# Synthesis and spectral characterization of coumarin mediated new chromophores

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***Abstract*—Coumarin mediated Schiff base chromophore is synthesized from 6-amino coumarin. It is characterized through single x-ray crystallography, Absorption and Emission Spectroscopy.**

***Index Terms*— Coumarin Schiff base, Crystal structure, Spectra.**

## I. INTRODUCTION

Coumarin is a phytochemical and is found in a variety of plants such as Tonka bean, lavender, sweet clover grass, licorice and also occurs in food plants such as strawberries, apricots, cherries, cinnamon. Coumarin derivatives have blood-thinning, anti-fungicidal, anti-tumor and anticoagulant activities. Photophysics and photochemistry of coumarin derivatives are also important and have been used as dye lasers. Considerable effort has now been given at present to functionalize coumarin so that metal–coumarin complexes may be synthesized that could display interesting excited state properties and be used in designing artificial photosynthetic systems, chemical sensors and molecular level devices [1-9].
The coumarinyl-derivatives have been obtained, namely (E)-6-(quinolin-8ylmethyleneamino)-2H-chromen-2-one ($L^1$), and 6-((E)-((E)-3-((E)-(2-oxo-2H-chromen-6-ylimino)methyl)benzylidene)amino)-2H-chromen-2-one ($L^2$) respectively. $L^1$ is characterised by X-ray crystallographic analysis whereas all other compounds have been characterized by elemental analysis, IR and UV-vis spectra, NMR and fluorescence spectrometry.

## II. EXPERIMENTAL

### 2.1. Materials

The binuclear imino ligands were synthesized by the reported procedure [10]. All chemicals and solvents used here were of reagent grade and used as received. The metal salts required for experiments were purchased from Merck, India.

### 2.2. Physical Measurements

Microanalytical data (C, H, and N) were collected on Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra by Perkin–Elmer UV–Vis spectrophotometer model Lambda 25; FTIR spectra (KBr disk, 4000–400 cm$^{-1}$) by Perkin–Elmer FT-IR spectrophotometer model RX-1; the $^1$H NMR spectra by Bruker (AC) 300 MHz FTNMR spectrometer. Emission was examined by LS 55 Perkin–Elmer spectrofluorimeter at room temperature (298 K) in DMF, Acetonitrile, EGME, Water solutions under degassed condition. The fluorescence quantum yield of the ligands were determined using anthracene as a reference with known $\Phi_R$ of 0.27 in ethanol [11]. The complex and the reference dye were excited at same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\frac{\phi_s}{\phi_R} = \left[\frac{A_S}{A_R}\right] \times \left[\frac{(Abs)_R}{(Abs)_S}\right] \times \left[\frac{\eta_S^2}{\eta_R^2}\right]$$

Here, $\Phi_S$ and $\Phi_R$ are the fluorescence quantum yield of the sample and reference, respectively. $A_S$ and $A_R$ are the area under the fluorescence spectra of the sample and the reference, respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and $\eta_S$ and $\eta_R$ are the values of refractive index for the respective solvent used for the sample and reference.

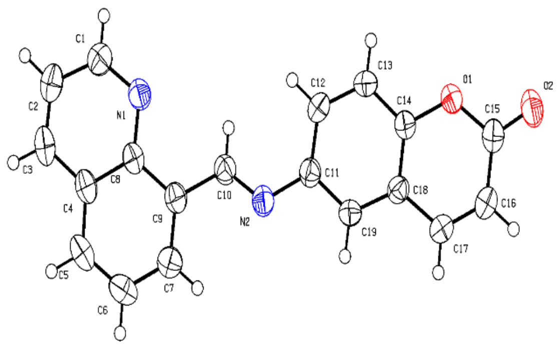
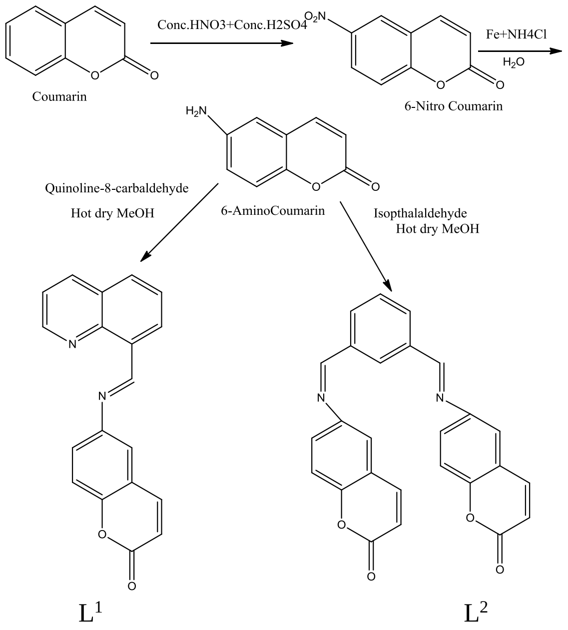


Fig. 1. ORTEP view of 8-(Coumarinyl -6-imino)-Quinoline, (L$^1$).Ellipsoids are drawn in 40 % probability level.

### 2.3. Preparation of the ligands.

#### 2.3.1. Syntheses of (E)-6-(quinolin-8ylmethyleneamino)-2H-chromen-2-one (L$^1$), and 6-((E)-((E)-3-((E)-(2-oxo-2H-chromen-6-ylimino)methyl)benzylidene)amino)-2H-chromen-2-one(L$^2$)

The steps include the synthesis of 6-nitrocoumarin (step 1), 6-aminocoumarin (step-2) and then condensation with aldehydes (step-3).



Step-1: Synthesis of 6-nitrocoumarin

Coumarin was penetrated with mixed acid in ice bath. Coumarin (8 gm, 54.8 mmol) was dissolved in conc. $H_2SO_4$ (40 ml) and temperature was maintained at -5°C and then 16 ml mixed acid ($HNO_3$ and $H_2SO_4$ (conc.) in 1:3 volume ratio) was added. The mixture was stirred under room temperature for 1 hour and then to it ice was added. A white precipitate of 6-nitrocoumarin was obtained. It was then filtered off and washed thorough with cold water (10 ml each for ten times) and dried over $CaCl_2$ and recrystallized from acetic acid. Yield: 9.2 gm (88 %). m.p.185±2 °C;

Step-2: Synthesis of 6-aminocoumarin

Reduction of 6-nitrocoumarin was done using iron powder and ammonium chloride in water. 6-Nitrocoumarin (8 gm, 41.9 mmol) in water (150 ml) was treated with Fe-powder (20 gm) and ammonium chloride (2.6 gm, 48.6 mmol). The mixture was kept in water bath for two hours with stirring. A dark brown precipitate was obtained which was then extracted with acetone. Evaporation of acetone yielded silky yellow precipitate of 6-aminocoumarin (m. p. 158 °C). It was then recrystallised from dil. HCl solution as 6-aminocoumarin hydrochloride. Yield: 5.1 gm (76%). m.p.>260°C;

Step-3: Synthesis of (E)-6-(quinolin-8ylmethyleneamino)-2H-chromen-2-one (L$^1$)

The ligand was prepared by the condensation of 6-aminocoumarin in hot dry Methanol followed by dropwise addition of hot methanolic solution of quinoline-8-carbaldehyde in a RB flask. Deep yellow color clear solution obtained and was crystallised from Ethanol by slow evaporation of solvent. Yield: 95% M.P. 264 ±2°c

#### 2.3.3. Synthesis of 6-((E)-((E)-3-((E)-(2-oxo-2H-chromen-6-ylimino) methyl)-benzylidene)amino)-2H-chromen-2-one (L$^2$)

The coumarin imino derivative was synthesized by the condensation of 6-aminocoumarin in hot dry methanol and followed by drop wise addions of hot methanolic solution of isophthaladehyde in a RB flask. The yellow precipitate was generated after three hours reflux and then washed with ethanol and recrystallised from methanol. All the steps involved are shown in Scheme 3. Yield: 85%, M.P. 245 ±2°C;

### 2.4. X-ray Crystallography

Details concerning crystal data, data collection characteristics and structure refinement are summarized in Table I. Single crystals of L$^1$ was mounted separately on capillaries and transferred to a goniostat. The diffraction data was collected at 293(2) under nitrogen stream, on a Bruker SMART CCD diffractometer with graphite-monochromated

Mo-Kα radiation. The $\omega$: $2\theta$ scan technique was applied within a $\theta$ range of 2.23–27.54° for $L^2$. No significant crystal decay was observed. Data were corrected for absorption empirically by means of $\psi$ scans. A total of 5680 reflections was collected, from which 2427 and 3253 independent [*R* (int) = 0.0415 and 0.1202, respectively] reflections were measured. The stability of the crystals was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted. During the data reduction, Lorentz, polarization and empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied [12]. The structures were solved with the direct method of SHELXS-97 [13] and refined on $F^2$ by full-matrix least-square techniques using the SHELXTL-97 [14] program. The functions minimized were $\Sigma w[|Fo|^2 - [|Fc|^2]^2$, where $w = [\sigma^2(I) + (0.0439P)^2 + 0.5317P]^{-1}$ and $w = [\sigma^2(I) + (0.0597P)^2 + 0.2248P]^{-1}$, with $P = (|Fo|^2 + 2|Fc|^2)/3$. The hydrogen atom positions were calculated and they were constrained to idealized geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom.

## III. RESULTS AND DISCUSSION

### 3.1. Crystal Structure of $L^1$

Compound $L^1$ crystallizes from methanol. The ORTEP representation is shown in Figure 1. Bond lengths and angles are listed in Table V. Both coumarinyl and quinolinyl are planar and bonded by –C=N- function. The C=N bond length is 1.261(2) Å. Other bond distances are comparable with literature data.

### 3.2. General Characterization

The (E)-6-(quinolin-8ylmethyleneamino)-2H-chromen-2-one($L^1$) derivative was prepared by condensation reaction and isolated as orange crystalline compound. The IR spectrum of compound shows ν(C=O) of coumarin at 1720 $cm^{-1}$, while ν(C=N) appears at 1620 $cm^{-1}$ (Table III). In DMF solution spectral properties was studied and it shows two sharp bands at 283 ($\pi \rightarrow \pi^*$) and 328 nm ($n \rightarrow \pi^*$) (Supporting information $S_5$). The $L^2$ was also characterised by $^1H$ NMR spectroscopy. The spectral data shows imine –CH proton at 11.46 ppm. The coumarin protons show signal at 6.5 – 7.7 ppm and only one singlet proton of coumarin show signal at 9.9 ppm whereas phenyl protons at 7.4 – 8.2 ppm (Supporting information $S_3$).

Another coumarinyl diimino derivative which was synthesized by condensation reaction of 6-Coumarin amine with benzene-1,3-dicarbaldehyde. FTIR spectrum of the pale yellow compound shows ν(C=O) of coumarin at 1733 $cm^{-1}$, while ν(C=N) appears at 1628 $cm^{-1}$ (Table III). Spectral properties was studied in DMF solution and it shows sharp band at 380 nm ($n \rightarrow \pi^*$) (Supporting information $S_5$). The spectral data of $^1H$ NMR study shows CH=N proton at 8.82 ppm. The isopthalic singlet proton comes at 8.5ppm (Supporting information $S_3$) and coumarin protons show signal at 6.4–8 ppm (Supporting information $S_4$).

### 3.3. Emission Spectroscopy

The $L^1$exhibits fluorescence when it is excited at both $\pi$ -$\pi^*$ band at 302 nm and n-$\pi^*$ band at 363 (Table 4). Free ligand exhibits transition at 487 nm at 298 K upon excitation at 397 nm. The emission is referred to n---$\pi^*$ emission *i.e.*, it may belong to intraligand charge transfer (ILCT), ligand-to-ligand charge transfer (LLCT) transitions or combination of both. The fluorescence quantum yield of the ligand ($L^1$) ($\phi$ = 0.05). It has been reported that the metal ions can enhance or quench the fluorescence emission depending on the strength interaction between ligand field potential and metal ion [20].

## IV. CONCLUSION

The fluorescent chromophore consisting multidentate sites has been synthesized and characterized by various spectral techniques. Besides, Coumarin mediated Schiff Base ligands are spectroscopically characterized. Additionally, Ligand $L^1$ is structurally characterized by X-ray diffraction analysis. Furthermore, two coumarin imino precursors manifesting with Quinoline-8-carbaldehyde and Isopthalic dicarbaldehyde have been generated and systematically characterized by spectral studies.

### Supporting Materials

All spectroscopic figures and Crystal data details along with experimental writeup data analyses are given in Supplementary Materials Section (Figs S1-$S_5$ and Tables $T_I$-$T_V$).

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