Molecular Properties of 5-(1*H*-Benzo[*D*]Oxa, Thia, Imid azole-2-YI)-2-Methyl Quinazolin-4-ol Fluorescent Brighteners: Theoretical And Experimental Approach

Vikas Patil, Nagaiyan Sekar, Vikas S. Padalkar, Jamatsing Rajput, Sharad R. Patil, Satish V. Patil

PII:	S0022-2860(19)31081-6
DOI:	https://doi.org/10.1016/j.molstruc.2019.126984
Article Number:	126984
Reference:	MOLSTR 126984
To appear in:	Journal of Molecular Structure
Received Date:	25 June 2019
Accepted Date:	24 August 2019

Please cite this article as: Vikas Patil, Nagaiyan Sekar, Vikas S. Padalkar, Jamatsing Rajput, Sharad R. Patil, Satish V. Patil, Molecular Properties of 5-(1*H*-Benzo[*D*]Oxa, Thia, Imid azole-2-Yl) -2-Methyl Quinazolin-4-ol Fluorescent Brighteners: Theoretical And Experimental Approach, *Journal of Molecular Structure* (2019), https://doi.org/10.1016/j.molstruc.2019.126984

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.



Quinazoline linked substituted Benzimidazole, Benzoxazole, Benzothiazole Fluorescent Brightening Agents: Theoretical and Experimental approach for Molecular Properties

Vikas Patil*, Nagaiyan Sekar, Vikas S. Padalkar, Jamatsing Rajput, Sharad R. Patil, Satish V Patil,



A series of novel oxazole, thiazole, imidazole substituted quinazoline representing fluorescent brightening agents and photophysics of fluorescence was optimised by experimental DFT computational.

Molecular Properties of 5-(1*H*-Benzo[*D*]Oxa, Thia, Imid azole-2-Yl)-2-Methyl Quinazolin-4-ol Fluorescent Brighteners: Theoretical And Experimental Approach

Vikas Patil^{ab*}, Nagaiyan Sekar^b, Vikas S. Padalkar^b, Jamatsing Rajput^c, Sharad R. Patil^d, Satish V. Patil^c

a) University Institute of Chemical Technology, North Maharashtra University, Jalgaon-425001 (India) Email: vikasudct@gmail.com

b) Department of Intermediate and Dyestuff technology, Institute of Chemical Technology, Mumbai-400019 (India)

c) School of Life Sciences, North Maharashtra University, Jalgaon 425001(India) d) SPDM Arts, Commerce, Science College Shirpur-425405 (India)

Abstract:

A series of seven new fluorescent brighteners 5-(1H-benzo[d]oxazole, thiazole, imidazole-2-yl)-2methyl quinazolin-4-ol were synthesized by chemical reaction of 2-Methyl-4-oxo-3,4dihydroquinazoline-5-carboxylic acid and derivatives of 2-aminophenol/2-aminothiophenol/1,2phenylenediamine attributes to its computational and experimental comparison. Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) calculations was performed by PCM model maintaining C₁ symmetry in ground state both in gas and DMF solvent. The electronic distribution over the molecules has built up strong relationship with its fluorescence quantum efficiency. HOMO and LUMO energies defined electron donor acceptor relationship and shows two distinct plane which are less responsive towards the π - π electronic transition and has inductive electronic effect control their fluorescence properties. The fluorescente brighteners **6a-6g** exhibits 0.6 -22% and 0.6 - 7.4% deviation for UV-absorption and fluorescence emission respectively. The theoretical and experimental results for absorption and emission are in well agreement that certainly believe to perform theoretical calculations before experimental setup. The thermally stable fluorescent brightening agents have been systematically investigated. The color space method was used to evaluate the brightening values on polyester fabrics in terms of L*, a* and b*.

Keywords: Benzimidazole, Benzoxazole, Benzothiazole, Quinazoline, DFT, Vertical excitation.

Introduction:

Thermally stable quinazoline based dyes are reported for coloring man-made fabrics due to excellent dyeing and optical brightening nature because of low sublimation nature [1]. While the base structure of quinazoline is utilized to carry chromophoric diazo as well as water solubilizing sulphonyl acid group [2-4]. The hybrid combination of bifunctional active compounds brings the synergistic effect and multiply the activity of quinazoline centric benzazole motif, where it found to be active

against the 60-tumour cell line panel and act as anticancer agent against leukemia, colon, melanoma, renal, breast cancer cell lines [5-7]. Computational structure-activity relationship (SAR) efficiently determines in vitro and in vivo cancer activities where in vitro activity against Versus Aurora was significantly noticed [8,9]. Substituent groups at different position has significant role on activity where this information is useful as future templates to investigate potential active molecules in medical science [10,11]. Where the chelating ability was utilized as chemical sensor against -CN⁻ and Pb²⁺ with high selectivity 0.05 µM lowest detection limit [11]. The fluorescent activity performance on-off' switch was designed for high Cu²⁺ ion selectivity and enhanced fluorescence was found for *in situ* generated Cu²⁺ complex as cyanide ion sensor [12]. Photophysical-electrooptical-optoelectronics properties are invented in electronics to obtain low turn on voltage efficient of red-light phosphorescent emitter with high external current, quantum and power efficiencies [13]. Quinazoline being active component in optics, medicinal, dyes, electronics and high-tech application the interest is focused to investigation of new infringing roots [14, 15, 16]. The structural analysis and molecular properties are investigated as predetermine strategy with the help of DFT computation. Where X-ray diffraction of regioselective system [17] and molecular vibrational spectroscopic analysis was performed [18,19]. This report is in continuation of our interest in guinazoline as well as new benzimidazole, benzoxazole and benzothiazole chemistry [22-26]. Summarized a complimentary relationship of theoretical results with respect to synthesis, photophysical properties by experimental. The new class of multifunctional heterocyclic azole-quinazoline system was introduced to obtain comparative discussion between actual and theoretical measures. The effects of various substituent groups significantly influence absorption and emission properties of structure in DMF solvent. The trends in vertical excitations obtained from Time Dependent Density Functional Theory calculations are in good agreement with the experimental absorptions.

Experimental

Materials and Methods

The materials and solvents used in the present work were pure and laboratory prepared. All the commercial chemical reagents and spectroscopic grade solvents were procured from S. D. Fine chemicals private limited Mumbai. The solvents and reagents were used as received without further purification. The reactions were monitored on silica gel aluminium based plates kisel gel 60 F254 Merck, India. The synthesized FBA's were purified by column chromatography technique. Spectronic Genesys 2 UV-Visible spectrophotometer was used for UV-Vis absorption spectra and emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer. 1×10^{-6} mol L⁻¹ concentration of freshly prepared solution was used for measurement. Absorption maxima from experimental and DFT was used as excitation wavelength in fluorescence measurement. Perkin-Elmer Spectrum 100 FTIR spectrometer was used for IR spectral analysis and VXR 300 MHz NMR was used

for ¹H NMR with TMS as internal standard. Finnigan mass spectrometer was used for mass spectra analysis and technique used was Electro Ionisation (EI) technique for low molecular weight. Fluorescent brightening agent application was performed using Rossari Labtech Flexi Dyer dyeing machine.

Relative Fluorescence Quantum Yield Calculations:

Comparative method of fluorescence quantum yield was used for evaluating the fluorescence quantum efficiency in DMF solvent. The internal standard anthracene was used and absorption and emission of five difference concentration was determined at 1 to 5 ppm. Slit width of emission measurement was kept constant at 2.5 unit. The phasor representation of absorption (X-axis) vs emission (Y-axis) was graphed for anthracene as well as new synthetic compounds i. e. **6a-6g**. Phasor was evaluated for the gradient calculation and these gradients were used in given formula (1). The terminal calculation gives the value of fluorescence quantum yield in given solvent at standard conditions [20,21, 23, 24].

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

Where: Φ_x = Fluorescence quantum yield of compound

- Φ_{st} = Fluorescence quantum yield of standard sample
- Grad_x = Gradient from the plot of integrated fluorescence intensity against absorbance of the studied 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

Synthesis

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

Ethyl ester of 3-nitrophtallic acid (5g) was prepared at refluxed in 15 mL of ethanol in catalytic amount of *p*-toluene sulphonic acid (0.1 g) to drive dehydration. After 2 hours of reflux separation of 3-nitrobenzene-1,2-dicarboxylate in ethyl acetate was obtained and un-esterified 3-nitrophtallic acid was drain in water by treatment of Na₂CO₃. Reduction of 3-Nitrobenzene-1,2-dicarboxylate in 5% Pd/C was performed under hydrogen gas pressure at 5 Kg/cm² in methanol gives diethyl 3-aminobenzene-1,2-dicarboxylate. HCl gas purging reaction of 3-aminobenzene-1,2-dicarboxylate (2.5 g) in acetonitrile (100 mL) was performed to yield intermediate ethyl 2-methyl-4-oxo-3,4-dihydroquinoline -5-carboxylate (**4**) separated by quenching in cold water under continuous stirring. Yield: 58 %, Melting point = 212 °C (Lit 212 °C) [21, 25].

FTIR (KBr): 2978 (CH₃ Out of plane), 2910 (-CH₂ methylene), 1739 (-C=O ester), 1674 (-C=O Amide), 1613 (C=N), 1590 (C=C Aromatic), 1503 (C=C Aromatic), 1468 (C-C-O), 1380 (-CH₃ First overtone), 1322 (C-H ion phase), 1273 (-CH₂), 1180, 1024, 873, 779, 678 (C-O-C sting) cm⁻¹. **¹H-NMR (CD₃)₂SO:** δ = 1.41 (t, 3H, -CH₃), 2.55 (s, 3H, -CH₃), 4.40 (q, 2H, -CH2), 7.42 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.7 (d, 2H, *J* = 9.9 Hz, Ar-H), 11.88 (s, 1H, NH). **Mass**: m/z 235 (M+1).

Synthesis of 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylic acid 5

A mixture of ethyl-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate **4** (5 g, 0.021 moles) and 4N HCl (20 mL) was stirred at room temperature for 4 hrs. The reaction mixture was poured onto crushed ice (500 g) whereby a white colored solid separated out. The solid was filtered, washed separately with ice-cold water to remove the trace of acid and dried to yield the crude product **5**. The compound **5** was crystallized from ethanol to get 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylic acid.

Yield: 4 g, 90 % m.p > 300 °C.

Synthesis of 5-(1H-benzo[d]oxazole, thiazole, imidazole-2-yl)-2 methylquinazolin-4-ol derivatives (6a-6g)

2-Methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylic acid **5** (2.45 mmol) and different 2aminophenol/2-aminothiophenol/1,2-phenylenediamine (2.45 mmol) were mixed in polyphosphoric acid. The mixture was heated to 150 °C for the appropriate time (3-7 hrs). After completion of the reaction (monitored by TLC) the reaction mixture was cooled to room temperature and made neutral with liquor ammonia (30 %). The separated product was collected by filtration and recrystallized from DMF **6a-6g**.

Synthesis of 5-(1,3-Benzoxazol-2-yl)-2-methylquinazolin-4(3H)-one 6a

Reaction time: 7h, Yield: 64 %, Melting point = 271 °C.

FT-IR (KBr): 3048 (-CH₃ Out of plane), 2981 (C-H benzoxazole), 2898, 1674 (C=O), 1610 (C=O amide), 1588 (C=C aromatic), 1471, 1406 (N-H amide), 1322, 1277 (C-O aromatic), 1235 (N-N oxadiazole), 1015, 1031, 960, 824, 743 (C-O oxazole), 685 cm⁻¹.

¹**H-NMR (CD**₃)₂**SO**: δ 2.19 (s, 3H, -CH₃), 7.12 (d, 2H, *J* = 9.1 Hz, Ar-H), 7.59 (d, 2H, *J* = 9.1 Hz, Ar-H), 7.78 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.93 (dd, 1H, *J* = 7.1 Hz, Ar-H), 8.13 (d, 1H, *J* = 7.8 Hz, Ar-H), 11.13 (s, 1H, NH-amide).

Mass: m/z 278 (M+1).

Synthesis of 5-(6-chloro-1,3-benzoxazol-2-yl)-2-methylquinazolin-4(3H)-one 6b

Reaction time: 3h, Yield: 71 %, Melting point = 282 °C. **FT-IR (KBr):** 3018 (-CH₃ Out of plane), 1676, 1618 (C=O amide), 1434 (N-H amide), 1176 (N-N oxadiazole), 1034, 898, 726 (C-O oxazole)., 711 cm⁻¹. ¹**H-NMR (CD₃)**₂**SO:** δ 1.91 (s, 3H, -CH₃), 7.26 (s, 1H, Ar-H), 7.40 (dd, 2H, *J* = 6.1, 8.4 Hz, Ar-H), 7.6 (s, 1H, Ar-H), 7.81 (dd, 2H, *J* = 11.4, 8.5 Hz, Ar-H), 12.03 (s, 1H, NH-amide). Mass: m/z 312 (M+1).

Synthesis of 2-methyl-5-(5-methyl-1,3-benzoxazol-2-yl)quinazolin-4(3H)-one 6c

Reaction time: 4h, Yield: 51 %, Melting point = 302 °C.

FT-IR (KBr): 3025 (-CH₃ Out of plane), 1672 (C=O), 1626 (C=O amide), 1467 (N-H amide), 1198 (N-N oxadiazole), 1034, 911, 734 (C-O oxazole)., 656 cm⁻¹

¹**H-NMR (CD₃)**₂**SO:** δ 1.78 (s, 3H, -CH₃), 1.98 (s, 3H, Ar-CH₃), 7.41 (s, 1H, Ar-H), 7.59 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.75 (s, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.98 (d, 2H, *J* = 9.8 Hz, Ar-H), 12.31 (s, 1H, -NH amide) Mass: m/z 292 (M+1).

Synthesis of 5-(1,3-benzothiazol-2-yl)-2-methylquinazolin-4(3H)-one 6d

Reaction time: 6h, Yield: 73 %, Melting point = 248 °C **FT-IR (KBr):** 3024 (-CH₃ Out of plane), 1670, 1621 (C=O amide), 1465 (N-H amide), 1180 (N-N oxadiazole), 1035, 913, 734, 656 (S-O thiazole) cm⁻¹. ¹**H-NMR (CD₃)**₂**SO:** δ 1.8 (s, 3H), 7.44 (s, 1H, Ar-H), 7.56 (dd, 2H, *J* = 8.5, 9.9 Hz, Ar-H), 7.79 (d, 2H, *J* = 6.9 Hz, Ar-H), 8.10 (dd, 2H, *J* = 8.0, 8.1 Hz, Ar-H), 12.08 (s, 1H, -NH amide). Mass: m/z 294 (M+1).

Synthesis of 5-(1H-benzimidazol-2-yl)-2-methylquinazolin-4(3H)-one 6e

Reaction time: 4h, Yield: 61 %, Melting point = 298-300 °C.

FT-IR (KBr): 3014 (-CH₃ Out of plane), 1675, 1633 (C=O amide), 1543 (C=C aromatic), 1167 (N-N oxadiazole), 1056, 943, 786 (C-N imidazole), 666 cm⁻¹.

¹**H-NMR (CD**₃)₂**SO:** δ 2.11 (s, 3H, -CH₃), 7.12 (d, 2H, *J* = 9.1 Hz, Ar-H), 7.59 (d, 2H, *J* = 9.1 Hz, Ar-H), 7.78 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.93 (dd, 1H, *J* = 7.1 Hz, Ar-H), 8.13 (d, 1H, *J* = 7.8 Hz, Ar-H), 11.13 (s, 1H, -NH amide).

Mass: m/z 277 (M+1).

Synthesis of 2-methyl-5-(6-methyl-1H-benzimidazol-2-yl)quinazolin-4(3H)-one 6f

Reaction time: 3h, Yield: 67 %, Melting point = 266 °C.

FT-IR (KBr): 3028 (-CH₃ Out of plane), 1678, 1623 (C=O amide), 1523 (C=C aromatic), 1345 (N-H amide), 1239, 1078 (N-N oxadiazole), 878, 773 (C-N imidazole). cm⁻¹.

¹**H-NMR (CD**₃)₂**SO**: δ 2.42 (s, 3H, -CH₃), 2.59 (s, 3H, Ar-CH₃), 7.22 (dd, 2H, *J* = 11.4, 8.4 Hz, Ar-H), 7.5 (s, 1H, Ar-H), 7.65 (dd, 2H, *J* = 14.7, 12.2 Hz, Ar-H), 7.85 (s, 1H, Ar-H), 8.7 (s, 1H, Ar-H), 12.31 (s, 1H, NH-amide).

Mass: m/z 291 (M+1).

Synthesis of 2-methyl-5-(6-nitro-1H-benzimidazol-2-yl) quinazolin-4(3H)-one 6g

Reaction time: 3h, Yield: 59 %, Melting point = 302 °C. **FT-IR (KBr):** 3024 (-CH₃ Out of plane), 1678, 1619 (C=O amide), 1534 (C=C aromatic), 1353 (N-H amide), 1218 (C-O aromatic), 1048 (N-N oxadiazole), 878, 771 (C-N imidazole). cm⁻¹. ¹**H-NMR (CD₃)**₂**SO:** δ 2.59 (s, 3H, -CH₃), 7.6 (s, 2H, Ar-H), 7.9-8.1 (m, 3H, *J* = 9.6, 14.6 Hz, Ar-H), 8.24 (s, 1H, Ar-H), 8.75 (s, 1H, Ar-H), 9.14 (s, 1H, Ar-H). Mass: m/z 322 (M+1).

Computational Details:

The effect of heteroatom and substituent was studied as function of photophysical properties, electronic state and energy level with respect to capacity as electron donor-acceptor. The density functional theory (DFT) calculations was performed at ground state C₁ symmetry fixed parameter in gas phase and DMF. In DMF Polarizable Continuum Model (PCM) solvation model was used [27]. The B3LYP function was used which is complementary combination of Becke's three parameter exchange functional (B3) [28,29] with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [30]. The 6-31G(d) basic set was computed to determines the vibrational frequencies of the optimized structures [31-34] corresponds to the local minima of potential energy surface verified by the optimized structures. The electronic conduction π - π system creates donor-acceptor continuous electron flow back and forth has no fused ring. The synergy was maintain between theoretical and excited computation level optimized in the framework of PCM model which has its own implications [34-37]. However, the general trend in the experimentally observed vertical excitations and emissions (in the same series of generic structures) was considered as an assess to the simple and traditional computational strategy. The ground-state vertical excitation energies in equilibrium geometries were calculated as TD-DFT function [38]. Using TD-DFT minimum energy and geometry was computed at less energetic first singlet excited state (S_1) of each tautomer. The vertical excitations equivalence to theoretical emission was obtained as energy difference between the ground state and first singlet excited state [39, 40]. Gaussian 09 program has additional function of calculation of theoretical emission [40]. As depicted in **Figure 1** ground state geometry computationally optimized minimum stereochemical interactions of compound **6a** shows two distinct planes for quinazoline and substituted benz-azoles. The two distinct planes imply maximum inductive effect and minimum π - π electron transfer over quinazoline core controlling the absorption and emission properties and fluorescence quantum efficiency of structure.





General procedure of fluorescent brightening application on polyester fiber:

High temperature-high pressure dying method was used in fluorescent brightening agent application with liquor ratio of 1:20. Comparing to weight of fabric 2 wt % fluorescent material was used initially solubilize in DMF and diluted to 15 mL by sodium acetate and acetic acid buffered solution of pH 5 prepared in water. Dispersing agent Metamol was used and further solution was ultra-sonicated for 15 to 20 minutes to obtain a high dispersion. Temperature was gradually raised at the rate of 3 °C min⁻¹ to 130 °C continued for next 60 minutes and cooled down to room temperature. The treated fabric was washed with cool water and allow to dry in open air [21, 40].

Results and Discussion:

The intermediate ethyl-2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylate **4** was prepared from 3nitrophthalic acid by esterification, reduction and followed by cyclisation reaction **Scheme 1** [25]. This intermediate was used for the synthesis of novel heterocyclic quinazolinone compounds by different strategy presented in **Scheme 1**.



Scheme1. Synthesis of 5-(1H-benzo[d]oxazole, thiazole, imidazole-2-yl)-2 methylquinazoline-4-ol derivatives **6a-6g**.

5-(1*H*-Benzo[*d*]oxazole (**6a-6c**), thiazole (**6d**) and imidazole (**6e-6f**)-2-yl)-2-methyl quinazolin-4-ol derivatives were synthesized from 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylic acid (**5**) by condensation reaction with different *o*-amino phenols or *o*-amino thiophenols or 1,2-phenylenediamine in polyphosphoric acid. The intermediate 2-methyl-4-oxo-3,4-dihydroquinazoline-5-carboxylic acid **5** was synthesized by acid hydrolysis of ethyl-2-methyl-4-oxo-3, 4-dihydroquinazoline-5-carboxylate **4**. The synthetic details for **6a-6g** are shown in **Scheme 1**.

Photophysical Properties of Fluorescent Brightening Agents (FBA) (6a-6g):

The absorption and emission properties of all the compounds **6a-6g** were studied in the solvent dimethylformamide (DMF). All the absorption-emission studies were performed at room temperature using solutions of concentration $1x10^{-6}$ M. The synthesized compounds are fluorescent in solution under irradiation of UV light. The effect of electron donor and electron acceptor groups on the absorption and the emission properties of the compounds were studied. The absorption and emission spectra of all the compounds are shown in **Figure 2**.



Figure 2: Absorption and Emission spectra of compounds 6a-6g in DMF

The two distinct planes of quinazoline-azole have less significant effect in absorption wavelength which was found in similar range for benzoxazole (**6a-6c**), benzothiazole (**6d**), and benzimidazole (6e-6g) derivatives. However, benzimidazole derivatives (6e-6g) uniformly emit at longer wavelengths compared to the benzoxazoles (6a-6c). The compounds 6e-6g containing the imidazole core showed a redshift as compared to the compounds containing thiazole 6d and oxazole 6a-6c cores. A large Stokes shift was observed for imidazole quinazolones (6e-6g) 127 nm, 109 nm, 140 nm respectively as compared to the thiazole (6d) 97 nm and oxazole (6a-6c) 88 nm, 89 nm and 100 nm respectively. As there is not momentous difference in absorption of the compounds while change in substituents plays important role in emission spectra. The absorption spectra occurs in the range of 310-322 nm range. Where 322 nm absorbance observed for methyl substituted benzimidazole (6f). While 310 nm absorption was given for all oxazole derivatives (6a-6c) and nitro substituted imidazole compound (6g). Benzthiazole substituent (6d) compound shows 319 nm absorption. The emission spectra arise through the excitation at particular absorption are ranging from 398 nm to 450 nm. The long-range emission 450 nm was observed for nitro substituted imidazole (6g) rather methyl substituted benzimidazole (6f) gives 431 nm and methyl substituted oxazole (6c) gives 410 nm emission. While unsubstituted benzoxazole, benzthiazole and benzimidazole gives emission to the 398 nm, 416 nm, 441 nm respectively. This suggest that emission is increasing from oxazole to thiazole to imidazole from 398 nm to 450 nm range. Fluorescence quantum yields of the compounds were evaluated in DMF using anthracene (Fluorescence quantum yield = 0.270) as the standard [20, 21, 23, 24]. Since the vertical excitation is govern by the only inductive effect which has significant effect on emission and fluorescence properties. The fluorescence quantum yield values of the compounds 6a (0.392), **6b** (0.275) and **6d** (0.202) are much higher as compared to the other synthesized compounds (6c = 0.076, 6e = 0.0887, 6f = 0.0363, 6g = 0.017) (Table 1). The fluorescence quantum efficiency is a

measure of its capacity to transfer the electrons in excited state is counted as its oxidation potential in excited state [20]. Fluorescence quantum yield of the compound **6c** is less as even having methyl substituent as compared to its analogy **6a** and **6b**. The fluorescence quantum yield is an intrinsic phenomenon of molecule which is truly controlled by the capacity to photoinduced electron transfer from ground state i. e. photo excitation oxidation potential which is higher for methyl substituent **6c** and secondary process of fluorescence emission from higher energy state to ground state. Even there is more excitation due to the methyl substituent in **6c** the capacity to accommodate that excited electrons (while returning to the ground state) i. e. reduction potential is lower due to high electron density due to methyl group. This is responsible for quantum yield which is balanced process of the oxidation potential in ground state and reduction potential in excited state of molecule [20, 41]. **Figure 3** depicts the transition of electrons in ground and excited state. Amongst imidazole substituents **6e** to **6g** compound **6g** has less quantum efficiency (0.017) due to less oxidation potential being nitro substituent.



Figure. 3. Predicted electron Shifting mechanism in quinazoline-benzazole derivatives during excitation and emission.

Computational Study

In azole series, the compounds absorb in the UV region between 310-322 nm and emit in the visible region 398-450 nm with good Stokes shift value in DMF (88-140 nm) as the difference in HOMO energy and LUMO energy was significantly large (**Figure 4**). The absorption and emission properties of the compounds **6a-6g** in DMF were correlated with the computed vertical excitations obtained from DFT and emission from TD-DFT and the results are summarized in **Table 1**. The large difference between the observed absorption and the vertical excitation is observed in (HOMO-LUMO) DMF (71 nm) for the compound **6g** where % deviation was maximum amongst all. Maximum populations of vertical excitation are from HOMO-LUMO (approximately 70%). Maximum % deviation between the experimental absorption and vertical excitation is 22 % for compound **6g** which was due to the presence of $-NO_2$ group on the imidazole core. The nitro group is likely to have increased electron withdrawing capacity causing a red shift in imidazole core. The computed emission using TD-DFT was

in close agreement with the observed emission **Table 1**, while there was some deviation in the case of vertical excitation and observed absorption. The maximum difference between the observed emission and the emission obtained by the TD-DFT computation is 28 nm and 31 nm for **6a** and **6b** respectively. The difference in experimental and theoretical emission are well in agreement and are acceptable level at the initial stage of calculation. Further refining of calculation tends to reach exact values by TD-DFT and experimental. The absorption wavelength and vertical excitations are precisely closed for **6a**, **6b**, **6c** and **6d** % deviation was in the range of 0.6 to 3.5 %. While for **6e**, **6f** and **6g** was 14, 14 and 22 % respectively. These results are highly promising and genuine efforts to optimize the large molecular weight fluorescent compounds to its optimized absorption and emission value by computational analysis.

Table 1: Observed UV-visible absorption, emission and computed vertical excitation and emission of compounds **6a -6g** in DMF.

	λ_{max}^{Expt} (nm)	Ve Exc	ertical itation	f	% D	Task	λ_{Em}^{Expt} (nm)	^a Stoke Shift	TD-DFT	% D	ьф
		nm	eV		D			(cm ⁻¹)	κ _{Em} (mm)		
6a	310	308	4.017	0.343	0.6	H→L (0.6857)	398	7132	426	6.7	0.392
6b	310	308	4.014	0.390	0.6	H→L (0.6882)	401	7320	432	7.4	0.275
6c	310	314	3.938	0.321	1.2	H→L (0.6930)	410	7867	428	4.3	0.076
6d	319	308	4.016	0.343	3.5	H→L (0.6857)	416	7309	426	2.4	0.202
6e	313	359	3.448	0.598	14	H→L (0.6991)	441	9273	438	0.6	0.088
6f	322	370	3.349	0.629	14	H→L (0.7009)	431	7854	452	4.8	0.036
6g	310	381	3.248	0.725	22	H→L (0.6995)	450	10003	444	1.3	0.017

^aStokes shift, ^bQuantum yield, *f* Oscillator strength, Analyses were carried out at room temperature (25°C); λ^{exp}

experimentally absorption and emission, [%]D-% Deviation between vertical excitation and experimental absorption and experimental emission and computed (TD-DFT) emission.

The frontier molecular orbitals and their energies were obtained from DMF. The HOMO and LUMO orbital diagrams with their energies are summarized in **Table 2** for the compounds **6a-6g**. In all the

molecules (except **6b**), the electron density is distributed across the molecule in the ground state (HOMO) as well as in the excited state (LUMO). In case of the molecule **6b** the electron density is surrounded on the benzioxazole core in the ground state (HOMO) and it acts as a donor and the quinazoline core acts as an electron acceptor, while in the excited state (LUMO), the electron density is localized along the quinazol-4-ol unit of the molecule. In the case of **6a-6d** the excited state is more planar as compared to ground state, but in the case of **6e-6g** the ground as well as an excited state are planar and the dihedral angle between azole core and quinazoline core is zero-degree **Table 3**.



Figure 4: HOMO-LUMO Energy level diagram of compounds 6a-6g in DMF

Table 2. HOMO-LUMO	Orbital diagram	of compound 6:	a-6g in DMF v	vith their energy.
		<u>-</u>	· · •	





Table 3: The dihedral angle of **6a-6g** between quinazolinone and azole ring in ground and excited state calculated by TD and TD-DFT

FBA's	Dihedral Angle	Dihedral Angle G	Dihedral Angle E	Quantum Yi
				(%)
6a	$C_2 - C_5 - C_{12} - O_{13}$	60.07	12.91	39.2
6b	-	61.33	13.27	27.5
6c		60.12	14.00	7.6
6d	_	60.00	12.00	20.2
6e	$C_2 - C_5 - C_{12} - N_{32}$	0.00	0.00	8.8
6f	_	0.00	0.00	3.6
6g	_	0.00	0.00	1.7

Thermogravimetric Analysis:

In order to give more insight into the dyes **6a-6g**, the thermal studies of the compounds have been carried out using thermal gravimetric techniques (TGA). 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. The TG curves of the compounds are shown in **Figure 5**. The TG results indicate that the frame works of the synthesized compounds are stable up to 300 °C (80%). Above 300 °C the thermogravimetric curves of the synthesized compounds show a loss in weight, but up to 600 °C compounds are not decomposes completely. The comparisons of the T_d (decomposition temperature) showed that compound **6g** is thermally not stable and shows continuous weight loss as compare to other compounds from the series. Thermal stability and their plausible degradation scheme were presented in **Figure 5**.



Figure 5: Thermo gravimetric analysis of compounds 6a-6g.

Fluorescent Brightening Study

The colorimetric parameters of the whitened polyester fabrics using synthesized fluorescent molecules **6a-6g** were recorded on a reflectance spectrophotometer CE-7000A Gretag-Macbeth [21, **42**]. CIE 1976 Color Space method was used to evaluate the color values of synthesized compounds **6a-6g** on polyester fabrics in terms of L*, a* and b* **(Tables 4)**. All the compounds have a 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 **6a-6g** are summarized in **Table 4**. The colorfastness properties of these dyes were correlated with commercially used whitening agents.

Parameters	Blank	6a	6b	6c	6d	6e	6f	6g	Leucoph BSB	Sera whi PB	Sera Wh PN	Hostalux ESR50
X	48.0	51.2	60.1	52.8	48.2	49.7	57.7	56.1	74.6	73.9	71.2	75.4
Y	50.8	53.5	61.4	55.8	50.9	52.7	60.2	59.1	80.1	77.7	75.0	79.9
Z	54.1	55.0	53.7	56.3	54.8	55.0	55.8	56.5	83.1	105.7	96.8	105.4
L*	76.5	78.2	82.6	79.5	76.6	77.7	81.9	81.3	91.7	90.6	89.4	91.6

Table 4: Color values of fluorescent dyes **6a-6g** polyester fabric and commercially used optical whiteners.

a*	-0.3	1.2	4.7	-0.2	-0.0	-0.7	1.5	0.3	-28.2	1.1	0.6	-0.1
b *	0.4	2.3	11.2	3.4	-0.1	1.5	8.1	6.4	2.1	-16.1	-12.2	-14.0
C*	0.5	2.6	12.1	3.4	0.1	1.7	8.2	6.4	3.5	16.1	12.2	14.0
hº	133.6	63.0	66.9	93.8	240	114.8	79.0	87.2	142.5	274.0	273.2	269.4
K/S	0.25	0.39	0.63	0.42	0.30	0.30	0.71	0.82	0.04	0.26	0.07	0.09
Stensbay Whiteness		74.7	63.2	68.5	76.8	70.9	62.0	38.1	0.5	142.4	128.0	134.0
Taube Whiten	e	59.4	30.6	57.6	66.6	61.8	42.3	48.5	92.1	189.7	162.3	181.8

Conclusion:

The novel synthetic compound has good response towards its computational B3LYP calculations with basic set of 6-31GD methods adapted in DFT as well as TD-DFT functions. The distribution of electron density over the molecules were obtained by HOMO and LUMO which was accredited to restricted electron transfer due to the bi-planer structure. Hence π - π electronic transition has relatively lower stake as compare to inductive transition defining the fluorescence properties of molecules. The vertical excitations of absorption were found a difference of only 2 nm for **1a** and **1b** compound with respect to its experimental values. In case of emission only 3 nm difference was observed for compound **6e** shows close resembles in theoretical and experimental results. The quantum efficiency was in lowest amount for 6g (0.017) compound being nitro (-NO₂) substituent at benzimidazole terminal reducing oxidation potential to electronic transition in excited state. The compounds were enough thermally stable to apply as fluorescent brightening agent and color space method gives L*, a* and b* values are in comparison with commercially available brightening agents on polyester fabric. The DFT and TD-DFT computation is theoretical technique has certainty of results in very close proximity with the experimental results. In near future the molecular chemist must adapt trend to obtain theoretical calculation before the experimental set-up and properties must be verified as an application point of view.

Acknowledgments: Vikas Patil and Vikas Padalkar are thankful to the Institute of Chemical Technology, Mumbai. Vikas Patil is thankful to University Grant Commission (UGC) New Delhi for UGC-FRP and Science and Engineering Research Board (SERB), Department of Science and Technology (DST) New Delhi for young scientist fastrack scheme (SB/FT/CS-106/2014).

References:

1] S. R. Patil, A. S. Choudhary, V. S. Patil, N. Sekar, *Fiber. and Polym.* Synthesis, Optical Properties, Dyeing Study of Dihydropyrimidones (DHPMs) Skeleton Green and Regioselectivity of Novel Biginelli Scaffold from Lawsone 16(11) (2015) 2349-2358.

2] H. S. Bhatti, S. Seshadri, Synthesis and fastness properties of styryl and azo disperse dyes derived from 6nitro substituted 3-aryl-2- methyl-4(3H)-quinazolinone *Color. Techn.* 120 (2004) 151-155.

3] H. S. Bhatti, S. Seshadri, Chromophoric potential of the 4(3H)- quinazolinones: a review *Color. Techn.* 120 (2004) 101-107.

4] V. S. Padalkar, V. S. Patil, K. R. Phatangare, V. D. Gupta, P. G. Umape, N. Sekar, Synthesis of nanodispersible 6-aryl-2,4-diamino-1,3,5-triazine and its derivatives *Mat. Sci. and Eng. B*, 170 (2010) 77-87. 5] F. A. M. Al-Omary, G. S. Hassan, S. M. El-Messery, H. I. El-Sub, Substituted thiazoles V. Synthesis and antitumor activity of novel thiazolo[2,3-b] quinazoline and pyrido[4,3-d]thiazolo [3,2-a]pyrimidine analogues *European Journal of Medicinal Chemistry* 47 (2012) 65-72.

6] A. Sharma, V. Luxami, K. Paul Synthesis, single crystal and antitumor activities of benzimidazolequinazoline hybrids *Bioorganic & Medicinal Chemistry Letters* 23 (11) (2013) 3288-3294.

7] K. Paul, A. Sharma, V. Luxami, Synthesis and in vitro antitumor evaluation of primary amine

substituted quinazoline linked benzimidazole Bioorganic Medicinal Chemistry Letters 24 (2014) 624-629.

8] W. W. Li, X.Y. Wang, R. L. Zheng, H. X. Yan, Z. X. Cao, L. Zhong, Z. R. Wang, P. Ji, L. L. Yang, L. J. Wang, Y. Xu, J. J. Liu, J. Yang, C. H. Zhang, S. Ma, S. Feng, Q. Z. Sun, Y. Q. Wei, S. Y. Yang, Discovery of the Novel Potent and Selective FLT3 Inhibitor 1-{5-[7-(3-Morpholinopropoxy) quinazolin-4-ylthio]-[1,3,4]thiadiazol-2-yl}-3-ptolylurea and Its Anti-Acute Myeloid Leukemia (AML) Activities in Vitro and in Vivo *J. Med. Chem.* 55 (2012) 3852-3866.

9] F. H. Jung, G. Pasquet, C. L. Brempt, J. J. M. Lohmann, N. Warin, F. Renaud, H. Germain, C. D. Savi, N. Roberts, T. Johnson, C. Dousson, G. B. Hill, A. A. Mortlock, N. Heron, R. W. Wilkinson, S. R. Wedge, S. P. Heaton, R. Odedra, N. J. Keen, S. Green, E. Brown, K. Thompson, S. Brightwell Discovery of Novel and Potent Thiazologuinazolines as Selective Aurora A and B Kinase

Inhibitors J. Med. Chem. 49 (2006) 955-970.

10] D. Hedou, R. Guillon, C. Lecointe, C. Log, E. Chosson, T. Besson, Novel synthesis of angular thiazolo [5,4f] and [4,5-h] quinazolines, preparation of their linear thiazolo [4,5-g] and [5,4-g] quinazoline analog *Tetrahedron* 69 (2013) 3182-3191.

11] P. Singla, V. Luxami, K. Paul, Quinazolinone-Benzimidazole Conjugates: Synthesis, Characterization, Dihydrofolate Reductase Inhibition, DNA and Protein Binding Properties Journal of Photochemistry and Photobiology B: Biology 168 (2017) 156-164.

12] V. Luxami, R. Rani, A. Sharma K. Paul Quinazoline-benzimidazole hybrid as dual optical sensor for Cyanide and Pb²⁺ ions and Aurora kinase inhibitor *Journal of Photochemistry and Photobiology A: Chemistry*, 311 (2015) 68-75.

13] L. Tang, N. Wang, Q. Zhang, J. Guo, R. Nandhakumar, A new benzimidazole-based quinazoline derivative for highly selective sequential recognition of Cu²⁺ and CN⁻ *Tetrahedron Letters* 54 (2013) 536-540

14] Z. Zhang, J. X. H. Wang, B. Shen, J. Zhang, J. Hao, J. Cao, Z. Wang, Synthesis, Photophysical and Optoelectronic Properties of Quinazoline-Centered Dyes and their Applications in Organic Light-Emitting Diodes *Dyes and Pigments* 125 (2016) 199-308.

15] P. Duy, Q. Dao, S. L. Ho, C. Sik Cho, Synthesis of N-Fused Benzimidazole-4,7-diones via Sequential Copper-Catalyzed C–N Coupling/Cyclization and Oxidation *ACS Omega* 3 (2018) 5643-5653.

16] S. Ambethkar, M. Kalaiselvi, J. Ramamoorthy, V. Padmini, I₂-Catalyzed Oxidative Cross-Coupling Reaction of Methyl Ketones and 2-(2-Aminophenyl) Benzimidazole: Facile Access to

Benzimidazo[1,2-c]quinazoline ACS Omega 3 (2018) 5021-5028.

17] A. H. Shinde, S. Arepally, M. D. Baravkar, D. S. Sharada Nickel-Catalyzed Aerobic Oxidative Isocyanide Insertion: Access to Benzimidazoquinazoline Derivatives via a Sequential Double

Annulation Cascade (SDAC) Strategy J. Org. Chem. 82 (2017) 331-342.

18] D. Gautam, P. Gautam, R. P. Chaudhary Spectral, DFT and X-ray diffraction studies on regioselective synthesis of thiazolo-quinazoline system *J. Mole. Structure* 1145 (2017) 268-277.

19] V. Krishnakumar, S. Muthunatesan, DFT studies of the structure and vibrational

assignments of 4-hydroxy quinazoline and 2-hydroxy benzimidazole *Spectrochimica Acta Part A* 66 (2007) 1082–1090.

20] V. S. Padalkar, A. Tathe, V. D. Gupta, V. S. Patil, K. Phatangare, N. Sekar, Synthesis and Photo-Physical Characteristics of ESIPT Inspired 2-Substituted Benzimidazole, Benzoxazole

and Benzothiazole Fluorescent Derivatives J. Fluoresc 22 (2012) 311–322.

21] V. S. Patil, V. S. Padalkar, N. Sekar, 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 *J. Fluoresc* 24 (2014) 1077–1086.

22] V. S. Padalkar, V. D. Gupta, V. S. Patil, K. R. Phatangare, P. G. Umape, N. Sekar, Indion 190 resin: efficient, environmentally friendly, and reusable catalyst for synthesis of benzimidazoles, benzoxazoles, and benzothiazoles *Green Chem Lett and Reviews*, 5(2) (2012) 139-145.

23] K. R Phatangare, B.N. Borse, V.S. Padalkar, V.S. Patil, V. D Gupta, P.G. Umape, N. Sekar, Synthesis, photophysical property study of novel fluorescent 4-(1,3-benzoxazol-2-yl)-2-phenylnaphtho[1,2-d] [1,3] oxazole derivatives and their antimicrobial activity J. Chem. Sci. 125 (1) (2013) 141-151.

24] V. S. Patil, V. S. Padalkar, K. R. Phatangare. V. D. Gupta, P. G. Umape, N. Sekar, Synthesis of new ESIPT-fluorescein: photophysics of pH sensitivity and fluorescence *J. Phys. Chem. A* 116 (2012) 536-545.

25] V. S. Patil, V. S. Padalkar, A. S. Chaudhari, N. Sekar, Intrinsic catalytic activity of an acidic ionic liquid as a solvent for quinazoline synthesis *Catal. Sci. Technol.*, 2 (2012) 1681-1684.

26] V.S. Padalkar, V.S. Patil, N. Sekar, Synthesis and characterization of novel 2, 2'-

bipyrimidine fluorescent derivative for protein binding Chem. Cent. J. 5 (72) (2011) 1-7.

27] O. Treutler R. Ahlrichs, Efficient molecular numerical integration schemes J. Chem. Phys., 102 (1995) 346-354.

28] Y. Z. Zhan, X. Zhao, Wei Wang, Theoretical study of the interaction energy of benzodifuranone dye molecule rings *Color. Technol.*, 133 (2016) 50-56.

29] A.D. Becke, A new mixing of Hartree–Fock and local densityfunctional theories *J. Chem. Phys.*, 98 (1993) 1372-1377.

30] C. Lee, W. Yang, R.G. Parr, Development of the Colic-Salvetti correlation-energy formula

into a functional of the electron density Phys. Rev. B, 37 (1988) 785-789.

31] C.H. Kim, J. Park, J. Seo, S.J. Park, T. Joo, Excited State Intramolecular Proton Transfer and Charge Transfer Dynamics of a 2-(2'-Hydroxyphenyl) benzoxazole Derivative in Solution *J. Phys. Chem. A*, 114 (2010) 5618-5629.

32] M. Kim Santra, H. Moon, M.H. Park, T.W. Lee, Y. Kim, K.H. Ahn, Dramatic Substituent Effects on the Photoluminescence of Boron Complexes of 2-(Benzothiazol-2-yl) phenols *Chem. Eur. J.*, 32 (2012) 9886-9893.

33] H. Kim Santra Li, L. Niu, X. Xu, S. Zhang, F. Gao, A Comprehensive Therotical Investigation

of Intramolecular Proton Transfer in the Excited States for Some Newly-designed Diphenylethylene Derivatives Bearing 2-(2-Hydroxy-Phenyl)-Benzotriazole Part *J. Fluoresc.*, 21 (2011) 1721-1728.

34] P. Wiggins, J.A. Gareth Williams, D.J. Tozer, Excited state surfaces in density functional theory: A new twist on an old problem *J. Chem. Phys.*, 131 (2009) 91101.1-91101.4.

35] R. Send, M. Kuhn, F. Furche, Assessing Excited State Methods by Adiabatic Excitation Energies *J. Chem. Theory Comput.*, 7(8) (2011) 2376-2386.

36] D. Jacquemin, A. Planchat, C. Adamo, B. Mennucci, Assessing Excited State Methods by Adiabatic Excitation Energies J. Chem. Theory Comput., 8 (7) (2012) 2359-2372.

37] L. Wiggins, S. Grimme, Assessment of TD-DFT methods and of various spin scaled CIS(D) and CC2 versions for the treatment of low-lying valence excitations of large organic dyes *J. Chem. Phys.*, 132 (2010) 184103.1-184103.9.

38] R. Bauernschmitt, R. Ahlrich, Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory *Chem. Phys. Lett.*, 256 (1996) 454-464.

39] V.S. Patil, V.S. Padalkar, N. Sekar, Environment-sensitive benzoxazole based fluorescein derivatives: synthesis and application to the design of ON-OFF fluorescent chemosensors for microenvironment J. Lumin. 158 (2015) 243-251.

40] V.S. Patil, V.S. Padalkar, A.B. Tathe, V.D. Gupta, N. Sekar, Synthesis, photophysical and DFT studies of ESIPT inspired novel 2-(20,40-dihydroxyphenyl) benzimidazole, benzoxazole and benzothiazole J. Fluoresc. 23 (2013) 1019-1029.

41] R. S. Patil, A. S. Patil, V. S. Patil, H. D. Jirimali, P. P. Mahulikar, Synthesis, photophysical, solvatochromic and DFT studies of (Z)-2-(2-Phenyl-4H-benzo[4,5]thiazolo[3,2-a]pyrimidin-4-ylidene)acetonitrile Derivatives J. Lumin. 210 (2019) 303–310.

42] V. S. Patil, V. S. Padalkar, N. Sekar, S. V. Patil, J. Rajput Synthesis of 2-methyl-5-(5-phenyl substituted-1,3,4 oxadiazole-2-yl) quinazolin-4-one fluorescent brightening agent: Computational and experimental comparison of photophysical structure *J. Mole. Structure*, 1182 (2019) 150-157.

Table and Figure captions

Table 1: Observed UV-visible absorption, emission and computed vertical excitation and emission of compounds **6a** -**6g** in DMF.

Table 2: HOMO-LUMO Orbital diagram of compound 6a -6g in DMF with their energy

 Table 3: The dihedral angle of 6a -6g between quinazolinone and azole ring in ground and excited state

 calculated by TD and TD-DFT

 Table 4: Colour values of fluorescent dyes 6a -6g polyester fabric and commercially used optical whiteners.

Figure 1: Molecular structure of substituted quinazoline 6a-6g extracted from DFT optimization.

Figure 2: Emission spectra of compounds 6a -6g in DMF.

Figure. 3. Predicted electron Shifting mechanism in quinazoline-benzazole derivatives during excitation and emission.

Figure 4: HOMO-LUMO Energy level diagram of compounds 6a -6g in DMF

Figure 5: Thermo gravimetric analysis of compounds 6a-6g.

Scheme1. Synthesis of 5-(1H-benzo[d]oxazole, thiazole, imidazole-2-yl)-2 methylquinazoline-4-ol derivatives **6a -6g**.

- > PCM model C₁ symmetry molecular DFT-TDDFT optimisation.
- > Two distinct planes has large resistance to the π - π electronic transition.
- > Inductive electronic effect of molecules controls fluorescence properties.
- > Future prospectus to reduce laboratory work rather to perform by computational.

boundance