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Synthesis and photosensitivity characterizations of 9-(6-bromo-4-oxo-4*H*-chromen-3-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2*H*-xanthene-1,8-(5*H*,9*H*)-dione(**BOCTTX**)

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ABSTRACT

Condensation reaction of 6-bromochromone-3-carboxaldehyde (**1**) with dimedone afforded 9-(6-bromo-4-oxo-4*H*-chromen-3-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2*H*-xanthene-1,8-(5*H*,9*H*)-dione (**3**, **BOCTTX**). Structure of **BOCTTX** was deduced based on its correct elemental analysis and spectral data (IR, ^{1}H NMR, ^{13}C NMR and mass spectra). Thin films of **BOCTTX** were prepared in this study by using spin coating technique. X-ray diffraction, scanning electron microscope analysis were studied for study the crystal and morphology characterization of **BOCTTX**. The results indicate that **BOCTTX** has a poly-crystalline nature with monoclinic structure. From differential scanning calorimetry, **BOCTTX** is found to be thermally stable up to 583 K and the chemical structure plays an important role in the thermal decomposition process. The optical absorption of the film was studied in the UV–Vis spectral range and the value of two allowed energy gaps of 2.2 and 3.3 eV. Current-voltage characteristics of **BOCTTX** based devices were studied in dark and under various illumination intensities in the range 20–100 mW/cm^2. Electrical and photoelectrical parameters were studied as a function of light intensity. The obtained results exhibits photoconductivity cauterization and suggest that the diode can be used as a photodiode in optoelectronic sensor application.

1. Introduction

Chromones have attracted attention from the point of view of both biological activity and organic synthesis [1–4]. They have been found to exhibit a broad range of biological activities including antifungal, antiviral, antimicrobial, antiallergenic, antitubulin, anticonvulsant and antitumor activity [5–10]. These derivatives also serve as intermediates to many products of fine chemical industries such as pharmaceuticals, agrochemicals and dyestuffs [11,12].

Chromones and its derivatives have promising electrical and photoelectrical characteristics similar to vital organic semiconductors which have considerable attention due to its infinite variety of compounds, high stability, low cost of technology, easy to manufacture, relatively low voltage processing, and their novel properties [13–16]. Moreover, organic semiconductor compounds can provide a wide range of electronic and optoelectronic devices [17]. In addition, thin organic films are characterized by low temperature, light weight, and high electrical and photoelectrical performance [17,18]. Accordingly, these organic films can be applied in semiconducting electronic devices as transistors, light emitting diodes and solar cells [17–20]. One of the benefits of organic electronics is their low cost compared to traditional inorganic electronics.

Due to its significantly lower manufacturing costs, low environmental impact during manufacturing and operations, suitability for thin film production, chemical and thermal stability, highly absorption coefficient, suitability for optoelectronic device application, **BOCTTX** is applied for this study.

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The aim of the present work is to synthesis a new oxygen heterocyclic organic compound containing both chromone and xanthenes moieties in one molecular frame, **BOCTTX**, and confirming its structure by different available techniques. The main challenges were by a new side for the validation of this new structure for the design of a photodiode in optoelectronic sensor application, in addition to its original purpose for drug design structure. Therefore, the specific goals of this work are:

1. Synthesis 9-(6-bromo-4-oxo-4*H*-chromen-3-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2*H*-xanthene-1,8-(5*H*,9*H*)-dione (**3**, **BOCTTX**) as a new oxygen heterocyclic organic compound.
2. Confirmation its structure by different techniques such as IR, ^{1}H NMR, ^{13}C NMR and mass spectra.
3. Study its crystalline structure by X-ray diffraction and morphological structure by scanning electron microscopy.
4. Study the optical absorption characteristics to detect the energy gap of the new structure as well as photoluminescence properties.
5. Designing a device based **BOCTTX** for checking the validity of this structure for optoelectronic sensor application.
6. Extracting the main important parameters of the prepared device, such as rectification ratio, series and shunt resistance, barrier height, ideality factor, responsivity and photosensitivity of the new device.

2. Experimental details

2.1. Reactions and molecular structure characterization

To a solution of carboxaldehyde**1** (0.51 g, 2 mmol) in dry pyridine (10 mL), dimedone (0.56 g, 4 mmol) was added and stirred at room temperature for 1 h, then acidified with 6N HCl. The solid deposited was filtered and crystallized from acetic acid to give compound (**3**, **BOCTTX**) as pale yellow crystals, yield 0.75 g (76%), mp > 300 °C. IR (KBr, cm^{-1}): 3090 (CH_{arom}), 2957, 2936, 2871 (CH_{aliph}), 1683, 1655 (2C = $O_{xanthene}$), 1638 (C=$O_{\gamma\text{-pyrone}}$), 1626 (C=C). ^{1}H NMR (DMSO-d_6): 0.88 (s, 6H, 2 CH_3), 1.03 (s, 6H, 2 CH_3), 2.00 (s, 2H, CH_2), 2.08 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 2.38 (s, 2H, CH_2), 4.35 (s, 1H, H-9$_{xanthene}$), 7.60 (d, 1H, J = 8.7 Hz, H-8$_{chromone}$), 7.90 (d, 1H, J = 8.7 Hz, H-7$_{chromone}$), 8.03 (s, 1H, H-5$_{chromone}$), 8.36 (s, 1H, H-2$_{chromone}$).^{13}C NMR (DMSO-d_6): 26.0 (2Me), 26.2 (2Me), 27.9 (2CH_2), 29.2 (C-9$_{xanthene}$), 32.1 (*2C*Me$_2$), 50.3 (2CH_2), 99.2, 112.0, 119.4, 120.2, 123.7, 127.8, 135.3, 149.6, 152.5, 154.9, 173.4 (C=$O_{\gamma\text{-pyrone}}$), 196.2 (2C = $O_{xanthene}$). MS (*m/z*, I %): 498 (M+2, 51), 496 (M^{+}, 50), 414 (100), 412 (95), 358 (9), 356 (9), 273 (23), 257 (23), 217 (13), 201 (9), 161 (15), 133 (10), 83 (29). Anal.Calcd for $C_{26}H_{25}BrO_5$ (497.39); C, 62.79; H, 5.07%. Found: C, 62.65; H, 4.90%.

2.2. Characterization methods

A digital Stuart SMP3 apparatus was used to determine melting points for all structures in this study. Different tools were used for identification the molecular structure such as infrared spectra by using Perkin–Elmer 293 spectrophotometer, using KBr disks.

Moreover, ^{1}H NMR spectrum (300 MHz) and ^{13}C NMR spectrum (75 MHz) were measured on Mercury-300BB, using DMSO-d_6 as a solvent and TMS (δ) as the internal standard. In addition, mass spectra were obtained using GC-2010 Shimadzu Gas chromatography instrument mass spectrometer (70 eV). Elemental microanalyses were performed on a Perkin–Elmer CHN-2400 analyzer. The electronic spectra of **BOCTTX** was measured with a JASCO model V-550 UV–Vis spectrophotometer (200–500 nm) using benzene, chloroform, dimethyl formamide, dioxane, methanol and ethanol as solvents. The molecular models of the **BOCTTX** was constructed the proposed structure with *Hyperchem 7.5* [21]. Geometry optimization was performed using Density Functional Theory (DFT) calculations.

Surface and morphological properties of **BOCTTX** structure was studied by using scanning electron microscopy (SEM) of type JEOL-JSM-636A OLA and the crystalline properties of powder and films were investigated by using a Shimadzu X-ray Diffractometer (Model 7000) with utilized monochromatic CuK_α radiation operated at 30 kV and 30 mA. Diffraction patterns were employed automatically in the scanning range $2\theta = 5–90°$and scan speed 2°/min.

Photoluminescence characteristics of **BOCTTX** was measured using Cary Eclipse Fluorescence Spectrometer, in the wavelength scan range 300–900 nm with scan speed of 500 nm min^{-1}.

Thermal analysis of **BOCTTX** was carried out by differential scanning calorimeter (DSC) using Shimadzu DSC-50.

Optical absorption was measured for films deposited on optically flat corning glass substrate using UV–Vis double beam PC scanning spectrophotometer labomed model UVD-2950 of spectral range 190–1100 nm with a step scan of 2 nm.

Single crystalline wafers of p-type Si was obtained from Nippon Mining Co with area of ~1 cm^2 each and 450 μm thick. The pieces were firstly cleaned and etched by using the CP4 solution (HF:HNO_3:CH_3COOH with ratio 1:6:1). Films of **BOCTTX** were deposited by spin coating on the crystalline substrates to obtain **BOCTTX**/p-Si diode. Ohmic contact was made by high vacuum evaporation of high purity of platinum onto the top of the film and onto the bottom of the substrate using a sputtering unit (Sputtering machine (Turbo Sputtering RF & DC Power Supplies Deposition System Model Hummer 8.1). The polarity of **BOCTTX** is checked in the present work. There are several experimental methods valid for determining conductivity type of the semiconductor. The *rectification method* is used in this study because of the suitability for high resistivity material such as **BOCTTX**. This method involves determining the sign of the majority carrier based on the polarity of a rectified AC signal at the point of contact with the semiconductor material (**BOCTTX**) [22].

Current–voltage characteristics of **BOCTTX** films were measured by means of high impedance electrometer type Keithley 2635 A attached with a personal computer interfaced *via* home-made software for recording and plotting for the extracted data from the electrometer. Photoelectrical characteristics was achieved by using a white halogen-tungsten with intensity measured using a solar power meter type TM-206.

3. Results and discussion

3.1. Synthesis characterization

In the present work, treatment of 6-bromochromone-3-carboxaldehyde (**1**) with dimedone in dry pyridine at molar ratio 1:1 and 1:2 afforded the same product which was identified as 9-(6-bromo-4-oxo-4*H*-chromen-3-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2*H*-xanthene-1,8-(5*H*,9*H*)-dione (**3**, **BOCTTX**). The simple condensation product **2** (1:1 product) was excluded based on the spectral data. Formation of compound **3** may obtained through condensation of aldehyde **1** with two molecules of dimedone with loss of one molecule of water leading to intermediate **A** which underwent further dehydration, *via* its enolic form **B**, producing the final product **3** (Fig. 1). The IR spectrum of compound **3** (Fig. 2) showed characteristic absorption bands at 1683, 1655 (2C = $O_{xanthene}$) and 1638 cm^{-1} (C=$O_{\gamma\text{-pyrone}}$). The ^{1}H NMR