



# Red and near-infrared emitting bis-coumarin analogues based on curcumin framework-synthesis and photophysical studies



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## ABSTRACT

Four fluorescent bis-coumarin analogues were synthesized having donor-acceptor-donor (D-A-D) system based on curcumin framework, where the 7-(diethylamino)coumarin-3-carbaldehyde has been employed as donor while the central 1,3-diketo or 1,3-diketofluoroborate is the acceptor core. The structural modifications have been made by functionalizing acetylacetone or 2-acetyl cyclopentanone to study the effect of imparting rigidity on the photophysical properties of the bis-coumarin analogues. The difluoroboron complexes of bis-coumarin analogues were synthesized to study the effect of difluoroboron complexation on the photophysical properties. The mono-coumarin analogue is synthesized to understand the nature and the contribution of the donor groups in bis-coumarin of the curcumin framework. The photophysical properties are studied in detail using solvents of differing polarity. The photophysical properties of the newly synthesized bis-coumarin molecules were compared with the previously reported bis-coumarin analogues.

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## 1. Introduction

Coumarin derivatives have their place as a class of highly fluorescent molecules. The coumarins occupies the largest class of laser dyes [1] for the blue-green region (400–520 nm). The prominence of coumarins in the field of optoelectronics [2–4], optical whitening [5] cellular imaging [6], and fluorescent markers for proteins [7] is well documented in the literature. Coumarins are attractive molecules due to their highly fluorescent nature [8] with moderate to good quantum yields [9]. The red and near infrared (NIR) emitting dyes are of importance in OLEDs and in bio-labelling to achieve greater penetration [10,11] and more cell viability. Design and synthesis of red and NIR emitting dyes are gaining interest in recent years [12–15]. To shift the emission of the coumarin molecules from blue-green region to the red/NIR region there are few strategies which are well documented in the literature which include the presence of electron donor at 7-position [16], rigidizing the donor and acceptor groups, increasing the  $\pi$ -conjugation [17] complexation with boron [18–20] and presence of electron acceptors at 3 and 4-positions [21]. The  $\pi$ -extended bis-coumarin analogues [22], monoketo bis-coumarins [23], biscoumarins bearing difluoroborn moiety [20]

are among the few fluorescent red/NIR emitting bis-coumarin analogues reported in the literature. In view of the above mentioned findings the present work describes the synthesis of novel bis-coumarin analogues based on the curcumin framework where the 7-(diethylamino)coumarin-3-carbaldehyde has been employed as donor while the central 1,3-diketo or 1,3-diketofluoroborate is the acceptor core. The synthesized bis-coumarin Fig. 1 molecules were studied in detail for their photo-physical properties in different solvent environment to understand their solvatochromic behavior and the results obtained were compared with the reported bis-coumarin analogues [18,20,22–24].

## 2. Experimental

### 2.1. Design synthetic strategy

Five different coumarin analogues were synthesized, and the synthesized chromophores **1a**, **1b**, **2a**, and **2b** have the donor-acceptor-donor (D-A-D) framework, the mono styryl coumarin **3c** is a donor-acceptor system. These dyes contain the 7-(diethylamino)coumarin-3-carbaldehyde as a donor fragment in all the five compounds Figs. 2 and 3. The structural modifications have been made by functionalizing acetylacetone or 2-acetyl cyclopentanone to study the effect of imparting rigidity on the photophysical properties of the bis-coumarin analogues **1a** and **1b**. The  $\text{BF}_2$ -complexes **2a** and **2b** of bis-coumarin analogues were

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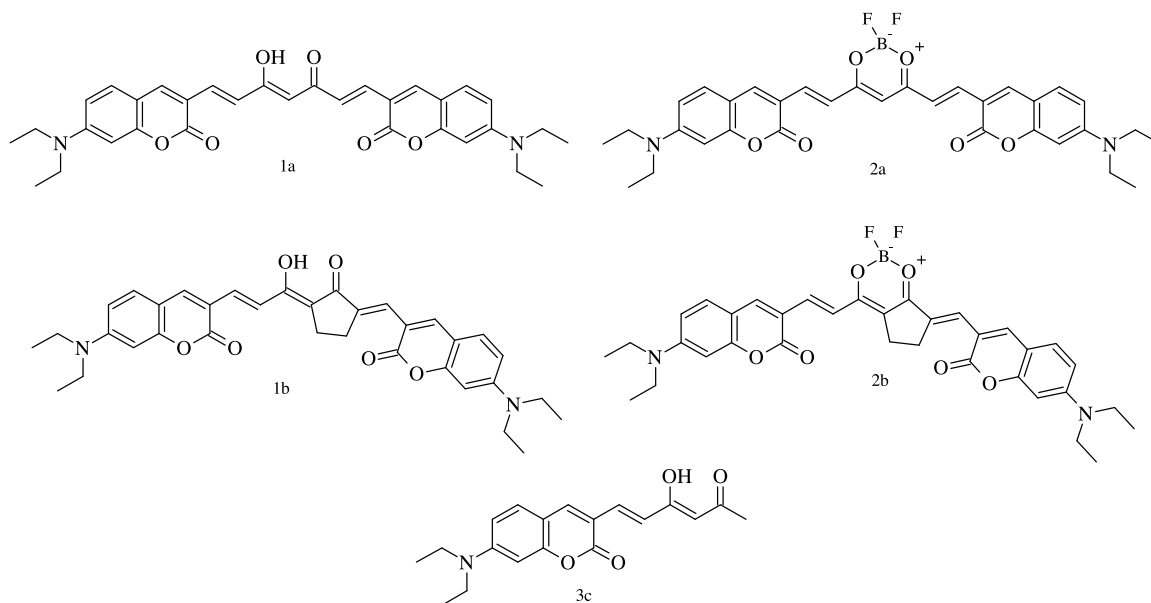


Fig. 1. Structures of the synthesized molecules.

synthesized to study the effect of  $\text{BF}_2$ -complexation on the photophysical properties. The mono styryl coumarin analogue **3c** is synthesized to understand the nature of the contribution of the donor groups in the curcumin framework. The synthesized dyes were well characterized by  $^1\text{H}$  NMR, LCMS and CHN analysis. The photophysical properties of the bis-coumarin analogues are measured in different solvent environment and the solvatochromic data was used to study the effect of solvent polarity on the ground state and excited state properties of the molecules by using different solvent polarity functions Lipperte-Mataga, Bakhshiev, Bilot-Kawskie, Liptay, Rettig, McRae, Weller and ETN correlations.

## 2.2. Materials and equipments

All the synthetic grade reagents were purchased from Sigma Aldrich and are used without purification, laboratory reagent grade solvents were purchased from Rankem, Mumbai. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel  $60\text{F}_{254}$  pre-coated plates, which were visualized with UV light (254 nm and 344 nm).  $^1\text{H}$  NMR spectra were recorded Agilent 500 MHz instruments using TMS as an internal standard. Mass spectra were recorded on FINNIGAN LCQ ADVANTAGE MAX instrument from Thermo Electron Corporation (USA). The absorption spectra of the

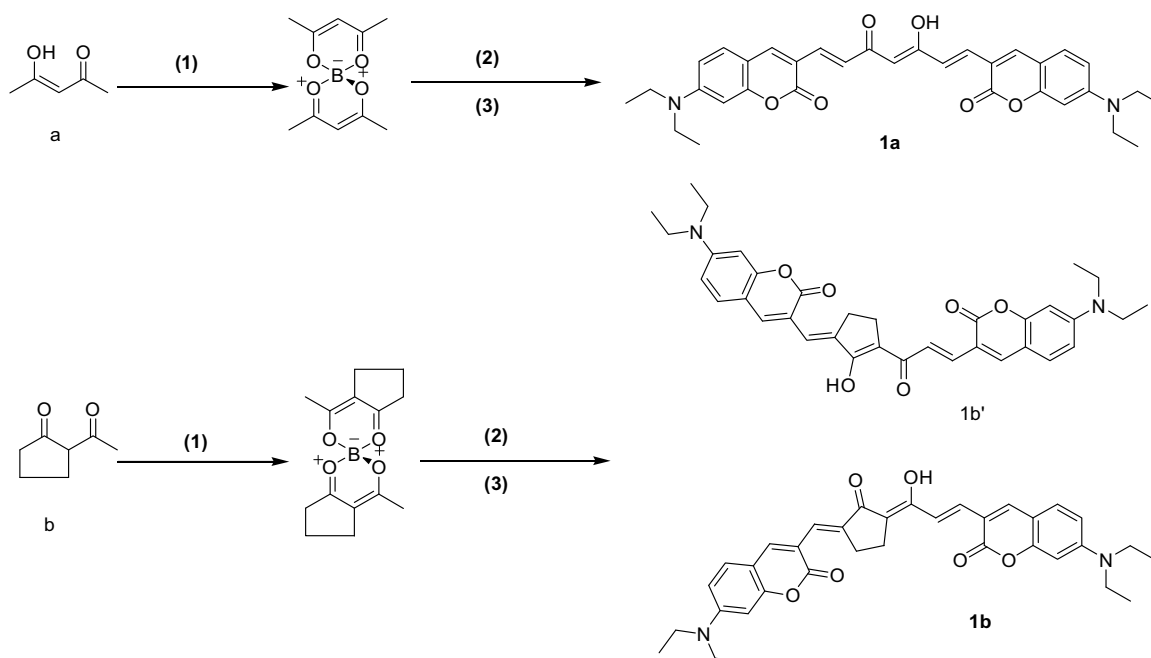


Fig. 2. Synthesis of bis-coumarin analogues **1a-1b** and reagents and conditions (1)  $\text{B}_2\text{O}_3$ /ethyl acetate,  $70^\circ\text{C}$ , 3 h (2) 2 eq. 7-(diethylamino)coumarin-3-carbaldehyde, tri-*n*-butyl borate/ethyl acetate, RT, 45 min, *n*-Butyl amine,  $70^\circ\text{C}$ , 24 h (3) 0.1 N HCl, 2 h,  $70^\circ\text{C}$ .

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