Optical Materials 62 (2016) 231–239

Contents lists available at ScienceDirect

Optical Materials

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

Synthesis and experimental-computational characterization of nonlinear optical properties of triazacyclopentafluorene-coumarin derivatives

Santiago García [a], Juan L. Vázquez [a], Marvin Rentería [a], Isis G. Aguilar-Garduño [a], Francisco Delgado [b], Mónica Trejo-Durán [c], Marco A. García-Revilla [a], Edgar Alvarado-Méndez [c, **], Miguel A. Vázquez [a, *]

[a] Chemistry Department, DCNE, University of Guanajuato, Noria Alta s/n, 36050, Guanajuato, Gto., Mexico
[b] Organic Chemistry Department, National School of Biological Sciences -IPN, Prol. Carpio y Plan de Ayala s/n, 11340, México, D. F., Mexico
[c] Engineering Division Campus Irapuato-Salamanca, University of Guanajuato, Palo Blanco s/n, 36885, Salamanca, Gto., Mexico

ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form
21 September 2016
Accepted 23 September 2016

Keywords:
Nonlinear optics
Triazacyclopentafluorene-coumarin
TD-DFT

ABSTRACT

A series of novel 3-(2,2*a*,3-triazacyclopenta[*jk*]fluoren-1-yl)-2*H*-chromen-2-one derivatives **5a-c** have been synthesized by [8 + 2] cycloaddition reaction between the corresponding 3-(imidazo[1,2-*a*]pyrimidines)-2-yl)-2*H*-chromen-2-one **4a-c** with 2-(trimethylsilyl)phenyl triflates as benzyne precursor in 65–80% yields. The strategic incorporation of triazacyclopentafluorene group at the 3-position of the coumarin molecules resulted in dyes with excellent nonlinear optical properties. The nonlinear optical properties of third order (compounds **5a-c**) were studied using Z-scan technique. The high nonlinear response is of 10^{-7} cm^2/W order. The nonlinearity of the compounds is an indication of a promising material for applications at low power, such as optical switching, waveguides, nonlinear contrast phase, among others. Theoretical results of HOMO-LUMO gaps and oscillator strengths are used to rationalize the high efficiency of the novel compound in the nonlinear optical behavior. In particular, **5b** displays the best nonlinear optical properties and at the same time the smaller HOMO-LUMO gap and the highest oscillator strength.

1. Introduction

Nonlinear optical (NLO) properties are consequence of the absorption-emission of more than one photon of molecules, some physical nonlinear effects are the self-diffraction, self-phase modulation, nonlinear absorption, third harmonic generation, and self-focusing [1,2]. NLO materials research is inspired by the demand for efficient molecules displaying high data rates to be used in communication technologies based on optical devices. Nowadays, such devices are based on inorganic compounds such as $LiNbO_3$ [2]. The impact of such inorganic materials in many applications have been proved due to the mechanical and chemical stability displayed and large NLO coefficients. Nevertheless, NLO materials based on organic molecules have been used as an alternative for the construction of such efficient optical devices. Some of the advantages displayed for such organic molecules over inorganic counterparts are: versatility on the design regarding with the demanded opto-electronic properties, fast optical nonlinearities. Therefore, NLO organic molecules are subjects to meet future requirements for ultrahigh bandwidth photonic devices [3]. Regarding high-speed third order NLO applications, devices having a refractive index dependent of the intensity are used in communications systems. High-speed third order NLO is generated with continuous or pulsed electromagnetic fields, as a consequence the nonlinear refractive index of the sample is modified.

For the design of organic NLO materials it is necessary to consider a π-conjugated systems, belonging to these systems are strong electron-donor and electron-drawing groups. With this regard, the benzo-α-pyrones, commonly called coumarins, are good candidates to NLO properties due to its electronic characteristics. Coumarins are commonly isolated from plants, either in the free or in the combined form [4]. Such molecules are used to develop

* Corresponding author.
** Corresponding author.
E-mail address: mvazquez@ugto.mx (M.A. Vázquez).

http://dx.doi.org/10.1016/j.optmat.2016.09.065
0925-3467/

applications in polymer science, medicine and biology [5]. They are used in cosmetics applications [6,7], fluorescent whiteners [8], biological labeling [9], photocaging [10,11] and laser dyes, just to name a few [12–16]. Due to their structural diversity and potential application in different areas of science [17–22], it is important to work on the modification of the different properties displayed by the introduction of different substituents in to the heterocyclic ring. Moreover, the family of cyclazines are molecules of great research interest owing to their special electronic properties [23–25], high fluorescence efficiency [26,27], wide range of biological activity [28,29] and the fact that their frameworks have been found in several natural products [30–35]. In particular, 1,2-benzannulated derivatives indolizine [3,4,5-*ab*]isoindole have recently been found to be excellent fluorophores with high emission quantum yields and tunable colors in the blue and green region [36].

A major issue in expanding the applications of coumarin derivatives is related to the problems of the overlap between absorption and emission spectroscopic bands displayed. A solution for this issue arises from increasing the delocalization of the conjugated π-electron system, which will allow us to obtain derivatives of coumarin with absorption bands located at longer wavelengths and with larger intensities. Moreover, an improvement of NLO properties can be achieved increasing the π-delocalized system, this would imply a big challenge, the introduction of a poly heterocyclic fragment in the coumarin ring attached to the 3-position. In order to reach this goal, we introduce a new triazacyclopentafluorene-coumarin derivatives **5a-c**. These systems are large π-conjugated structure obtained from benzyne precursors and imidazo [1,2-*a*]pyrimidines with coumarin moiety. Furthermore, we describe the analysis of electronic structure by molecular orbital calculations and their nonlinear optical properties.

Regarding to the characterization of the optical properties of molecules, the Time Dependent Density Functional Theory (TD-DFT) [37] is the most used computational methodology to rationalize the absorption and emission of molecules from the Quantum Chemistry perspective. The advances in TD-DFT [38] enable us to study the physical reasons of the optical properties of relatively big systems. Additionally, to the experimental section, in this contribution, we perform a theoretical characterization of the optical properties of the synthesized molecules using the TD-DFT approach. Coumarin derivatives have been one of the most studied molecules from the optical properties perspective. Several theoretical studies are devoted to the characterization of the ground and excited states of commercial coumarins [38]. Some theoretical studies are devoted to the characterization of the solvent effects in optical properties [39], some others are centered on the characterization of properties of coumarin-based dyes [40,41]. The goal of the present study is the experimental and theoretical characterization of new triazacyclopentafluorene-coumarin derivatives that have never been reported.

2. Experimental

2.1. Chemistry materials

We dried the solvents before use, THF and Et_2O were distilled over Na°, ethanol was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen and CH_3CN was distilled over $CaCl_2$. All other chemicals and solvent were commercially available and used without further purifications. The products were purified by column chromatography over silica gel (MN Kieselgel 60, 230–400 mesh). Mixtures of ethyl acetate and hexane were used as eluents. Analytical TLC was used (aluminum sheets, silica gel 60 F/UV_{254}). Visualization was carried out with UV light and iodine.

2.2. Chemistry instrumentation

Melting points were measured on using a digital Electrothermal 90100 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz, a Varian VNMR System 500 MHz, a Bruker Ascend 400 MHz, or a Bruker Ultrashield 500 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as a solvent. Chemical shifts are reported in ppm, relative to tetramethylsilane as internal reference. IR spectra were recorded on potassium bromide plates with a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. UV absorption spectra were recorded on a Perkin Elmer lambda 50 and the emission were recorded on Fluorescence spectrophotometer HITACHI F-7000. High-resolution mass spectra (HRMS) were determined with electrospray ionization on a Bruker micrOTOF-Q II or electronebulization ionization on a Bruker QTOF mass spectrometer.

2.3. Synthesis of benzo-indolizine-coumarin (*5a-c*)

The coumarin **2a-c** were prepared following a literature procedure [42,43] Representative procedure and data for compound **2a**: The aldehyde **1a** (4.1 mmol), morpholine (10% mmol) and ethyl acetoacetate (4.9 mmol) were dissolved in 10 mL of ethanol and the mixture was irradiated by microwave during 5 min at 140 °C (140 W). The solvent was removed and using recrystallization afforded product **2a** (90%) as a yellow solid [42]. m.p. 107–109 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.52 (s, 1H, −CH═C−), 7.66 (d, *J*(H,H) = 2.8 Hz, 2H, Ar), 7.41–7.33 (m, 2H, Ar), 2.74 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS) δ = 195.5, 159.2, 155.3, 147.4, 134.3, 130.2, 125.0, 124.9, 118.3, 116.7, 30.5; IR (KBr) ν = 1741 cm^{-1} (C═O), 1678 cm^{-1} (−O−C═O); UV–vis (CH_2Cl_2) λ_{max} = 246 nm.

For the halogenation procedure of **2a-c**: The coumarin **2a** (1 mmol) were dissolved in CH_3CN (10 mL), trifluoroacetic acid (2 mmol) and NBS (1.1 mmol) were added. The mixture was irradiated by microwave during 15 min at 140 °C. Water was added, the mixture was extracted three times with CH_2Cl_2 and the combined organic extract was dried over sodium sulfate and evaporated. Flash chromatography was performed using 230–400 MESH and mixture hexane/ethyl acetate 9:1 to give **3a** (95%) [44]. m.p. 163–164 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.64 (s, 1H, −CH═C−), 7.71 (t, *J*(H,H) = 7.2 Hz, 2H, Ar), 7.44–7.35 (m, 2H, Ar), 4.76 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 188.90, 158.88, 155.43, 149.54, 135.12, 130.43, 125.31, 122.19, 118.15, 116.91, 35.59; IR (KBr) ν = 1727 cm^{-1} (C═O), 1685 cm^{-1} (−O−C═O); UV–vis (CH_2Cl_2) λ_{max} = 247 nm.

2.4. Synthesis of *4a-c*

In a 50 mL round-bottom flask we add compound **3a-c** (1 mmol), 2-amino-4-methylpyrimidine (1.2 mmol) and $NaHCO_3$ (1.8 mmol). Anhydrous ethanol (15 mL) was added and the reaction mixture was irradiated by microwave for 30 min. The reaction time is determined by observing the disappearance of starting materials by TLC, a CH_2Cl_2/hexane (1:1; v/v) system was used. The reaction mixture is filtered and washing with H_2O. Then the dry product is purified by column chromatography. Finally, the derivative is recrystallized from CH_2Cl_2/petroleum ether.

2.4.1. Compound *4a*

Yield 72%; m.p. 301–303 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.92 (s, 1H, −CH═C−), 8.43 (s, 1H, −CH═C−), 8.30 (d, *J* (H,H) = 6.7 Hz, 1H, Ar), 7.65 (d, *J* (H,H) = 7.6 Hz, 1H, Ar), 7.55 (t, *J* (H,H) = 7.6 Hz, 1H, Ar), 7.39 (d, *J* (H,H) = 8.3 Hz, 1H, Ar), 7.33 (t, *J* (H,H) = 7.3 Hz, 1H, Ar), 6.76 (d, *J* (H,H) = 6.8 Hz, 1H, Ar), 2.65 (s, 3H,