

Synthesis and Characterization of Anchoring Group Containing 3-(4-nitro phenyl)-2H-coumarins

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Abstract—A facile and efficient sonochemical approach was developed for the synthesis of 3-(4-nitrophenyl)-2H-coumarin derivatives. The target compounds were synthesized through the condensation of 4-nitrophenyl acetonitrile with salicylaldehyde and substituted salicylaldehyde derivatives in the presence of piperidine and ethanol under ultrasonic irradiation. The reactions were completed within a short period and afforded the corresponding coumarin derivatives in good yields. The synthesized compounds were characterized by FT-IR, ^1H NMR, mass spectrometry, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). The spectral data confirmed the formation of the coumarin framework and the presence of characteristic carbonyl, nitro, and ether functionalities. The SEM studies revealed distinct surface morphologies, while EDS analysis confirmed the presence of carbon, oxygen, and nitrogen. The developed sonochemical method provides a simple, efficient, and comparatively mild route for the preparation of nitrophenyl-substituted coumarins. Owing to their fluorescent properties and structural features, these compounds may be useful as functional materials for optoelectronic applications, particularly in organic light-emitting devices (OLEDs).

Index Terms—Sonochemical synthesis; 3-(4-nitrophenyl)-2H-coumarin; Ultrasonic irradiation; Knoevenagel condensation; Optoelectronic materials; OLED

I. INTRODUCTION

Organic fluorescent dyes based on the π -conjugated system are intensively investigated as active materials in organic field-effect transistors and light-emitting diode.¹ Organic light-emitting diodes (OLEDs) have been extensively researched because of their potential application in full-color flat-panel displays.² Significant progress in materials synthesis and device construction had led to the realization of full color as well as white OLEDs with improved efficiencies and lifetimes. Great effort has been made to develop high performance materials with desirable

properties and devices with optimized architecture to develop marketable OLEDs.^{3,4} Coumarin dyes exhibit unique photochemical and photophysical properties, which make them useful applications such as optical brighteners, laser dyes, non-Linear optical chromophores, fluorescent labels and solar energy collectors. Also, the Coumarin dyes find their use as blue, green and red dopants in organic light-emitting diodes (OLEDs).⁵⁻⁷ It is well known that the electron donating groups substituted on Coumarin will increase the intermolecular electron transfer there by enhancing the fluorescence of Coumarin derivatives. Due to the exhibition of fluorescent properties, Coumarin acts as a good donor. Coumarins are recognized as good organic dye photosensitizes by injecting electrons effectively into the conduction band of semiconductors.⁸ The lasing range covered by Coumarin dyes has been appreciably extended when the substituents occupy at 3rd position in a heterocyclic moiety,^{9, 10} which are most efficient photostable laser dyes, emitting in the blue green region in the visible spectrum. Therefore, the synthesis and study of electronic properties of Coumarin bearing different heterocycles at 3rd position have gained much attention in order to obtain highly sensitive fluorescent Coumarin brighteners.¹¹⁻¹³ Coumarins substituted an electron – donating group or by lengthened π - conjugation are known to influence the fluorescent properties. Coumarin itself is not fluorescent, but it exhibits intense fluorescence after the substitution of various functional groups at different positions.^{14,15} In general, electron-donating substituent tend to enhance emission intensity, while electron-withdrawing substituent tend to diminish it. Coumarins substituted at 7th position with an electron-donating group are known to exhibit strong fluorescence and are used as fluorescent probes.^{17, 18} Encouraged by the OLEDs

properties exhibited by coumarin derivatives and in continuation of our effort to develop new OLED molecules.^{19,20}

In the present investigation we report one pot sonication method of synthesis of structurally distinct 3-(4-nitrophenyl)-2H-coumarin derivatives 3(a-b) by using 4-nitrophenyl acetonitrile and various substituted salicylaldehyde compounds. Most of the methods reported in the literature suffer drastic reaction conditions, low yield and use of expensive starting materials. In order to overcome these difficulties, we made an attempt to synthesis substituted coumarin derivatives by using relatively less expensive materials with good yield.

II. EXPERIMENTAL

2.1. Materials and methods

Chemicals and reagents used for the synthesis and analysis were procured from a commercial supplier, Sigma Aldrich, India. Analytical grade solvents were purchased from SD Fine chemicals Pvt Ltd., Mumbai, India and used as such without purification. Melting points of the synthesized compounds were carried out by an open capillary method using electrical heating apparatus. The wave number range from 650 cm^{-1} to 4000 cm^{-1} was used for recording Fourier-Transform Infrared (FT-IR) spectra of the samples using Agilent FT-IR Spectrometer. Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectrum was recorded using Agilent NMR instrument at 400 MHz.

2.2. Procedure for the synthesis of 3-(4-nitrophenyl)-2H-coumarin (3a):

A mixture of 2-hydroxybenzaldehyde (1.22 g, 0.01 mole) and 4-nitrophenyl acetonitrile (1.62 g, 0.01 mole) in 0.5mL piperidine and 10mL ethanol was Sonicated for 25 minutes, then acidified, followed by acidification with 10N Glacial Acetic acid (10mL). The reaction mixture was again sonicated for 10 minutes the reaction completion was confirmed by thin layer chromatography [petroleum ether and ethyl acetate (8:2 v/v)] and the solvent was removed under reduced pressure. The reaction mixture was poured into cold water to afford a solid product, which was purified by column chromatography using silica gel 60-120 mesh, 7:3 hexanes: ethyl acetate v/v as eluent to afford pure product

2.3. Procedure for the synthesis 8-ethoxy-3-(4-nitrophenyl)-2H-chromen-2-one (3b):

A mixture of 3-ethoxysalicylaldehyde (1.22 g, 0.01 mole) and 4-nitrophenyl acetonitrile (1.62 g, 0.01 mole) in 0.5mL piperidine and 10 mL ethanol was Sonicated for 25 minutes. After acidification with 10N Glacial Acetic acid (10mL) the reaction mixture was again subjected to sonicated for 10 minutes. The reaction completion was confirmed by TLC and the solvent was removed under reduced pressure. The solid product obtained after pouring the reaction mixture into cold water. The product was purified by column chromatography (silica gel 60-120 mesh, 7:3 hexanes: ethyl acetate v/v).

2.4. Spectral characterization

Spectral data for 3-(4-nitrophenyl)-2H-coumarin (3a)
Appearance: Light yellow color solid; Yield : 80% ;
M.P.: 253-254°C; MF: $\text{C}_{15}\text{H}_9\text{NO}_4$; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3044 (Aromatic C-H stretching), 1632 (C=O), 1342 (N-O), 1149 (C-O-C). $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): δ =7.40 (t, J=7.60 Hz, 1H), 7.46 (d, J=8.00 Hz, 1H), 7.65 (t, J=1.20 Hz, 1H), 7.86 (t, J=74.00 Hz, 1H), 8.01 (d, J=8.80 Hz, 2H), 8.31 (d, J=8.80 Hz, 2H), 8.46 (s, 1H)ppm.

Mass spectra of the compound showed molecular ion peak at $m/z = 267.0$ [M^+].

Spectral data of 8-ethoxy-3-(4-nitrophenyl)-2H-chromen-2-one (3b)

Appearance : light yellow color solid; Yield : 82 % ;
M.P.: 253-254°C; MF: $\text{C}_{17}\text{H}_{13}\text{NO}_5$; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3087 (Aromatic C-H stretching), 2995 (Aliphatic C-H), 1698 (C=O), 1341 (N-O), 1147 (C-O-C). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ =1.52 (t, J=6.80 Hz, 3H), 4.18 (q, J=6.80 Hz, 2H), 6.97 (dd, J=7.60, 15.40 Hz, 2H), 7.06 (d, J=7.60 Hz, 1H), 7.27 (d, J=16.00 Hz, 1H), 7.84-7.87 (m, 2H), 8.26 (d, J=8.80 Hz, 2H)ppm.

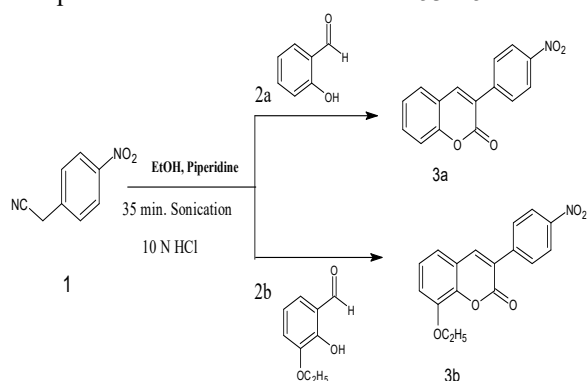
Mass spectra of the compound showed molecular ion peak at $m/z = 311.0$ [M^+].

III. RESULTS AND DISCUSSION

3.1. Synthesis

The method of synthesis of 3-(4-nitrophenyl)-2H-coumarin derivatives 3(a-b) is depicted in Scheme.1. The sonication experiment made use of an equimolar mixture of 4-nitrophenyl acetonitrile (1) and 2-hydroxyl benzaldehyde (2a) in the presence of

piperidine and ethanol. The mixture was sonicated for 25 minutes in an ultrasonic bath followed by acidification using 10N Glacial acetic acid (10mL). The reaction mixture was again subjected to sonication for 10 minutes. The progress of the reaction was checked by thin layer chromatography and the solvent was removed under reduced pressure and poured the reaction mixture into cold water. The crude product obtained after pouring was purified by column chromatography (silica gel 60-120 mesh, 7:3 hexanes: ethyl acetate v/v). The melting point of the compound obtained was found to be 253–254°C.

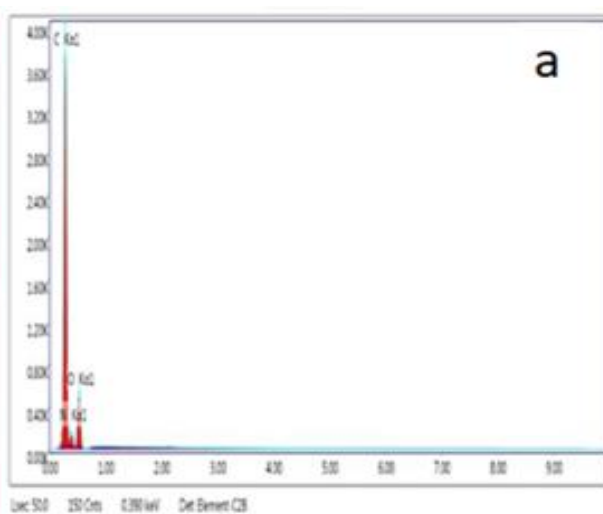
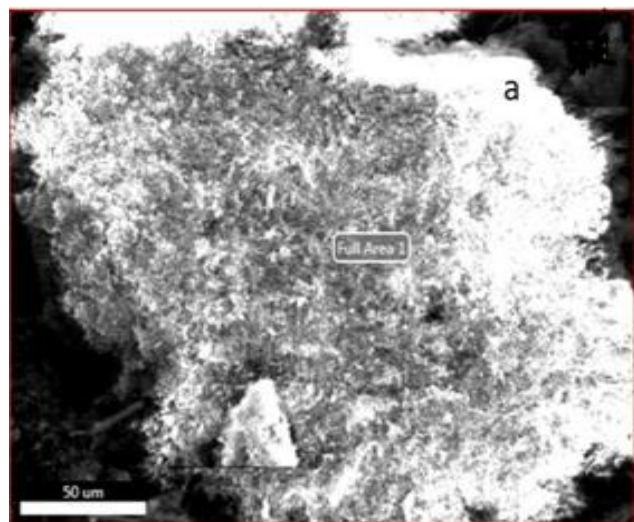


Scheme-1: Synthetic route of 3-(4-nitrophenyl)-2H-coumarins 3(a-b) The synthesized compounds were

thoroughly characterized by FT-IR, ^1H NMR and Mass spectral analysis. In its FT-IR spectrum, it showed absorption peak at 1707 cm^{-1} due to $\text{C}=\text{O}$ stretching. Absorption bands at 1342 and 1149 cm^{-1} are due to $\text{N}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations respectively. In ^1H NMR spectrum of 6a the 9 aromatic protons showed three triplet at 7.40 ppm, 7.65 ppm, 7.86 ppm due to 3 protons and three doublet at 7.46 ppm, 8.01 ppm, 8.31 ppm due to 4 protons also singlet at 8.46 ppm. The mass spectrum showed molecular ion peak at $m/z = 267.0$ $[\text{M}^+]$. Based on the spectral data, it was confirmed that the compound was 3-(4-nitrophenyl)-2H-coumarin (3a) and its derivative (3b) was prepared.

3.2. SEM and EDS studies

Scanning Electron Microscope was used to study the Surface morphology of the Coumarin dyes 3a and 3b and images were shown in Fig. 1. SEM micrograph of the 3a shows irregular lumpy mushroom with rough crystal type structure and 3b shows irregular cloudy shape with luminescent appearance was observed. The EDS spectra confirmed the elemental composition of carbon, oxygen and nitrogen in 3a and 3b.



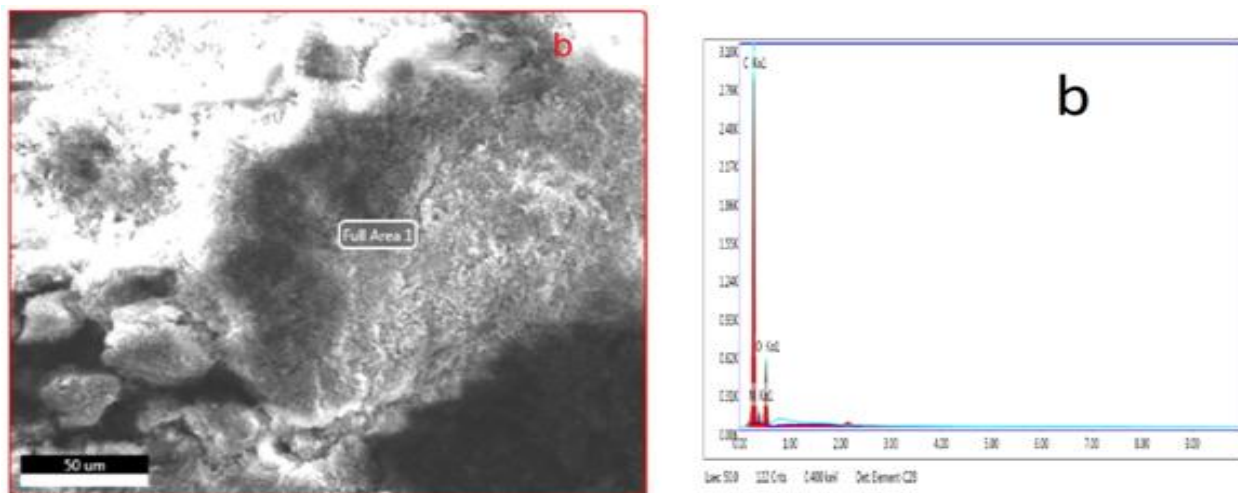


Fig. 1: SEM images and EDS spectra of 3a and 3b

Table. 1: Elemental Composition of 3a

Element	Weight %	Atomic %	Net Int.	Error %	Kratio
C K	58.81	64.38	472.10	4.36	0.4508
N K	15.12	14.20	21.18	15.39	0.0185
O K	26.07	21.42	73.18	11.26	0.0459

Table. 2: Elemental Composition of 3b

Element	Weight %	Atomic %	Net Int.	Error %	Kratio
C K	61.86	67.16	446.92	4.27	0.4849
N K	15.08	14.04	17.62	18.92	0.0175
O K	23.07	18.80	54.70	14.74	0.0389

IV. CONCLUSION

We have successfully synthesized 3-(4-nitrophenyl)-2H-coumarins by condensation reaction between benzaldehyde and acetonitrile with piperidine under ultrasonic irradiation in ethanol leads to good yield of the products. The applied sonochemical method is an efficient and safe. Ultrasound hastens the reaction, increases yields of products by means of creating the activation energy in micro surroundings. The significant features of ultrasound approach for the preparation of highly sensitive fluorescent coumarins for OLEDs.

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