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Photophysical Properties of Coumarin 4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one ($C_{23}H_{18}O_4$) and Estimation of Ground-State and Excited- State Dipole Moments by Solvatochromic Approaches

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Abstract: ***The absorption and emission fluorescent properties of coumarin-4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one - ($C_{23}H_{18}O_4$) (4MPPC) at room temperature are investigated in pure polar and nonpolar solvents. The pure solvents influence on spectral characteristics. This is investigated by applying theories such as the Lippert-Mataga polarity function, Reichardt's microscopic solvent polarity parameter, and Kamlet and Catalan's multiple linear regression techniques. The main role of solute and solvents interactions in pure solvents, particularly dielectric interaction and hydrogen bonding. The computed HOMO and LUMO energies of these compounds indicate that they are chemically active with a tendency for molecular interactions and is supported by the electrostatic potential data. The hydrogen bonding interactions dominate the contribution of dielectric interactions. The electric dipole moments of both the ground state and excited states had been estimated using Solvatochromic method. The value of electric dipole moment of the excited state. We concluded that polar and polar solvents change fluorescent properties of coumarin.***

Keywords: Density Functional Theory, Optimized Vector, HOMO and LUMO, Molecular electrostatic potential surface, Solvent effect on absorption and fluorescence spectra, Dipole moments and Polarizability

1. Introduction

The study of effect of solvents on the absorption and fluorescence properties of organic fluorophores had been an interesting investigation from last decade. These investigations have considerable importance in the field of photophysical and photochemistry [1] [3]. This is very importance for the determination of ground and excited state dipole moments and investigations of photophysical properties like fluorescence quantum yield(Φ_f), fluorescence life time(τ_f), absorption and fluorescence spectral shift, etc. The knowledge of the excited state dipole moments of electronically excited molecules is quite useful in designing nonlinear optical materials [2]. Differential stabilization of ground and excited states are observed when the polarities of the solvents are varied [4] [15]. The most widely accepted method is based on solvatochromism due to the high linear correlation between spectroscopic parameters and solvent polarity functions. Solvatochromic method has been used for the determination of dipole moments of ground and excited state of various fluorescent molecules such as coumarins [16]. The present investigation focuses on the estimation of ground and excited state dipole moments of coumarin 4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one- **($C_{23}H_{18}O_4$) (4MPPC)** molecule using solvents with different polarities [5] [18]. The effects of pure solvents on spectral properties of the molecule were studied by employing Bilot-Kawski, Lippert-Mataga bulk solvent polarity parameter, Bakhshiev and Kawski-Chamma-Viallet and Reichardt solvatochromic shift methods [8] [16].

The solvatochromic study of coumarin **($C_{23}H_{18}O_4$) (4MPPC)** has been done using Kamlet-Abboud-Taft and Catalan solvent polarity parameters to study about specific and nonspecific interactions between the solute and solvents [17] [18]. In fact, to the best of our knowledge there have been no reports on the determination of ground and excited state dipole moment values of **($C_{23}H_{18}O_4$) (4MPPC)** [6] [12].

4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one is a coumarin (chromen-2-one) derivative containing multiple aromatic rings and heteroatoms(o). because of its extended π – conjugation, substituent effects, and possible intramolecular interactions, Density Functional Theory (DFT) is an appropriate method to study its optimized geometry and electronic structure.

DFT Structure of 4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one

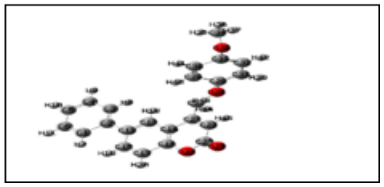

Figure 1: DFT Structure

Optimized Vector (OPT-Vector)

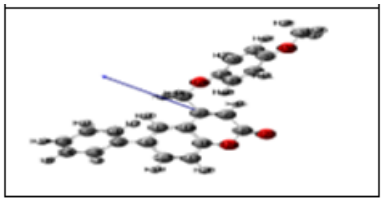

Figure 2: OPT Vector

Molecular electrostatic potential surface

Electrostatic potential created by the molecule's electron distribution and atomic nuclei. The molecular electrostatic potential surfaces show the charge distributions of molecules in three dimensions [9] [15]. It is used to understand how molecules interact and optimize their electrostatic complementary [12] [18] [27]. It shows regions of positive and negative electrostatics potential around a molecule. ESP (Expert System Prediction) computational method that uses artificial intelligence to predict the properties of the molecules [7] [17]. If the discussion is about molecular properties or molecular interactions, it likely refers to Electrostatic Potential. If the discussion is about computational methods for predicting chemical behaviour, it could be an Expert System Prediction [14] [26].

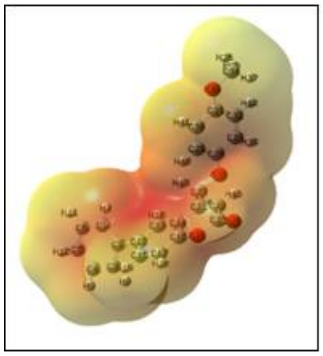

Figure 3: Electrostatic potential surface

The MEP mapped the surface of **4MPPC** was computed using DFT basis set and the MEP surface is plotted in Fig. The computed MEP surface Fig. shows the electrophilic regions that are mostly exist over O_2 in the compound. So, O_2 behaves as an electron donor in the compound [15] [24]. The positive regions are over the CH_4 group in the compound which are nucleophilic and behave like acceptors in the compound and the unbalanced distribution of charge results in higher dipole moment [16] [18] [26]. The molecular electrostatic potential (MEP) is useful in determining electrophilic attack sites, nucleophilic reactions, and hydrogen-bonding interactions[8] [17].

Core Molecular Features

- Formula: $C_{23}H_{18}O_4$.
- Exact Mass: 358.1205 Da.
- Molar Mass: 358.392 g·mol^{-1}.
- Double Bond Equivalents (DBE): 15 (high aromaticity and conjugation) [17].
- LogP: ~4.0-4.6 (hydrophobic, organic soluble).
- Topology: Lactone (chromen-2-one core) + 6-phenyl + methoxy-phenoxy methyl (electron-donating substituent).

Photophysical Properties

Absorption and Emission

UV-Vis Absorption: Dominant π–π* band typically 320–380 nm, with the maximum (λ_{max}) shifting to the higher 300 nm due to the electron-donating substituents and extended conjugation [17] [18] [22].

Emission: Blue-green region (400–520 nm), with emission red-shifting in polar solvents; the Stokes shift is moderate (60–140 nm).

Quantum Yield (Φ_f): Predicted 0.3–0.8; higher in non-protic, rigid media and lower with H-bonding or quenching processes [16] [26].

Lifetime (τ_f): ~1–5 ns in air-saturated solution; longer in deoxygenated /nonpolar Environments [17] [18] [25].

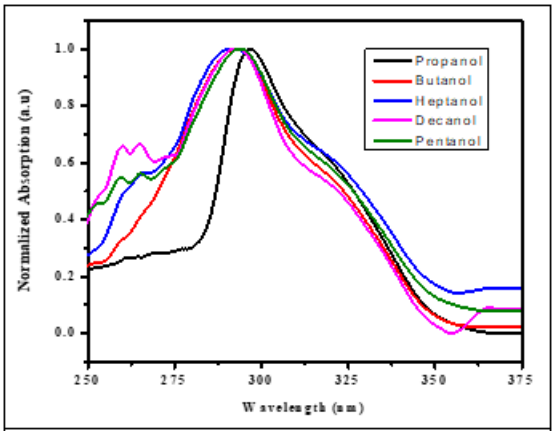

Figure 4: Absorption Vs Wavelength

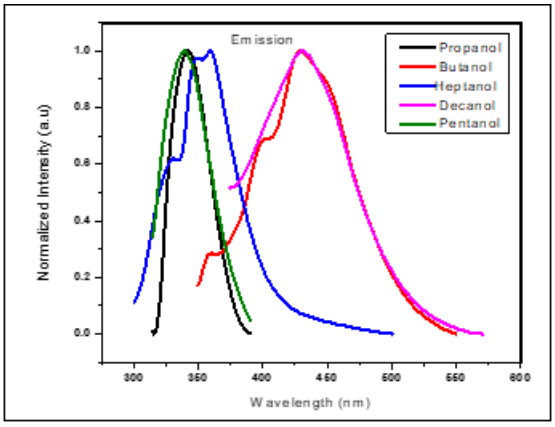

Figure 5: Intensity Vs Wavelength

Effect of solvents on absorption and fluorescence spectra of coumarin ($C_{23}H_{18}O_4$):

The absorption and fluorescence spectra of coumarin **($C_{23}H_{18}O_4$) (4MPPC).**were recorded in different solvents in the increasing order of their polarity at room temperature [16] [26]. Maximum absorption and fluorescence wavelength of coumarin **($C_{23}H_{18}O_4$) (4MPPC)** [18] [20]**.** was found to be in the range of 258–298 nm and 339–434 nm respectively in the chosen solvents [12] [14]. Absorption maxima ($\bar{\nu}_a$), emission maxima ($\bar{\nu}_f$), Stokes shifts ($\bar{\nu}_a - \bar{\nu}_f$) and the arithmetic mean of Stokes shift values (in cm^{-1}) were calculated and tabulated [17] [25].

Equations for the estimation of dipole moments

The independent equations used for the estimation of ground and excited state dipole moments in various solvents with varied dielectric constant (ε) and refractive index (n) are as follows.

Lippert-Mataga Equation-

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f_1(\varepsilon\ n) + Constant$$

Bakhshiev's Equation –

$$\bar{\nu}_a - \bar{\nu}_f = m_2 f_2(\varepsilon\ n) + Constant$$

Kawski-Chamma-Viallet's Equation [15] [27].

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_3 f_3(\varepsilon\ n) + Constant$$

Where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and emission maxima wave number in cm^{-1} [11] [26].

Estimation of excited state dipole moments

The $\mu_e$of coumarin ($C_{23}H_{18}O_4$) (4MPDC) compound was determined with the help of Bakshiev's, Kawski-Chamma-Viallet's relations [15] [18] [27]. Using these polarity parameters, the following expressions can be obtained to estimate μ_e and $\mu_g$which are parallel to one another [16] [26].

$$\mu_g = \frac{m_2 - m_1}{2} \left(\frac{hca^3}{2m_1}\right)^{1/2}$$

$$\mu_g = \frac{m_2 + m_1}{2} \left(\frac{hca^3}{2m_1}\right)^{1/2}$$

The slopes m_1 and m_2 are obtained from the plots of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $f_1(\varepsilon\ n)$, and $\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2}$ versus $f_2(\varepsilon\ n)$ for different solvents, respectively.

Where h Planck's constant, a is Onsager radius of a molecule C is velocity of light [8].

If μ_e and μ_g are not parallel to one another, then the angel ϕ between μ_e and μ_g can be estimated using the below

$$\cos\emptyset = \frac{1}{2\mu_g\mu_e}\left[\left({\mu_g}^2 + {\mu_e}^2\right) - \frac{m_2}{m_1}\left({\mu_e}^2 - {\mu_g}^2\right)\right]$$

The μ_e is also estimated by means of E_N^T using the below

$$(\bar{\nu}_a - \bar{\nu}_f) = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_s}\right)^2 \left(\frac{a_s}{a}\right)^3\right] E_N^T + \text{Constant}$$

Where $\Delta\mu_B$ is the change in dipole moment
a_s is the Onsager radius of the solvent
Δμ and a are the corresponding parameters of the compound [16]

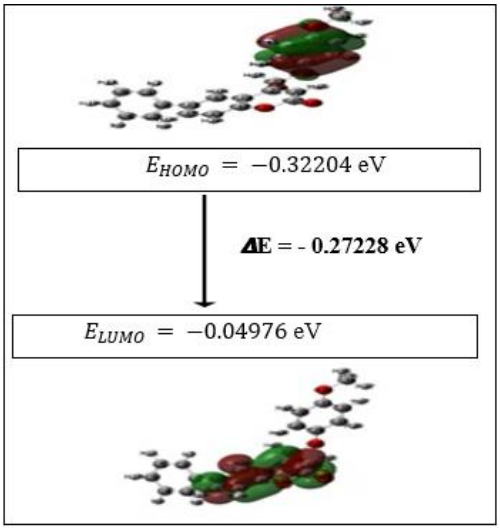

Figure 6: Absorption Vs Wavelength

Mulliken Charges

Table 1

1	**1C**	-0 .166318		**12**	**12C**	-0.026952
2	**2C**	0.025081		**13**	**13C**	-0.105289
3	**3C**	-0.173991		**14**	**14C**	-0.169349
4	**4C**	-0.120805		**15**	**15C**	-0.085132
5	**5C**	-0.150161		**16**	**16C**	0.275590
6	**6C**	-0.119310		**17**	**17C**	-0.194183
7	**7H**	0.145568		**18**	**18H**	0.170937
8	**8H**	0.152438		**19**	**19H**	0.156613
9	**9H**	0.145380		**20**	**20H**	0.175212
10	**10H**	0.146480		**21**	**21C**	0.089796
11	**11H**	0.144390		**22**	**22C**	-0.445558

23	**23C**	0.637218		**34**	**34C**	-0.189105
24	**24O**	-0.367949		**35**	**35H**	0.129435
25	**25O**	-0.447181		**36**	**36H**	0.155540
26	**26O**	-0.323972		**37**	**37H**	0.129846
27	**27C**	-0.285909		**38**	**38O**	-0.388242
28	**28C**	0.157570		**39**	**39H**	0.170492
29	**29C**	-0.200801		**40**	**40H**	0.175151
30	**30C**	-0.150347		**41**	**41H**	0.164120
31	**31C**	0.218166		**42**	**42H**	0.171802
32	**32C**	-0.197305		**43**	**43H**	0.303736
33	**33C**	-0.196414		**44**	**44H**	0.262227
				45	**45H**	0.201483

Mulliken Charges and Chemical Reactivity

Electron-rich the (nucleophilic) centres: Oxygens (−0.3679 to −0.4471), carbons like C6, C12, C22.Electron-poor (electrophilic) centres: C23 (+0.6372), C16 (+0.2755), C31 (+0.2181).Strong intramolecular charge transfer (ICT) axis, especially across C23 and adjacent Oxygens, governs absorption or emission shifts [26].This charge polarization boosts *solvatochromic fluorescence* and targets for reactivity or coordination [17] [18].

Table 2

Calculated values for solvent polarity parameters λ_a , ν_a and $\bar{\nu}_a$				
ABSORPTION				
SL	Solvents	λ_a(nm)	ν_a	$\bar{\nu}_a$
1	Propanol	296	1013513	33783
2	Butanol	226	1327433	44247
3	Heptanol	292	1027397	34246
4	Toluene	290	1034482	34482
5	DMSO	281	1067615	35587
6	Benzene	286	1048951	34965

Table 3

Calculated values for solvent polarity parameters λ_f , ν_f and $\bar{\nu}_f$				
EMISSION				
SL	Solvents	λ_f (nm)	ν_f	$\bar{\nu}_f$
1	Propanol	299	1003344	33444
2	Butanol	324	925925	30864
3	Heptanol	359	835654	27855
4	Toluene	294	1020408	34013
5	DMSO	344	872093	29069
6	Benzene	295	1016949	33898

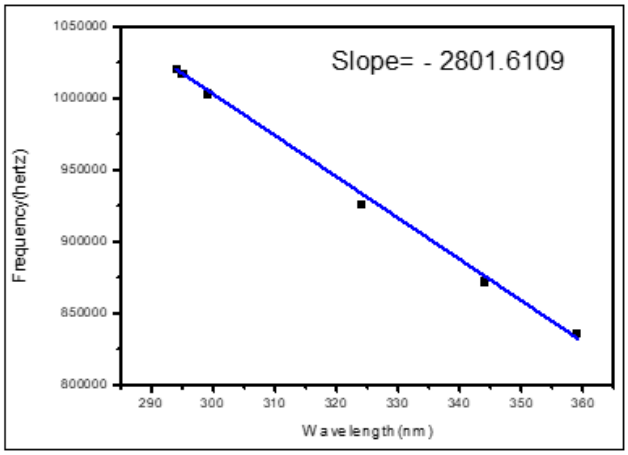

Figure 7: Frequency Vs Wavelength (Absorption)

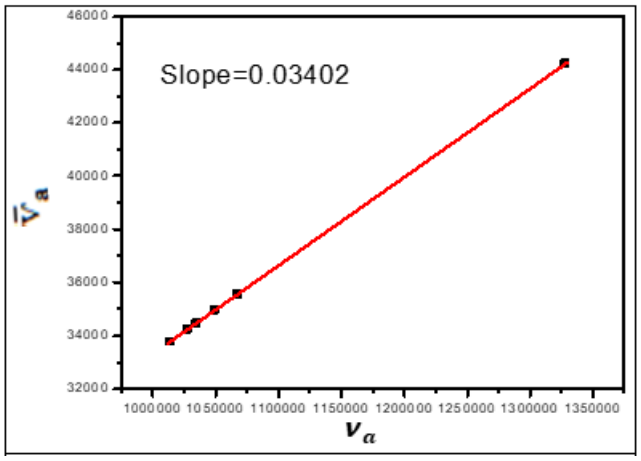

Figure 8: $\bar{\nu}_a$ Vs ν_a (Absorption)

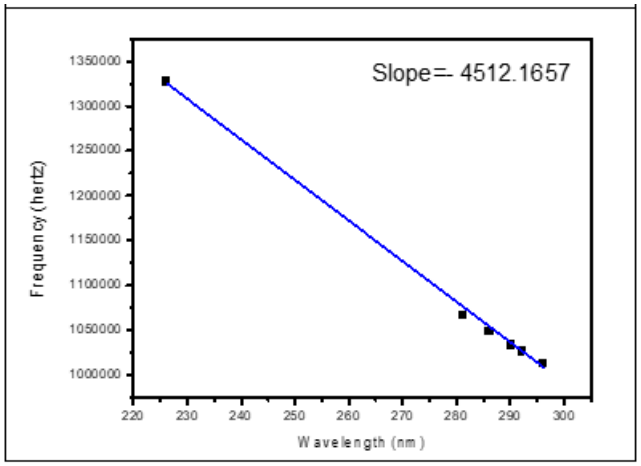

Figure 9: Frequency Vs Wavelength (Emission)

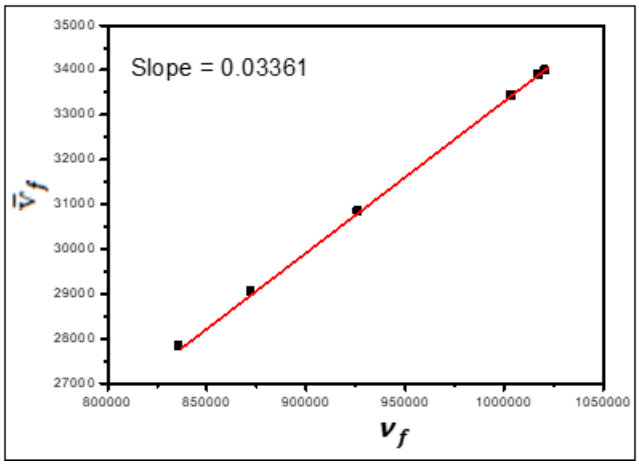

Figure 10: $\bar{\nu}_f$ Vs ν_f (Emission)

Table 4

Calculated values for solvent polarity parameters $\bar{\nu}_a - \bar{\nu}_f$, $f_1(\varepsilon, n)$ and m_1			
Solvents	$\bar{\nu}_a - \bar{\nu}_f$	$f_1(\varepsilon, n)$	m_1
Propanol	10169	0.2746	37032.046
Butanol	401508	0.2633	1524906.95
Heptanal	191743	0.2525	929456.148
Toluene	14074	0.3351	41999.403
DMSO	195522	0.2684	728472.429
Benzene	32002	0.0475	673726.315

Table 5

Calculated values for solvent polarity parameters $\bar{\nu}_a - \bar{\nu}_f$, $f_2(\varepsilon, n)$ and m_2			
Solvents	$\bar{\nu}_a - \bar{\nu}_f$	$f_2(\varepsilon, n)$	m_2
Propanol	10168	0.524	19406.488
Butanol	401508	0.79	1524906.95
Heptanal	191743	0.652	929456.148
Toluene	14074	0.142	41999.403
DMSO	195522	0.841	728472.429
Benzene	32002	0.475	673726.315

Table 6

Calculated values for solvent polarity parameters f_1 (ε, n), g(n).f_1 (ε, n) + g(n)			
Solvents	f_1 (ε, n)	g(n)	f_1 (ε, n) + g(n)
Propanol	0.2746	0.262	0.5366
Butanol	0.2633	0.271	0.5343
Heptanal	0.2525	0.285	0.5375
Toluene	0.3351	0.477	0.5001
DMSO	0.2684	0.324	0.841
Benzene	0.0475	0.225	0.475

Table 7

Calculated values for solvent polarity parameters $f_2(\varepsilon, n)$, 2g(n) and $f_2(\varepsilon, n)$ + 2g(n).			
Solvents	$f_2(\varepsilon, n)$	2g(n)	$f_2(\varepsilon, n)$ + 2g(n)
Propanol	0.781	0.524	1.305
Butanol	0.749	0.542	1.291
Heptanal	0.652	0.575	1.227
Toluene	0.142	0.67	4.926108
DMSO	0.648	0.648	42.310275
Benzene	0.45	0.45	9.729729

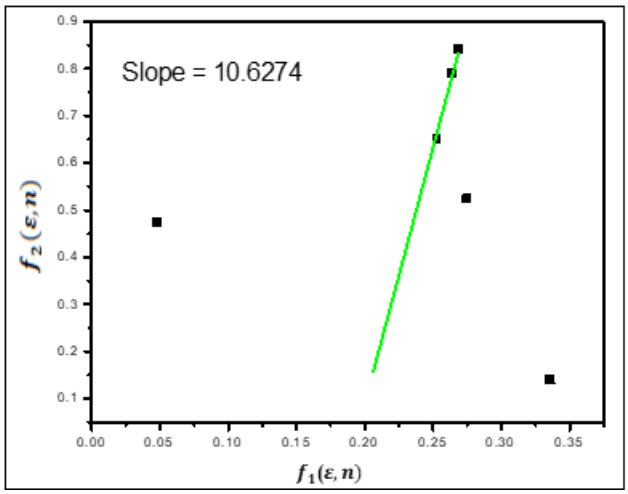

Figure 11: $f_2(\varepsilon,n)$ Vs $f_1(\varepsilon,\mathrm{n})$)

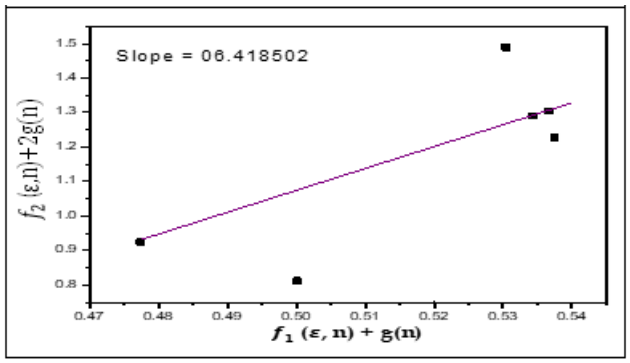

Figure 12: $f_2(\varepsilon,n)$ + 2g(n) Vs $f_1(\varepsilon,\mathrm{n})$ + g(n)

Dipole Moment and Polarizability (NLO Potential)
Ground-state dipole: 7.3195 D (strong, anisotropic; dominates along X-axis)
Isotropic polarizability (αiso): 2351 au (~34.85×10^{-24} cm³) [26].
First hyperpolarizability (βtot): ~5799 au (strong NLO response; Z-axis dominant)

High polarizability and hyperpolarizability make this chromophore a candidate for NLO applications (frequency doubling, electro-optic modulation) [8].

Applications
Fluorescent probes/dyes: Blue-green emitter with microenvironment sensitivity [13] [17].
Optoelectronics (OPV/OLED): Extended π-system, strong photostability, NLO activity [9] [21].
Sensors: FRET donor capability, ratio metric sensors tuneable by substituent modification.
Bioimaging: Stable fluorescence, solvatochromic response, low toxicity.
The IR spectrum features several **diagnostic bands** related to functional groups present in the coumarin-based molecule [10] [18].

Molecular Structure and Evidence

Lactone carbonyl:
Strong doublets around **1725 cm⁻¹** (very strong, conjugated C=O) and **1815 cm⁻¹** (lactone C=O) [12] [23].Indicates coumarin-type core; lower C=O due to aromatic conjugation.

Aryl and ether motifs:
Intense features from **1202–1243 cm⁻¹** and **1049 cm⁻¹** validate multiple **phenoxy/methoxy substituents**. **Aromatic substitution:**
Several strong out-of-plane modes (810–910 cm⁻¹) reveal various aromatic substitution environments.

Aliphatic/aromatic C–H stretches:
Multiple sharp signals at **2640–2780 cm⁻¹** fit the expected methoxy/benzylic hydrogens, though the region appears shifted low, as noted in the data comments

Table 8

Wavelength (nm)	Intensity (ε, $M^{-1}cm^{-1}$)	Assignment	Structural Origin
1815, 1725	Strong, very strong	C=O stretch (lactone/ester)	Chromen-2-one coumarin carbonyl
1654,1509	Moderate/ strong	Aromatic C=C stretch	Phenyl/coumarin aromatic rings
1202–1243	Strong cluster	C–O–C stretch, C–O, ring modes	Methoxy, phenoxy, aryl ethers, in-plane C–H bends
1049	Very strong	Alkyl/aryl C–O stretch	Phenoxy, methoxy ether group
810,851, 910	Strong	Aromatic C–H bend (oop)	Substituted aromatic environments
2650–2770	Multiple, moderate	Aliphatic/ aromatic C–H stretches	Methoxy/benzylic/ aromatic hydrogens

Fingerprint region:
Rich, complex, indicative of multiple ring systems and ether linkages.

2. Summary

The molecule 4-(4-Methoxy-Phenoxymethyl)-6-phenyl-chromen-2-one (**4MPPC)** ($C_{23}H_{18}O_4$) offers a rich conjugated framework that endows it with distinctive photophysical and nonlinear optical properties [15] [18] [27]. Its strong absorption and tenable emission, environment-sensitive behaviour, and pronounced IR fingerprints are tied to the extended aromaticity and functional group diversity. The charge distribution, dipole, and hyperpolarizability underline its capacity for nonlinear optics and sensing, while practical characterization is supported by IR/NMR/UV–Vis spectral features. Its robust fluorescence, polarizability, and photostability position it for diverse use in advanced imaging, sensing, and optoelectronic applications [16] [19].

3. Conclusion

Photophysical properties of coumarin **($C_{23}H_{18}O_4$) (4MPPC).** molecule have been investigated and their ground and excited state dipole moments were determined as a function of solvent polarity [9] [17]. Different solvent polarity correlation methods were used to analyse solvent effects on the excitation and emission spectra. Gaussian 16 W software was used to theoretically determine the ground state dipole moment. The experimental excited state dipole moment of coumarin **($C_{23}H_{18}O_4$)(4MPPC).**was determined by Lippert-Mataga, Bakshiev [12].

Section snippets: Reagents and apparatus

All chemicals and solvents used in this study were of spectroscopic grade obtained from Sigma-Aldrich Chemical Company and S.D. Fine Chemicals Ltd., India respectively. Absorption and fluorescence spectra were recorded by UV–visible spectrophotometer, USIC Gulbarga University, Kalaburagi and Spectro fluorophotometer, USIC Dharwad University, Dharwad respectively at room temperature. All sample solutions were prepared in various solvents with different polarities at low concentrations (10^{-5} M) to avoid self-absorption.

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