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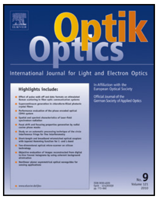

Original research article

Design, characterization and nonlinear optical properties of coumarin appended chalcones: Use of a dual approach

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ABSTRACT

In present investigation, we present designing and characterization of coumarin appended chalcone hybrids using a dual approach consisting of experimental and computational techniques. For the first time, the parent compound **2** ((E)-2-(3-(2,4-dimethoxyphenyl)acryloyl)-3H-benzo[*f*]chromen-3-one) is successfully synthesized in our lab. The compound **2** is characterized experimentally as well as quantum computational techniques. The results of absorption and emission spectra are compared with those of computationally calculated spectra. A good agreement is found among the experimental and calculated spectra of compound **2**. The experimental absorption spectra show maximum absorption and emission peaks at 392 and 461 nm, which are found to be in agreement with their experimental absorption and emission peaks at 393 and 501 nm, respectively. Additionally, we perform analysis of its nonlinear optical (NLO) properties by calculating its second-(β) and third-order $<\gamma>$ nonlinear polarizabilities. The compound **2** shows reasonably good NLO response with its β and $<\gamma>$ amplitudes mounting to 120.23×10^{-30} esu and 677.12×10^{-36} esu, respectively. These β and $<\gamma>$ amplitudes of compound **2** are ~6 and ~20 times larger than those of para-nitroaniline (PNA) at BMK/6-311G** level of theory. Based on above structure-property relationship, we also check the effect of substitution of donor groups in the form of further four derivatives i.e. **2a**, **2b**, **2c** and **2d**. Interestingly, among these derivatives, the derivative **2d** shows a robust NLO response with its β and $<\gamma>$ amplitudes as large as 218.84×10^{-30} esu and 1515×10^{-36} esu, respectively. The present investigation not only reports the first synthesis of compound **2** but also explores the potential of compound **2** and its derivatives as efficient NLO-phores.

1. Introduction

Among the advanced functional materials of modern scientific era, optical and NLO materials are the most intriguing materials. Optical materials are used as semiconducting materials and light emitting diodes while NLO materials functions in telecommunication, optical data storage and laser frequency conversion etc. [1–3]. With the advancement of modern technology, there is always a dire need to produce new NLO materials with more efficient NLO properties. Over the past

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several years, NLO properties have studied in several types of materials [4] mainly including organic [3], inorganic [5], organometallic [6] and other types hybrid materials [7]. It is important to pinpoint that every class of materials has different pros and cones owing to their practical applications. Nevertheless, organic class is considered to be the most studied class of material for NLO properties [8]. Due to the vast variety of functional groups and a great diversity among designing strategies, organic class has been always the best choice for tuning NLO properties. Additionally, organic NLO materials also enjoy the advantage of being cost effectiveness and ease of their fabrication for the device applications [4].

Among several organic compounds, the chalcone derivatives are extensively studied materials for their biological activity and electrochemical properties. Recently, several studies focused on the chalcones for their interesting NLO properties [9–11]. Furthermore, chalcone derivatives also possess excellent electrochemical and optical properties like high extinction coefficients and broad absorption range in UV spectrum etc. [12]. On the other hand, the coumarin compounds are important member of organic class of materials, which occur and synthesized naturally among many plants. The coumarin compounds have a range of pharmaceutical applications ranging from anti-cancer to antioxidant activities [13]. In view of above interesting properties of chalcone and coumarin compounds, some recent attempts have been made to synthesize the hybrid coumarin-appended chalcone derivatives [14–16]. These coumarin-appended chalcone derivatives have been studied for their potential spectroscopic and optical properties. In most of the coumarin-appended chalcone derivatives, the coumarin moiety acts as electron acceptor group establishing the donor acceptor type configurations [17]. Huang et al. reported the synthesis and characterization of indole and anthracene based coumarines having two photon induced fluorescent properties [14]. The synthesis and characterization of chalcone and coumarin-based chromophores are also important to mention here, where benzocoumarin systems showed significant bathochromic effect i.e. ~100–500 cm^{-1} as compared to the coumarin systems [16]. Similarly, Sun et al. have also reported the synthesis of coumarin-based chromophores having azo and pyrazoline moieties [15]. Along above lines, Xue et al. report another important study, which theoretically explains the structure and optical properties of coumarin-based chromophores [17]. In our recent studies, we have explored several novel strategies to tune the NLO properties of chalcone compounds, which include the effect of number and position of methoxy groups [18], tuning of push-pull configuration [19] as well as the effect of bridging groups [20] etc. To the best of our knowledge, there is no experimental and/or computational study that targets the nonlinear optical properties (second- and/or third-order polarizability) of coumarin-appended chalcone derivatives. The coumarin compounds possesses important photophysical properties due to their structural resemblance with other heterocyclic dyes [21]. Several compounds with heterocyclic moieties showed interesting NLO properties. So, it will be interesting to explore the potential of coumarin-appended chalcone derivatives possessing push-pull configurations for NLO applications. The present study will not only highlight the synthesis of important coumarin-appended chalcone derivative but also extends the number of derivatives through the use of quantum chemical methods to get a structure-NLO property relationship among these derivatives as it will be discussed in succeeding sections.

2. Methodology

2.1. Experimental details

Analytical grade chemicals and solvents used in this study were used without further purification. Reaction was monitored by thin layer chromatography (TLC) with the aid of UV light. 2-Hydroxy-1-naphthaldehyde, 2, 4-Dimethoxybenzaldehyde and ethylacetoacetate were purchased from Sigma–Aldrich and Merck. Stock solution of the title compound and its dilutions were prepared for UV–vis and fluorescent study at different concentrations. Gallenkamp melting point apparatus was used to determine the melting point and the infrared (IR) spectra were recorded on Shimadzu FT-IR 8400S infrared spectrophotometer using KBr pellets. The NMR (^1H and ^{13}C) spectra were recorded on a Bruker DPX-600 at 600 MHz and 150 MHz, respectively, using TMS as the internal standard. The chemical shift values are documented on δ scale and coupling constants (J) in Hertz; Splitting patterns were entitled as follows: s: singlet; d: doublet; m: multiplet. PG UV-160A spectrophotometer was used to record the UV–vis electronic absorption spectra, and the steady-state fluorescence spectra were measured using Varain Cary Eclipse spectrofluorophotometer using a rectangular quartz cell of dimensions 0.2 cm × 1 cm.

Procedure for the Synthesis of 3-acetyl-3*H*-benzo[*f*]chromen-3-one (**1**)

To a solution of 2-Hydroxy-1-naphthaldehyde (860 mg, 5 m mol) and ethylacetoacetate (650 mg, 5 m mol) in ethanol (40 ml), 0.3 mL of piperidine and 2–3 drops of glacial acetic acid were added. The mixture was refluxed for 5 h. After the completion of the reaction as identified by TLC, the reaction mixture was cooled to room temperature and 20 mL of ice cold water was added. The solid product was collected by filtration, dried and recrystallized from ethanol to give 2 (480 mg). Yield 69%, off white solid, Melting point: 168 °C; IR (KBr, $v\,cm^{-1}$): 1660 (CO), 1735 (CO), 1497, 1420, 1232, 792, 657; ^1H NMR (600 MHz, $CDCl_3$): δ 8.2 (d,1H, Ar-H), 7.84(d,1H, Ar-H), 7.64 (m, 4H, Ar-H), 8.72 (s,1H, Ar-H), 2.27 (s, 1H, $-CH_3$); ^{13}C NMR assignments ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.20 (—CO—CH3), 140.2 (C=C), 138.9 (C=C), 142.2 (C=C), 145.6 (C=C), 150.96 (C=C), 131.27 (C=C), 165.07(O—CO ring), 125.22 (C=C), 123.90 (C=C), 127.40(C=C), 149.45 (C=C), 22.18 (—CH3), 124.03 (C=C), 124.72 (C=C).

Procedure for the Synthesis of 2-[3-(2,4-Dimethoxy-phenyl)-acryloyl]-benzochromene-3-one **(2)**

To a solution of 3–Acetyl coumarin (480 mg, 2 m mol) and 2, 4-Dimethoxybenzaldehyde (335 mg, 2 m mol) in ethanol (50 ml), 0.3 mL of piperidine and 2–3 drops of glacial acetic acid were added. The mixture was refluxed for 12 h. After the completion of the reaction as identified by TLC the solvent was removed under vacuum. The residue thus obtained was