



Chemiluminescence properties of isoluminol related mono azo disperse dyes: Experimental and DFT based approach to photophysical properties



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ABSTRACT

A six novel isoluminol derivatives containing azo unit were synthesized by coupling different *N,N*-disubstituted anilines with the diazotized 5-nitro and 7-nitro-6-amino-2,3-dihydrophthalazine-1,4-dione. The chemiluminescent properties were studied in hydrogen peroxide, potassium hexacyanoferrate(III) and sodium hydroxide solution. The chemiluminescence properties were compared with the standard isoluminol systems it was observed that the chemiluminescence properties of the novel derivatives were nearly same to isoluminol. The geometries of the synthesized disperse dyes for their azo and hydrazone tautomeric forms were optimized using density functional theory and their electronic excitation properties were evaluated using density functional theory and time dependent density functional theory.

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1. Introduction

In recent years, compounds exhibiting chemiluminescence (CL) has been an attractive detection technique in the high-performance liquid chromatography (HPLC) [1]. A convenient labelling reagent having a luminol-isoluminol moiety has not been reported due to the fact that the CL intensity is always low and the synthesis method is difficult. On the other hand, various reagents containing an isoluminol moiety like isoluminolisothiocyanate (ILITC) [2], *N*-amino-butyl-*N*-ethylisoluminol (ABEI) [3,4], 4,5-diaminophthalhydrazide (DPH) [5] and 6-aminomethylphthalhydrazide (6-AMP) [6] have been widely used for the microanalyses of biological compounds. The presence of electron donating substituents (alkyl or aryl) on the amino group of luminol causes a decrease the CL intensity. While the electron donating group (alkyl or aryl) on the amino of isoluminol causes an increase in the CL intensity [7,8].

In addition, azobenzenes are widely used in liquid crystalline displays (LCD) and non-linear optical devices [9,10]. The

azobenzenes also show interesting properties of reversible *cis-trans* photoisomerization [11–13]. Also, their syntheses have good atom economy and are easy to prepare. The azo disperse dyes containing aromatic heterocyclic moiety have been investigated due to their superior properties like brilliant color and chromophoric strength, high level-dyeing property and excellent fastness properties [14,15]. The presence of acetamido groups at ortho position relative to the azo bridge is attributed to the hydrogen bonding with azo groups as well as protect reductive cleavage from light [16].

We have already developed some luminol-isoluminol related compounds; viz. 6,7-diaminophthalazine-1,4(2H,3H)-dione and 5,6-diaminophthalazine-1,4(2H,3H)-dione as a chemiluminescent derivatization reagent for carbonyl compounds [17]. Next, we will aim to develop a new isoluminol type chemiluminescence derivatization reagent for azo, which has a cyclic phthalhydrazide group as a light emitter of the chemiluminescence, and a hydrazino or hydrazono group moiety as a reaction site. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) computations were used to study the geometrical and electronic properties of the synthesized molecules. Their structures were determined by FT-IR, ¹H-NMR, HRMS, Mass spectra.

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2. Experimental

2.1. Materials and equipments

4-Nitrophthalic acid, *N,N*-diethylaniline, *N*-(3-(diethylamino)phenyl)acetamide, *N*-(3-(diethylamino)-4-methoxyphenyl)acetamide, sodium hydroxide and conc. H₂SO₄ were purchased from s.d. fine chemicals Ltd, Mumbai, India. The solid reagents were characterized by their melting points and used without purification. The liquid reagents were purified by simple distillation at their boiling points and used thereafter. The solvents were used after distillation at their boiling point and drying according to the standard processes.

All the reactions were monitored on a precoated silica gel aluminum based plates kisel gel 60 F₂₅₄ Merck, India. Purification of all the compounds was achieved by recrystallization. Melting points were recorded on the instrument from Sunder Industrial Product Mumbai by using open capillary and are uncorrected. The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ¹H NMR spectra were recorded on a Varian Cary Eclipse Australia (600 MHz), USA instrument using TMS as an internal standard. Mass spectra were recorded on Finnigan Mass spectrometer. The chemical shifts are expressed in δ ppm using DMSO as the solvent and TMS as the internal standard. Simultaneous DSC-TGA measurements were carried out on SDT Q600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd. The UV–visible absorption and chemiluminescence of the dyes were performed on a Perkin–Elmer Lambda 25 and Varian Cary Eclipse at room temperature respectively. NaOH solution of the hydrogen peroxide and potassium hexacyanoferrate(III) as an oxidizing agent for chemiluminescence measurements.

The DFT and TD-DFT calculations were performed using Gaussian 09W software package. The ground state geometry was optimized at B3LYP level of theory using the basis set 6-31G(d) for all the atoms.

2.2. Computational methods

The geometry of the synthesized azo dyes in their azo and hydrazone tautomeric forms was optimized in the ground state at B3LYP/6-31G(d) level [18]. The ground state (S₀) geometries of the dyes in vacuum and in solvents were optimized in their C₁ symmetry using DFT [19]. The Becke's three parameter exchange functional (B3) [20] combining with nonlocal correlation functional by Lee, Yang and Parr (LYP) [21] and the basis set 6-31G(d) was used for all the atoms. The same method was used for the vibrational analysis to verify that the optimized structures correspond to the local minima on the energy surface. The TDDFT computations were used to obtain the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries using the same hybrid functional and basis set [22–24]. The Self-Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM) [25,26] was used for optimizing the geometries of the dyes in solvents of different polarities.

2.3. Examination of the chemiluminescent properties

2.3.1. Standard procedure

The chemiluminescence reaction was initiated by the simultaneous automatic injections of 100 μL of hydrogen peroxide solution and 100 μL of potassium hexacyanoferrate(III) solution dissolved in sodium hydroxide to the 100 μL portion of a 10 nM solution of each chemiluminophore. The chemiluminescence intensities were

recorded immediately after the injection of oxidizing agent solution. The integrated photon counts for 1 min after the injections were explained as the chemiluminescence intensities.

2.3.2. Optimization of the chemiluminescence conditions

To establish the optimum chemiluminescence conditions the concentrations of the oxidizing reagents (hydrogen peroxide, potassium hexacyanoferrate(III) and sodium hydroxide) were varied one at a time. The temporarily settled conditions were DMF solution of chemiluminophore, 5.0 mM hydrogen peroxide and 5.0 mM potassium hexacyanoferrate(III) prepared in 1.5 M sodium hydroxide.

2.4. Synthetic strategy

A six novel chemiluminescent D-π-A azobenzenes have been synthesized by the conventional synthesis methods. These dyes have *N,N*-diethylaniline as the electron donor, nitro and phthalazine ring as the electron acceptors which are conjugated through the azo π-bridge. They were synthesized by the traditional azo coupling reaction [27] using nitrosylsulfuric acid selected as diazotizing agent because of its high reactivity which helps in the protonation of the N-atom [28]. The resulting diazonium salt was further coupled with different aromatic amines (**a–c**) to give the target azo disperse dyes (**3a–3c** and **4a–4c**) Scheme 1.

3. Synthesis and characterization

The synthetic scheme for the preparation of the dyes **3a–3c** and **4a–4c** are shown in Scheme 1. 6-Amino-7-nitrophthalazine-1,4(2*H*,3*H*)dione **1** and 6-amino-5-nitrophthalazine-1,4(2*H*,3*H*)dione **2** were prepared by the reported procedure [29] from 4-nitrophthalic acid.

3.1. Preparation of azo dyes (3a–3c and 4a–4c)

3.1.1. Preparation of diazotization salt (3 and 4)

A solution of amine (**3** or **4**) (2.2 g, 10 mmol) in concentrated sulfuric acid (10 ml) was slowly added to 1.56 M nitrosylsulfuric acid at 0–5 °C within 1 h. The completion of the diazotization was checked using starch iodide paper. Urea (0.02 g) was added to consume the excess of nitrous acid.

3.1.1.1. General method for preparation of nitrosylsulfuric acid. 1.56 M Nitrosylsulfuric acid was prepared by adding 63 g of dry sodium nitrite to 500 ml 98% sulfuric acid at 0–5 °C. The addition was made slowly; so that there was no formation of brown fumes. When the addition was completed the reaction mass was heated to 80 °C till a clear solution was obtained. The reaction mass was cooled before the diazotization.

3.1.2. General method of coupling

The coupler **a–c** (10.1 mmol) was dissolved in 100 ml ethanol at 0–5 °C. The diazonium salt 10 mmol (**3** and **4**) was added dropwise to the coupler solution at 0–5 °C over a period of 2 h. After the addition was completed, the pH was adjusted between 5 and 6 by using cold aqueous 10% sodium hydroxide solution. The reaction mixture was stirred overnight and monitored by using H-acid and starch iodide paper. The precipitated product was filtered and washed with water, recrystallized from DMF/*N,N*-dimethylacetamide to give the dyes **3a–3c** and **4a–4c** respectively. The low solubility of the compounds **3a–3c** and **4a–4c** made the ¹³C-NMR characterization of these substrates not possible. Only the IR, ¹H-NMR, mass and HRMS are recorded.

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