



Green Chemiluminescence of Highly Fluorescent Symmetrical Azo-based Luminol Derivative

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ABSTRACT

A symmetrical azo-based Luminol derivative **2** was synthesized using catalytic dehydrogenative coupling reaction procedure. This symmetrical molecule shows blue fluorescence in polar aprotic solvents ($\lambda_{\text{max}} = 450 \text{ nm}$). With an increase in aqueous content **2** was exhibiting aggregation caused fluorescence quenching (ACQ) with a red shift of 30 nm ($\lambda_{\text{max}} = 480 \text{ nm}$). Distinct emission features were observed for this molecule with a variation in the pH range. In basic medium, deprotonated form of **2** shows fluorescence quenching followed by enhancement of green chemiluminescence ($\lambda_{\text{max}} = 490 \text{ nm}$) with $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ -catalytic system. The fluorescence and chemiluminescent (CL) properties of **2** were compared with its parent luminol **1**. The CL emission intensity of **2** was found to be about 16 times higher than that of **1**. In addition, HOMO-LUMO energy gap for **2** was also calculated using density functional theory (DFT) studies.

Keywords: Luminol, Azo-derivative, Fluorescent, Hydrogen peroxide, Green Chemiluminescence.

INTRODUCTION

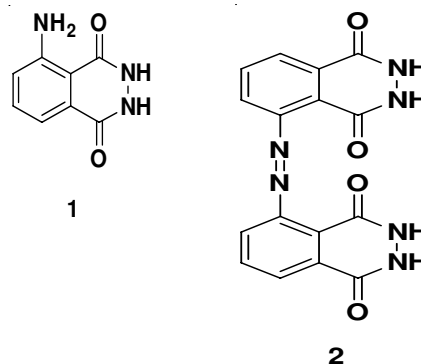
Luminol **1** is a classic chemiluminescent (CL) reagent¹ first reported by Albrecht in 1928², extensively used for different analytical applications^{3,4}. The basic solution of Luminol exhibits a striking blue glow when mixed with an oxidizing agent and an Iron catalyst.¹ Various luminol derivatives were reported with an intention to improve emission properties.⁵⁻⁸ Luminol derivatives

with electron-releasing substituents show red shift with an enhancement of CL quantum yield.⁹⁻¹⁴ and White *et al.*, have synthesized alkyl derivatives of luminol to maximize the CL ($\lambda_{\text{max}} = 410 \text{ nm}$) quantum yield.¹² While substitution of amino or methoxy groups on luminol increases its CL intensity¹³, electron withdrawing substituents like chloro and nitro groups make it non fluorescent.⁹⁻¹⁴ Zaitsu *et al.*, have synthesized *N*-(4-substituted benzyl) isoluminol with substituents like, 4-bromo,4-methoxy



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and 4-nitro groups. The chemiluminescent intensities of these compounds were 0.03-4.7 times that of luminol.¹² Naphthalene analogues of luminol have an extended aromaticity which leads to green chemiluminescence ($\lambda_{\text{max}} = 490$ to 550nm).¹⁵ It is noteworthy that green chemiluminescence in longer wavelength region is of great interest for biological applications.¹⁶ The increase of aromaticity leads to a redshift with a green CL. Balaban *et al.*, have synthesized 5-(azo-para-phenylene-*N*-aza-15-crown-5)-phthalhydrazide, an azo derivative of Luminol¹⁷ which shows a weak fluorescence but a significant chemiluminescence at 425nm . But the chemiluminescent emission was found around 425nm similar only to its parent luminol. Another azo derivative of luminol, phthalhydrazide-5-azo-2-naphthol, synthesized by coupling diazotized 5-aminophthalhydrazide with 2-naphthol which shows fluorescence at 350nm .¹⁸ This derivative was used to complex with metal ions, but chemiluminescent studies were not reported. Reddy *et al.*, have reported the synthesis of a series of symmetrical azobenzenes from various aromatic amines using Cu(I) catalyzed dehydrogenative homocoupling using mild reaction conditions.¹⁹⁻²⁰ The catalytic system employed was Cu(I)Br along with DMAP (Dimethylamino pyridine) and AIBN (Azobisisobutyronitrile). Luminol 1 is also basically an aromatic amine with a phthalhydrazide group. Dehydrogenative homo coupling of luminol would also result in a symmetrical azo product of luminol, which is actually a dimer with an extended conjugation between two luminol units through an azo link 2. To the best of our knowledge, this kind of homocoupling of luminol was not known. So we have decided to synthesize a symmetrical luminol derivative with an objective to increase the CL intensity and a significant red shift. In the present work, we have performed the homo coupling of 1 and optimized the conditions for a maximum yield. Azobenzene and its derivatives are commonly used as dyes and fluorescent materials. Linking chemiluminescent luminol units through an azo group would also result in interesting fluorescent properties through the short and compact π -conjugated structure. The presence of two phthalhydrazide groups guarantee its chemiluminescent nature, which can be taken advantage for applications like biosensing.



EXPERIMENTAL

Materials

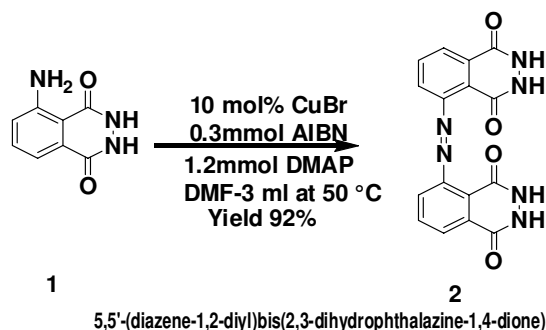
Luminol(99%), Copper bromide(99%), Azobisisobutyronitrile(AIBN), (98%) and 4-Dimethylaminopyridine (DMAP) (99%) were purchased from Sigma-Aldrich and used as received. Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$, (97%) Hydrogen peroxide (30%), Sodium hydroxide was purchased from Merck Dimethyl sulfoxide (DMSO) (98%), Dimethylformamide (DMF) (97%), Ethyl acetate (97%), Tetrahydrofuran(THF) (98%) Hexane (96%), were purchased from Merck & Co. and vacuum distilled before further used.

METHODS

Thin-layer chromatography was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence lamp. Silica gel (particle size 100-200 mesh) purchased from Merck & Co, was used for chromatography. ^1H NMR spectra were recorded on a Bruker 400 MHz instrument. Spectra were reported relative to DMSO- d_6 residual peak (δ 2.5 ppm). (^{13}C 100 MHz NMR) were reported relative to DMSO- d_6 (δ 40.16 ppm). The first-order peak patterns are indicated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet), and m (multiplet). UV-Visible spectra were recorded on Perkin Elmer spectrophotometer (Model: Lambda 35). Chemiluminescence spectra were recorded by Jasco Spectrofluorometer instrument (Model: F8300). Density Functional Theory calculations were carried out with B3LYP level using Gaussian 09 program.

Synthesis of Compound 2

Compound 2 was synthesized according to the procedure earlier reported by Reddy *et al.*,¹⁹⁻²⁰ Accurately weighed Luminol (250 mg, 1.0 mmol) was taken in a dry 100 ml two necked round bottom flask followed by the addition of 4-dimethyl aminopyridine (DMAP) (150 mg, 1.2 mmol), cuprous bromide (14.3 mg, 0.10 mmol) and Azobisisobutyronitrile (AIBN) (50 mg, 0.3 mmol) under an inert atmosphere condition. To these contents, 3 ml of DMF was added. The reaction mixture was allowed to stir under inert conditions for a period of 7 h at 50 °C, after which the reaction mass, was filtered. The filtrate obtained was concentrated under high vacuum and the resultant sticky crude product was purified using column chromatography (silica gel, hexane/ethyl acetate, 85/15 as an eluent). The product was obtained in a pure form as a yellow colour solid in 92% of isolated yield and its structure was established using various analytical techniques. ¹H NMR (400 MHz, DMSO-d₆, TMS) 6.90 (1H, d); 6.95 (1H, d); 7.42 (1H, t) ¹³C NMR (100 MHz, DMSO-D₆, TMS) δ (ppm): 162.97; 152.72 ; 134.41 :129.70128.56: 126.13; 125.63 ppm. HRMS was calculated for C₁₆H₁₀N₆O₄ (M+): 351.08. Found: 351.17 (M+1).



Scheme 1. Synthesis of Luminol azo derivative

General procedure for the absorbance, Fluorescence and Chemiluminescence (CL) Studies

1 (1.8×10^{-5} M) was dissolved in DMF whereas 2 (2.5×10^{-5} M) was dissolved in various solvents like DMF, DMSO, ethyl acetate and THF. For CL studies, both 2 (2.5×10^{-5} M) and 1 (1.8×10^{-5} M) were dissolved in DMF. 2 mL of these solutions were taken in a quartz cuvette, followed by addition of 100 μ L of potassium ferricyanide (1.8×10^{-5} M) in 9 μ M sodium hydroxide solution. To initiate CL, H₂O₂

(1-9 μ M) was added to this solution. Solutions of same concentrations were used for all absorbance, fluorescence and CL spectroscopic studies unless otherwise specified.

General procedure for calculating Density functional theory studies:

Density functional theory calculations were carried out with B3LYP level using Gaussian 09 program. The dihedral angle (Φ) between the plane of the optimized energy structure is found to be $\sim 50^\circ$. The Frontier molecular orbitals of compound 2 obtained from DFT calculations.

RESULTS AND DISCUSSION

In the earlier work by Reddy *et al.*, homocoupling of simple and substituted aromatic amines at ambient temperature under mild conditions was reported¹⁹⁻²⁰. Luminol is a basic aromatic amine with a phthalhydrazide group. Following the mentioned reported procedure dehydrogenative homocoupling of luminol 1 was done using the catalytic system. The catalytic system employed was 10 mol% CuBr, 0.3 mmol of AIBN and 1.2 mmol of DMAP at room temperature as well as 50 °C which resulted in 2, a symmetric molecule 2 (Table 1) has two phthalhydrazide groups which can produce chemiluminescence as like the parent luminol molecule. The yield of coupling product was less when reactions were performed at room temperature. (Entries 1, 4, 6). To increase the yield slightly higher temperature a 50 °C was used with DMF (Entries 2). The yield of the desired coupling product 2 was 92%. At higher temperature of 80 °C (Entry 3) the yield was not found to be increasing (72%). At this stage it was almost confirming the better activity of the catalytic system only at 50 °C. The reaction was also performed in DMSO at ambient temperature (Entry 4) as well as (Entry 5) 50 °C. The yield was higher at 50 °C (83%) compared to room temperature (27%) but still lower than that in DMF (Entry 2). The reaction was also performed in acetonitrile at ambient temperature (Entry 6) and 50 °C (Entry 7) as well as DCM at 50 °C (Entry 8). Only with the DMF solvent, the highest conversion was obtained.

Table 1: Experimental Optimizing conditions for dehydrogenative homocoupling of Luminol to Compound 2

Entry	Metal Catalyst	Solvent	Temperature(°C)	Time (hr)	% Yield
1.	Cu(I)Br	DMF	RT	8	20
2.	Cu(I)Br	DMF	50	7	92
3.	Cu(I)Br	DMF	80	7	72
4.	Cu(I)Br	DMSO	RT	8	27
5.	Cu(I)Br	DMSO	50	7	83
6.	Cu(I)Br	ACN	RT	8	17
7.	Cu(I)Br	ACN	50	7	79
8.	Cu(I)Br	DCM	50	7	46

All the reactions were carried out using 1.2 mmol of DMAP, 10 mol% catalysts, 0.3 mmol of Azobisisobutyronitrile (AIBN)

The product 2 is symmetrical and shows fluorescence because of the extended conjugation as two phthalhydrazide groups are also present, it is obvious to expect chemiluminescence also. 2 was found to be highly soluble in polar solvents like DMF, DMSO, Ethyl acetate and THF. These solutions were fluorescent with varying intensities. Compared with 2, the parent luminol molecule was found to be non-fluorescent when dissolved in DMF. (Fig. 1. black background under UV lamp).

Solutions of 2 with various solvents were prepared and the absorption and fluorescence spectra were recorded using these solutions. The absorption spectra of 2 in different solvents are given in (Fig. 2) Compared with parent luminol (DMF), the absorbance maxima of 2 shows red shifted due to the increase in conjugation. 1 shows two absorption bands at 300nm and 350nm due to $\pi-\pi^*$ transitions. 2 shows two absorption bands one in the wavelength range of 250-300 nm due to $\pi-\pi^*$ transitions of aromatic group and a shoulder in the range of 300-390 nm which is due to $\pi-\pi^*$ transitions of $-N=N-$ group with all solvents. The intensity of absorption spectra was found to be varying in accordance with the dielectric constant of the solvents employed.²¹ High dielectric constant, solvents like DMSO ($\epsilon = 46.7$) and DMF, ($\epsilon = 36.7$), compound 2 show two bands at 262 nm and 275 nm due to $\pi-\pi^*$ transitions of aromatic groups and another shoulder at 385 nm and 370 nm

correspond to the azo group.²¹⁻²² In solvents with low dielectric constant like THF ($\epsilon = 7.52$) and Ethyl acetate ($\epsilon = 6.02$), 2 show two absorption band with a λ_{max} at 253 and a shoulder at 315, 253 and 375nm respectively which is evident for negative solvatochromism. This type of observation may be due to more polarisation of 2 in polar solvents with a high dielectric constant.

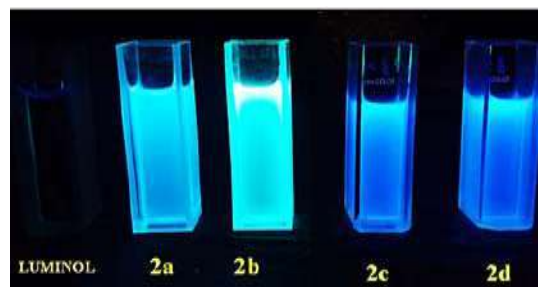


Fig. 1. Luminol (in DMF) and 2 in DMF (2a), DMSO(2b), Ethyl acetate(2c), THF(2d) under UV at 365 nm

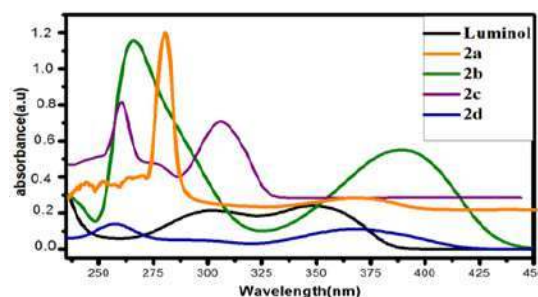


Fig. 2. UV-Visible Spectrum of Luminol in DMF and Compound 2 in various polar solvents like DMF (2a), DMSO (2b), Ethyl acetate (2c), THF (2d)

The compound 2, is a symmetrical homocoupling product of Luminol and was found to be highly fluorescent in polar solvents. Compared with parent luminol, 2 shows blue fluorescence with a λ_{max} at 458 nm in DMF (Fig. 3). In other polar solvents like DMSO, Ethyl acetate, and THF, maximum fluorescence was found at 467, 445 and 449 nm respectively. (Fig. 4) A clear redshift was noticed in DMSO. This may be due to the intermolecular charge transfer taking place between the solvents and compound 2 and also the compound 2 is more polar in the excited state²¹. In Ethyl acetate a blue fluorescence with a λ_{max}

at 445 nm. (Fig. 4).which is due the negative solvatochromism appeared in compound 2. In less dielectric constant solvent like Ethyl acetate ($\epsilon=6.02$) and THF ($\epsilon=7.02$) compound 2 is freely rotating which leads to a blueshift.²¹⁻²²

Self-aggregation is a well known phenomenon among the azo dyes caused due to hydrophobic and/or vanderwaals forces, which results in fluorescence quenching, prevalently called as aggregation caused quenching (ACQ)²³ which affect its development as a solid-state fluorescent materials.

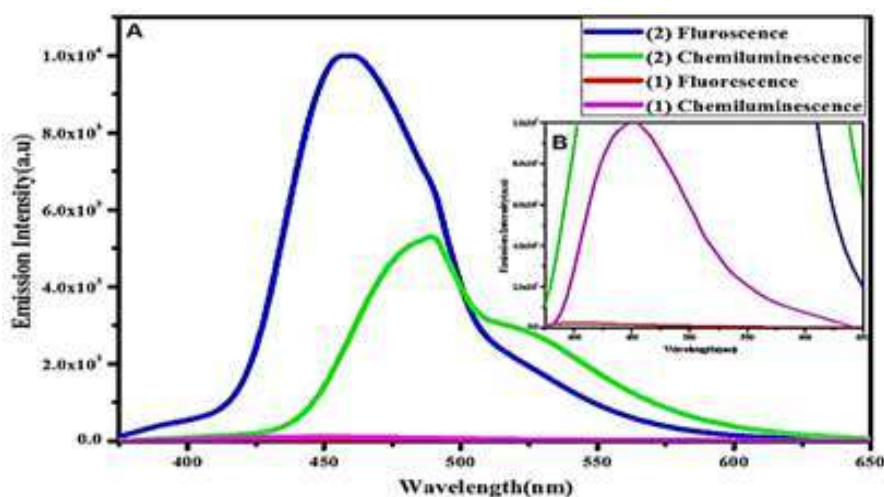


Fig. 3. (A) Emission spectra of 2 and Inset (B) Emission spectra of 1

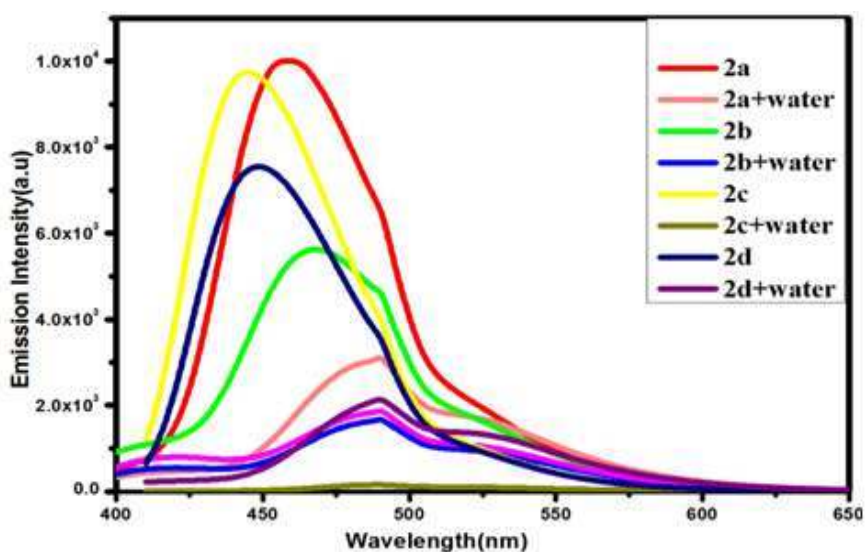


Fig. 4. Fluorescence spectra of Compound 2 in various polar solvents like DMF (2a), DMSO (2b), Ethyl acetate (2c), THF (2d) and by varying water fractions

The symmetric luminol azo derivative **2** was also expected to show ACQ. Compound **2** in their respective solvents were prepared. By varying the proportion of water 10-90% *v/v* using these solutions the Fluorescence spectra were recorded. (Fig. 4) With an increase in water content the fluorescence bands got in different solvents gets quenched and also get red shifted to 480 nm. In aqueous media the intramolecular rotations are limited due to the formation of aggregates (ACQ) which block the radiative excitations getting the molecule quenched.²⁴ In the case of **2a**/water, **2b**/water mixtures fluorescence intensity of

2 gradually decreases with an increase in water upto 10-40% *v/v*. Further increase in the percentage of water to 50%*v/v*, ACQ breaks quenched intensity of the fluorescence band gets improved. (Fig. 5 & 6). But furthermore addition of water from 60% - 90% *v/v* results in a gradual quenching of fluorescence. So for all other studies like effect of pH and CL emission 50% *v/v* DMF-water mixture of **2** was used.

In ethyl acetate and THF also the fluorescence intensity of **2** gradually decreased with the increase in the water fraction (10-90%) and got redshifted to 480nm. (Figure 7 and 8).

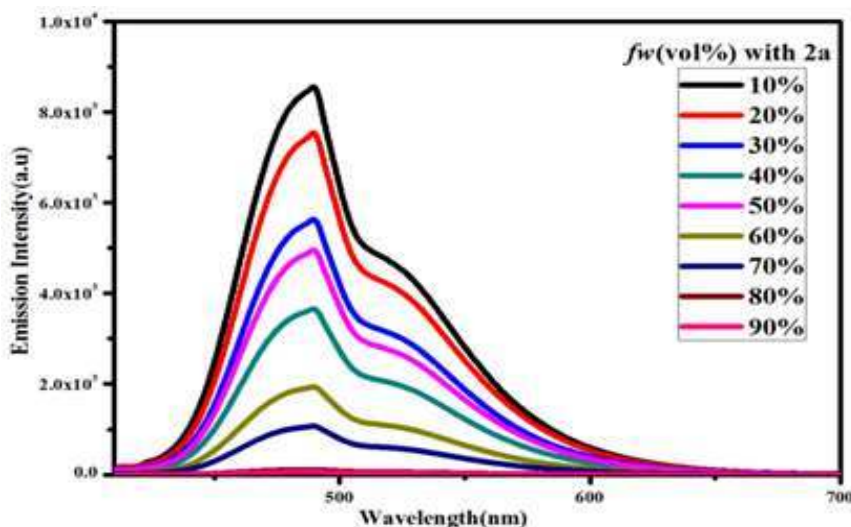


Fig. 5. Fluorescence spectra of **2** in DMF (**2a**) by varying water fractions

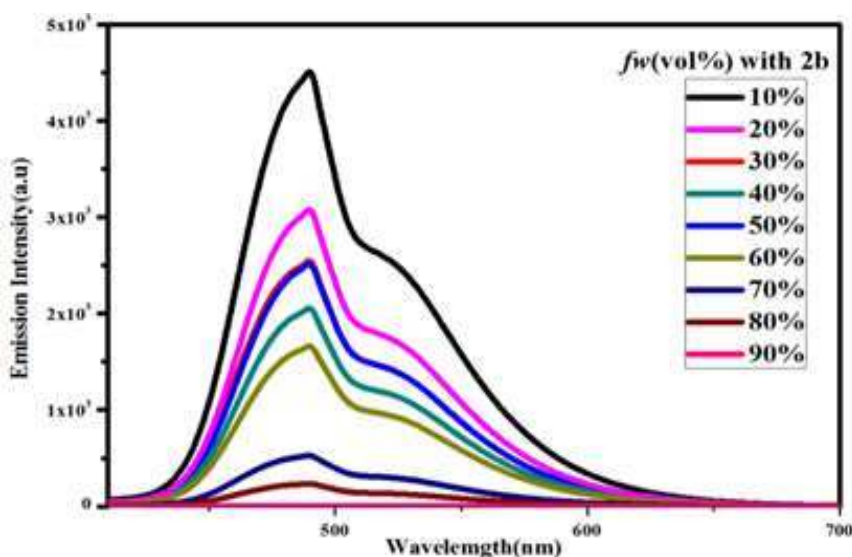


Fig. 6. Fluorescence spectra of **2** in DMSO (**2b**) by varying water fractions

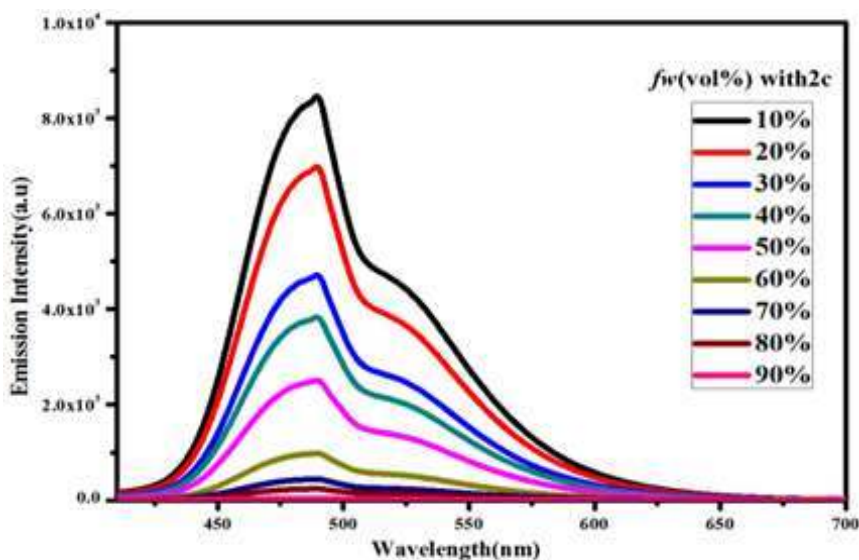


Fig. 7. Fluorescence spectra of 2 in Ethyl acetate (2c) by varying water fractions

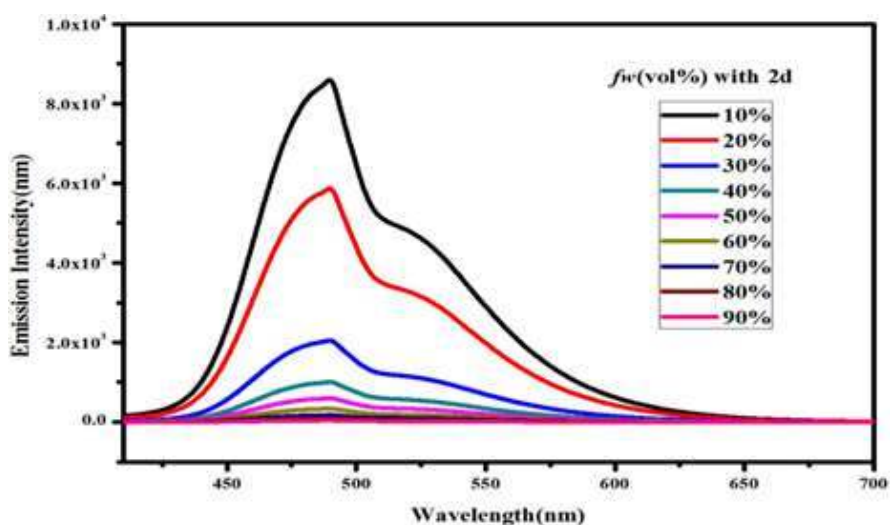


Fig. 8. Fluorescence spectra of 2 in THF (2d) by varying water fractions

A solution of 2 was adjusted to the required pH using sodium phosphate buffer solution. Using this solution, absorption and fluorescence spectra were recorded. The effect of pH on absorption and fluorescence spectra of 2 are shown in Fig. 9 & 10. The absorption spectra of 2 in lower pH 4 show one prominent band at 280nm and a shoulder at 380nm. In neutral pH, the absorption band shows two prominent bands at 280 and 390 nm similar to luminol. In an alkaline pH 9, three bands were observed with the $\lambda_{\text{max}} = 280$ nm, 340 and 360 nm. The fluorescence spectra of 2 at lower pH 4 gave a single band with $\lambda_{\text{max}} = 445$ nm with a decrease in intensity compared to the band in neutral medium this may be due to

the protonation of one nitrogen atom of azo chromophore Scheme 2 (I). There was no change in the structural and electronic environment of solution 2²⁵ in neutral pH, which was confirmed by a prominent peak at 450 nm Scheme 2(II) In an alkaline pH 9 the fluorescence spectra with a $\lambda_{\text{max}} = 477$ nm which is due to the anion formed by the deprotonation of the phthalhydrazide groups in 2 Scheme 2 (III). This symmetrical luminol azo derivative 2 exhibits CL with only molecular oxygen and base in aprotic solvents like DMF and DMSO a phenomenon similar to the parent luminol molecule^{6-8,26} The addition of base in an aprotic solvent to 2 produces a spectral red shift to 477 (Fig. 10) nm and a quenching effect in fluorescence intensity.

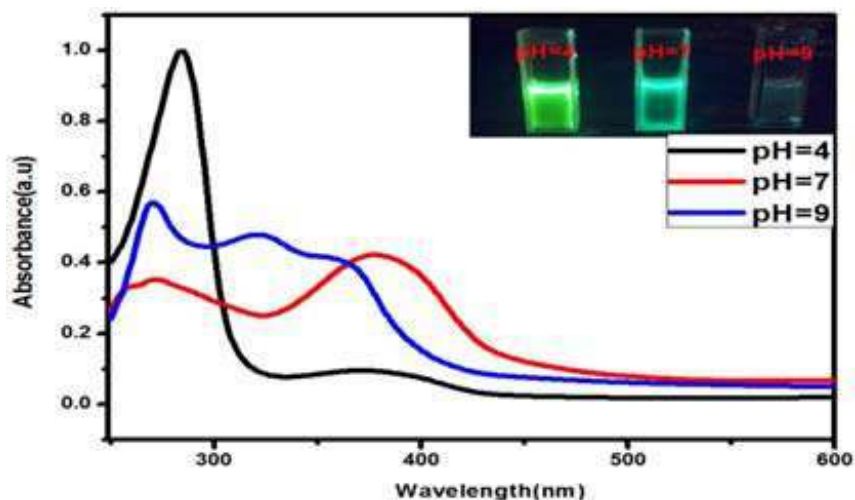


Fig. 9. UV-Visible Spectrum of 2 by varying the pH

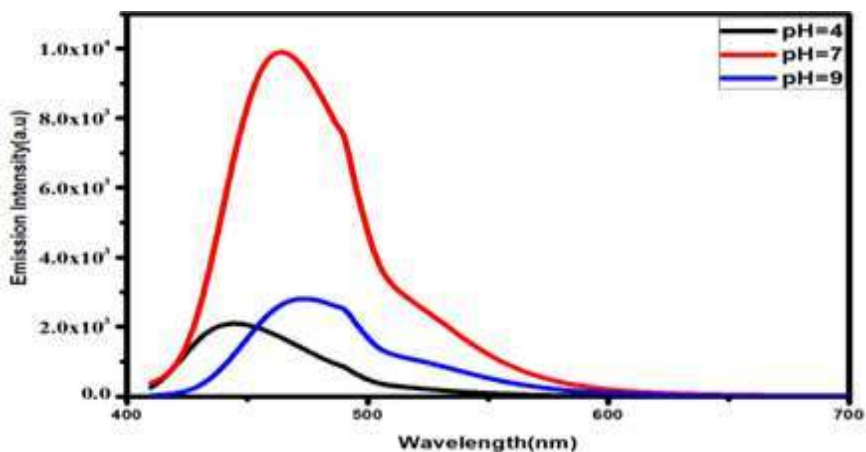
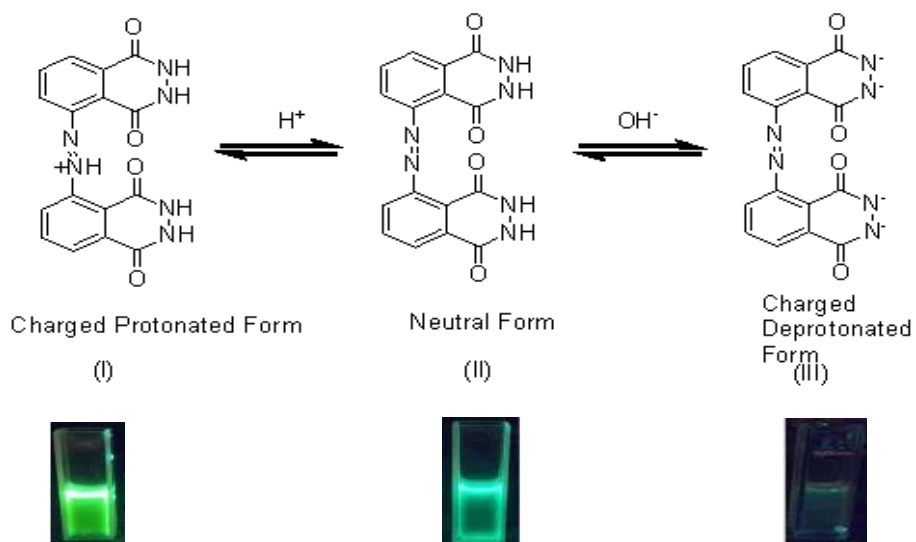


Fig. 10. Fluorescence spectra of 2 by varying pH



Scheme 2. Effect of pH in 2 Picture of 6(I) (II) (III) under UV at 365 nm

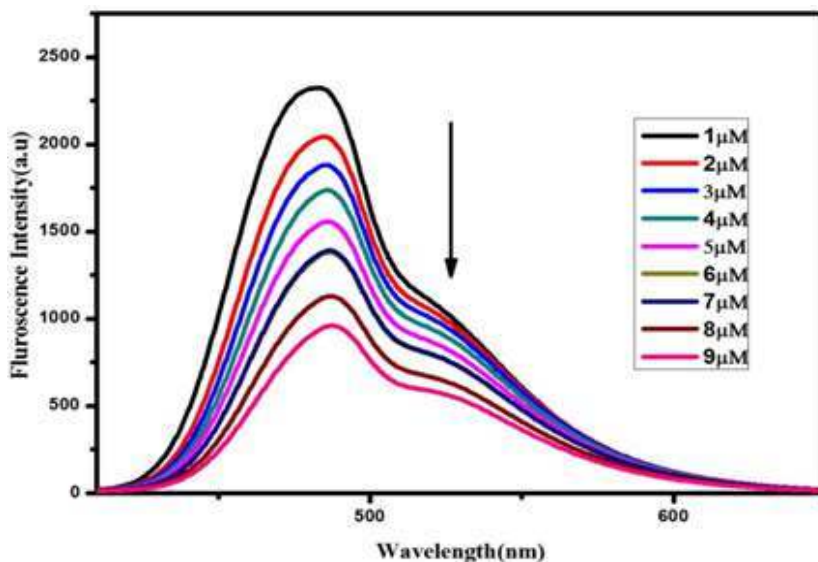


Fig. 11. Fluorescence spectra of 2 observed upon various NaOH (15 μ) concentrations showing quenching

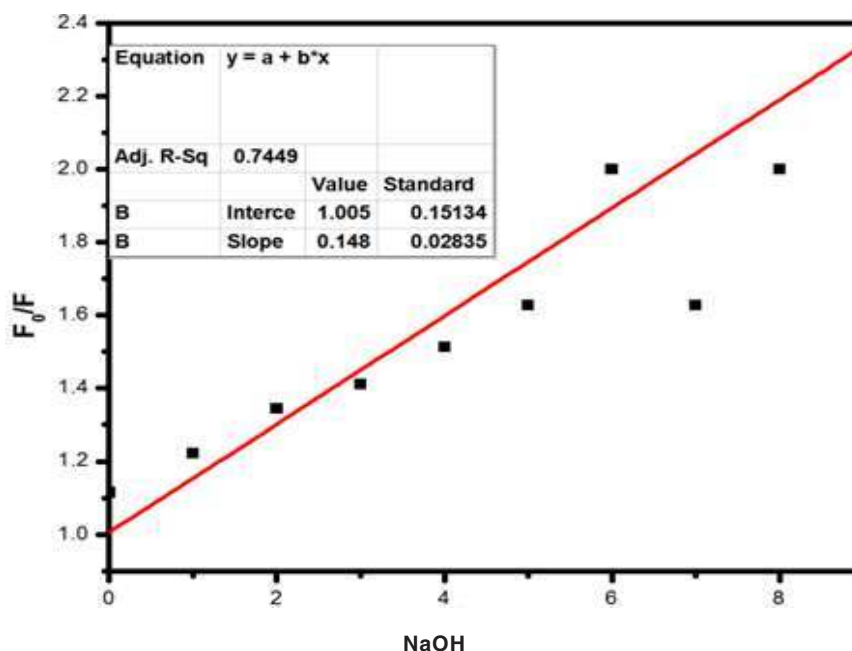


Fig. 12. Stern-Volmer plot for fluorescence quenching of the compound 2 by NaOH Solution

White *et al.*,⁶⁻⁸ have proposed CL studies of Luminol in aprotic solvents like Dimethylsulfoxide (DMSO), Dimethylformamide (DMF) exhibiting the CL with presence of oxygen and based without a need for peroxide/catalyst system. In those solvents, the CL reactions relatively free of complications and amino phthalate ion have been identified as the

products of the reaction^{6-8,26} The fluorescence quenching behavior of compound 2 was studied in DMF and NaOH Solution. To the solution of 2 in DMF taken in a quartz cuvette (1-9 μ M) NaOH solution was added and the fluorescence spectra were recorded. With the increase in the concentration of NaOH, fluorescence intensity was

found to be decreasing. (Fig. 11). In aprotic solvents like DMSO, DMF base like NaOH are not solvated and can exhibit their intrinsic basicity. But in aqueous solutions the base is not strong enough to remove the proton in both 1 and 2 because of the levelling effect of water. Formation of dianion is responsible for the initiation of the CL in both 1 and 2. Increasing the aqueous of NaOH content solution in aprotic solvents like DMF, DMSO with compound 2 considerably reduce the concentration of dianion by shifting the $\lambda_{max} = 480$ nm and quenches its fluorescence intensity.

Fluorescence quenching is quantitatively measured with the Stern–Volmer equation.

$$F_0/F = K_{SV} [Q] + 1$$

Where K_{SV} represents Stern–Volmer constants indicating the sensitivity of the quenching effects of compound 2. F_0 and F are the fluorescence intensities before and after the addition of the analytes, and $[Q]$ is the molar concentration of the analyte. Fig. 12 shows the Stern–Volmer plot for quenching effect in OH^- ion in compound 2. K_{SV} Value was calculated as $2.8 \times 10^5 \text{ M}^{-1}$. This suggested that the dynamic nature of quenching process playing a role in higher quencher concentration.

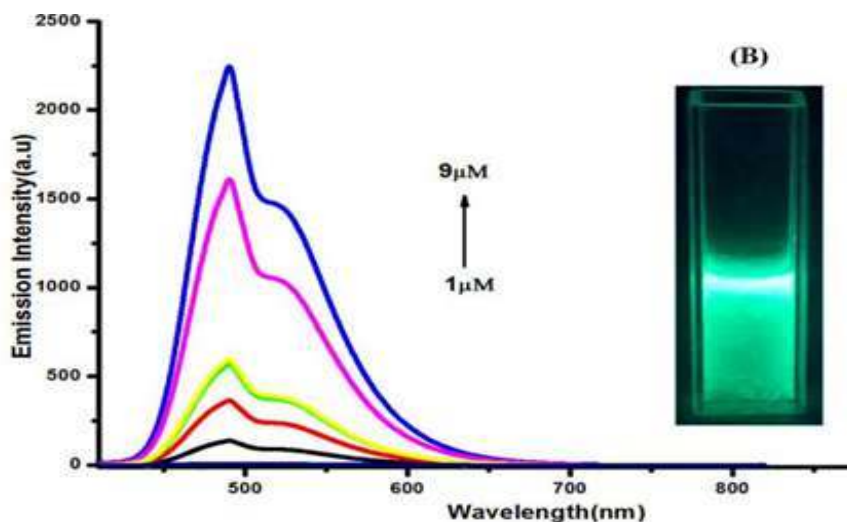


Fig. 13. Effect of H_2O_2 concentration (B). Inset shows a green CL emission at 490 nm under UV at 365nm

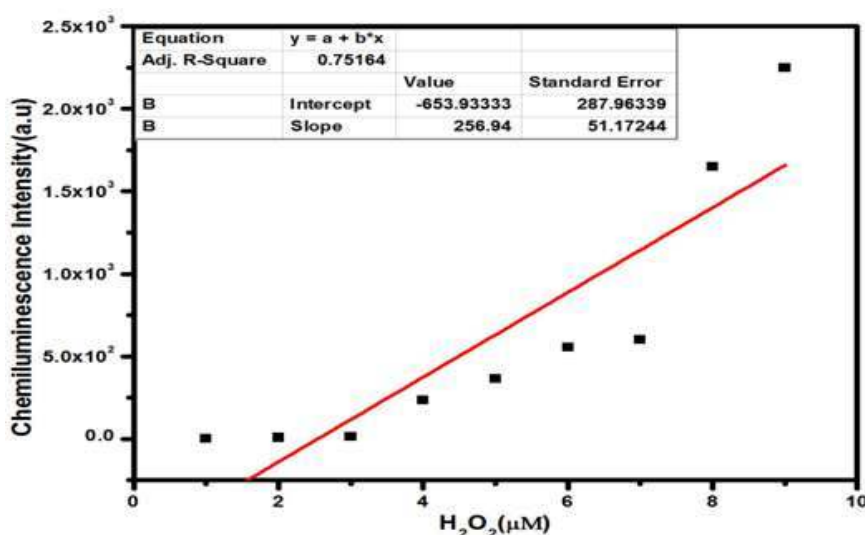
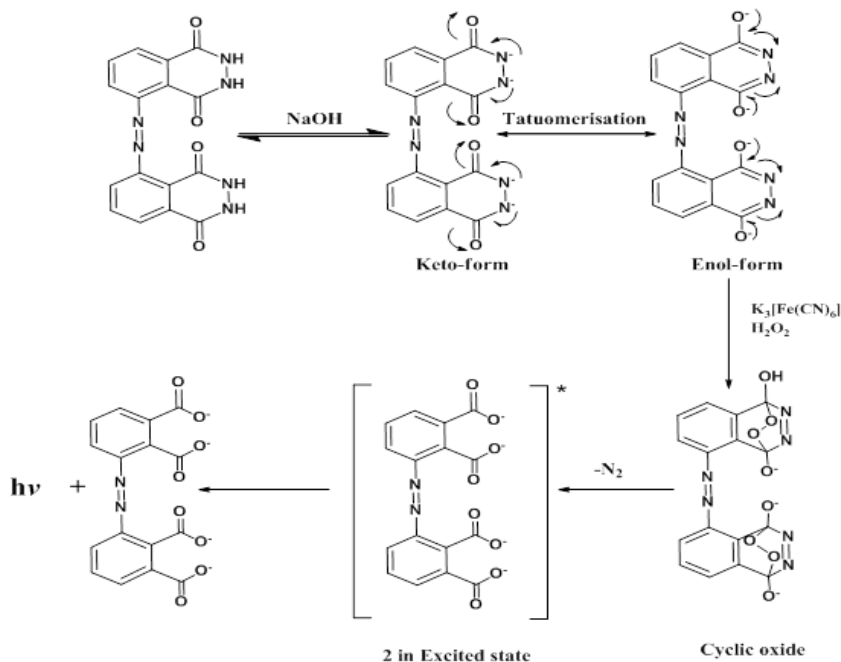


Fig. 14. Changes in Chemiluminescence intensity upon addition (1-9 μ M) of H_2O_2 at 490nm

The luminescence of Luminol (3-amino-phthalhydrazide) and chemiluminescence during oxidation process have been widely studied. Luminol chemiluminescence has limitations in bioimaging and sensing applications due to its solubility. The fluorescence titration of compound 2 with gradual addition of NaOH quenches the fluorescence intensity progressively at 480 nm. (Fig. 11) due to the increase in the concentration of dianion. But this basic solution can initiate CL reaction, provided the necessary conditions. To initiate the chemiluminescence in 2, (100 μ L of 1.8×10^{-5} M) alkaline potassium ferricyanide, followed by varying amounts (1-9 μ M) of hydrogen peroxide solution were added.¹⁰ With an increase in the concentration of peroxide,

CL emission intensity was found to be increasing and the lower detection limit (LOD=3 σ /s) was found to be 0.76 μ M. This CL spectra shows a redshift with an emission peak at 490nm and a shoulder from 510nm to 600nm covering the with a green light region (Fig. 13 and 14). An appreciable red shift was shown by 2 ($\lambda_{\text{max}}=490\text{nm}$) compared to 1 ($\lambda_{\text{max}}=435\text{nm}$). The CL reaction of 2 produced a fluorescent green colour under UV light (Fig. 16). Compared to the short life time of luminol's blue glow, this fluorescence green colour was long lasting for several hours. The mechanism of CL shown by 2 should be similar to that of parent luminol molecule, 1 (Scheme 3). It should be convincing because of the structural similarity with both these molecules having CL active phthalhydrazide groups.



Scheme 3. Probable CL mechanism of 2

More structural variations in 2 would further enhancement result in enhancement of CL intensity and longer red shift. With this objective we are now involved in synthesizing the derivatives of 2 with more structural variations and their applications in sensing/imaging.

Density functional theory studies

Density functional theory calculations were carried out with B3LYP level using Gaussian

09 program. The Frontier molecular orbitals of compound 2 obtained from DFT calculations are shown in (Fig. 15) which reveals the energy gap between HOMO and LUMO that reflects the chemical activity of compound 2. HOMO has the ability to donate an electron and LUMO represents an electron acceptor. The calculated energy gap between HOMO and LUMO was 3.502 eV. This reveals that the charge transfer interaction may be taking place within the molecule through the π -conjugated bridge.²⁸⁻³¹

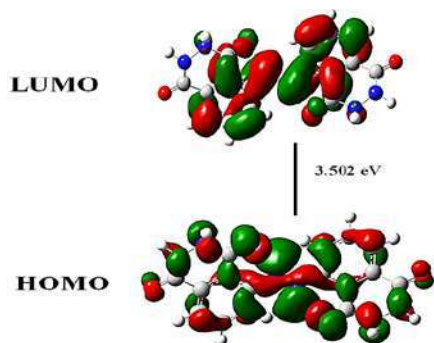


Fig. 15. Frontier molecular orbitals of compound 2 obtained from DFT calculations using Gaussian 09 program

CONCLUSION

Structural variation in chemiluminescent Luminol is widely studied to improve its emission properties. In the present study a symmetrical dimer

like molecule of luminol bridged by azo link has been prepared. This azo based luminol derivative is highly fluorescent and also shows aggregation caused quenching (ACQ) with an increase in the aqueous content. Its fluorescence also gets affected by the pH of the medium. In an alkaline medium, fluorescence of luminol derivative gets quenched and green chemiluminescence can be initiated at this stage with $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ system. This kind of behaviour shown by this derivative can be successfully utilized for sensing applications.

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