



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

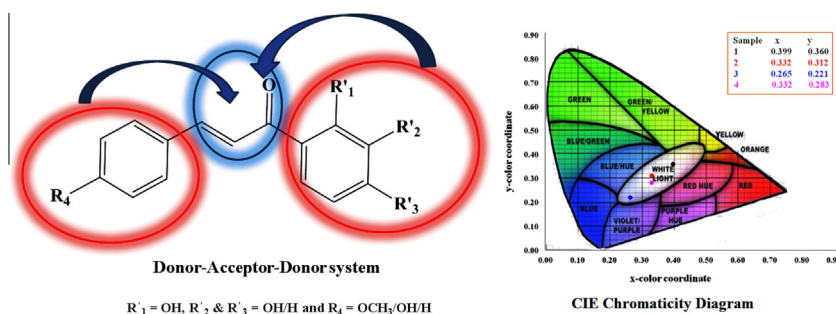
Synthesis and detailed spectroscopic characterization of various hydroxy-functionalized fluorescent chalcones: A combined experimental and theoretical study

M. Jagadeesh^a, M. Lavanya^b, B. Hari Babu^c, Kiryong Hong^a, Rory Ma^a, Joonghan Kim^{d,*}, Tae Kyu Kim^{a,*}^a Department of Chemistry and Chemical Institute of Functional Materials, Pusan National University, Busan 609-735, Republic of Korea^b Department of Chemistry, Sri Venkateswara University, Tirupati 517502, Andhra Pradesh, India^c Department of Surgery, Montreal General Hospital, McGill University, Montreal, Canada^d Department of Chemistry, The Catholic University of Korea, Bucheon 420-743, Republic of Korea

HIGHLIGHTS

- Interpretations of IR and Raman spectra of hydroxyl-substituted chalcones.
- Prepared hydroxyl-substituted chalcones as good semiconducting materials.
- The white-light emitting property of prepared hydroxyl-substituted chalcones.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 January 2015
 Received in revised form 16 May 2015
 Accepted 20 May 2015
 Available online 9 June 2015

Keywords:

Hydroxy-substituted chalcones
 DFT calculations
 HOMO–LUMO
 Vibrational spectra

ABSTRACT

Four different bright yellow to orange hydroxy-substituted chalcones (i.e., 2',4-di-hydroxy (**1**), 2',3',4-trihydroxy (**2**), 2',3',4'-trihydroxy (**3**), and 2'-hydroxy-4-methoxy (**4**) chalcones) were synthesized and characterized by LC–MS, FT-IR, FT-Raman, and fluorescence spectroscopy and thermogravimetric analysis. UV–visible absorption spectroscopy was also used. The experimental (theoretical) bandgaps of **1**, **2**, **3**, and **4** are 2.89 (2.90), 2.93 (2.95), 3.04 (3.09), and 3.01 (2.91) eV, respectively. The hydroxy-substituted chalcones exhibited strong dual emissions as a consequence of the locally excited states followed by internal charge transfer processes. The molecular structures, lowest energy transitions, vibrational frequencies, and spectroscopic information were calculated using density functional theory and time-dependent density functional theory methods at the B3LYP/6-31G(d,p) theoretical level. The experimental and theoretical data were compared and the relationship between them was briefly discussed.

© 2015 Elsevier B.V. All rights reserved.

Introduction

Benzylideneacetophenones, which are commonly known as chalcones, have gained significant attention in modern chemistry

because of their wide range of applications [1]. These bichromophoric molecules, which have two chromophoric groups separated by a hetero-vinyl chain, serve as precursors of several heterolytic compounds like flavonoids, flavones, and pyrazolones [2–5]. Chalcones are excellent models for studying photo-induced electron transfer processes, which play a key role in different fields such as polymer, photo, optic, and laser physics [6,7]. These chromophores, which feature electron-donor and

* Corresponding authors.

E-mail addresses: joonghankim@catholic.ac.kr (J. Kim), tkkim@pusan.ac.kr (T.K. Kim).

electron-acceptor groups connected via a π -conjugated spacer, are called donor- π -acceptor (D- π -A) systems [8]. Chalcones are classified into symmetrical and asymmetrical donor-acceptor-donor (D-A-D) systems based on the electron-donating substituents attached to the aromatic rings at the end of the carbonyl functional group: Symmetrical D-A-D chalcones contain electron donors on both phenyl rings, while asymmetrical D-A-D chalcones have electron donors at only one of the two phenyl rings [9]. Hence, these molecules can show highly efficient intramolecular charge transfers, and thus they are particularly useful in the development of nonlinear optical systems (NLO materials) [10]. They are also used for ultrafast optical nonlinearities [11] and as absorption filters for UV light [12].

Among the various chalcone derivatives, hydroxy chalcones and related derivatives have proven to be challenging candidates that attract wide biological interest. For example, a number of pharmacological applications of these derivatives have been investigated because of their antitumor [13–15], antidiabetic [16], antimalarial [17], antioxidant [18], antifungal [19], anti-angiogenic [20], and anti-inflammatory activities [21]. In particular, electron-releasing groups that induce high polarization of the ring enhance the antibacterial [22–24] and enzyme-inhibition activity [25,26]. In addition, 2'-hydroxy chalcones like chalcone **1** and **4** are suitable for quantitative analysis of metal ions because of their good complexing ability [27]. The applications of chalcones also extend to agrochemicals and artificial sweeteners [7].

Although hydroxy-substituted chalcones have a variety of applications, especially in pharmacological fields, detailed elucidations of the structural and spectroscopic properties of these hydroxy-substituted chalcones have rarely been reported. Detailed spectroscopic assessments may aid in generating facile syntheses of new chalcone derivatives and advance the pharmacological applications of hydroxy-substituted chalcones. In this work, we report the preparation and structural elucidation of four hydroxy-substituted chalcones, i.e., 2',4'-dihydroxychalcone (**1**), 2',3',4'-trihydroxychalcone (**2**), 2',3',4'-trihydroxychalcone (**3**), and 2'-hydroxy-4-methoxychalcone (**4**) using a variety of spectroscopic methods. In addition, theoretical approaches including DFT and TD-DFT calculations are used to study their molecular vibrations, frontier orbitals, and electronic transitions. The experimental and calculation data are compared and the relationship between them is briefly discussed.

Materials and methods

Chemicals and syntheses of hydroxy chalcone derivatives

All chemicals and solvents used in the present work were obtained from commercial sources and used without any further purification. 4-Hydroxybenzaldehyde, 2'-hydroxyacetophenone, 2',4'-dihydroxyacetophenone, benzaldehyde, 2',3',4'-trihydroxyacetophenone, and 4-methoxybenzaldehyde were purchased from Sigma Aldrich. The target chalcones were prepared according to the conventional base-catalyzed Claisen-Schmidt reaction as per the literature [28]. Equivalent molar amounts of an ethanolic solution of the hydroxy-substituted acetophenone with the corresponding benzaldehyde were mixed in a round-bottom flask. After adding 10% NaOH solution, the mixture was stirred at room temperature for 8–10 h. After complete consumption of the corresponding aldehyde, the solution was neutralized using 10% HCl. The precipitate was collected by filtration, dried, and recrystallized from ethanol.

Spectroscopic characterizations

FT-IR spectral measurements were recorded in the solid state using KBr pellets on a JASCO FTIR 5300 spectrophotometer between 4000 and 400 cm^{-1} . UV-visible spectra of the synthesized compounds were recorded using a JASCO V-570 UV-visible spectrophotometer. Mass spectra of the molecules were recorded using an Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS. Raman spectra were measured using a confocal Raman microscope (Lab Ram HR 800, Horiba Jobin Yvon SAS, France) equipped with a 432 nm He-Ne laser (Torus Laser, Laser Quantum, France) at a power of 50 mW and a 50 \times LWD air-dry visible objective (NA = 0.5 wd 10.6 MM LIEU Microsystems of Model BX 41) that was attached to a Fieltyar multichannel CCD detector; two scans were recorded. Each Raman spectrum was measured in the range of 400–1800 cm^{-1} at a spectral resolution of 0.35 cm^{-1} /pixel with an 1800 g/mm grating at the confocal pinhole, which was set at 400 nm. Fluorescence studies of the solid samples were recorded using a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The chalcones were thermally analyzed using a Labsys TG-DSC 1600 model instrument under a N_2 atmosphere at a scan rate of 10 $^\circ\text{C}/\text{min}$. Scanning electron microscopy (SEM) images of the chalcone molecules were obtained using a Carl Zeiss EVO MA 15 Thermoionic Emission scanning electron microscope.

DFT calculations

To determine the properties of these chalcone molecules (**1–4**) at the molecular level, density functional theory (DFT) [29,30] was employed. The geometries of the chalcone molecules were fully optimized using Becke's three parameter hybrid functional [31] combined with the Lee, Yang, and Parr [32] correlation functional (B3LYP) using the standard Pople basis set, i.e., 6-31G(d,p), [33,34] for all atoms (i.e., H, C, N, and O atoms) in the gas phase. To validate that these optimized structures were global minima, the vibrational frequencies were also calculated using the same level of theory. Moreover, time-dependent DFT (TDDFT) calculations were used to investigate the optical properties of these four chalcone molecules. The DFT-optimized structures were employed and the same level of theory was used for TDDFT. We also used an integral equation formalism variant of the polarizable continuum model (IEFPCM) [35,36] for ethanol to account for the bulk solvent effects for all TDDFT calculations. All DFT and TDDFT calculations were performed using the Gaussian 09 program [37].

Results and discussion

FT-IR and FT-Raman spectral investigations

FT-IR spectroscopy can serve as an important basic tool for characterization of organic and inorganic molecules. In this work, experimental IR spectra of hydroxy chalcones (**1–4**) were compared and analyzed with respect to those obtained from DFT calculations (B3LYP/6-31G(d,p) level). The DFT-optimized molecular structures of **1–4** are shown in Fig. 1. The FT-IR and FT-Raman spectra of the synthesized chalcone derivatives are shown in Figs. 2 and 3, respectively. The theoretical spectra are also shown for comparison. We assigned only the important peaks in the FT-IR and FT-Raman spectra because there are only a limited number of references for the IR spectra of other chalcone molecules for comparison. As shown in Figs. 2 and 3, the experimental patterns of the IR and Raman peaks are much more complex because of overlapping peaks and the presence of highly active vibrational groups. The specified vibrations that occur at similar

Download English Version:

<https://daneshyari.com/en/article/1231647>

Download Persian Version:

<https://daneshyari.com/article/1231647>

[Daneshyari.com](https://daneshyari.com)