linear with slopes S , S_1 and S_2 respectively and are given as,

$$S = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (7)$$

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (8)$$

and

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} \quad (9)$$

Where μ_e and μ_g are excited and ground-state dipole moments respectively. Here the term 'h' is Planck's constant, 'c' is the velocity of light in vacuum and 'a₀' is the Onsager cavity radius of the probe molecule and is calculated using Edward's [38] atomic increment method (Table 5).

The Stoke's shift vs. $F(\epsilon, n)$, Stoke's shift vs. $F_1(\epsilon, n)$, and arithmetic mean of Stoke's shift vs. $F_2(\epsilon, n)$ plots for fluorescent dyes are shown in Fig. 3. The statistical data like slopes, intercepts, and correlation coefficients for all molecules are reported in Tables 2–4. It is observed that the correlation coefficient values are greater

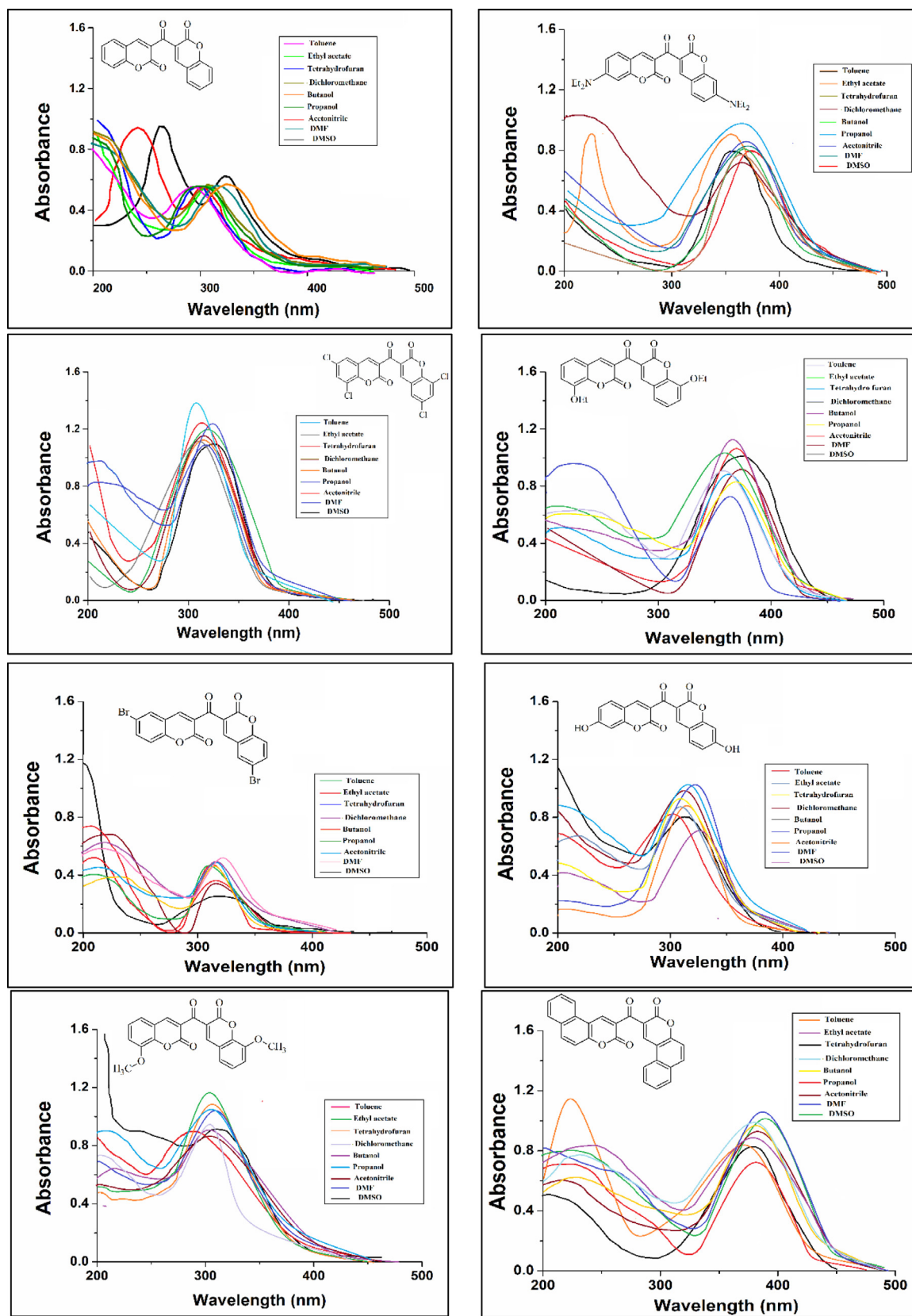


Fig. 1. Absorption spectra of 3a-3h in different solvents.

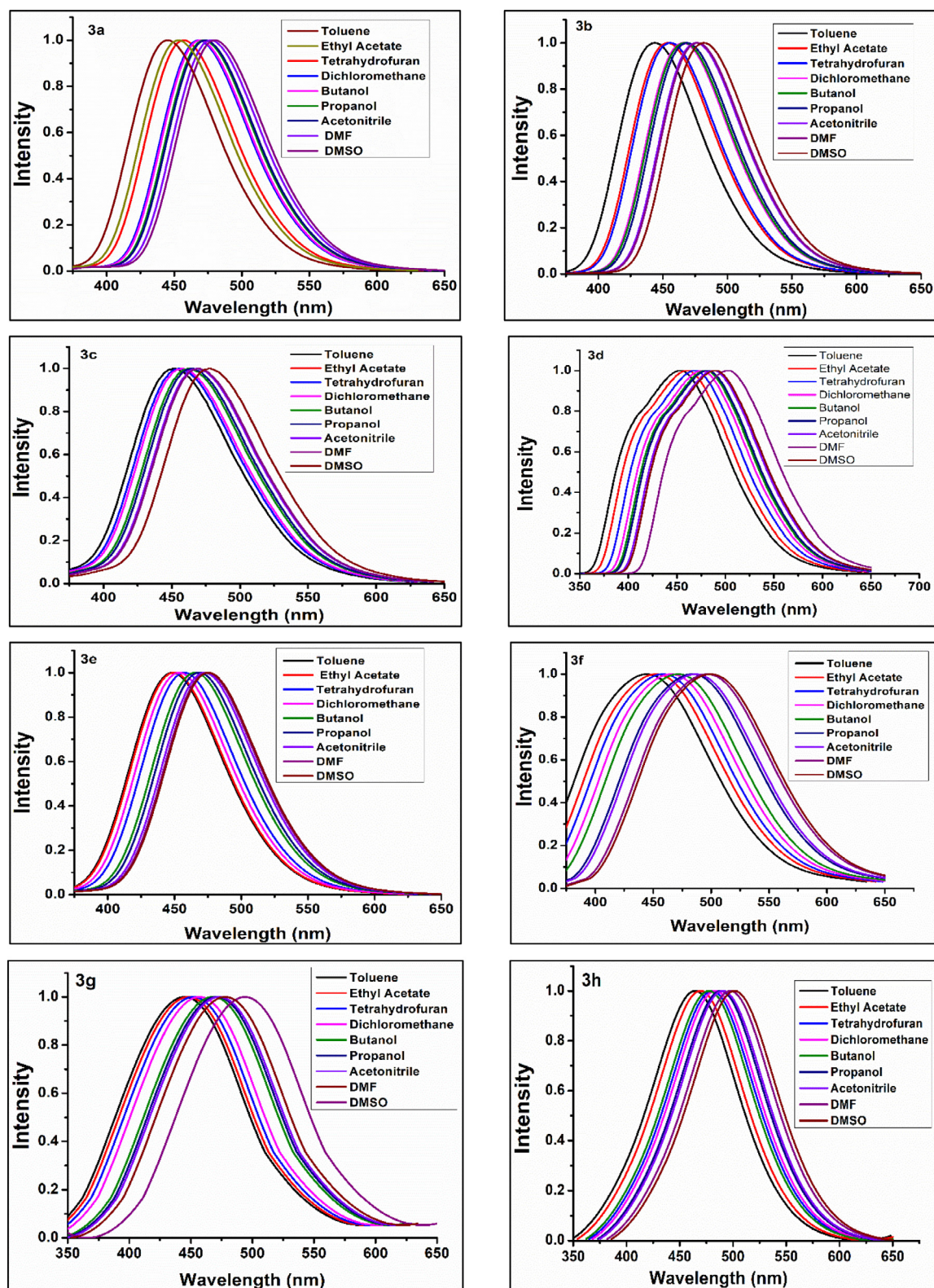


Fig. 2. Fluorescence spectra of 3a-3h in different solvents.

than 0.8, which indicates good linearity for the slopes S , S_1 , and S_2 .

Assuming that the symmetry of the probe molecule remains unchanged upon electronic transition and considering the ground and excited-state dipole moments to be parallel, the expression

for ground-state dipole moment (μ_g), excited state dipole moment (μ_e), and the ratio of μ_e and μ_g are given by,

$$\mu_g = \frac{S_2 - S_1}{2} \left[\frac{hca_0^3}{2S_1} \right]^{1/2} \quad (10)$$

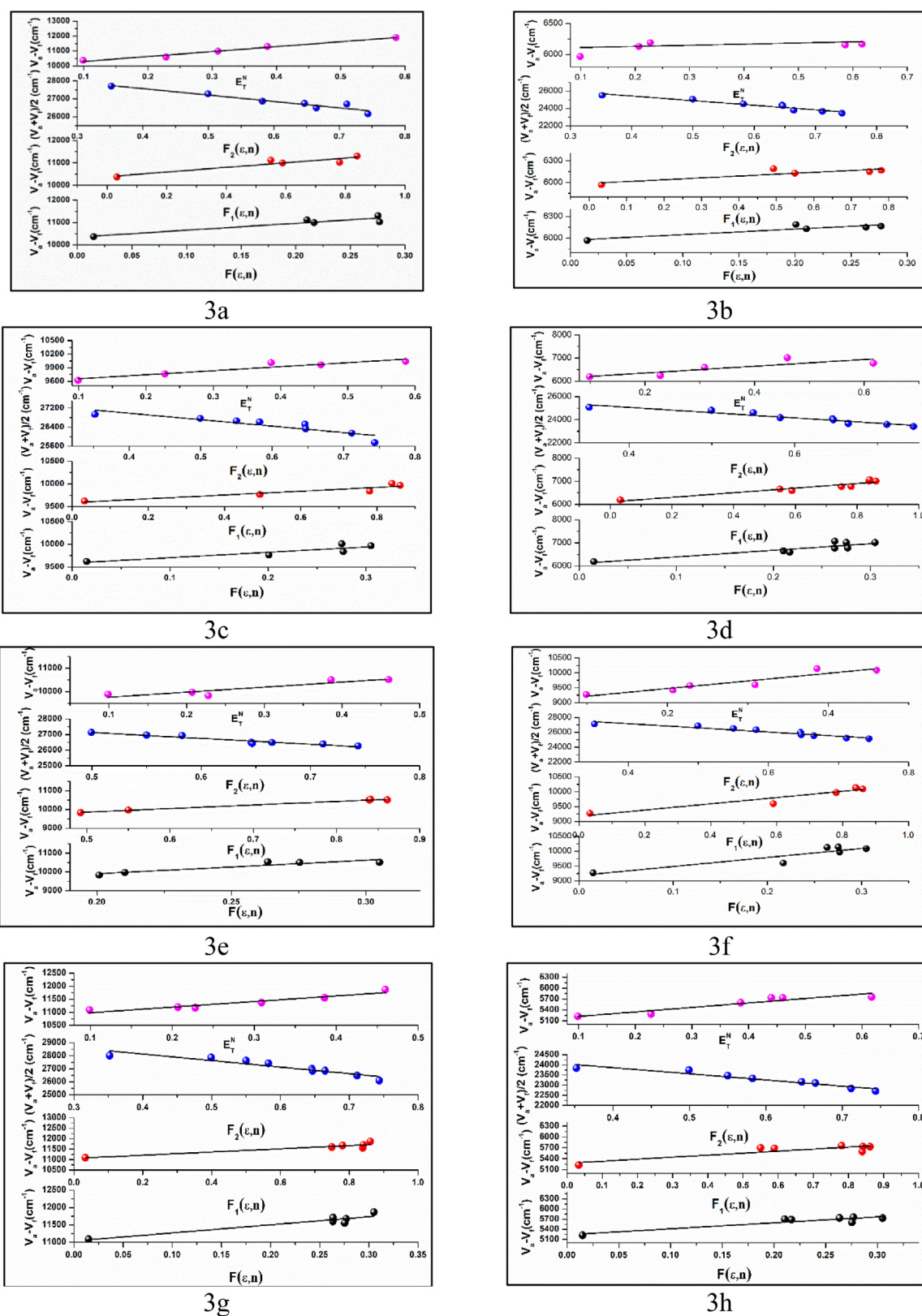


Fig. 3. Plot of Lippert's (Stoke's shift vs. $F(\epsilon, n)$), Bakhshiev's (Stoke's shift vs. $F_1(\epsilon, n)$), Kawski-Chamma-Viallet's, (arithmetic mean of Stoke's shift vs $F_2(\epsilon, n)$), and Stoke's shift vs. (E_T^n) of synthesized fluorescent dyes.

Table 2

Slope, intercepts, and correlation coefficient of Lippert's plot of 3a–3h molecules.

Molecule	Slope (cm ⁻¹)	Intercepts (cm ⁻¹)	Correlation coefficient	No. of data
3a	3086	10351	0.880	5
3b	769	5972	0.828	5
3c	1186	9585	0.896	5
3d	2870	6106	0.819	8
3e	7214	8460	0.867	5
3f	3035	9183	0.840	6
3g	2331	11037	0.899	6
3h	1761	5239	0.844	7

Table 3

Slope, intercepts and correlation coefficient of Bakhshiev's correlation of 3a–3h molecules.

Molecule	Slope (cm ⁻¹)	Intercepts (cm ⁻¹)	Correlation coefficient	No. of data
3a	1040	10384	0.878	5
3b	254	5988	0.842	5
3c	417	9588	0.869	5
3d	998	6107	0.906	8
3e	1901	8908	0.994	5
3f	1051	9176	0.913	6
3g	770	11053	0.872	6
3h	555	5276	0.871	7

Table 4

Slope, Intercepts, and Correlation coefficient of Kawski-Chamma-Viallet's correlation plot of 3(a–h) molecules.

Molecule	Slope (cm ⁻¹)	Intercepts (cm ⁻¹)	Correlation coefficient	No. of data
3a	3583	29001	0.920	7
3b	4721	27272	0.894	8
3c	1733	27586	0.870	8
3d	4205	26715	0.874	8
3e	2605	54312	0.889	8
3f	4961	29089	0.864	9
3g	4056	29656	0.855	9
3h	2498	24815	0.903	8

Table 5

Ground and Excited-state dipole moment values of 3(a–h).

sample	Radius (Å)	Theoretical Ground State Dipole Moment μ_g (in D)	Excited State Dipole moment μ_e (D) according to					
			Ground State Dipole Moment μ_g (in D)	Lippert	Bakhshiev	Kawski-Chamma-Viallet	Solvatochromic method	Solvent Polarity Parameter
3a	4.67	5.95	3.97	9.55	7.21	7.21	7.21	7.14
3b	4.69	8.69	14.16	16.97	15.78	15.78	15.78	18.16
3c	4.27	4.70	2.84	5.88	4.64	4.64	4.64	4.29
3d	4.39	5.73	4.65	9.39	7.55	7.55	7.55	6.58
3e	4.19	4.55	1.69	7.93	4.42	4.42	4.42	6.89
3f	4.10	7.74	4.99	9.58	7.67	7.67	7.66	7.29
3g	4.24	6.60	5.15	9.35	7.56	7.56	7.56	7.37
3h	4.40	5.64	3.79	7.65	5.96	5.96	5.96	5.53

$$\mu_e = \frac{S_1 + S_2}{2} \left[\frac{hca_0^3}{2S_1} \right]^{1/2} \quad (11)$$

$$\frac{\mu_e}{\mu_g} = \frac{S_1 + S_2}{S_2 - S_1}; (S_2 > S_1) \quad (12)$$

Using the slopes S_1 and S_2 , the values of μ_g , μ_e , and their ratio μ_e/μ_g were calculated according to Eqs. (10)–(12) and the results are given in Tables 5 and 6. Further, by substituting the value of μ_g calculated from Eq. (10), the excited state dipole moment (μ_e) is calculated according to Lippert's, Bakhshiev's, and Kawski-Chamma-Viallet's method i.e. from Eqs. (7), (8) & (9) respectively, and the results are presented in Table 5.

If the angle between ground and excited state dipole moments are not parallel, then the angle θ between the two dipole moments

is determined from the following equation.

$$\cos\theta = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{S_2}{S_3} (\mu_e^2 - \mu_g^2) \right] \quad (13)$$

The angle between ground and excited state dipole moments is calculated according to Eq. (13) and the results are presented in Table 6.

The parameters S , S_1 and S_2 occurring in (1) (3) and (f) for the difference $\bar{\nu}_a - \bar{\nu}_f$ and the sum $\bar{\nu}_a + \bar{\nu}_f$ of the wavenumbers, which are linear functions of the solvent polarity parameters $F(\epsilon, n)$, $F_1(\epsilon, n)$ and $F_2(\epsilon, n)$, can be determined from the slopes of the straight lines. With this method we use the extrapolation technique of the linear fit to the experimental data corresponding to the gaseous phase. In this way we obtain dipole moments of an isolated molecule, free from solvents. The problem of determination of authentic dipole moments from solvatochromic shifts based on the theories of different authors [35–37] has been discussed

Table 6Change in dipole moment, ratio, and angle between μ_e & μ_g .

Molecule	Change in Dipole moment ($\Delta\mu$) (D) from		The ratio of Excited & Ground state dipole moment	Angle between μ_g & μ_e
	Solvatochromic Method	Solvent Polarity Parameter	μ_e/μ_g	θ in Degree
3a	3.24	3.17	1.82	0
3b	1.62	4.45	1.11	0
3c	1.80	1.45	1.69	0
3d	2.90	1.93	1.62	0
3e	2.73	2.18	2.61	0
3f	2.68	2.31	1.54	0
3g	2.42	2.22	1.47	0
3h	2.17	1.74	1.57	0

in detail in [39]. It should be stressed that the short-range specific interactions between the solute and the solvent molecules, as hydrogen bonding, the tendency of polar solvent molecules to form aggregate of two or more molecules (alcohols) are not taken into account in the mentioned theories. Having this in mind one has to select appropriate solvents which should possess moderate electric permittivity ϵ . Moreover, anisotropic solvent media such as nematic liquid crystals [39] cannot be used to determine the real dipole moment both in the ground and excited state based on the mentioned theories. However, the change in ϵ and n in an aprotic solvent can be obtained by increasing temperature T in a high-pressure cell (thermochromic method) provided that the solute does not undergo any kind of a chemical change. In this way, the values of ϵ and n can be changed continually, which supports the analysis of the absorption and fluorescence shift observed [40,41].

3.3. Change in dipole moment ($\Delta\mu$) and excited state dipole moment (μ_e) by solvent polarity parameter (E_T^N)

This method is based on solvent polarity parameter (E_T^N) to estimate the change in dipole moment ($\Delta\mu$) proposed by Reichardt [45] and developed by Ravi et al. [46]. In this method, the problem associated with the estimation of Onsager cavity radius has been minimized.

The expression for Stoke's shift according to Reichardt and Ravi et al. is,

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + \text{const} \quad (14)$$

where $\Delta\mu_B$ ($= 9D$) and a_B ($= 6.2 \text{ \AA}$) is the change in dipole moment on excitation and Onsager cavity radius of reference betaine dye molecule and $\Delta\mu$ and 'a' are the change in dipole moment and molecular radius of the molecule under investigation.

The change in dipole moment ($\Delta\mu$) is determined from the following equation.

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a_0} \right)^3 11307.6}} \quad (15)$$

Where m is the slope obtained from the linear plot of Stoke's shift versus (E_T^N).

Then by using Eq. (15) and knowing the value of μ_g (From Eq. (10)), the excited state dipole moment is determined from the following equation.

$$\mu_e = \Delta\mu + \mu_g \quad (16)$$

The relevant plots of Stoke's shift vs. (E_T^N) required for the determination of change in dipole moment ($\Delta\mu$) for all the probe molecules are shown in Fig. 3. Using the slopes calculated from Stoke's shift versus E_T^N , the excited state dipole moment (μ_e) and

change in dipole moment ($\Delta\mu$) for both the molecules were calculated using Eq. (16) and the results are presented in Tables 5 and 6.

The ground state dipole moment of 3b is higher as compared to other molecules (Table 5) and it may be due to the substitution tertiary amine at the 7 position of 3,3'- Carbonylbiscoumarin electronegativity difference between oxygen and carbon atoms. The introduction of an electronegative atom decreases the bond length and increases polarizability, which may lead to the increase in the dipole moment of the 3b molecule [43,44]. It is also observed from Table 5 that, the excited state dipole moment (μ_e) for molecule 3c is less than the other molecule. The decrease of excited-state dipole moment (μ_e) for molecule 3c may suggest different geometry for the singlet excited state than the remaining molecules, indicating a significant difference in the charge distribution.

As it is evident from Table 5, the excited state dipole moment (μ_e) determined by using Bakhshiev's, KawskiChamma-Viallet's, and solvatochromic equations were found to be in good agreement with each other. The higher values of excited-state dipole moment (μ_e) observed in the case of Lippert's method compared to other methods may be due to the non-accountability of polarizability. However, μ_e calculated by using solvent polarity parameter E_T^N (Eq. (16)) is found to be smaller than μ_e determined from Bakhshiev's, Kawski-Chamma-Viallet's, and solvatochromic methods. This may be due to the reason that these methods do not take into account specific solute-solvent interactions like hydrogen bonding, complex formation, and molecular aspects of solvation, whereas they are incorporated in the solvent polarity parameter [44].

The μ_e values are found to be higher than μ_g values for all the molecules (Table 5). The higher values of μ_e indicate that the probe molecules are more polar in the excited state than the ground state. The angle between the ground and excited-state dipole moment for both the molecules are found to be zero degrees (Table 6) which suggests that, μ_g and μ_e are parallel to each other and the molecular symmetry remains the same upon electronic transition [42]. Further, it is observed that the change in dipole moment ($\Delta\mu$) value is found to be higher. The higher values of $\Delta\mu$ may indicate the existence of a more relaxed excited state and which may be due to ICT. The possible intramolecular charge transfer may be attributed to the resonance structures of 3a molecules as shown in Fig. 4 and the remaining molecule resonance structures are shown in Figs.S23-S30.

3.4. Computational analysis

The absorption and emission spectra of all molecules in different solvents were computed by using Gaussian 09W to compare with the experimental results. For this purpose, the molecule is optimized for the ground and excited state using DFT and TD-DFT with the basis sets B3LYP/3-211G combined with integral equa-

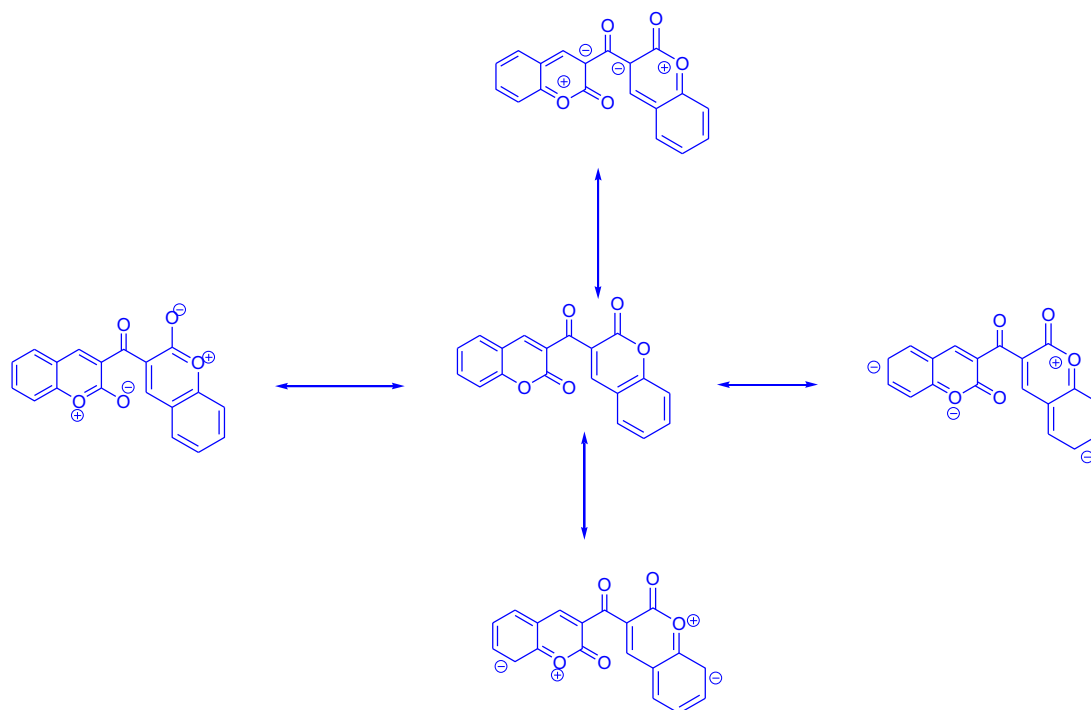


Fig. 4. Possible resonance structures of 3a.

Table 7
Theoretical ground state dipole moment (μ_g) of 3(a-h) in different solvents.

Solvent	3a in D	3b in D	3c in D	3d in D	3e in D	3f in D	3g in D	3h in D
Toluene	7.18	10.44	5.61	6.57	5.50	9.32	8.00	6.48
Ethyl Acetate	8.25	12.07	6.31	7.12	6.30	10.97	8.98	6.66
Tetrahydrofuran	8.40	13.48	6.43	7.20	6.40	12.36	9.14	6.78
Dichloromethane	8.50	12.51	6.51	7.27	6.48	11.12	9.26	6.97
Butanol	8.77	12.96	6.74	7.44	6.70	12.34	9.59	7.12
Propane-2-ol	8.82	13.01	6.76	7.46	6.72	13.45	9.69	7.23
Acetonitrile	8.93	13.23	6.87	7.57	6.83	11.71	9.82	7.32
DMF	8.95	13.24	6.88	7.58	6.84	13.69	9.86	7.39
DMSO	8.97	14.53	6.91	7.62	6.87	11.76	9.87	7.44

tion formalism variant-Polarizable Continuum Model (IEFPCM) solvation model.

The ground-state dipole moment of the probe molecule in the gaseous state is also estimated theoretically by using DFT with basis sets B3LYP/3-11G and the result is presented in Table 5. The optimized molecular geometry of all molecules along with the direction of dipole moment is shown in Fig. 5.

It is observed from Tables 5 and 6 that the theoretically computed μ_g value is higher than the experimental μ_g value. It is to be noted that the experimental methods take solvent and environmental effects like solute-solvent interactions into account, whereas the *ab initio* computations are based on the gaseous phase [37–38]. Further, to analyze the solute-solvent interactions, the ground dipole moments are estimated theoretically for all the studied solvents by using the IEF-PCM solvation model and the results are given in Table 7, and it is noticed that the ground-state dipole moment values for each of the solvents are found to be higher than the ground-state dipole moment value of the probe molecule in the gaseous phase. The increase in the dipole moment value is due to the consideration of environmental effects like solute-solvent interactions in the IEF-PCM solvation model. Further, the excited-state dipole moment values were found to be higher than the corresponding ground-state dipole moment values for all the solvents and this suggests that the probe molecule is

more polar in the excited state than the ground state. It is interesting to note that the computational studies also reproduce a similar trend as observed experimentally. However, the theoretically computed ground- and excited-state dipole moments were found to be higher than the experimental dipole moments [47].

The 3D plots of HOMO and LUMO of synthesized fluorescent dye are shown in Fig. 6. The HOMO, LUMO energies, and HOMO-LUMO energy bandgap (ΔE) values for the probe molecule are presented in Tables S9–S16. The optical band gap E^{opt}_g is determined from the absorption threshold wavelength for all molecules in different solvents and the result is tabulated in Tables S9–S16. It is observed that the HOMO-LUMO energy bandgap is in order with the experimental optical energy bandgap. The lower values of the energy gap for the probe molecule also support the observed higher values of excited-state dipole moments. The determination of HOMO-LUMO energies also helps in understanding the chemical stability of a molecule in terms of a parameter known as chemical hardness (η). The molecules possessing a large HOMO-LUMO energy gap are considered as hard, whereas molecules possessing small HOMO-LUMO energy gaps are considered soft molecules [38,42]. The chemical hardness (η) of a molecule [44] is determined from Eq. (17).

$$\eta = \frac{E_L - E_H}{2} \quad (17)$$

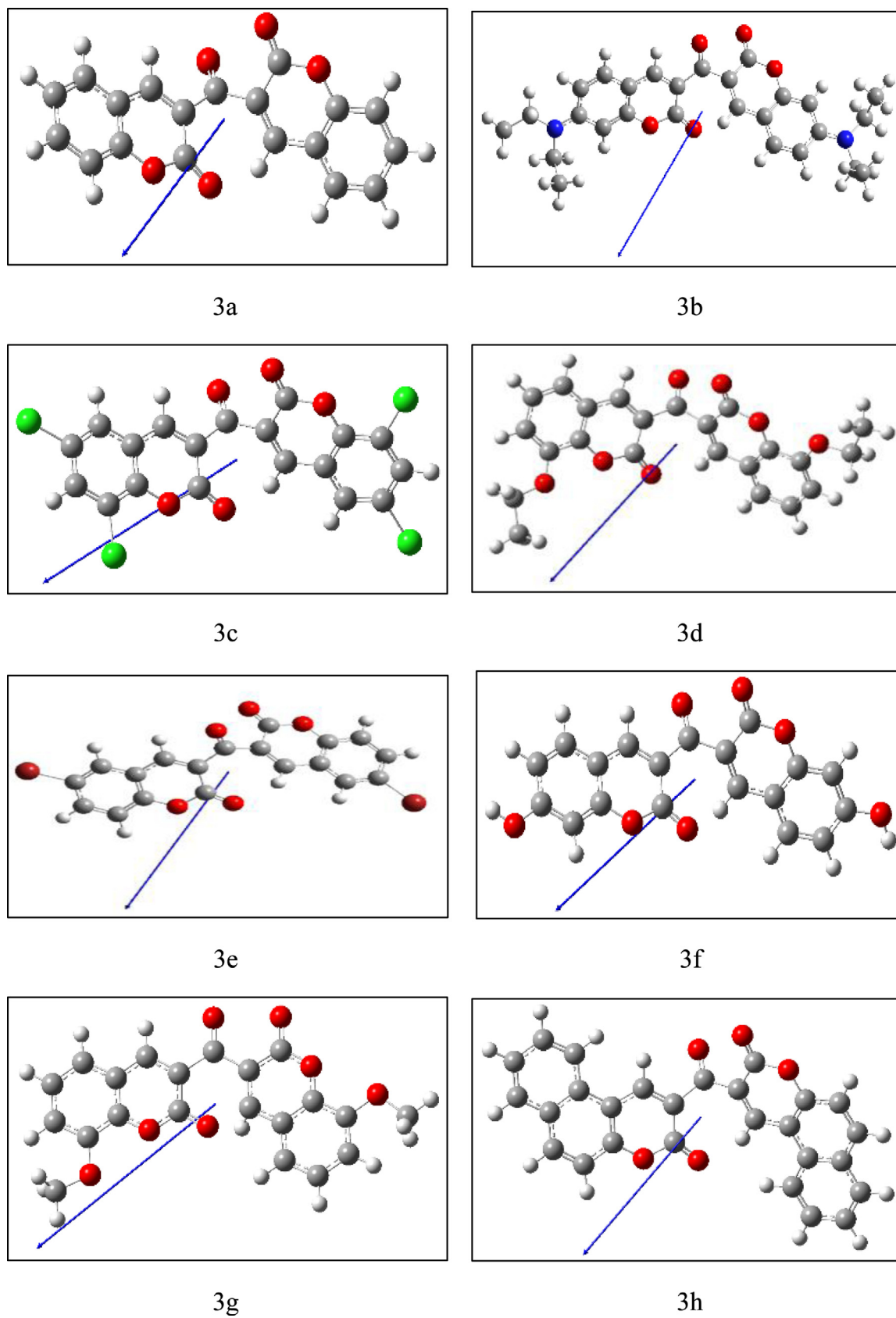


Fig. 5. Ground-state optimized molecular geometries of fluorescent dyes. The arrow mark indicates the direction of dipole moment.

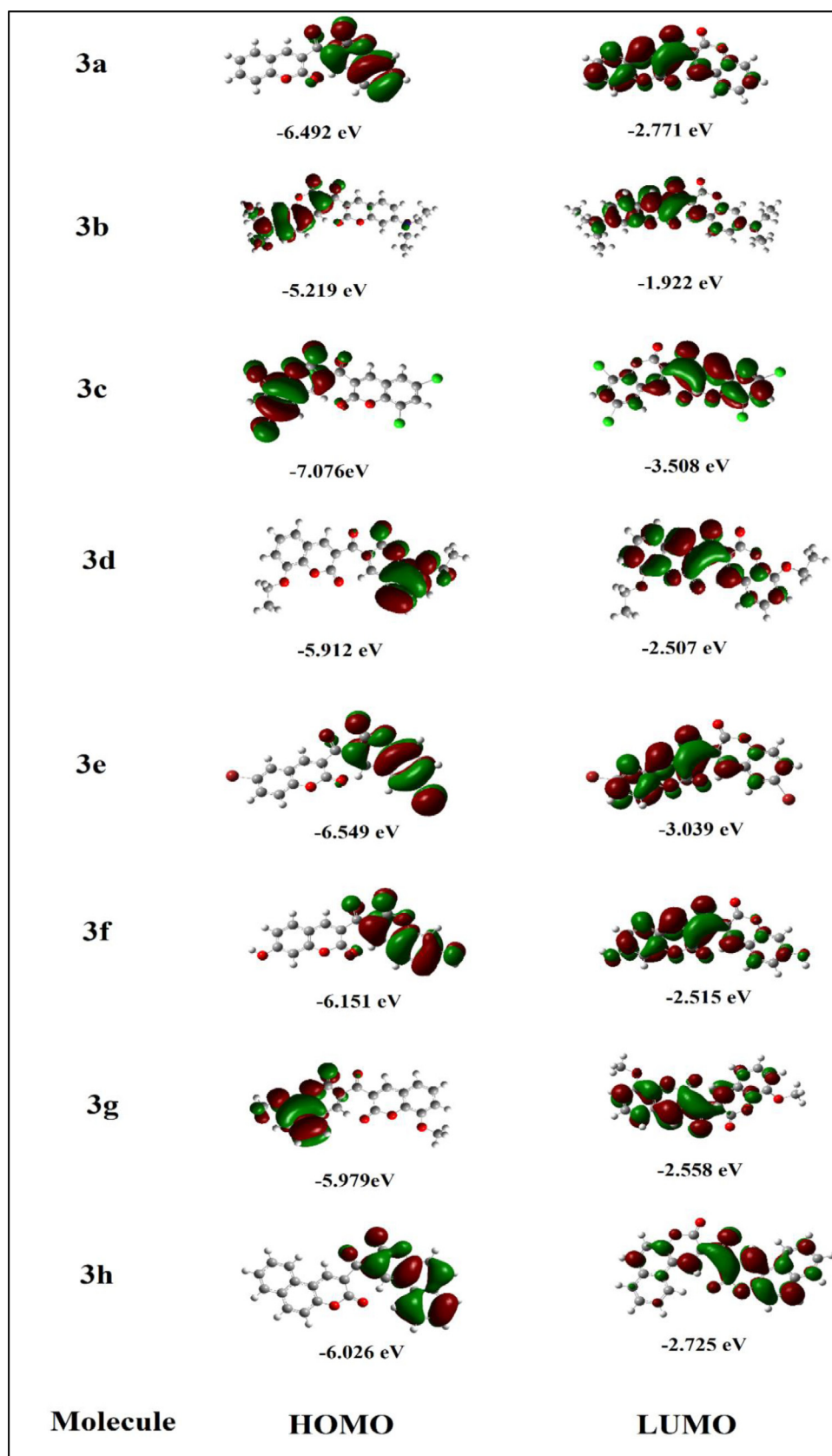


Fig. 6. 3D plots of HOMO-LUMO with energy levels.

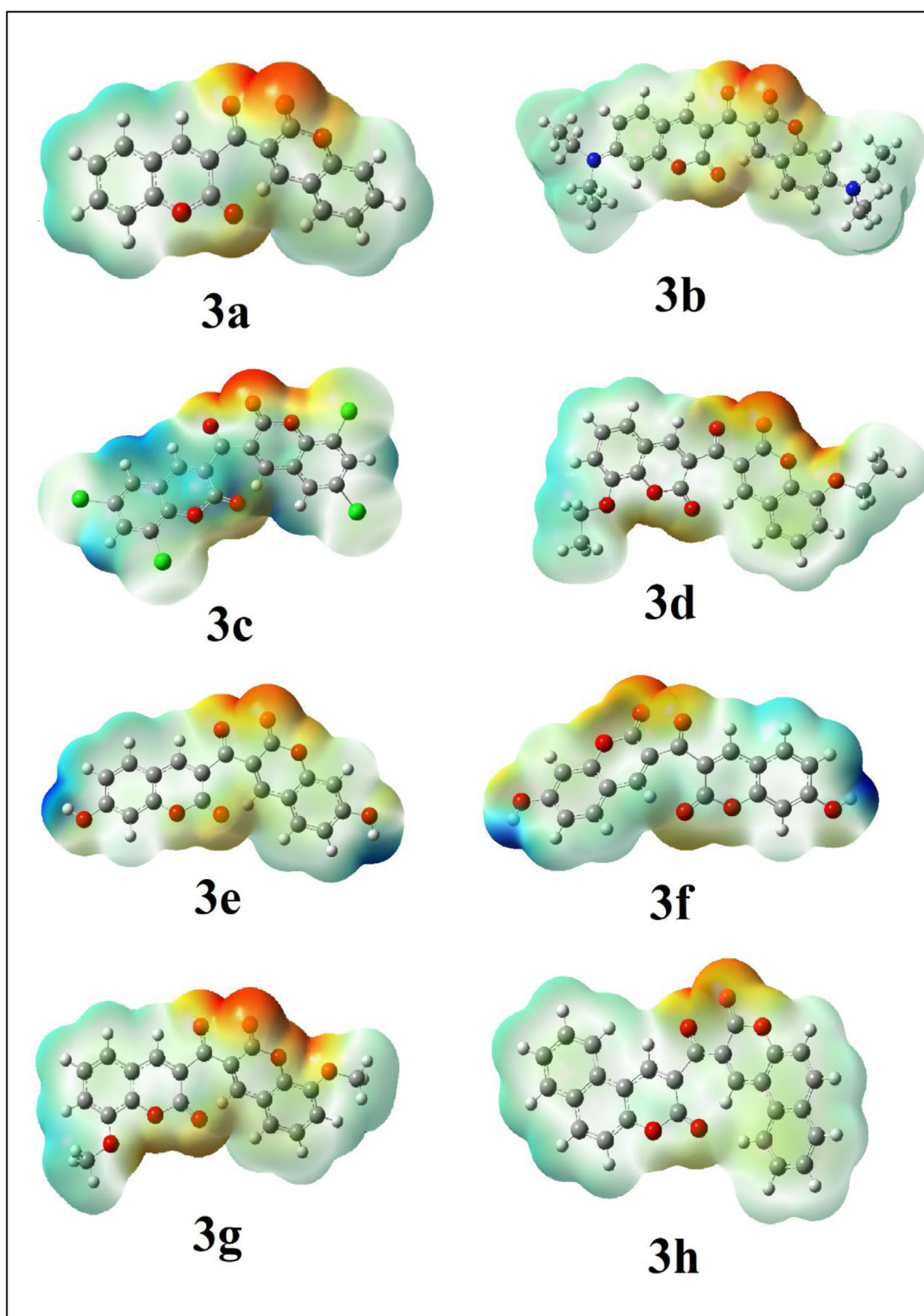


Fig. 7. Molecular electrostatic potential (MESP) plots. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where E_H and E_L are the HOMO and LUMO energies

The chemical hardness (η) is estimated for all fluorescent dyes and is given in Tables S9–S16. The small values of chemical hardness (η) and HOMO–LUMO energy gaps suggest that the molecule may be considered as a soft molecule [44]. These results also support the observed higher values of μ_e .

The molecular electrostatic potential (MESP) plots provide the information for determining a suitable position for nucleophilic and electrophilic attacks along with the hydrogen bonding interactions of solvent. The MESP 3D plot of the fluorescent dyes is shown in Fig. 7. In this plot, different colors correspond to different values of the electrostatic potential at the surface. The red color represents the negative phase, which can be related to the electrophilic site, and the blue color represents the positive phase, which corresponds to the nucleophilic site. From Fig. 7, it is observed that the MESP plot of all molecules shows negative phases around 2-oxo-2H-pyran-3-carbaldehyde whereas positive phases around all hydrogen atoms.

4. Conclusions

In the present studies, we have synthesized a library of 3,3'-Carbonylbiscoumarin derivatives via a one-pot chemical reaction. To investigate the solvatochromic behavior and dipole moments, the absorption and fluorescence spectra of the fluorescent dyes were recorded in different solvents. The ground state dipole moments for fluorescent dyes are estimated theoretical and experimental methods. The result shows that the theoretical ground state dipole moments (μ_g) values are higher than the experimental ground state dipole moments values. Further, the ground state dipole moments of the probe molecules in different solvents are also estimated theoretically by using the IEF-PCM solvation model. By using Lippert's, Bakhshiev's, Kawski-Chamma-Viallet's, and solvent polarity parameter equation, the excited state dipole moments are determined. It is observed that the excited state dipole moments (μ_e) determined from Bakhshiev's, Kawski-Chamma-Viallet's, solvatochromic equations are found to be in good agreement with each other. Further, the excited state dipole moments determined from all the methods are found to be higher than the ground state dipole moments for all molecules under investigation and this suggests that the fluorescent dyes are more polar in the excited state than in the ground state. It is observed that the angle between μ_g and μ_e all molecules are found to be zero degrees, which suggests that, μ_g and μ_e is parallel to each other and there is no change in the symmetry upon electronic transition. The changes in dipole moment ($\Delta\mu$) values are found to be higher for all the molecules, which may indicate the existence of a more relaxed excited state. The HOMO–LUMO energy band gaps determined from DFT computations and also from optical energy band gaps using absorption threshold wavelengths are found to be in good agreement. Using HOMO–LUMO energies, the chemical hardness of the molecules is studied and the results suggest that all the molecules exhibit a soft nature. The computational studies performed using DFT calculations imply that the fluorescent dyes exhibit both nucleophilic and electrophilic sites. These preliminary observations and results suggest that the fluorescent dyes may be considered as potential and interesting candidates for luminescence materials, fluorescent probes, and dye-sensitized solar cell materials in the future.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Lohit Naik reports financial support, administrative support, and statistical analysis were provided by Hirasugar Institute of technology, Belgaum.. Shashashikant Walki reports a relationship with Hirasugar Institute of technology, Belgaum that includes: employment. Shashikant Walki has patent Nil pending to nil.

CRediT authorship contribution statement

Shashikant Walki: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software. **G.H. Malimath:** Conceptualization. **K.M. Mahadevan:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Soniya Naik:** Data curation, Methodology. **Suraj M. Sutar:** Conceptualization, Data curation, Formal analysis. **Hemantkumar Savanur:** Writing – review & editing. **Lohit Naik:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Acknowledgment

Dr. K. M. Mahadevan thankful to the department of science and technology, ministry of science and Technology, India for providing financial supports. The authors are thankful to the authorities of USIC, Karnatak University, Dharwad, for providing the instrumental facility for our research work. One of the author Shashikant walki is thankful to the principal, Hirasugar Institute of technology, Belgaum, for their continuous support and encouragement.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2021.130781](https://doi.org/10.1016/j.molstruc.2021.130781).

References

- [1] S. Stanchev, G. Momekov, F. Jensen, I. Manolov, Synthesis computational study and cytotoxic activity of new 4-hydroxycoumarin derivatives, *Eur. J. Med. Chem.* 20 (2007) 1–13.
- [2] I. Kostava, I. Manolov, I. Nicolova, S. Konstantinov, M. Karaivanova, New lanthanide complexes of 4-methyl-7-hydroxycoumarin and their pharmacological activity, *Eur. J. Med. Chem.* 36 (2001) 339–347.
- [3] Z.H. Chohan, A.U. Shaikh, A. Rauf, C. Supuran, Antibacterial, antifungal and cytotoxic properties of novel N-substituted sulfonamides from 4-hydroxycoumarin, *J. Enzym. Inhib. Med. Chem.* 21 (2006) 741–748.
- [4] J.W. Hinman, H. Hoeksema, E.L. Caron, W.G. Jackson, The partial structure of novobiocin (streptonivcin), *J. Am. Chem. Soc.* 78 (1956) 1072–1074.
- [5] J.H. Lee, H.B. Bang, S.Y. Han, J.G. Jun, An efficient synthesis of (+)-decursinol from umbelliferone, *Tetrahedron Lett.* 48 (16) (2007) 2889–2892.
- [6] H. Zhao, N. Neamati, H. Hang, A. Mazumder, S. Wang, S. Sunder, G.W. Milne, Y. Pommier, Coumarin-based inhibitors of HIV integrase, *J. Med. Chem.* 40 (2) (1997) 242–249.
- [7] R.S. Manian, J. Jayashankaran, R. Raghunathan, A rapid access o indolo [2,1-a] pyrrolo [4',3': 4,5] pyrano [5,6-c] coumarin / [6,5-c] chromone derivatives by domino Knoevenagel intramolecular hetero Diels-Alder reactions, *Tetrahedron Lett.* 48 (8) (2007) 1385–1389.
- [8] M.M. Asimov, V.M. Nikitchenko, A.I. Novikov, A.N. Rubinov, New high-efficiency biscoumarin laser dyes, *Chem. Phys. Lett.* 149 (1988) 140–144.
- [9] M.R. Padhye, S. Varadarajan, A.V. Deshpande, Biscoumarins -new laser dyes in coumarin series, *Spectrosc. Lett.* 17 (1984) 369–376.
- [10] A. Khatyr, H. Maas, G. Calzaferri, Synthesis of new molecules containing head, spacer, and label moieties, *J. Org. Chem.* 67 (19) (2002) 6705–6710.
- [11] J.P. Chen, P.S. Horns, B.R. Hsieh, Fluorescent bis-coumarins for organic light-emitting devices, Patent no. US 2003164499; 2003.
- [12] A. Chandrasekhar, S. Padmanabhan, S. Seshadri, Synthesis of biscoumarins and biscoumarinyl ketones, *Dyes Pigments* 7 (1986) 13–21.
- [13] H. Tuncer, C. Erk, The synthesis of chromophore ended glycols, part IV. bis-coumarin derivatives ended polyglycols, *J. Heterocycl. Chem.* 43 (2006) 1135–1139.
- [14] N.O. Mahmoodi, F. Ghanbari-Pirbasi, Z. Jalalifard, Recent advances in the synthesis of coumarin derivatives, *J. Chin. Chem. Soc.* 65 (2018) 383–394.
- [15] J. Khurana, S. Kumar, Ionic liquid: an efficient and recyclable medium for the synthesis of octahydroquinazolinone and biscoumarin derivatives, *Monatshfte für Chem. Chem. Mon.* 141 (2010) 561–564.

- [16] H. Mehrabi, H. Abusaidi, Synthesis of biscoumarin and 3,4-dihydropyrano [c]chromene derivatives catalysed by sodium dodecyl sulfate (SDS) in neat water, *J. Iran. Chem. Soc.* 7 (2010) 890–894.
- [17] W. Li, Y. Wang, Z. Wang, L. Dai, Y. Wang, Novel SO₃H-functionalized ionic liquids based on benzimidazolium cation: efficient and recyclable catalysts for one-pot synthesis of biscoumarin derivatives, *Catal. Lett.* 141 (2011) 1651–1658.
- [18] R. Rezaei, M. Fatemeh, M.M. Doroodmand, Propane-1,2,3-triyl tri(hydrogen sulfate): a mild and efficient recyclable catalyst for the synthesis of biscoumarin derivatives in water and solvent-free conditions, *Chin. Chem. Lett.* 25 (2014) 183–186.
- [19] M.A. Zolfigol, A.R. Moosavi-Zare, M. Zarei, Friedel-Crafts alkylation of 4-hydroxycoumarin catalyzed by sulfonic-acid-functionalized pyridinium chloride as a new ionic liquid, *C. R. Chim.* 17 (2014) 1264–1267.
- [20] A.R. Kiasat, L. Hemat-Alian, Phospho sulfonic acid: a versatile and efficient solid acid catalyst for facile synthesis of bis-(4-hydroxycoumarin-3-yl) methanes under solvent-free conditions, *Res. Chem. Intermed.* 41 (2015) 873–880.
- [21] M. Sedighi, N. Montazeri, Synthesis of biscoumarin derivatives as biological compounds using cellulose sulfonic acid, *Adv. Stud. Biol.* 7 (2015) 89–95.
- [22] F. Shirini, M. Abedini, S. Zamani, H.F. Moafi, Introduction of W-doped ZnO nanocomposite as a new and efficient nanocatalyst for the synthesis of biscoumarins in water, *J. Nanostruct. Chem.* 5 (2015) 123–130.
- [23] S. Zahiri, M. Mokhtary, Bi(NO₃)₃•5H₂O: an efficient catalyst for one-pot synthesis of 3-(aryl)(diethylamino)methyl-4-hydroxy-2H-chromen-2-ones and biscoumarin derivatives, *J. Aibah Univ. Sci.* 9 (2015) 89–94.
- [24] A. Zhu, S. Bai, L. Li, M. Wang, J. Wang, Choline hydroxide: an efficient and biocompatible basic catalyst for the synthesis of biscoumarins under mild conditions, *Catal. Lett.* 145 (2015) 1089–1093.
- [25] B. Maleki, Green synthesis of bis-Coumarin and Dihydropyrano [3,2-c]chromene Derivatives Catalyzed by o- Benzenedisulfonimide, *Org. Prep. Proced. Int.* 48 (2016) 303–318.
- [26] F. Shirini, A. Fallah-Shojaei, L. Samavi, M. Abedini, A clean synthesis of bis(indolyl)methane and biscoumarin derivatives using P₄VPy-CuO nanoparticles as a new efficient and heterogeneous polymeric catalyst, *RSC Adv.* 6 (2016) 48469–48478.
- [27] M. Sedighi, F. Shirini, M. Mamaghani, Sulfonated rice husk ash (RHA-SO₃H) as a highly efficient and reusable catalyst for the synthesis of some bis-heterocyclic compounds, *RSC Adv.* 3 (2013) 24046–24053.
- [28] K. Niknam, A. Jamali, Silica-bonded N-propylpiperazine sodium n-Propionate as recyclable basic catalyst for synthesis of 3,4-Dihydropyrano [c]chromene derivatives and biscoumarins, *Chin. J. Catal.* 33 (2012) 1840–1849.
- [29] H.O. Foroughi, A. Khalafi-Nezhad, Synthesis of Bis-4-hydroxycoumarins via a multi component reaction using silica boron- sulfuric acid nanoparticles (SB-SANs) as an efficient heterogeneous solid acid catalyst, *Org. Chem. Res.* 2 (2016) 148–161.
- [30] K.P. Boroujeni, P. Ghasemi, Synthesis and application of a novel strong and stable supported ionic liquid catalyst with both Lewis and Bronsted acid sites, *Catal. Commun.* 37 (2013) 50–54.
- [31] A. Tzani, A. Douka, A. Papadopoulos, E.A. Pavlatou, E. Voutsas, A. Detsi, Synthesis of biscoumarins using recyclable and biodegradable task-specific ionic liquids, *ACS Sustain. Chem. Eng.* 1 (2013) 1180–1185.
- [32] J. Li, C.W. Lv, X.J. Li, D. Qu, Z. Hou, M. Jia, X.X. Luo, X. Li, M.K. Li, Synthesis of biscoumarin and dihydropyran derivatives and evaluation of their antibacterial activity, *Molecules* 20 (2015) 17469–17482.
- [33] M.V.R. Reddy, E.P. Reddy, 3-Acyl coumarins, thiochromones and quinolones and therapeutic uses, here of field of invention, PCT Patent no:WO 2006132947
- [34] D. Huang, J. Sun, L. Ma, C. Zhang, J. Zhao, Preparation of ketocoumarins as heavy atom-free triplet photosensitizers for triplet-triplet annihilation upconversion, *RSC Photochem. Photobiol. Sci.* 12 (2013) 872–882.
- [35] E. Lippert, Spekreijse & opisohe b&hnmng dee Dipolmomentes ammatiseber Verbindqen im ersten amregten SingdeMzmstand, *Z. für Elektrochem.* 61 (1957) 962–975.
- [36] N.G. Bakhshiev, Universal intermolecular interactions and their effect on the position of the electronic spectra of molecules in 2-component solutions, *Opt. Spectrosc.* 16 (1964) 821–832.
- [37] A. Kowski, On the estimation of excited state dipole moments from solvatochromic shifts of absorption and fluorescence spectra, *Z. Naturforsch.* 57A (2002) 255–262.
- [38] J.T. Edward, Molecular volumes and the Stokes-Einstein equation, *J. Chem. Educ.* 47 (1970) 261–270.
- [39] M.S. Zakerhamidi, M. Ghanadzadeh, A.M. Tajalli, Anisotropic and isotropic solvent effects on the dipole moment and photophysical properties of rhodamine dyes, *Spectrochim. Acta Part A* 77 (2010) 767–777.
- [40] I. Gryczynski, A.Z. Kowski, Temperatura bhängigkeit der statischen Dielektrizitätskonstante und des optischen Brechungsindex von Flüssigkeiten, *Z. Naturforsch.* A 30a (1975) 287.
- [41] A. Kowski, B. Kuklinski, P. Bojarski, Thermochromic shifts of absorption and fluorescence spectra and excited state dipole moment of PRODAN, *Z. Naturforsch.* 55a (2000) 550.
- [42] L. Naik, C.V. Maridevarmath, I.A.M. Khazi, G.H. Malimath, Photophysical and computational studies on optoelectronically active thiophene substituted 1,3,4-oxadiazole derivatives, *J. Photochem. Photobiol. A Chem.* 368 (2019) 200–209.
- [43] C.V. Maridevarmath, L. Naik, G.H. Malimath, Synthesis, photophysical, DFT and solvent effect studies on biologically active benzofuran derivative: (5-methyl-benzofuran-3-yl)-acetic acid hydrazide, *Chem. Data Collect.* 21 (2019) 100221.
- [44] C.V. Maridevarmath, L. Naik, G.H. Malimath, Synthesis characterization and photophysical studies on novel benzofuran-3-acetic acid hydrazide derivatives by solvatochromic and computational methods, *J. Mol. Struct.* 1188 (15) (2019) 142–152.
- [45] C. Reichardt, Solvatochromic dyes as solvent polarity indicators, *Chem. Rev.* 94 (8) (1994) 2319–2358.
- [46] M. Ravi, T. Soujanya, A. Samanta, T.P. Radhakrishnan, Excited state dipole moments of some coumarin dyes from a solvatochromic method using the solvent polarity parameter, *J. Chem. Soc. Faraday Trans.* 91 (1995) 2739–2742.
- [47] M.B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 6th Ed., Wiley, New York, 2012.
- [48] D.P. Specht, P.A. Martic, S. Farid, A new class of triplet sensitizers, *Tetrahedron* 38 (9) (1982) 1203–1211.