

Indolino-oxazolidine Photochromic System Insights by NMR and DFT Calculations

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In the past decades organic switchable molecules have been shown to be very versatile building blocks with a wide range of applications.^[1] Among them, indolino-oxazolidine (BoX) derivatives have recently triggered interest as multi-addressable systems. Besides being photo-, electro-, and acido-chromic, these molecular switches also display nonlinear optical properties,^[2] with promising potential applications in communication and material science. Even if switching processes have already been reported,^[3] only few attempts to characterize and rationalize them are to be noticed.

Our study is hereby focused on some thienyl-substituted BoX, linked by allylic bridge as well as Bi-BoX dyad compounds associated by thienyl or phenyl junctions. The basic of BoX switching relies on two processes: (i) photo- and acido-opening of the oxazolidine ring (C-O bond breaking) and (ii) *trans* > *cis* photo-isomerization of the double bond between the BoX and the aromatic moiety (Fig. 1).

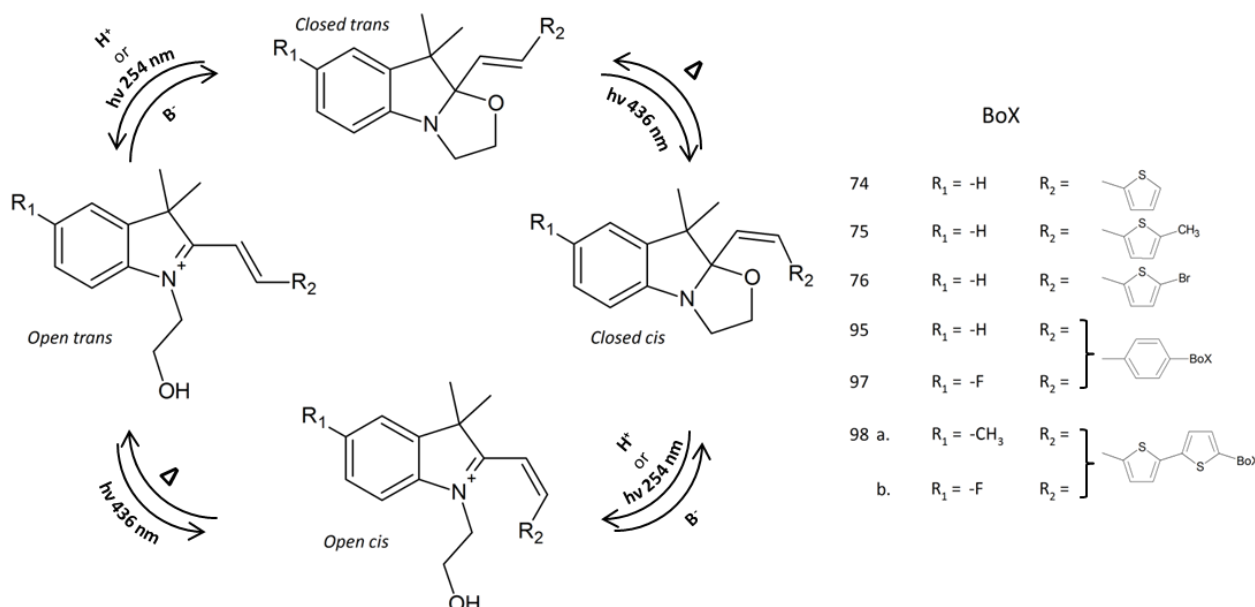


Figure 1. Commutation principles for substituted BoX systems. From the parent Closed *trans* compound (up), one can reversibly isomerize the double bond to a *cis* isomer (right) by mean of 436 nm irradiation light, or open the oxazolidinic ring to an Open *trans* isomer (left) with a 254 nm line or acidified medium. Then, the Open *cis* isomer (down) can be obtained by isomerization of the latter, or opening of the first.

In this work, we propose a coupled experimental and theoretical approach in order to push forward the understanding of the system mechanism, and set pathways to design optimised substituted BoX moiety for suitable application. In this perspective, Nuclear Magnetic Resonance (NMR) spectroscopy coupled to irradiation sources is used for structural assignment and kinetic study, while Density Functional Theory (DFT) calculations will pave the way to highlight energetic and electronic processes that are involved. Substitution as well as solvent effects towards the reactivity of the compounds are experimentally studied, and combined with theoretical calculations.

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