



Coumarinyl(thienyl)thiazole Molecules as Fluorescent Photoswitches

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Light sensitive coumarinyl(thienyl)thiazole derivatives exhibiting photochromism and fluorescence were synthesized, characterized and their behavior was investigated theoretically using density functional theory (DFT). In presence of UV light, the molecules switch to the bridged cyclic isomeric form and on irradiation with visible light, they revert back to their original molecular form. These molecules are sensitive to both UV and visible light, and switch themselves between open ring isomers and closed ring isomers. The photo-regulated-switching energy (ΔE) from open to closed isomeric form is approximately 6.3 kcal/mol. All the synthesized derivatives exhibit fluorescence only in their open form. Theoretical data is compared with the experimental data and both show similar results.

Keywords: Coumarinyl(thienyl)thiazoles, Fluorescence, Photochromism, Density functional theory.

INTRODUCTION

The photochromic molecules received greater attention due to their varied benefits, ranging from medicinal importance to various potential applications such as molecular level switches, optical memory display devices and photochromic fluorescent proteins [1-5]. In general, upon irradiation with ultraviolet light, the open dihetarylethene conformer undergoes photocyclization reaction to the closed form while the closed ring isomer absorbs in the visible region and returns to the initial open form. Switching between the two isomers can result in the structural changes and hence in the fundamental change of molecular electronic properties [6-8].

Of all the molecules, dihetarylethenes are considered the best molecular switching devices because of their high thermal dual stability, excellent fatigue resistance and easily detectable forms. Due to this reason, many fused aromatic and heterocyclic ring systems are synthesized and the photochromic properties of diaryl / diheteroarylethene derivatives are extensively explored.

Continuous efforts are being made to identify new heterocyclic compounds with potential photochromic activity to meet various social needs. Literature reveals that a fusion of coumarin ring and thiazole with dieny system had enhanced functionality and exhibited both photochromic and fluorescent behaviour

[9-18]. The fluorescence behaviour and photochromic nature of coumarinyl(thienyl)thiazoles [19,20], prompted us to synthesize a series of 3-(4-(thiophen-3-yl)-2-(arylamino)thiazol-5-yl)-2H-chromen-2-ones as photoswitches.

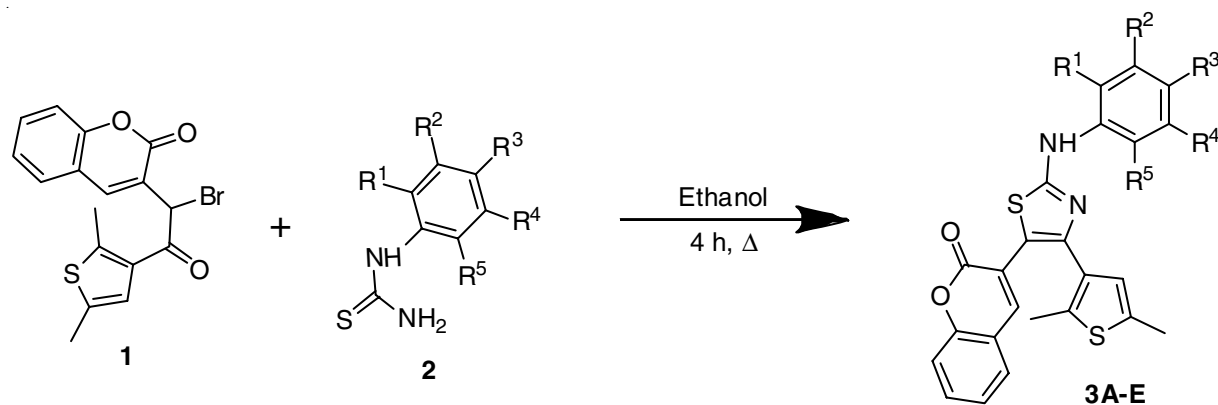
EXPERIMENTAL

Melting points were measured in open capillary tubes and uncorrected. ¹H NMR spectra were taken using Bruker-Avance (400 MHz) Spectrometer with TMS as an internal standard and DMSO-*d*₆ as solvent. ¹³C NMR spectra were collected using the same instruments at 100 MHz. The EI-MS mass spectra were measured on a Q-TOF mass spectrometer. Purity of the compounds was tested by TLC on silica gel plates.

Synthesis: A mixture of 0.25 mmol bromoketone (1) and 0.3 mmol thioamide (2) were dissolved in ethanol (25 mL) and refluxed for 4 h. It was cooled and then transferred into 2% K₂CO₃ solution. The residue was then filtered and recrystallized using ethanol to get the coumarinyl(thienyl)thiazole derivatives (3A-3E) (Scheme-I).

Spectral data

3-(2-((2,4-Difluorophenyl)amino)-4-(2,5-dimethylthiophen-3-yl)thiazol-5-yl)-2H-chromen-2-one (3A): Yield: 84%, m.p.: 165-167 °C; IR (KBr, ν_{\max} , cm⁻¹): 3313, 2916, 1708; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.07 (s, 3H), 2.32



3A: R₁ = F, R₂ = H, R₃ = F, R₄ = H, R₅ = H; **3B:** R₁ = CH₃, R₂ = H, R₃ = H, R₄ = F, R₅ = H; **3C:** R₁ = Cl, R₂ = H, R₃ = Cl, R₄ = H, R₅ = Cl; **3D:** R₁ = H, R₂ = CF₃, R₃ = H, R₄ = CF₃, R₅ = H; **3E:** R₁ = CH₃, R₂ = H, R₃ = CH₃, R₄ = H, R₅ = CH₃

Scheme-I: Pathway towards synthesis of coumarinyl(thienyl)thiazoles (**3A-E**)

(s, 3H), 6.71 (s, 1H), 7.01-7.12 (m, 3H), 7.16-7.25 (m, 2H), 7.26-7.50 (m, 3H), 9.01 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 15.1, 17.2, 121.2, 124.2, 126.1, 128.1, 128.8, 131.2, 133.3, 136.1, 140.1, 141.2, 144.8, 148.1, 149.8, 153.0, 155.1, 159.0, 162.1, 163.2, 165.1, 169.3; EIMS 70 eV, *m/z*: 466 [M]⁺.

3-(4-(2,5-Dimethylthiophen-3-yl)-2-((5-fluoro-2-methylphenyl)amino)thiazol-5-yl)-2H-chromen-2-one (3B): Yield: 87%, m.p.: 169-171 °C; IR (KBr, *v*_{max}, cm⁻¹): 3034, 2916, 1718; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 1.85 (s, 3H), 2.08 (s, 3H), 2.23 (s, 3H), 6.52 (s, 1H), 6.70-6.72 (m, 3H), 6.77-6.81 (m, 2H), 6.86-7.29 (m, 3H), 8.92 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 15.0, 18.3, 19.1, 122.9, 124.7, 127.6, 128.1, 130.5, 132.1, 137.5, 140.9, 141.7, 144.9, 148.1, 149.3, 152.8, 156.1, 162.1, 165.8, 169.1; EIMS 70 eV, *m/z*: 463 [M]⁺.

3-(4-(2,5-Dimethylthiophen-3-yl)-2-((2,4,6-trichlorophenyl)amino)thiazol-5-yl)-2H-chromen-2-one (3C): Yield: 81%; m.p.: 173-175 °C; IR (KBr, *v*_{max}, cm⁻¹): 3151, 2914, 1720; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.01 (s, 3H), 2.25 (s, 3H), 6.37 (s, 1H), 6.62-6.69 (m, 2H), 6.75-6.81 (m, 2H), 6.92-7.07 (m, 3H), 8.88 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 14.9, 17.8, 113.9, 128.1, 128.9, 130.1, 132.8, 132.9, 136.2, 140.7, 141.8, 145.1, 147.3, 151.8, 154.3, 157.7, 161.1, 63.9, 169.8; EIMS 70 eV, *m/z*: 533 [M]⁺.

3-(2-((3,5-bis(Trifluoromethyl)phenyl)amino)-4-(2,5-dimethylthiophen-3-yl)thiazol-5-yl)-2H-chromen-2-one (3D): Yield: 79%, m.p.: 176-178 °C; IR (KBr, *v*_{max}, cm⁻¹): 3305, 2910, 1718; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.08 (s, 3H), 2.20 (s, 3H), 6.69 (s, 1H), 6.98-7.02 (m, 3H), 7.11-7.22 (m, 2H), 7.25-7.41 (m, 3H), 9.25 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 13.8, 16.7, 125.7, 126.9, 128.1, 129.2, 130.1, 131.8, 134.9, 137.8, 141.2, 145.6, 147.4, 149.8, 152.7, 156.2, 158.1, 159.2, 160.5, 161.9, 163.1, 163.2, 168.1; EIMS 70 eV, *m/z*: 567 [M]⁺.

3-(4-(2,5-Dimethylthiophen-3-yl)-2-(mesitylamino)thiazol-5-yl)-2H-chromen-2-one (3E): Yield: 75%, m.p.: 169-171 °C; IR (KBr, *v*_{max}, cm⁻¹): 3147, 2914, 1718; ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 1.62-1.98 (m, 9H), 2.05 (s, 3H), 2.25 (s, 3H), 6.47 (s, 1H), 6.73-6.75 (m, 2H), 6.77-6.81 (m, 2H), 6.84-7.01 (m, 3H), 8.92 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 13.5, 14.9, 17.8, 19.4, 21.8, 128.1, 129.2, 130.1, 132.9,

133.1, 137.1, 141.1, 142.2, 144.7, 148.8, 149.9, 152.3, 156.1, 162.3, 169.8; EIMS 70 eV, *m/z*: 473 [M]⁺.

DFT studies: Density functional theory (DFT) B3LYP method with 6-31G basis set in Gaussian software was employed to assess and explore molecular and electronic structures of coumarinyl(3-thienyl)thiazole derivatives.

RESULTS AND DISCUSSION

The photoinduced isomerization brings the remarkable changes in the physico-chemical properties of both isomers (Fig. 1). The UV-visible and fluorescence studies were performed for all the synthesized coumarinyl(3-thienyl)thiazole derivatives and their photochromic behaviour was explored. It was observed that the closed isomer modulated by light showed a decrease in absorbance maxima, fluorescence and dipole moment when compared to that of its open form. The photo-isomerization of the open form of coumarinyl(thienyl)thiazoles lead to fluorescence quenching due to intramolecular energy transfer which in turn resulted in structural changes of coumarin moiety.

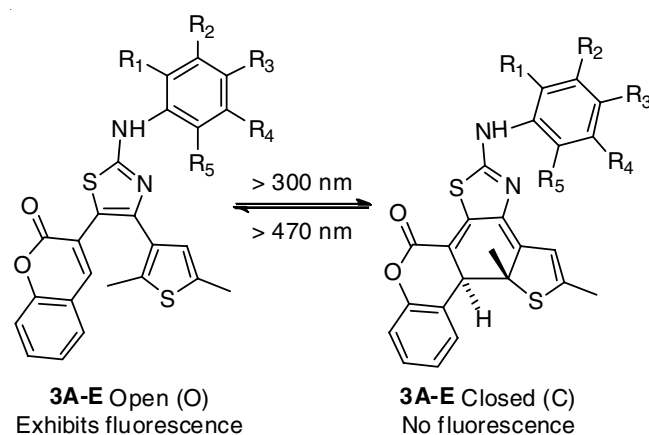
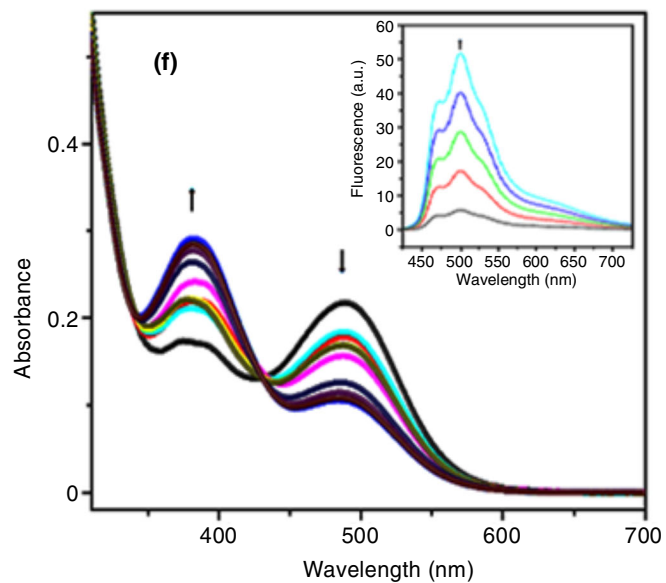
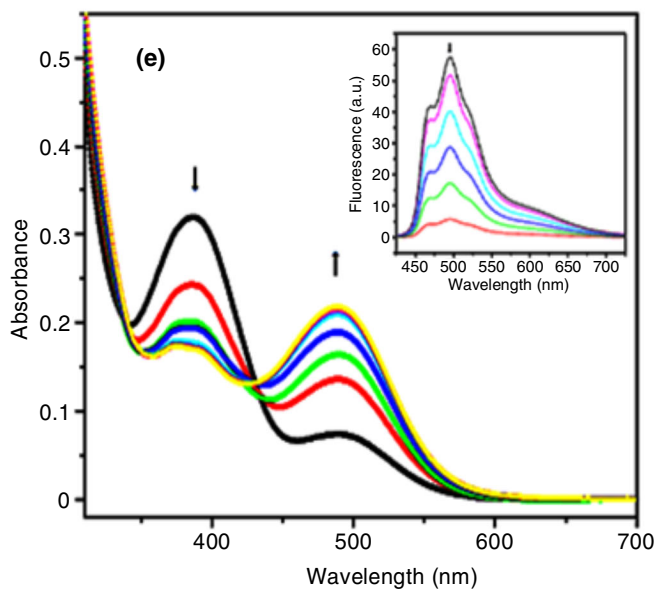
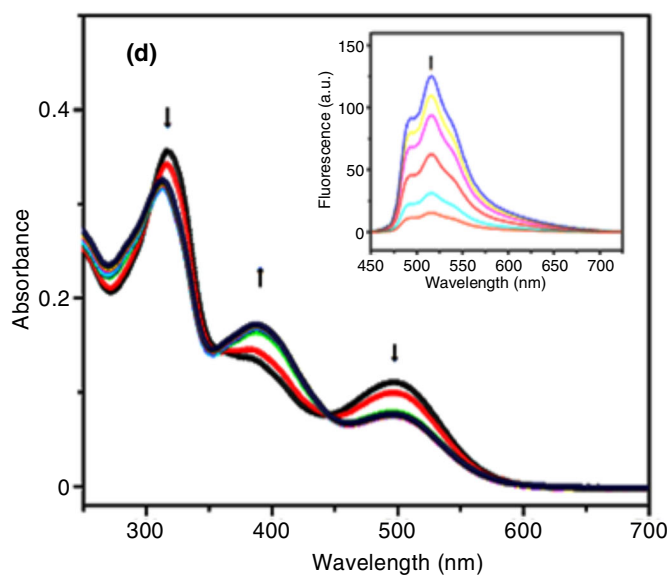
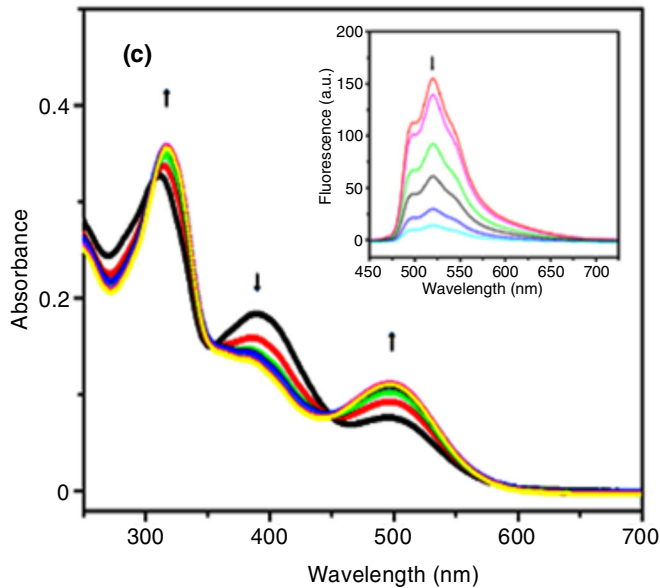
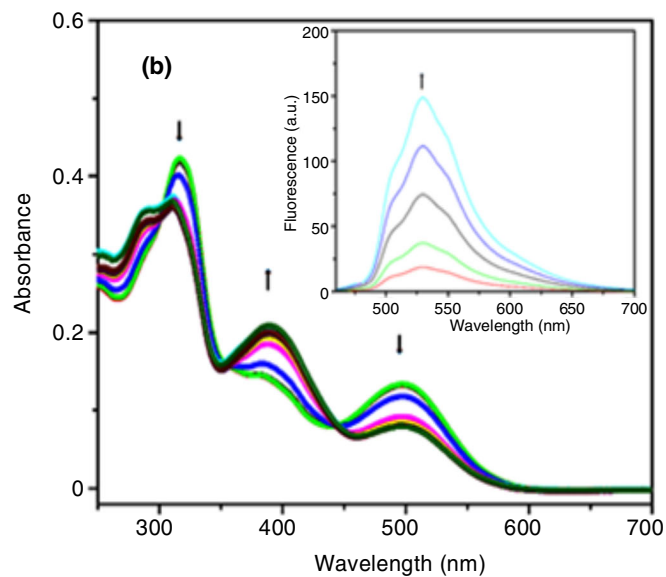
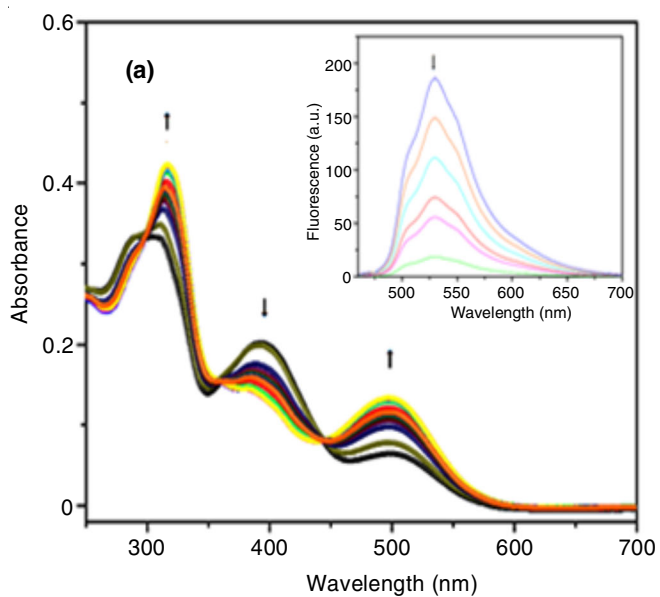


Fig. 1. Photoinduced isomerization of coumarinyl(thienyl)thiazoles (**3A-E**)

The UV-visible spectrum for coumarinyl(thienyl)thiazole derivatives was taken using acetonitrile solvent (Fig. 2). When sample solutions of the derivatives **3A-E**, were irradiated with



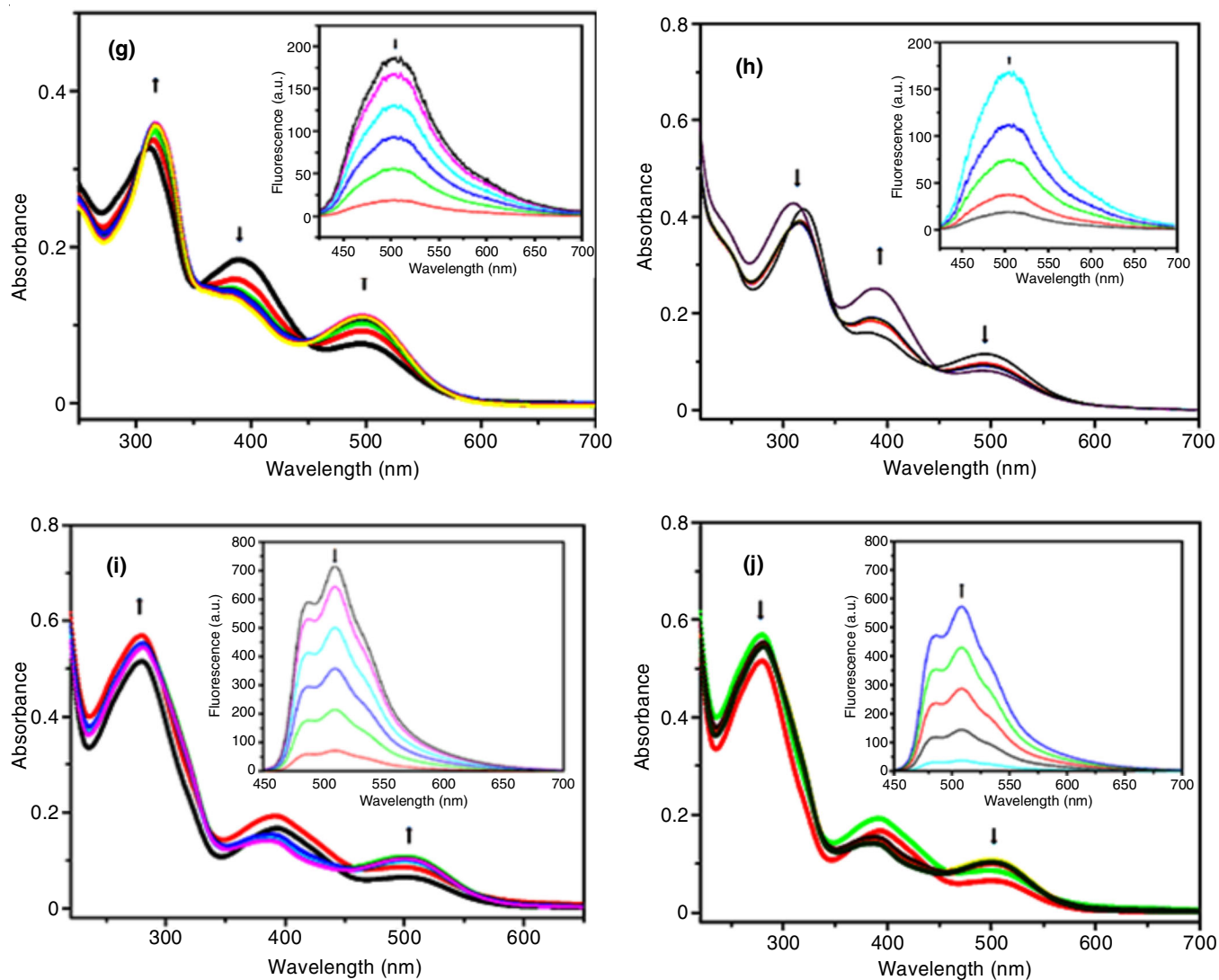


Fig. 2. UV Visible absorption spectrum of **3A(O)** (a); **3A(C)** (b); **3B(O)** (c); **3B(C)** (d); **3C(O)** (e); **3C(C)** (f); **3D(O)** (g); **3D(C)** (h); **3E(O)** (i); and **3E(C)** (j) in CH_3CN (0.2×10^{-6} M at $T = 293$ K), before (line 1) and lines 2-6 (with a time interval of 3 s) irradiation at 365 nm UV light. Inset picture shows fluorescence spectrum

Hg-Xe lamp the open form spectra was characterized by an absorption band from 383-394 nm.

The photoisomerization of molecule **3A** from open(O) form to closed(C) form and its absorption and fluorescence spectra are presented in Fig. 2a and Fig. 2b, respectively. The UV-visible spectrum obtained when molecule **3A(O)** was irradiated with wavelength 365 nm at different time intervals is shown in Fig. 2a. It explains about the disappearance of absorption maxima at 394 nm and decrease in intensity with an increase in time of radiation.

In Fig. 2a, the reappearance of another band is noted at 500 nm for the closed isomeric form whose maxima increases with the increase in exposure time of **3A**. The UV-visible spectrum of **3A(C)**, at different time intervals when exposed to monochromatic light of more than 470 nm is shown in Fig. 2b. The figure states that for the closed form, the absorption band at 500 nm disappeared and a new band of isomer **3A(O)** appeared at 394 nm. A gradual increase in intensity of the band along with a gradual increase in the exposure time was also observed (Fig. 2b).

Emission spectral characteristic features of both isomeric forms of dihetarylethenes were also studied in acetonitrile solutions at 293 K using Jasco spectrofluorometer. Fluorescence spectra of compound **3A(O)** is displayed in the inset of Fig. 2a. The spectra revealed that with the increased time of irradiation of **3A(O)** with UV light of wavelength 365 nm, the concentration of the cyclic form at 527 nm increases, resulting in decrease of fluorescence intensity.

The fluorescence quenching (inset Fig. 2a) was due to the molecular energy transfer in the transition state of photocyclization and structural changes that occurred in the coumarin moiety. Similarly, the fluorescence spectra of compound **3A(C)** is displayed in inset Fig. 2b. An increase in intensity of fluorescence of **3A(C)** with increase in time of irradiation of visible light is noted in the inset. This increase in fluorescence intensity at the same $\lambda_{\text{max}}^{\text{fl}}$ of around 527 nm is due to cycloreversal to the open form. Fluorescence quantum yields in the range 0.004-0.005 are noted for all the synthesized dihetarylethene molecules (**3A-3E**) [20-25].

The extended conjugation length due to the aryl groups decrease the antibonding character of central photogenerated carbon-carbon bond resulting in a decrease of quantum yield values. These fluorescent single molecule switches possess the remarkable fatigue resistance. They are thermally stable, so they don't interconvert in large temperature ranges. Their detectable high coloration sensitivity makes them to be used as colorimetric chemo sensors [26].

DFT studies: The molecules were built using Gaussview 5.0.8 and the geometries were optimized. Gaussian 09 package [27] was employed to perform density functional theory (DFT) calculations using B3LYP/6-31G(d,p) functional. The hybrid functional B3LYP, was chosen due to its computational cost and accuracy of results [28].

Single point energy values were computed for the stable molecular geometries. The absorption maxima $\lambda_{\text{abs}}^{\text{max}}$, oscillator strengths, frontier molecular orbital data and dipole moment values were obtained using TD-DFT (time dependent density functional theory) method. The molecular stability and chemical reactivity of dihetarylethenes were analyzed from HOMO and LUMO energy gaps and ionization energies.

The molecular orbital energy diagrams of 3A(O) and 3A(C) (Fig. 3) disclosed that the delocalization of electron density is greater for open isomer than the closed form. This is also reflected from relatively low energy values of the open form when compared to that of the closed one, indicating the stability of the open form isomer (Table-1). The data state that the photoinduced switching $\Delta E_{\text{OPEN} \rightarrow \text{CLOSED}}$ is of the order of ~ 6.3 kcal/mol when compared to $\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$, which is of the order of ~ 70 kcal/mol.

The molecular orbital energy data from DFT calculations is shown in Table-2. The HOMO value with a negative sign is the ionization energy (IE) and LUMO value is the electron affinity (EA). The ionization energy and electron affinity of coumarinyl(thienyl)thiazoles in open form are of the order of 5 eV and 2.3 eV, respectively. The $\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$ gap of each of the photochromic isomers is of the order of ~ 3 eV. This energy barrier can result in variable functionality leading to potential applications of the molecular switches [29-31].

The DFT studies infer that the dipole moment of the closed isomeric form is larger than that of the open form and with increase in electronegativity of the substituent, an increase in

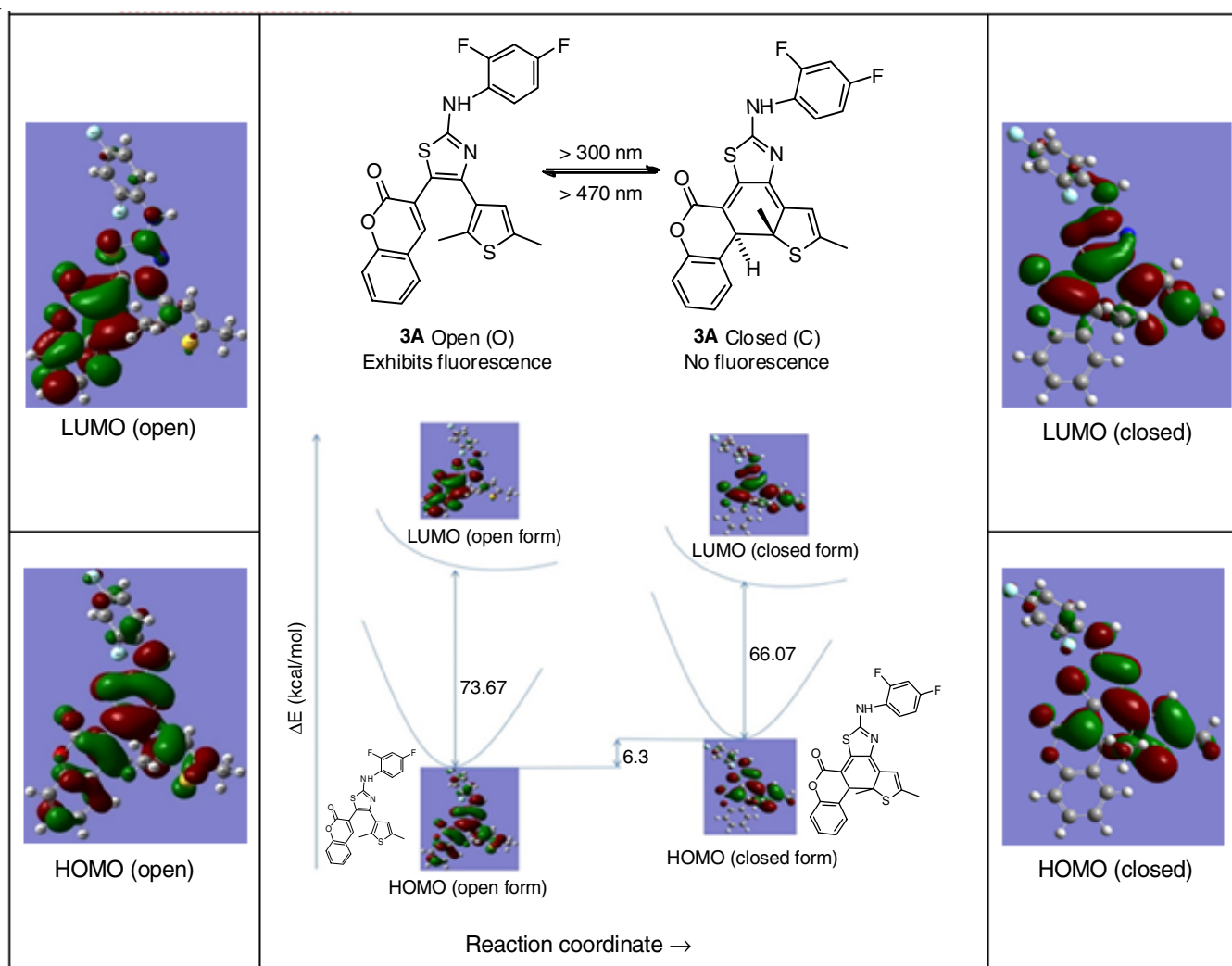


Fig. 3. HOMO and LUMO molecular orbital energy diagrams of 3A and a schematic representation of potential energy (E, kcal/mol) against reaction coordinate (arbitrary units) of the photoisomerization of 3A (open to closed form)

TABLE-1
 $\Delta E_{\text{OPEN} \rightarrow \text{CLOSED}}$ (PHOTOISOMERIZATION) AND $\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$ CALCULATIONS (kcal/mol) FOR OPEN (O)
 AND CLOSED (C) ISOMERIC FORMS OF **3A-E** USING DFT B3LYP/6-31G(d,p) METHOD

Molecule	Total energy (a.u.) (open form)	Total energy (a.u.) (closed form)	$\Delta E_{\text{OPEN} \rightarrow \text{CLOSED}}$ (kcal/mol)	$\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$ (kcal/mol)	
				Open	Closed
3A	-2179.77	-2179.76	6.27	73.67	66.07
3B	-2119.87	-2119.86	6.27	72.10	64.94
3C	-3360.06	-3360.05	6.27	74.83	66.20
3D	-2655.27	-2655.26	7.53	74.63	64.98
3E	-2099.27	-2099.26	6.30	82.26	65.64

TABLE-2
 IONIZATION ENERGY (IE), ELECTRON AFFINITY (EA), DIPOLE MOMENTS OF THE
 DIHETARYLETHENES (**A-E**) OF OPEN (O) AND CLOSED (C) ISOMERIC FORMS USING DFT METHOD

Molecule	Open (O)			Closed (C)			Dipole moment (Debye)	
	IE = $-E_{\text{HOMO}}$ (eV)	EA = E_{LUMO} (eV)	$\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$	IE = $-E_{\text{HOMO}}$ (eV)	EA = E_{LUMO} (eV)	$\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$	Open (O)	Closed (C)
3A	5.42	2.22	3.20	5.25	2.38	2.87	3.99	6.42
3B	5.41	2.28	3.13	5.26	2.44	2.82	5.23	7.50
3C	5.55	2.31	3.24	5.33	2.46	2.87	4.29	5.35
3D	5.77	2.53	3.24	5.56	2.74	2.82	8.35	8.75
3E	5.49	1.92	3.56	5.09	2.24	2.85	4.14	5.11

TABLE-3
 ABSORPTION AND FLUORESCENCE SPECTRAL DATA IN ACETONITRILE SOLUTIONS
 AT 293 K AND COMPUTED DFT DATA OF THE OPEN AND CLOSED FORMS **3A-E**

Molecules	Open form (O) $\lambda_{\text{abs}}^{\text{max}}$, nm (Oscillator strength)		Closed form (C) $\lambda_{\text{abs}}^{\text{max}}$, nm (Oscillator strength)		Fluorescence $\lambda_{\text{fl}}^{\text{max}}$, nm (Oscillator strength)
	Experiment	DFT	Experiment	DFT	
3A	394 (0.34)	372 (0.13)	500 (0.13)	459 (0.22)	527 (192)
3B	383 (0.18)	392 (0.11)	498 (0.10)	503 (0.15)	521 (162)
3C	388 (0.32)	400 (0.11)	488 (0.21)	516 (0.23)	498 (58)
3D	388 (0.21)	373 (0.24)	492 (0.11)	480 (0.25)	513 (179)
3E	392 (0.48)	412 (0.11)	502 (0.10)	482 (0.21)	515 (708)

dipole moment is observed. Insertion of $-\text{CF}_3$ polarizes the molecule more and hence large dipole moment ~ 8 D is observed. The symmetrical 2,4,6-phenyl substituted coumarinyl(thienyl)-thiazoles **3C** and **3E** have their resultant dipole moment values low, unlike the unsymmetrical forms **3A**, **3B** and **3D**.

Absorption and fluorescence spectral data of theory and experiment of the photoinduced cyclization of the open and closed isomeric forms of **3A-3E** are displayed in Table-3. The theoretical absorption maxima $\lambda_{\text{abs}}^{\text{max}}$ of coumarinyl(thienyl)-thiazoles derivatives (**3A-3E**) are comparable with that of the experimental values.

A careful investigation throws light on the fact that the presence of electron donating groups on R_3 position shows remarkable fluorescence with high intensity and substitution at other positions show no significant change. For 2,4,6-methyl substituted phenyl (**3E**), a highly intense fluorescence absorption can be attributed to the electron donating nature of methyl groups.

Conclusion

The synthesized coumarinyl(thienyl)thiazole derivatives (**3A-3E**) exhibit fluorescence and behave as molecular photo-

switches. These photofluoric molecular switches cyclize with UV light and undergo cycloreversion with the visible light. Thus, introduction of coumarin moiety and also a judicious substitution of electron donating groups at *para*-position in dihetarylthiazoles can have a remarkable fluorescence increase of the open isomeric form. In these new photomodulated fluorophores, electron donating groups provide more stability than electron withdrawing groups. The $\Delta E_{\text{HOMO} \rightarrow \text{LUMO}}$ gap of each of the photochromic isomers is of the order of 3 eV, the band gap similar to that of ZnO and other semiconductors used in the optoelectronics. A blend of photochromic organic molecules with semiconductors can induce charge transport and can result in better molecular switches, leading to potential applications. The structural modification, the viability of light-controlled energy-level manipulation at various interfaces in photoswitchable optoelectronic devices may be further investigated for these coumarinyl(thienyl)thiazoles.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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