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ORIGINAL PAPER

2-Methyl-4-oxo-*N*-(4-oxo-2-phenyl substituted-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamides—A New Range of Fluorescent Whiteners: Synthesis and Photophysical Characterization

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Abstract Fluorescent quinazolinones were synthesized form ethyl 2-methyl-4-oxo-3,4-dihydroquinazoline −5-carboxylate intermediate. The photophysical properties of the compounds were evaluated in DMF solvent. The experimental absorption and emission of the compounds were compared with the vertical excitation and emission obtained Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) computation. Application of the fluorescent compounds as a fluorescent brightening agent was tested on polyester fiber. Changes in the electronic transition, energy levels, and orbital diagrams of quinazolin-4(3*H*)-one analogues were investigated using the DFT computations and were correlated with the experimental spectral data. The experimental absorption and emission wavelengths are in good agreement with those predicted using the DFT and TD-DFT.

Keywords Quinazoline · DFT · TD-DFT · Absorption · Emission · Photophysical properties

Introduction

A large number of alkaloids contain quinazolinone nucleus and they are known to have biological activities [1]. In addition to pharmaceutical applications, quinazolinone derivatives are widely used as coloring materials in dyestuff industry [2, 3]. The azo colorants based on quinazolinone have industrial importance [3, 4]. The substituted quinazolinone are reported as fluorescent compounds for different applications [5–10]. Quinazolinone derivatives are known to be fluorescent brightening agents [2, 3, 8]. Optical whiteners are characterized by a strong absorption below 400 nm with well separated intense emission beyond 400 nm [11]. The optical bleaching agents are chemicals that increase the whiteness when applied on the natural and synthetic textile materials [12]. The surface of textile materials therefore appear whiter to the human eye [13]. Fluorescent brighteners are substances which normally have a system of conjugated double bonds and electron-donating groups to show high fluorescence [14, 15].

Fluorescent brightening agents (FBAs) are used in textile industry to enhance the whiteness and brightness of textile substrates; they also significantly increase the UV-blocking properties of the medium to which they are applied [16, 17]. They are also used in pulp and paper industries for the improvement of brightness [18]. In addition to the above mentioned applications they are also used in pH chemosensing materials [19], chemosensors [20], photo-induced electron transfer sensors [21], light emitting diodes [22], biological staining [23] and polyurethane fluorescent brightener dispersions [24].

Fluorescent whitening agents are derivatives of triazine [25], stilbene [26], pyrazole [27], naphthalimide [28], quinoline [29], iso-quinoline [30], quinoxaline [31], oxadiazole [32], triazole [33], benzoxazole [34], benzotriazole [35] and tinopol-CBX [36] based compounds. The fluorescent quinazolinone are also reported as fluorescent brightening agents for polyester fibers [2, 3]. A fluorescent brightener should present a high quality of whiteness and fastness. However, as the fluorescent brightener is exposed to the sunlight, its whiteness is diminished [3]. This happens because the

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chemical structure of fluorescent brightener is destroyed by the autoxidation from free radical generated from the sunlight [3]. Fluorescent whiteners with enhanced chemical, thermal and photostability are needed today for high performance textile substrates.

Reported quinazolinone derivatives are 2 and 6-substituted in which the electron donor is at the 2-position and the acceptor at the 6- position [2, 3]. A study of the literature reveals that, electron donor substitution at the 2-position along with an acceptor at the 6-position gives red shifted absorption and hence red shifted emission, because such a substitution pattern leads to an effective donor acceptor chromophore [9]. To achieve blue shifted emission it is necessary to reduce the donor strength.

In this paper, attempts have been made to synthesize fluorescent quinazolinone thiazolidines. The synthesized quinazolinone derivatives contain electron donor at the 2-position and an acceptor at the 5-position. The photophysical properties like absorption, emission and quantum yields of the compounds were recorded in the solvent dimethylformamide (DMF). Fluorescent compounds were used for whitening polyester fiber for optical brightening study. The changes in the electronic transition, energy levels, and orbital diagrams of the quinazolinone derivatives were studied by TD-DFT computation. The computational results were correlated with the experimental photophysical properties.

Methodology

Materials and Methods

All the commercial reagents and solvents were purchased from S. D. Fine Chemicals Pvt. Ltd. and they were used without purification and all the solvents were of spectroscopic grade. The absorption spectra of the dyes were recorded on a Spectronic Genesys 2 UV-Visible spectrophotometer, and emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer using freshly prepared solutions in solvents of different polarities at the concentration of 1×10^{-6} mol L^{-1}. The excitation wavelength used for the fluorescence measurements was absorption maxima of the compounds in respective solvents. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. ^{1}H NMR spectra were recorded on VXR 400 MHz instrument using TMS as an internal standard. Mass spectra were recorded on Finnigan mass spectrometer.

Computational Methods

The ground state geometries of the compounds **7a–7e** in their C_1 symmetry were optimized using the tight criteria in the gas phase using (DFT) [37]. The functional used in this study was B3LYP [38, 39]. The basis set used for all atoms was 6-31G(d) [40–42]. The vibrational frequencies of the optimized structures were computed using the same method to verify that the optimized structures correspond to local minima on the potential energy surface. The vertical excitation energies at the ground-state equilibrium geometries were calculated with TD-DFT [43–45]. The low-lying first singlet excited state (S_1) of each tautomer was relaxed using the TD-DFT to obtain its minimum energy geometry. The difference between the energies of the optimized geometries in the first singlet excited state and the ground state was used in computing the emissions [46–52]. All electronic structure computations were carried out using the Gaussian 09 program [53].

Relative Quantum Yield Calculations

The quantum yields of compounds **7a**–**7e** in DMF were evaluated. Anthracene was used as the standard. Quantum yields were calculated using the comparative method [54, 55]. The absorption and emission characteristics of the standards and for the compounds in polar solvents were measured at different concentrations (1, 2, 3, 4, and 5 ppm level). The emission intensity values were plotted against absorbance values and linear plots were obtained. The gradients were calculated for the compounds in each solvent and for the standards. All the measurements were done by keeping the parameters such as solvent and slit width constant. The relative quantum yields of the synthesized compounds in different solvents were calculated by using the Eq. 1 [54, 55].

$$\phi_x = \Phi_{st} \times \frac{Grad_x}{Grad_{st}} \times \frac{\eta_x^2}{\eta_{st}^2} \tag{1}$$

Where:

Φ_x	Quantum yield of compound
Φ_{st}	Quantum yield of standard sample
$Grad_x$	Gradient of compound
$Grad_{st}$	Gradient of standard sample
η_x	Refractive index of solvent used for synthesized compound
η_{st}	Refractive index of solvent used for standard sample

General Procedure of Dyeing

Dyeing of polyester fabric was carried out using high temperature high pressure method in Rossari Labtech Flexi Dyer dyeing machine at a material to liquor ratio of 1:20. 2 %

Fluorescent compounds were used for the dying (calculated on weight of the fabric). All the synthesized fluorescent compounds are having less solubility in water. Initially the compounds were dissolved in 5 mL DMF and diluted with 15 mL buffered solution of pH 5 made by using sodium acetate and acetic acid in water. The mixture was ultrasonicated for 15 min to obtain a fine dispersion. Metamol was used as a dispersant. The polyester fabric was dyed using the above solution and metamol as the dispersing agent. The dye bath temperature was raised at a rate of 3 °C min^{-1} to 130 °C, maintained at this temperature for 60 min, and rapidly cooled to room temperature as shown in Fig. 1. The dyed fabrics were rinsed with cold water and allowed to dry in the open air.

Experimental

Synthesis Details

Ethyl 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate 4

The intermediate **4** was prepared according to the known procedure [56].

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide 5

Ethyl-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate (5 g) on reaction with hydrazine hydrate (15 mL) for 2 h under reflux condition gave 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5**.

Yield: 89 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.20 (s, 3H), 5.26 (s, 2H), 7.72 (d, 1H, *J*=22.00 Hz), 7.79 (d, 1H, *J*=6.7 Hz), 7.82 (dd, 1H, *J*=22.00, 6.7 Hz).

FT-IR (KBr): 3165, 3103, 2981, 2917, 2871, 1665, 1607, 1562, 1478, 1383, 1325, 1261, 1193, 1158, 1103, 1041, 843, 788, 721, 663 cm^{-1}.

2-Methyl-4-oxo-N′-[(Z)-phenylmethylidene] -3,4-dihydroquinazoline-5-carbohydrazide 6a

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** (1 g, 4.58 mmol) was reacted with benzaldehyde (0.46 g, 4.58 mmol) in methanol in presences of catalytic amount of sulfuric acid at reflux condition for 2 h to give 2-methyl-4-oxo-*N′*-[(*Z*)-phenylmethylidene]-3,4-dihydroquinazoline-5-carbohydrazide **6a**.

Yield: 67 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.36 (s, 3H), 2.50 (s, 1H), 3.16 (s, 1H), 7.45 (d, 2H, *J*=7.7 Hz), 7.78 (d, 1H, J=8.5 Hz), 7.86 (m, 5H, *J*=8.0, 11.09 Hz), 12.01 (s, 1H)

FT-IR (KBr): 3011, 1678, 1613, 1567, 987, 673 cm^{-1}.

Mass: m/z 307 (M^+).

2-Methyl-N′-[(Z)-(4-nitrophenyl)methylidene] -4-oxo-3,4-dihydroquinazoline-5-carbohydrazide 6b

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** (1 g, 4.58 mmol) was reacted with *p*-nitro benzaldehyde (0.69 g, 4.58 mmol) in methanol in the presences of catalytic amount of sulfuric acid at reflux condition for 6 h to give 2-methyl-*N′*-[(*Z*)-(4-nitrophenyl) methylidene]-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6b**.

Yield: 87 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.23 (s, 3H), 7.34 (d, 2H, *J*=7.7 Hz), 7.62 (d, 2H, *J*=7.7 Hz), 7.75 (dd, 2H, *J*=7.7, 9.1 Hz), 8.15 (d, 2H, *J*=13.2 Hz), 8.3 (d, 1H, *J*=13.2 Hz), 11.75 (s,1H).

FT-IR (KBr): 2965, 2900, 2644, 1691, 1665, 1584, 1478, 1406, 1309, 1264, 908, 740, 711. cm^{-1}.

Mass: m/z 349 (M-2).

N′-(anthracen-9-ylmethylidene) -2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide 6c

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** (1 g, 4.58 mmol) was reacted with anthracene 9-carbaldehyde (0.94 g, 4.58 mmol) in methanol in the presences of catalytic amount of sulfuric acid at reflux condition for 4 h to give *N′*-(anthracen-9-ylmethylidene)-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6c**.

Yield: 83 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.24 (s, 3H), 7.34 (d, 1H, *J*=7.7 Hz), 7.59 (d, 1H, *J*=7.0 Hz), 7.62 (dd, 4H, *J*=8.1, 7.9 Hz), 7.76 (d, 4H, *J*=8.1, 9.7 Hz), 7.73 (s, 1H), 9.25 (s, 1H), 11.72 (s, 1H).

FT-IR (KBr): 2991, 1778, 1623, 1637, 1557, 967, 656 cm^{-1}.

Mass: m/z 407 (M^+).

2-Methyl-N′-[(Z)-(4-N, N-diethyl, 2-hydroxy)methylidene] -4-oxo-3,4-dihydroquinazoline-5-carbohydrazide 6d

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** (1 g, 4.58 mmol) was reacted with 4-(diethylamino)-2-hydroxybenzaldehyde (0.88 g, 4.58 mmol) in methanol in the presences of catalytic amount of sulfuric acid at reflux condition for 7 h to give 2-methyl-*N′*-[(*Z*)-(4-N, N-diethyl, 2-hydroxy)methylidene]-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6d**.

Yield: 79 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.21 (s, 3H), 2,48 (t, 3H, *J*=7.0 Hz), 3.35 (d, 2H, *J*=7.0 Hz), 7.30 (d, 1H, *J*=8.1 Hz), 7.60 (d, 1H, *J*=7.7 Hz), 7.74 (dd, 1H, *J*=9.8, 7.7 Hz), 8.81 (m, 3H, *J*=9.8, 6.9 Hz), 12.21 (s, 1H), 10.39 (s, 1H),

FT-IR (KBr): 3027, 1781, 1622, 1645, 1534, 2511, 978, 656 cm^{-1}.

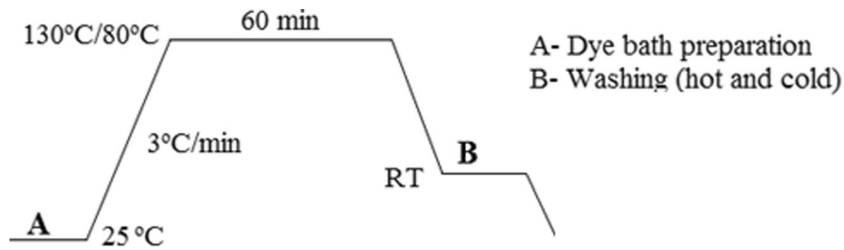


Fig. 1 Dyeing profile of polyester used

Mass: m/z 395 (M^+).

N′-[(Z)-(1-Tert-butyl-4-chloro-1H-pyrazol-5-yl)methylidene]-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide 6e

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** (1 g, 4.58 mmol) was reacted with 2-*tert*-butyl-5-chloro-1*H*-imidazole-4-carbaldehyde (0.85 g, 4.58 mmol) in methanol in the presences of catalytic amount of sulfuric acid at reflux condition for 4 h to give *N′*-[(*Z*)-(1-*tert*-butyl-4-chloro-1*H*-pyrazol-5-yl)methylidene]-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6e**.

Yield: 85 %, Melting point => 300 °C.

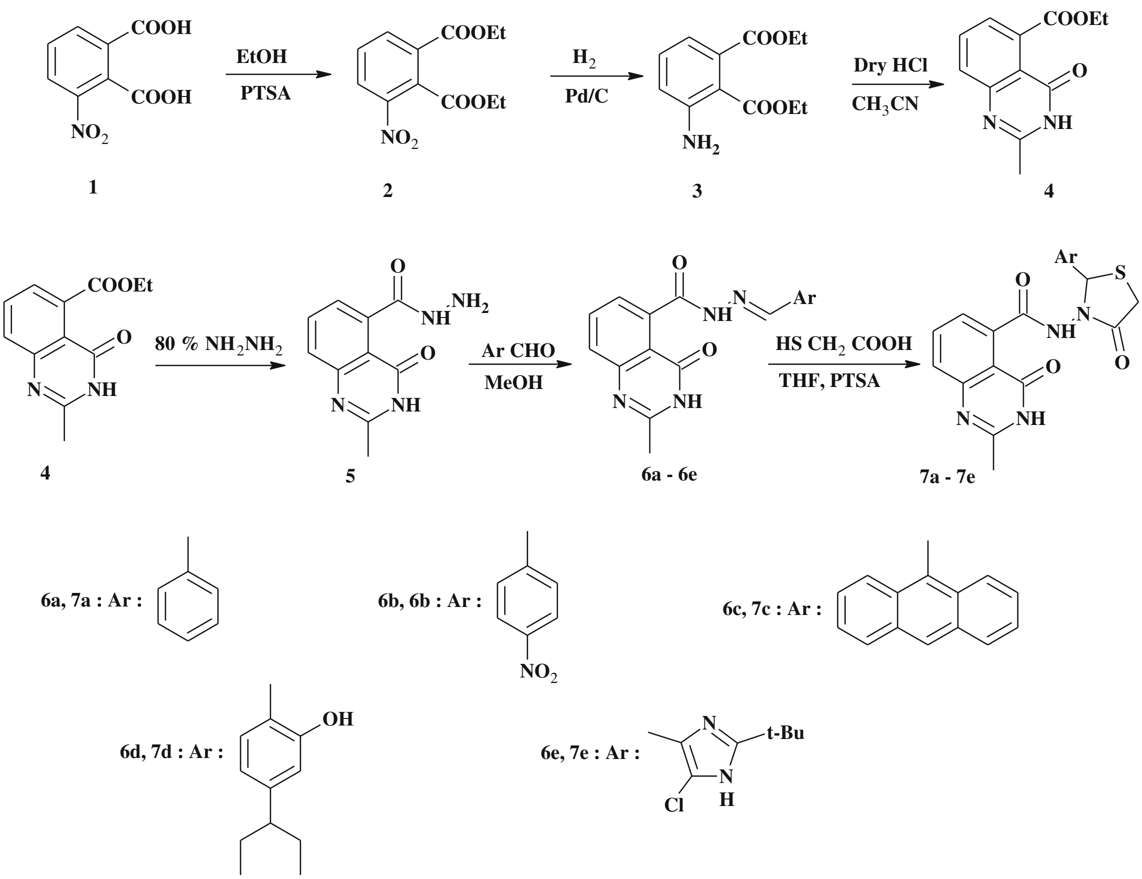
^{1}H-NMR $(CD_3)_2SO$: δ 2.5 (s, 3H), 2.65 (s, 9H), 7.30 (d, 1H, *J*=8.1 Hz), 7.60 (d, 1H, *J*=7.7 Hz), 7.74 (dd, 1H, *J*=8.1, 7.7 Hz), 11.72 (s, 1H).

FT-IR (KBr): 3014, 1771, 1643, 1655, 1521, 1456, 1378, 1218, 978, 698, 651 cm^{-1}.

Mass: m/z 388 (M^+).

2-Methyl-4-oxo-N-(4-oxo-2-phenyl-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide 7a

2-Methyl-4-oxo-*N′*-[(*Z*)-phenylmethylidene]-3,4-dihydroquinazoline-5-carbohydrazide **6a** (1.42 mmol) was reacted with thioglyconic acid (1.42 mmol) in tetrahydrofuran (THF) at reflux condition for 6 h to give 2-methyl-4-oxo-*N*-(4-



Scheme 1 Synthesis of 2-methyl-4-oxo-*N*-(4-oxo-2-phenyl substituted-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamides

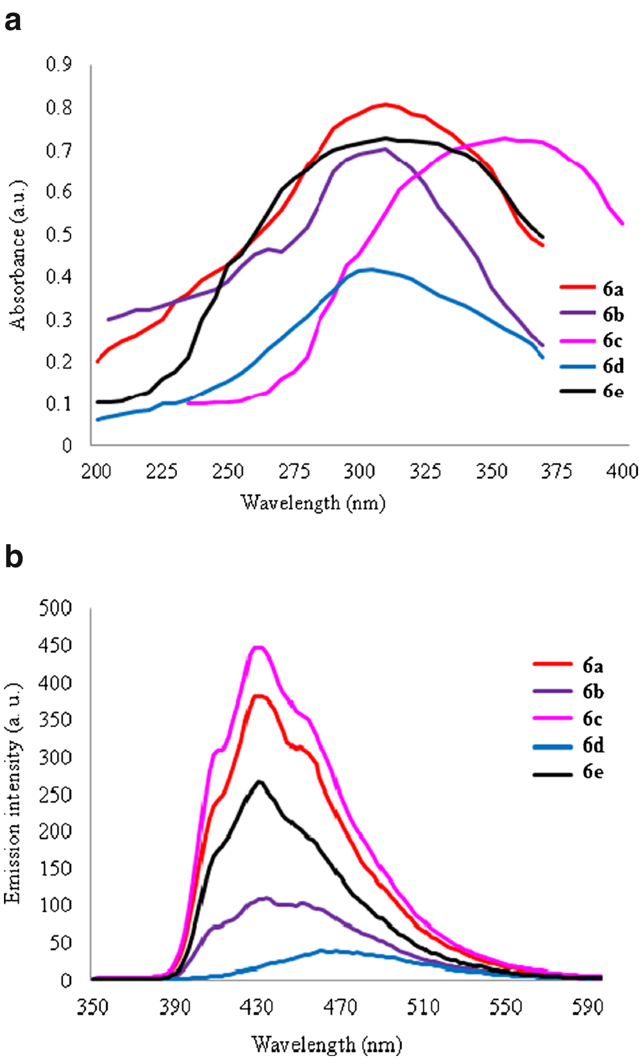


Fig. 2 Absorption and emission spectra of compounds **6a**–**6e. a** Absorption spectra of compounds **6a**–**6e. b** Emission spectra of compounds **6a**–**6e**

oxo-2-phenyl-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide **7a**.

Yield: 69 %, Melting point => 300 °C.

^{1}H-NMR (CD$_3$)$_2$SO: δ 2.25 (s, 3H), 2.5 (s, 2H), 3.45 (s, 1H), 7.33 (d, 1H, *J*=7.7 Hz), 7.63 (d, 1H, *J*=7.7 Hz), 7.74 (dd, 1H, *J*=8.1, 7.3 Hz), 7.80–7.88 (m, 3H, *J*=8, 8.1, 7.7 Hz), 8.15 (d, 1H, *J*=8.1 Hz), 8.36 (d, 1H, *J*=8 Hz), 9.71 (s, 1H), 11.78(s, 1H)

FT-IR (KBr): 2978, 1789, 1768, 1628, 1667, 1581, 1458, 1335, 1267, 1211, 970, 689, 651 cm^{-1}.

Mass: m/z 388 (M^{+}).

2-Methyl-N-[2-(4-nitrophenyl)-4-oxo-1,3-thiazolidin-3-yl] -4-oxo-3,4-dihydroquinazoline-5-carboxamide 7b

2-Methyl-*N′*-[(*Z*)-(4-nitrophenyl)methylidene]-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6b** (1.42 mmol) was reacted with thioglyconic acid (1.42 mmol) in THF at reflux condition for 12 h to give 2-methyl-*N*-[2-(4-nitrophenyl)-4-oxo-1,3-thiazolidin-3-yl]-4-oxo-3,4-dihydroquinazoline-5-carboxamide **7b**.

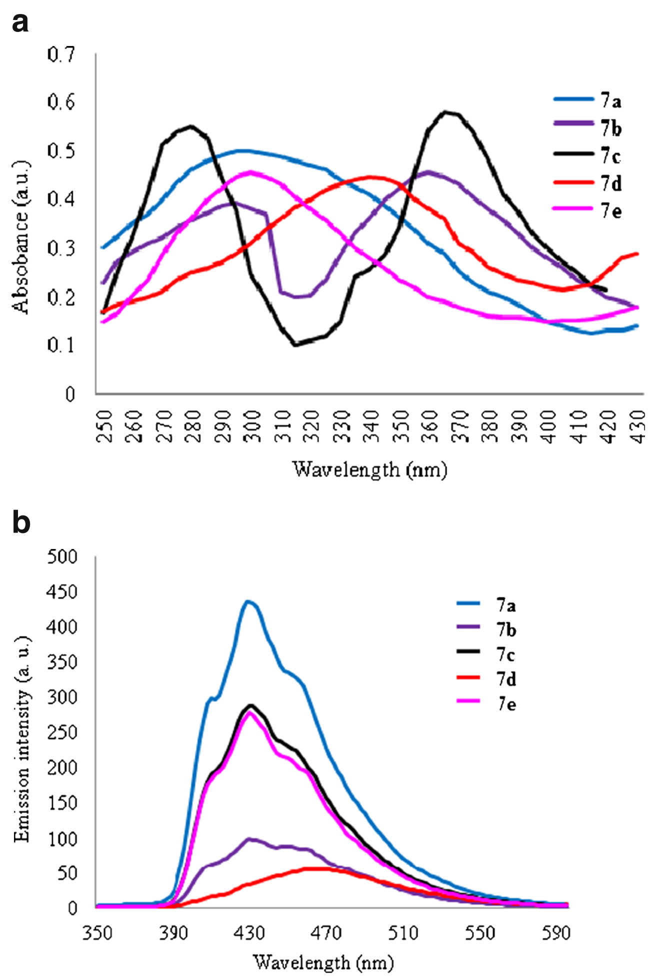


Fig. 3 Absorption and emission spectra of compounds **7a**–**7e**. a Absorption spectra of compounds **7a**–**7e** in DMF. **b** Emission spectra of compounds **7a**–**7e** in DMF

Yield: 61 %, Melting point => 300 °C.

^{1}H-NMR (CD$_3$)$_2$SO: δ 2.28 (s,1H), 2.50 (s, 1H), 3.65 (s, 1H), 7.37 (d, 1H, *J*=7.7 Hz), 7.69 (d, 1H, *J*=7.7 Hz), 7.69 (d, 1H, *J*=7.7 Hz), 7.76 (dd, 1H, *J*=8.1, 7.3 Hz), 8.16 (d, 2H, *J*=8.8 Hz), 8.37 (d, 2H, *J*=8.8 Hz), 9.71 (s, 1H), 11.85 (s, 1H)

FT-IR (KBr): 2981, 2823, 2761, 1629, 1558, 1478, 1419, 1338, 1167, 1089, 1044, 876, 779, 698 cm^{-1}.

Mass: m/z 427 (M^{+}).

2-Methyl-4-oxo-N-(4-oxo-2-anthracene-1,3-thiazolidin-3-yl) -3,4-dihydroquinazoline-5-carboxamide 7c

N′-(Anthracen-9-ylmethylidene)-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6c** (1.42 mmol) was reacted with thioglyconic acid (1.42 mmol) in THF at reflux condition for 14 h to give 2-methyl-4-oxo-*N*-(4-oxo-2-

Table 1 Observed UV-visible absorption, emission and computed vertical excitation and emission of compounds **7a -7e** in DMF

Comp	$\lambda_{max}^{Expt}(nm)$ (nm)	TD-DFT vertical excitation		*f*	% D	$\lambda_{Em}^{Expt}(nm)$	λ_{Em}^{DFT}	% D	[a]Stokes shift Δλ (cm^{-1})	[b]Φ
		nm	eV							
7a	300	307	4.029	0.120	2	431	345	19	10131	0.002
7b	341	362	3.417	0.003	6	432	426	1	6177	0.017
7c	354	402	3.083	0.010	13	464	440	4	6696	0.021
7d	342	383	3.233	0.0003	11	431	473	9	6037	0.102
7e	312	303	4.083	0.007	2	428	470	9	8686	0.253

[a] Stokes shift in cm^{-1}

[b] Quantum yield

Analyses were carried out at room temperature (25 °C); experimentally observed λ_{max}

(% D) % Deviation between vertical excitation and experimental absorption and experimental emission and computed (TD-DFT) emission

f: Oscillator strength

anthracene-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide **7c**.

Yield: 71 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.28 (s, 3H), 2.50 (s, 2H), 3.65 (s, 1H), 7.37 (d, 1H, *J*=7.7 Hz), 7.67 (d, 1H, *J*=7.7 Hz), 7.70–7.82 (m, 12H, *J*=18.6, 7.7, 8.0 Hz), 11.85 (s, 1H).

FT-IR (KBr): 3018, 1801, 1757, 1625, 1681, 1580, 1448, 1345, 1255, 1210, 978, 667, 644 cm^{-1}.

Mass: m/z 488 (M^+).

2-Methyl-4-oxo-N-(4-oxo-2-(4-(diethylamino) 2-phenol-1,3-thiazolidin-3-yl) -3,4-dihydroquinazoline-5-carboxamide 7d

2-Methyl-*N*′-[(*Z*)-(4-N, N-diethyl, 2-hydroxy)methylidene]-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6d** (1.42 mmol) was reacted with thioglyconic acid (1.42 mmol) in THF at reflux condition for 10 h to give 2-methyl-4-oxo-*N*-(4-oxo-2-(4-(diethylamino)2-phenol-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide **7b**.

Yield: 69 %, Melting point => 300 °C.

^{1}H-NMR $(CD_3)_2SO$: δ 2.43 (s, 3H), 2.51 (6H, t, *J*=14.3 Hz), 2.64 (2H, s), 3.36 (1H, s), 3.92 (q, 4H, *J*=14.3 Hz), 6.92 (s, 1H), 7.63 (d 1H, *J*=7.7 Hz), 7.72 (d, 1H, *J*=8.1), 7.92 (dd, 1H, *J*=7.7, 8.1 Hz), 8.03 (d, 1H, *J*=9.3 Hz), 8.23 (d, 1H, *J*=7.9 Hz), 8.88 (dd, 1H, *J*=9.3, 7.9 Hz), 10.39 (s, 1H), 12.25 (s, 1H), 12.51 (s, 1H).

FT-IR (KBr): 3028, 1777, 1759, 1631, 1667, 1568, 1440, 1320, 1245, 1264, 957, 678, 621 cm^{-1}.

Mass: m/z 469 (M^+).

2-Methyl-4-oxo-N-(4-oxo-2-1-tert-butyl-4-chloro-1 H-pyrazole-1,3-thiazolidin-3-yl) -3,4-dihydroquinazoline-5-carboxamide 7e

N′-[(*Z*)-(1-*Tert*-butyl-4-chloro-1*H*-pyrazol-5-yl)methylidene]-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **6e**

Graph 1 HOMO-LUMO energies of compounds **7a**–**7e** in different solvents

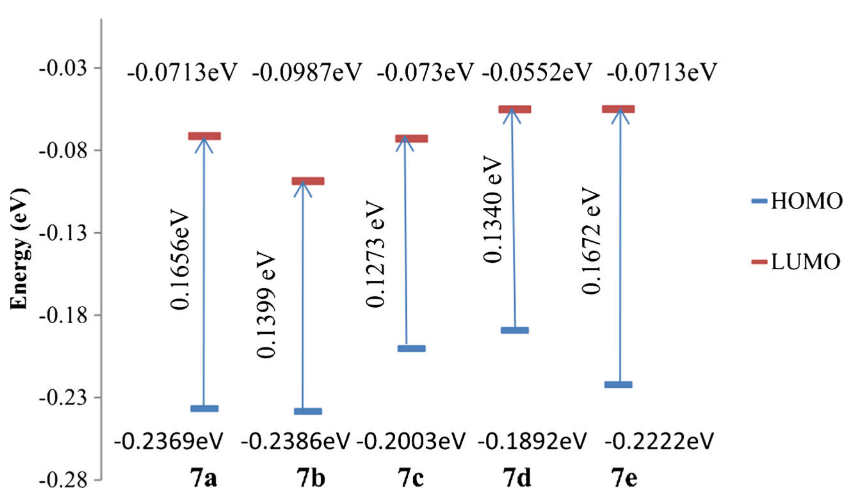
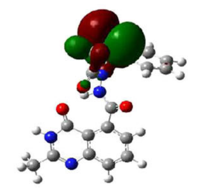
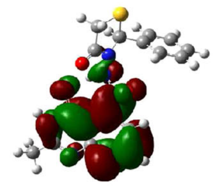
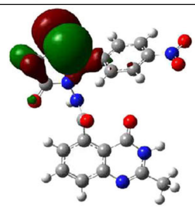
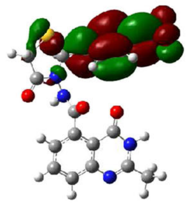
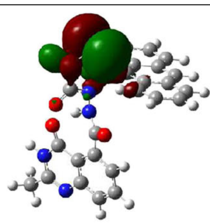
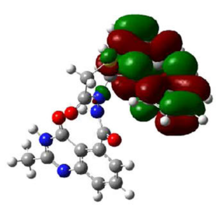
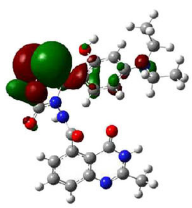
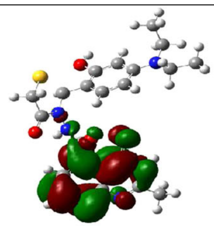
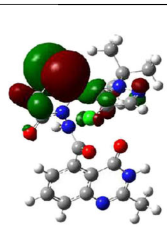
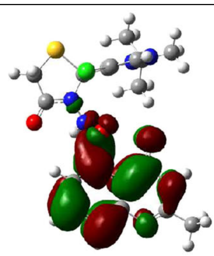


Table 2 Frontier molecular orbitals of compounds **7a-7e**

Compounds	HOMO	LUMO
7a		
7b		
7c		
7d		
7e		

(1.42 mmol) was reacted with thioglyconic acid (1.42 mmol) in THF at reflux condition for 18 h to give 2-methyl-4-oxo-*N*-(4-oxo-2-1-*tert*-butyl-4-chloro-1*H*-pyrazole-1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide **7e**

Yield: 61 %, Melting point => 300 °C.

^{1}H-NMR ($(CD_3)_2SO$): δ 2.22 (s, 3H), 2.48 (s, 9H), 3.16 (s, 1H), 3.35 (s, 1H), 7.30 (d, 1H, *J*=8.7 Hz), 7.61 (d, 1H, *J*=8.7 Hz), 7.74 (dd, 1H, *J*=6.1, 8.7 Hz), 11.72 (1H, s)

FT-IR (KBr): 3034, 1759, 1721, 1645, 1621, 1545, 1435, 1341, 1257, 1222, 950, 669, 602 cm^{-1}.

Mass: m/z 462 (M^+).

Result and Discussion

Chemistry

Synthesis of 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** was performed by reacting ethyl-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate with 98 % hydrazine hydrate under reflux condition for 2 h. Initially ethyl-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate was insoluble in hydrazine hydrate at room temperature and it gets solubilized after heating at reflux condition. The product was separated from the reaction mass as the reaction goes to completion. On completion of the reaction the reaction mixture was cooled, the product was separated by filtration, washed with cold water, and dried.

The intermediate 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carbohydrazide **5** was reacted with different aldehydes in methanol at reflux condition to give the corresponding Schiff base 2-methyl-4-oxo-*N′*-[(*Z*)-phenyl substituted methylidene]-3,4-dihydroquinazoline-5-carbohydrazide (**6a**–**6e**). In this step the formation of Schiff base requires nearly 2 to 7 h. The reaction was initiated in the presence of catalytic amount of H_2SO_4. On completion of the reaction the reaction

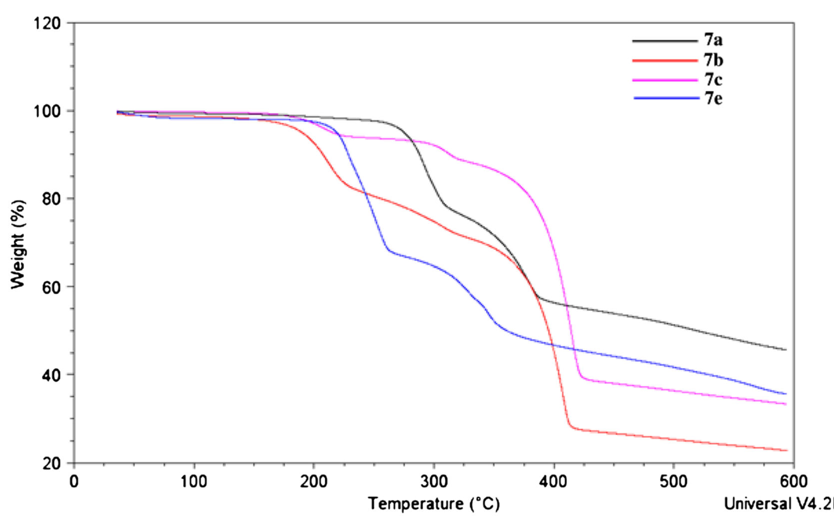


Fig. 4 TGA of compounds **7a**, **7b**, **7c** and **7e**

mixture was cooled, and neutralized with Na_2CO_3 at low temperature to precipitate the products. The products were filtered and dried. The yields of the compounds **6a**–**6e** range from 67 to 87 %.

2-Methyl-4-oxo-N-(4-oxo-2-phenyl substituted −1,3-thiazolidin-3-yl)-3,4-dihydroquinazoline-5-carboxamide (**7a**–**7b**) was prepared by reacting the Schiff base 2-methyl-4-oxo-*N*′-[(*Z*)-phenyl substituted methylidene]-3,4-dihydroquinazoline-5-carbohydrazide (**6a**–**6e**) with thioglyconic acid in THF in the presence of catalytic amount of PTSA. The reaction details are summarized in the experimental procedure and the synthetic strategy is presented in Scheme 1.

Photophysical Properties

The absorption and emission properties of the compounds **6a**–**6e** and **7a**–**7e** were studied in the solvent DMF. All the absorption-emission studies were performed at room temperature using solutions of concentration 1×10^{-6} M. The synthesised compounds are fluorescent in solution under irradiation of UV light. The absorption and emission spectra of the compounds **6a**–**6e** and **7a**–**7e** are presented in Figs. 2 and 3 respectively. The effect of electron donor and electron acceptor groups on the absorption and the emission properties of the compounds were studied. All the compounds absorb in the ultraviolet region and emit in the visible region. The absorption and the emission properties of the compounds show that they are well suitable to function as fluorescent brightening agents. In other words they absorb in the ultra-violet region and emit in the visible region. The observed photophysical properties of the compounds are compared with the computational results obtained by DFT and TD-DFT and the results are summarised in Table 1.

The absorption and emission properties of the compounds depend on the quinazolone unit as there is no direct conjugation between quinazolone and thiazolyl units. This is also supported by the fact that the compound **6a**–**6e** and **7a**–**7e** have similar photophysical properties. The compounds **6a**–**6e** absorb at 300 nm except the compound **6c** which absorbs at 354 nm in DMF. The experimental absorption properties of the compounds are well in agreement with the computed energy difference between HOMO and LUMO Graph 1. In the case of the compound **6c** the energy difference between HOMO and LUMO is less as compared to the other compounds and it shows a red shifted absorption. The analogous behavior is observed for the compounds **7a**–**7e**. The compounds **6a**–**6e** emit at 430 nm except the compound **6c** which emits at 470 nm in DMF. The emission properties of the compound **6a**–**6e** and the compounds **7a**–**7e** are almost the same in DMF. This clearly indicates that the quinazolone unit is responsible for the absorption as well as the emission properties. The compounds **7b** and **7c** show dual absorption. The short wavelength absorption is in the range 274–294 nm and the long wavelength absorption is at 350 nm. In the case of the emission spectra of the compound **7a**–**7e** a single intense emission was observed. The quantum yields of the compounds are in range of 0.002 to 0.353. The compound **7e** shows a higher quantum yield as compared to the compounds **7a**–**7d** in DMF.

Computational Study

The observed experimental absorption properties of the compounds were compared with the vertical excitation data obtained computationally and they are in good agreement with each other. The maximum difference is observed for the compounds **7c** and **7d**. In the case of the compounds **7a**, **7b** and **7e** the experimental absorption and the vertical excitation are almost the same. In the case of the emission a large difference was observed between the experimental emission and the calculated emission for the compound **7a** (19 %) and a

Table 3 Color properties of compounds **7a-7e**

	Standard blank polyester	7a	7b	7c	7d	7e
X	48.025	56.532	51.414	57.805	48.921	53.635
Y	50.82	59.421	54.689	61.766	51.823	56.874
Z	54.138	56.284	55.871	61.848	54.815	57.327
L*	76.57	81.522	78.862	82.789	77.175	80.109
a*	−0.396	0.525	−1.111	−1.797	−0.54	−0.696
b*	0.416	6.879	2.687	3.915	0.799	3.451
C*	0.574	6.899	2.908	4.308	0.964	3.52
H*	133.608	85.601	112.491	114.682	124.075	101.434
K/S	0.2515	0.5506	0.3152	0.5626	0.2739	0.4152
Berger whiteness		−299.914	−145.533	−275.681	−16.865	−168.12
Stensbay whiteness		62.46	67.468	65.653	73.158	67.668
Taube whiteness		46.873	59.417	62.094	63.791	58.686

larger difference was observed for the compounds **7d** and **7e**. In the case of the compounds **7c** and **7d** the experimental emission and the calculated emission are very close to each other. A large Stokes shift was observed for the compounds **7c** and **7e**. The % deviation between the experimental photophysical properties and the calculated photophysical properties and oscillator strength obtained by DFT computation are summarised in Table 1.

The most probable electronic transitions occurring in the molecules were understood using the frontier molecular orbitals (HOMO and LUMO) generated using Gaussview 05 program for compounds **7a**–**7e** in the solvent DMF Table 2. All the compounds may be considered to be consisting of three cores—quinazolinone, thiazolidine and aromatic cores. The electron density for the compounds **7a**–**7e** is concentrated on the thiazolidine core, but the LUMO energy distribution pattern is not linear. In the case of compounds **7a**, **7d** and **7e** the electron density is spread over quinazolinone unit. The electron distribution is on the aromatic system of the thiazolidine for compounds **7c** and **7b**. The electron distribution patterns of compounds **7a**–**7e** indicates that the thiazolidine core acts as donor and quinazolinone and aromatic cores of the compound **7c** and **7b** act as acceptor units.

Thermogravimetric Analysis

Thermal stability of the compounds **7a**–**7e** was evaluated by thermogravimetric analysis (TGA). The compounds are thermally stable up to 200 °C. The compounds start decomposing after 200 °C and the decomposition is complete at 600 °C. Compound 7c is thermally more stable as compared to the compounds **7a**, **7b** and **7e**. The compound **7d** is a semi-solid and so thermal stability of the compound **7d** was not evaluated. The thermogravimetric studies have been carried out in the temperature range 50–600 °C under nitrogen gas at a heating rate of 10 °C min^{-1} Fig. 4.

Color Assessment

The colorimetric parameters of the whitened polyester fabrics using synthesized fluorescent molecules **7a**–**7e** were recorded on a reflectance spectrophotometer CE-7000A Gretag-Macbeth. CIE 1976 Color Space method was used to evaluate the color values of the synthesized compounds **7a**–**7e** on polyester fabrics in terms of L*, a* and b* (Table 3). All the compounds have good affinity towards the polyester fabrics at high temperature and gave whitening with a blue tinge on polyester fabrics. The whiteness index values of the fabrics dyed with compounds **7a**–**7e** are summarized in Table 3.

Conclusion

Fluorescent compounds are synthesised from the intermediate ethyl 2-methyl-4-oxo-3, 4-hydroquinazoline-5-carboxylate. Photophysical properties of the compounds in DMF were evaluated experimentally and the results are compared with the theoretical data. The experimental results are in good agreements with the theoretical results. The % deviation between the experimental absorption and the emission is in the range between 1 and 19 %. The fluorescent compounds show good brightness on polyester fibres and have good thermal stability.

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