Computational and Theoretical Chemistry 963 (2011) 63–70

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Photochromic properties of a dithienylethene–indolinooxazolidine switch: A theoretical investigation

Denis Jacquemin [a,b,*], Eric A. Perpète [b,1], François Maurel [c], Aurélie Perrier [c,*]

[a] Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS No. 6230, Université de Nantes, 2 rue de la Houssinière – BP 92208, 44322 Nantes Cedex 3, France
[b] Unité de Chimie Physique Théorique et Structurale (UCPTS), Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, B-5000 Namur, Belgium
[c] Laboratoire Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), CNRS UMR 7086, Université Paris 7 – Paris Diderot, Bâtiment Lavoisier, 15 rue Jean Antoine de Baïf, 75205 Paris Cedex 13, France

ARTICLE INFO

Article history:
Received 8 September 2010
Accepted 29 September 2010
Available online 13 November 2010

Keywords:
Diarylethenes
Indolinooxazolidine
Molecular switches
TD-DFT
Absorption spectroscopy
Excited-states

ABSTRACT

Using ab initio spectroscopic tools, we have studied the structural and electronic properties of an hybrid dithienylethene–indolinooxazolidine switch synthesized by Pozzo and coworkers [Photochem. Photobiol. Sci. 9 (2010) 131]. To simulate the electronic absorption spectra of this mixed photochrome, we relied on a PCM-TD-DFT approach. Several functionals have been considered, namely the PBE0 global hybrid as well as four range-separated hybrids (CAM-B3LYP, LC-ωPBE, ωB97X and ωB97XD). On average, considering all four closed/open structures, ωB97XD provides the best compromise for estimating the transition wavelengths. It is shown that the TD-DFT procedure combined with an analysis of the molecular orbitals implied in the absorption bands provide insights into the observed photochromic pathways.

1. Introduction

Photochromic molecules, which undergo a light-induced reversible transformation between two isomers presenting different absorption spectra [1,2], can act as binary units. Consequently, these compounds have attracted a considerable interest as potential building blocks for molecular-scaled optoelectronic devices such as switches, logic gates and memories. Recently, experimental investigations have focused on the development of multicomponent systems encompassing several covalently-linked photochromic units. First, one can find architectures designed with two or more identical molecular switches [3–10]. These symmetric systems often rely on dithienylethene units (also referred to as diarylethenes, DA) which are well-known for their fatigue resistance, large quantum yields, short response times and high thermal stability [11]. Single DA presents a colorless open-form, **Do**, which undergoes a ring-closure reaction under UV irradiation leading to the colored closed form, **Dc** (see Fig. 1). In symmetric twin-DA compounds, the successive photocyclisations might possibly lead to three different states: doubly open (**DoDo**), mixed closed-open (**DcDo**) and doubly closed (**DcDc**). However, experimental studies have shown two limitations: (i) the doubly closed system remains unseen in several cases [3,5,6]; (ii) even when full photochemical reactivity is preserved, the color alteration resulting from the **DcDo** to **DcDc** reaction is rather limited [7–9] and "only" a doubling of the intensity of the visible absorption band is observed. The second strategy proposed to conceive candidates for multifrequency optical memories relies on the combination of two photochromic systems belonging to different families [12–17]. For instance, four-ways switches have efficiently been obtained by combining a DA to a phenoxynapthacenequinone [15], to a naphtopyran [16] and to an indolinooxazolidine [17]. The latter system, represented in Fig. 2, has been recently synthesized by Pozzo and coworkers and contains a DA covalently linked through an ethylenic bridge to an indolino[2,1-b]oxazolidine moiety. In the single colorless indolinooxazolidine moiety **Ic** (Fig. 1), UV irradiation induces a cleavage of the relatively weak bond between the sp^3 carbon atom and the oxygen atom of the oxazolidine core, subsequently leading to a colored zwitterionic structure **Io**. For the hybrid compound, referred to as **ID** in the following, the four different states corresponding to all open/closed possibilities have been successfully characterized in chlorobenzene [17]. Additionally, reversible light-triggered commutations have been obtained for three isomers, namely **IcDo**, **IoDo** and **IcDc**. On the contrary, the conjugated colored structure, **IoDc**, constitutes a deadlock as attempts to restore **IcDc** or **IoDo** lead to the formation of side products [17]. **IoDc** presents a relatively poor fatigue resistance but benefits from a large contrasts: the color can be switched between

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* Corresponding authors.
E-mail addresses: Denis.Jacquemin@univ-nantes.fr (D. Jacquemin), aurelie.perrier-pineau@univ-paris-diderot.fr (A. Perrier).
[1] Senior Research Associate of the Belgian National Fund for Scientific Research.

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doi:10.1016/j.comptc.2010.09.009

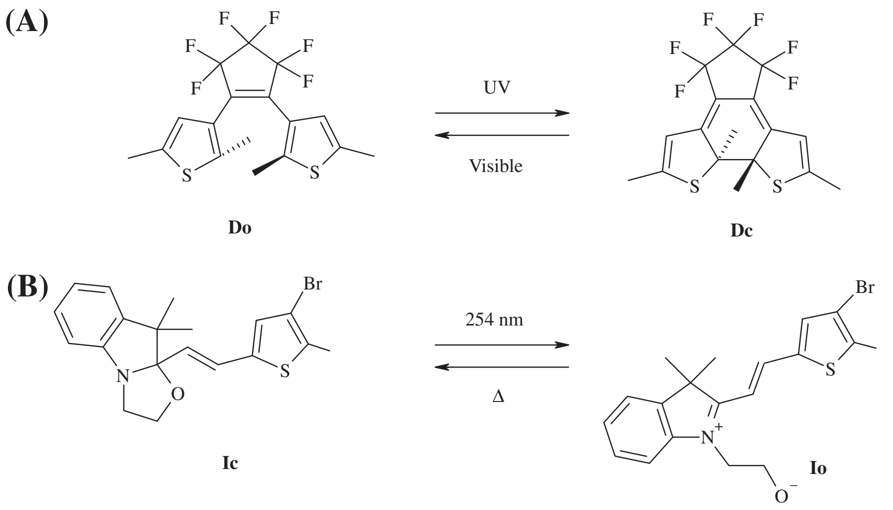

Fig. 1. Representation of the dithienylethene (A) and indolinooxazolidine (B) model compounds.

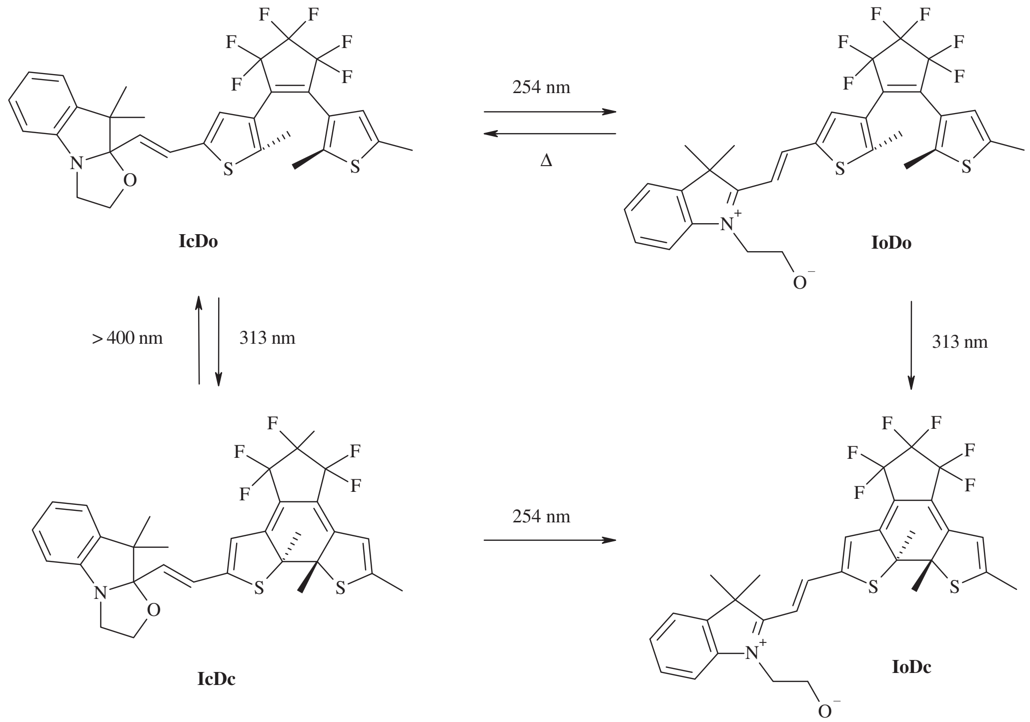

Fig. 2. Schematic representation of the four states of the dithienylethene–indolinooxazolidine photochrome of Ref. [17].

colorless (**IcDo**) to yellow (**IoDo**), pink (**IcDc**) or green (**IoDc**). Consequently, the bottleneck constituted by the most conjugated colored isomer has to be overcome to obtain an efficient four-color mode switch.

In the framework of multi-addressable molecular structures, theoretical tools can certainly be a valuable complement to experimental investigations. Recently, we have shown that investigating the excited-states with Time-Dependent Density Functional Theory (TD-DFT) [18,19] and analyzing the nature of the molecular orbitals involved in the short-wavelength absorption bands of the hybrid open/closed structures might indeed help in rationalizing the full or partial photochromism of DA dimers [20–23] and trimers [24,25]. To the best of our knowledge, the **ID** has never been modelled by theoretical tools. Our first goal in this paper is thus to fill this gap by defining a computation protocol able to accurately predict the absorption spectra of **ID**. For DA, numerous TD-DFT calculations have already been performed, and it is known that CAM-B3LYP [26], a range-separated hybrid (RSH) provides accurate absorption wavelengths [27,28]. However, for the indolinooxazolidine moiety, the zwitterionic nature of the open form may be a concern. As a matter of fact, for the spirooxazine family which is close to the indolinooxazolidine series, it turned out that no global hybrid could correctly describe the absorption spectra of the merocyanine isomers [29]. For **ID** that is built upon two different families of photochromic compounds, the set up of the computational procedure therefore represents a real challenge. In a second step, we aim at rationalizing the spectroscopic and photochromic properties of this hybrid photochromic compound.