ANALYSIS OF QUINOXALINE DERIVATIVE FOR OPTOLUMINESENCE TECHNIQUES

Suma M, Sushma G.N, Nadaf Y.F., Department of Physics and Materials Research Center, Maharani Science College for Women, Maharani Cluster University, Bengaluru, India-560001.
A K. Maniyar Department of Physics Government First Grade College, Hubballi. 580032.
Alande Balaji D Rani Channama University, Sagoli Rayanna First Grade Constituent College, Belagavi,India-590077 : dryfnadaf@gmail.com

Abstract

Introduction: Benzene and Pyrazine are two aromatic rings to form Quinoxaline molecule. The drug industries used for quinoxaline derivative have high efficiency against the diseases namely imuno regulatory, tumour, hypoglycaemia, they have very less side effects. Heterocyclic compounds which containing the nitrogen atoms is well known for various applications [1-4]. DFT and TDDFT became the very popular method in determining the energies, electronic structure in excited state with excited and emission wavelength, it is also helpful in the determination of atomic charge distribution, optical spectral analysis and photochemical reactions studies [5-6]. From the structural, optical and charge distribution analysis studies we can understand the nature of the molecule [7-9]. Besides biological activities quinoxaline derivatives were helpful in industrial applications due to its thermal stability and less energy bang gap of molecule shows good luminescence property and it can be used in display applications like photovoltaics. Quinoxaline based compounds containing polymers used in optical devices and used in quantum dot light emitting diodes (QLEDs) as transport layers. quinoxalines were active against fungal infection and also part of several chronic and metabolic disease treatment.

Objectives: Quinoxaline derivatives are widely used in separation of metal ions from industrial waste by using solvent extraction process. Our Quinoxaline derivative is named as 2-chloro-5,6-dimethyl-3-(methylsulfanyl)quinoxaline molecule to study the structural and thermodynamic properties using density functional theory (DFT) with the help of B3LYP functional and 6-311G(d,p) basis set. The energy band gap of the molecule in vacuum, alkane and alcohol solvents were calculated using HOMO and LUMO values, Mulliken charge distribution on each atomic site of the molecule explain the nucliophilic and electrophilic site of the molecule and Molecular electrostatic potential mapping of 2Cl5,6Dm3MsQ molecule in vacuum is exported.

Methods: The molecular structure was designed with the help of Gauss view 5.0 and calculations were done using density functional theory (DFT), time dependent density functional theory (TDDFT) with a basis set of 6-311G(d,p) with a functional of B3LYP, using Gaussian 09 software. CIE chromatography of molecule by Osram Sylvania software for photoluminescence study.

Results: The optimized structure of 2Cl5,6Dm3MsQ is found using Gaussian and its atomic bomd length and bond angle values are been exreacted. Its HOMO and LUMO and MEP 3D pictures are represented. Optoelectronic properties of the molecule are calculated and that value gives good agreement with OLED applications that coincide with CIE values.

Conclusions: This molecule acts differently in vacuum, alkane medium of hexane and alcohol medium of octonal. It shows that, the band gap between different molecular orbital (HOMO to LUMO) is increases with solvent polarity. In vacuum of Energy gap is 6.416 eV, hexane is 6.2716 eV and in octonal is 6.3213 eV. The optoelectronic properties like global electrophilicity(ω), ionization potential (I), chemical softness (s), chemical hardness (η), chemical potential (μ), electron affinity (E) were also increases with increase in polarity of the medium. MEP helps in understanding of molecular parameters and nucliophilic atomic positions by using the color code and stability of the molecule.

Keywords: HOMO, LUMO, CIE, MEP and optoelectronic properties.

1. Introduction

Benzene and Pyrazine are two aromatic rings to form Quinoxaline molecule.. The drug industries using quinoxaline derivative have high efficiency against the diseases namely imuno regulatory, tumour, hypoglycaemia, they have very less side effects. Heterocyclic compounds which containing the nitrogen atoms is well known for various applications [1-4]. DFT and TDDFT became the very popular method in determining the energies, electronic structure in excited state with excited and emission wavelength, it is also helpful in the determination of atomic charge distribution, optical spectral analysis and photochemical reactions studies [5-6]. From the structural, optical and charge distribution analysis studies we can understand the nature of the molecule [7-9]. Besides biological activities quinoxaline derivatives were helpful in industrial applications due to its thermal stability and less energy bang gap of molecule shows good luminescence property and it can be used in display applications like photovoltaics. Quinoxaline based compounds containing polymers used in optical devices and used in quantum dot light emitting diodes (QLEDs) as transport layers. quinoxalines were active against fungal infection and also part of several chronic and metabolic disease treatment.

2. Objectives

Quinoxaline derivatives are widely used in separation of metal ions from industrial waste by using solvent extraction process. Our Quinoxaline derivative is named as 2-chloro-5,6-dimethyl-3-(methylsulfanyl)quinoxaline molecule to study the structural and thermodynamic properties using density functional theory (DFT) with the help of B3LYP functional and 6-311G(d,p) basis set. The energy band gap of the molecule in vacuum, alkane and alcohol solvents were calculated using HOMO and LUMO values, Mulliken charge distribution on each atomic site of the molecule explain the nucliophilic and electrophilic site of the molecule and Molecular electrostatic potential mapping of 2Cl5,6Dm3MsQ molecule in vacuum was exported and compared with various parameters of media.

3. Methods

The molecular structure was designed with the help of Gauss view 5.0 and analysis were done using density functional theory (DFT), time dependent density functional theory (TDDFT) with a basis set of 6-311G(d,p) with a functional of B3LYP, using Gaussian 09 software.CIE chromatography of molecule by Osram Sylvania software for photoluminescence studies.

4. Results

4.1 Structural Properties

The optimized structure of 2Cl5,6Dm3MsQ molecule is shown in Figure and bond length [Å] and bond angle [º] of 2Cl5,6Dm3MsQ molecule is presented in Table 1.
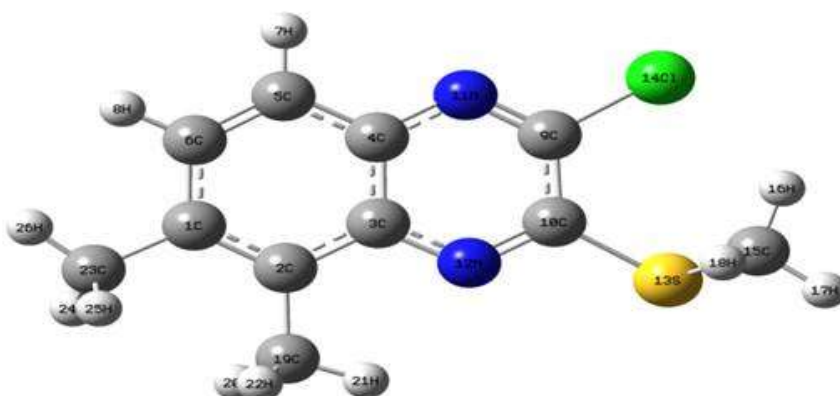

Figure 1: Optimized molecular structure of 2Cl5,6Dm3MsQ.

The bond length between the carbon and sulfur atoms shows higher value than carbon-carbon (C-C) and carbon-hydrogen (C-H), the bond length between 7H-5C shows 1.0827Å and Bond length between carbon and nitrogen (11N-4C) is 1.2914 Å. Between carbon and sulphur, we observed a higher bond length for 15C-13S. The highest bond angle is observed between 14Cl-9C-4C which is 148.075º and lowest for 11N-9C-4C is 31.820º [10].

Table 1: Bond length (Å), bond angle (º) and dihedral angle (º) of 2Cl5,6Dm3MsQ.

Atoms	Bond length (Å)	Atoms	Bond angle (º)
2C-1C	1.3911	3C-2C-1C	118.414
3C-2C	1.4260	4C-3C-2C	120.544
4C-3C	1.4252	5C-4C-3C	119.760
5C-4C	1.4080	6C-5C-4C	118.954
6C-5C	1.3735	7H-5C-4C	118.675
7H-5C	1.0827	8H-6C-5C	119.382
8H-6C	1.0848	9C-4C-3C	90.178
11N-4C	1.2973	10C-9C-4C	91.197
10C-9C	1.4413	11N-9C-4C	31.820
11N-9C	1.2914	12N-10C-9C	119.032
12N-10C	1.3090	13S-10C-9C	124.585
13S-10C	1.7934	14Cl-9C-4C	148.075
14Cl-9C	1.7631	15C-13S-10C	102.737
15C-13S	1.8338	16H-15C-13S	112.096
16H-15C	1.0877	17H-15C-13S	104.966
17H-15C	1.0906	18H-15C-13S	110.405
18H-15C	1.0894	19C-6C-5C	121.523
19C-2C	1.5059	20C-2C-1C	110.995
20H-19C	1.0951	21H-20C-2C	110.662
21H-19C	1.0875	22H-20C-2C	111.047
22H-19C	1.0948	23H-20C-2C	120.743
23H-1C	1.5090	24H-19C-1C	111.458
24H-23C	1.0945	25H-19C-1C	111.460
25H-23C	1.0948	26H-19C-1C	111.174
26H-23C	1.0909	-	-

4.2 Mulliken Atomic Charge Distribution

Mulliken charge on each atom of 2Cl5,6Dm3MsQ molecule (Table 2), in which the atoms, 1C, 2C, 5C,6C,10C,11N, 12N, 14Cl, 15C and 23C were donor atoms and carbon atom which share bond with sulfur atom (15C) and nitrogen atom (3C, 4C,10C) acts as acceptor like hydrogen atoms and sulphur atom (3C,4C,7H, 8H, 9C,13S, 16H,17H, 18H, 19H, 20H, 21H,22H 24H and 26H). The atomic charge of sulfur atom (13S) also increases with solvent polarity like carbon, hydrogen, nitrogen and chlorine atoms but in the case of nitrogen atoms its vice versa[11, 12].

Table 1. Mulliken atomic charges of 2Cl5,6Dm3MsQ by DFT method in Vaccum, Hexane and Octanol solvents

Atoms	Mulliken atomic charge		
	vacuum	**hexane**	**octanol**
1C	-0.11778	-0.12005	-0.12149
2C	-0.07115	-0.07288	-0.07419
3C	0.100023	0.104313	0.107286
4C	0.123007	0.129404	0.13408
5C	-0.04407	-0.05218	-0.05882

6C	-0.05151	-0.05605	-0.05789
7H	0.105566	0.109823	0.112858
8H	0.092603	0.103009	0.111868
9C	0.077231	0.083432	0.087565
10C	-0.01953	-0.00791	0.000754
11N	-0.2669	-0.28138	-0.29317
12N	-0.28593	-0.2966	-0.30534
13S	0.14725	0.123265	0.101968
14Cl	-0.05328	-0.06126	-0.06804
15C	-0.45329	-0.4524	-0.45109
16H	0.16185	0.164898	0.167664
17H	0.15023	0.158034	0.164484
18H	0.150033	0.156107	0.161381
19C	-0.24267	-0.24338	-0.24368
20H	0.12075	0.126301	0.131157
21H	0.143553	0.13508	0.126973
22H	0.118089	0.124092	0.129558
23C	-0.24846	-0.25083	-0.25208
24H	0.127442	0.131151	0.134289
25H	0.127522	0.131514	0.135011
26H	0.10941	0.114478	0.118892

4.3 Molecular Orbitals and Energy Band Gap

The energy band gap of 2Cl5,6Dm3MsQ molecule in vacuum, alkane and alcohol solvents were studied. This molecule in vacuum shows lowest energy gap than the other solvents. The 3D energy band gap between HOMO-LUMO, HOMO-1-LUMO+1 and HOMO-2-LUMO+2 in vacuum is shown in Figure 2. Energy band gap (E_g) between HOMO and LUMO in vacuum medium is 6.2738 eV, energy gap between HOMO-1 to LUMO+1 are 6.6313 eV. The E_g between HOMO+2 to LUMO-2 in vacuum is 7.4944 eV. The green area the 3D plots represents the green and red region indicates positive region and the negative region of molecular orbital[13].

To analyse the molecular orbitals, we used the job type as energy and method DFT in Gaussion programming after the optimization of the molecules. The FMO gives us the information about the chemical reaction and structure of the molecule with its symmetry. HOMO, HOMO-1, HOMO-2 are the orbitals like HOMO, HOMO1, HOMO2 is π-bonding symmetry and the orbitals such as LUMO, LUMO+1, LUMO+2 reprasents π* antibonding symmetry.
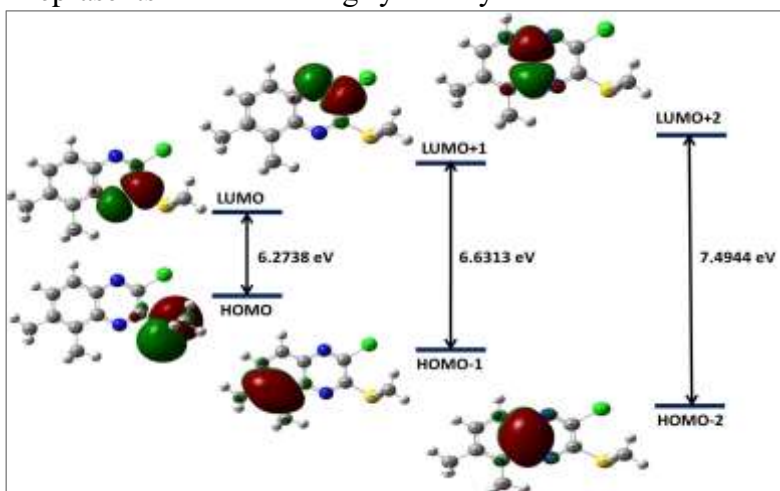

Figure 2: Molecular orbital with energy band gap of 2Cl5,6Dm3MsQ.

4.4 Frontier Molecular Orbitals and Optoelectronic Properties of Quinoxaline Derivatives.
FMO study is an important concept in the field of quantum chemistry. FMO helps us to identify the donor and acceptor group and the charge transfer between them by π-conjugate. HOMO is the electron-donating group which associated with ionization potential and LUMO is electron-accepting group associated with electron affinity of the molecule. From DFT theory of global reactivity descriptors can be analysed by using optical parameters, the ionization potential (I) can be obtained by negative of HOMO energy is and negative of LUMO energy is considered as electron affinity (E). Ionisation potential, electron affinity of the molecules and the energy band gap were helpful in the calculation of various terms like chemical hardness (η), chemical potential (μ), chemical softness (s), global electrophilicity(ω) of the quinoxaline derivatives. These properties are useful in understanding the reactivity of the molecule and in the interpretation of electronic spectra. The energy band gap (E_g) is the gap between the bound state and free state, which can be obtained from values of HOMO and LUMO.

$$E_g = E_{HOMO} \sim E_{LUMO} \qquad (1)$$

The capacity of atoms to attract the electrons which are shared when forming chemical bonding represents electronegativity (χ)

$$\chi = (I+E)/2 \qquad (2)$$

The half value of the energy band gap is Chemical hardness (η)

$$\eta = (I-E)/2 \qquad (3)$$

The chemical softness (s) is stability of the compound that can be calculated using Chemical hardness

$$s = 1/2\eta \qquad (4)$$

The chemical potential (μ) is considered as the negative of electronegativity value.

$$\mu = -\chi \qquad (5)$$

Hence global electrophilicity (ω) can be analysed .which is the capacity of electrophile to promote a covalent (soft) reaction.

$$\omega = \mu^2/2\eta \qquad (6)$$

The optoelectronic properties of the quinoxaline molecule in different solvents including vaccume were studied using B3LYP/6-311+G(d,p) method and presented below (Table.3).

TableError! No text of specified style in document.**. Optoelectronic properties of 2Cl5,6Dm3MsQmolecule in vacuum and different solvents.**

Solvents	Vacuum	Hexane	Octanol
HOMO (eV)	-6.7546	-6.8779	-6.9951
LUMO (eV)	-0.4808	-0.5614	-0.6392
Energy band gap (E_g)	6.2738	6.3165	6.3559
Ionization potential (I)	6.7546	6.8779	6.9951
Electron affinity (A)	0.4808	0.5614	0.6392
Electro negativity (χ)	3.6177	3.7196	3.8172
Chemical hardness (η)	3.1369	3.1582	3.1780
Chemical potential (μ)	-3.6177	-3.7196	-3.8172
Chemical Softness (s)	1.5684	1.5791	1.5890
Global Electrophilicity (ω)	20.5274	21.8479	23.1526

4.5 Molecular Electrostatic Potential of 2Cl5,6Dm3MsQ Molecule
In 2Cl5,6Dm3MsQ molecule, contour values are in the range of -1.2235 to 1.2235 eV in vacuum shown in Figure Error! No text of specified style in document.. The negative charge distribution (red) region of 2Cl5,6Dm3MsQ is mainly distributed around 11N and 12N and which is surrounded with yellow colour represents that, they can easily be attacked by nucleophiles, making them electron accepter. Hydrogen atoms attached to the benzene ring (7H, 8H) and dimethyl groups (21H, 22H, 23H, 24H, 25H and 26H) of the molecule bear the maximum positive charge (blue region), hence

they are susceptible to attacks by electrophiles and can loss charges, making them electron donors. The neutral (green) region is spread more on the sites of carbon atoms of benzene ring structure (1C, 2C, 3C, 4C, 5C and 6C), methyl group (15C) joined to sulphanyl compound and near chlorine atomic position (10Cl). MEP helps in understanding of molecular parameters like charge density, polarity of the molecule, electrophilic and nucliophilic atomic positions of quinoxaline derivatives by using the color code.
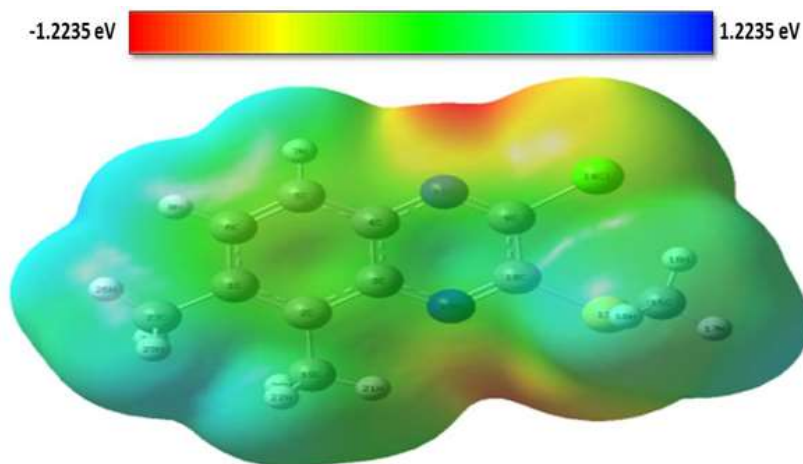
Figure Error! No text of specified style in document.. **Molecular electrostatic potential mapping of 2Cl5,6Dm3MsQmolecule in vacuum**

4.6 CIE Chromaticity of 2Cl5,6Dm3MsQ Molecule

The colour coordinates (x, y) of 2Cl5,6Dm3MsQ molecule calculated by using the emission spectrum in different solvents were presented in Figure.4 which were located in deep blue region. The x coordinate value of the molecule vary from 0.1408 to 0.148 and y coordinate ranges from 0.06 to 0.07 with correlated temperature of 5928 to 5947 K. the error value of Du'v. The colour rendering index is about 98 % for this molecule.
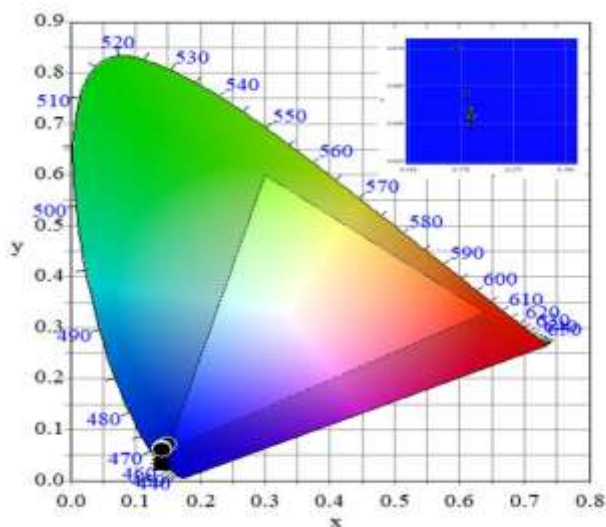
Figure.4: CIE Plot for 2Cl5,6Dm3MsQ in all studied solvents.

5.   Discussion

 The 2Cl5,6Dm3MsQ molecule acts differently in vacuum, alkane medium of hexane and alcohol medium of octonal. it shows that, the band gap between different molecular orbital (HOMO to LUMO) is increases with solvent polarity. In vaccume of Energy gap is 6.416 eV, hexane is 6.2716 eV and in octonal is 6.3213 eV. The optoelectronic properties like ionization potential (I), global

electrophilicity(ω), chemical hardness (η), chemical softness (s), electron affinity (E),chemical potential (μ), were also increases with increase in polarity of the medium. MEP helps in understanding of molecular parameters and nucliophilic atomic positions by using the color code and stability of the molecule.

.

Refrences

1. P. B. Devaraja *et al.*, "Spectroscopic and photoluminescence properties of MgO : Cr 3 + nanosheets for WLEDs," *Displays*, 2015, doi: 10.1016/j.displa.2015.10.006..

2. I Sıdır and Y. G. Sıdır, "Solvatochromism and intramolecular hydrogen-bonding assisted dipole moment of phenyl 1-hydroxy-2-naphthoate in the ground and excited states," *J. Mol. Liq.*, vol. 221, pp. 972–985, 2016, doi: 10.1016/j.molliq.2016.06.019.

3. J M. Chem, Y. Jay, and T. J. Chow, "Journal of Materials Chemistry," pp. 3091–3099, 2011, doi: 10.1039/c0jm03109g.

4. A. Manuscript, "Materials Chemistry C," 2016, doi: 10.1039/C6TC00480F.

5. "Gaussview/Gaussian Guide and Exercise Manual.".

6. M S. Mehata, A. K. Singh, and R. K. Sinha, "Experimental and theoretical study of hydroxyquinolines: hydroxyl group position dependent dipole moment and charge-separation in the photoexcited state leading to fluorescence," *Methods Appl. Fluoresc.*, vol. 4, no. 4, p. 045004, Nov. 2016, doi: 10.1088/2050-6120/4/4/045004.

7. B. F. Minaev *et al.*, "Computational and Experimental Investigation of the Optical Properties of the Chromene Dyes," *J. Phys. Chem. A*, vol. 119, no. 10, pp. 1948–1956, 2015, doi: 10.1021/acs.jpca.5b00394.

8. B. F. Minaev *et al.*, "Computational and Experimental Investigation of the Optical Properties of the Chromene Dyes," *J. Phys. Chem. A*, vol. 119, no. 10, pp. 1948–1956, 2015, doi: 10.1021/acs.jpca.5b00394.

9. S A. El-Daly *et al.*, "Photophysical parameters and laser activity of 3(4-dimethylamino-phenyl)-1- (2, 5-dimethyl-thiophen-3-yl)-propenone (DDTP): A new potential laser dye," *Opt. Laser Technol.*, vol. 45, no. 1, pp. 605–612, 2013, doi: 10.1016/j.optlastec.2012.05.024.

10. Warde and N. Sekar, "NLOphoric mono-azo dyes with negative solvatochromism and in-built ESIPT unit from ethyl 1,3-dihydroxy-2-naphthoate: Estimation of excited state dipole moment and pH study," *Dye. Pigment.*, vol. 137, pp. 384–394, 2017, doi: 10.1016/j.dyepig.2016.10.032.

11. G N. Sushma and Y. F. Nadaf, "Computational Studies , Molecular Orbital and Thermodynamic Analysis of 9-Chloro-1 , 2- Dimethyl-10 (Methylsulfanyl) Quinoxaline," vol. XX, pp. 1–13, 2022.

12. G. N. Sushma, M. Suma, A. G. Pramod, and Y. F. Nadaf, "Structural , thermal , chemical and optoelectronic properties of the quinoxaline with DFT Structural , Thermal , Chemical and Optoelectronic Properties of the Quinoxaline with DFT," vol. 130027, no. May, 2020.

13. Abbaz, A. Bendjeddou, and D. Villemin, "theoretical investigations on molecular structure, homo, lumo, nbo analysis and hyperpolarizability calculations of mono and extended-tetrathiafulvalenes (mono/ex-ttfs)," 2018.

14. G N. Sushma, M. Suma, and Y. F. Nadaf, "Quantum chemical and photophysical properties of 9-Chloro 2, 6-Dimethyl 10(Methylsulfanyl)Quinoxaline," *Mater. Today Proc.*, 2022, doi: https://doi.org/10.1016/j.matpr.2022.02.502.

15. A G. Pramod, C. G. Renuka, and Y. F. Nadaf, "Electronic Structure, Optical Properties and Quantum Chemical Investigation on Synthesized Coumarin Derivative in Liquid Media for Optoelectronic Devices," *J. Fluoresc.*, vol. 29, no. 4, pp. 953–968, 2019, doi: 10.1007/s10895-019-02409-w.