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BENZAZOLO-OXAZOLIDINE UNIT: FROM ITS SYNTHESIS TO THE ELABORATION OF MULTI-ADDRESSABLE SYSTEMS

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Abstract

The benzazolo-oxazolidine (BOX) derivatives can be considered as a new family of molecular switches but are also often considered as a sub-class of spiropyrans. Since

their first appearance in the 1970ies, these compounds have already demonstrated some impressive acido-, photo- and electrochromic behaviours [1]. Moreover, the simplicity of their preparation and the high structural diversity offered by chemical modifications either on the indoline moiety or on the associated –system allow to prepare numerous molecular switches with fine-tuning chromophoric properties.[1b, 2]. The introduction of one indolino-oxazolidine moiety as a BOX unit in a molecular system has already demonstrated its efficiency in order to modulate the optical properties such as the absorption, the luminescence, and the first hyperpolarizability but also some physico-chemical properties i.e complexation constants over two different states.

Going further, in order to promote the metastable states possibilities, the condensation of two identical BOX units connected around a pi conjugated system has allowed the observation of a stepwise commutation by using indifferently different kinds of stimulation (proton, photon and electron).[4] These new molecular switches lead to the modulation of new molecular properties such as two-photon absorption and the modulation of others over 3 discrete levels.

This concept was successfully extended to 3 identical BOX units connected by using pi conjugated systems based on symmetrical triarylamine and conducts to obtain some molecular switches exhibiting up to 4 different metastable states. More important, breaking the C3v symmetry by the introduction of 3 different substituents on triarylamine core should theoretically conduct to consider 23 different states. Nevertheless, we have demonstrated that the conjugation of the whole a system is a key parameter in order to promote the regioselective addressability of the three identical BOX units of the system.

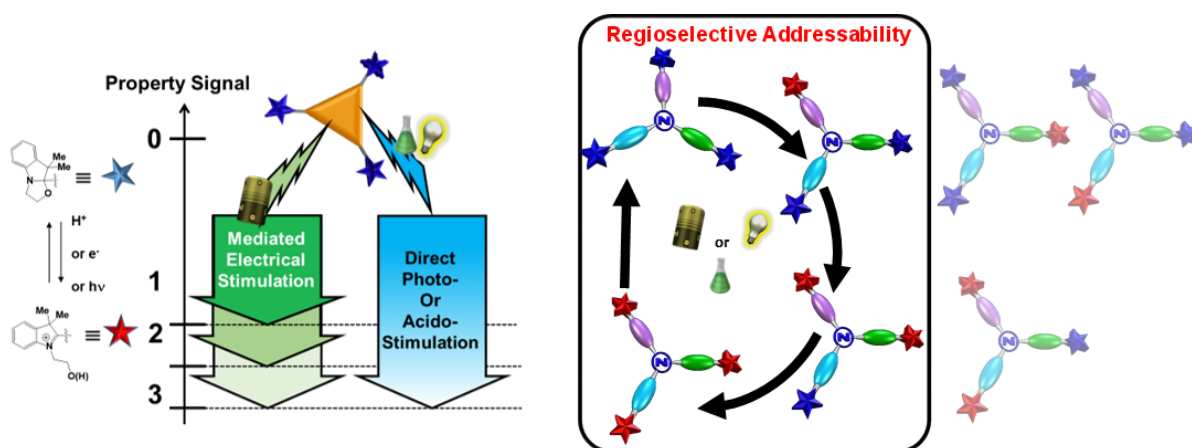


Figure 1. Schematic representation of the observed stepwise (left) and regioselective (right) addressability of symmetrical and unsymmetrical triarylamine-BOX systems respectively.

References

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[3] (a) K. Pielak ; F. Bondu; L. Sanguinet; V. Rodriguez; F. Castet; B. Champagne, Dyes Pigments 2019, 160, 641. (b) C. Guerrin; Y. Aidibi; L. Sanguinet; P. Leriche; S. Aloise; M. Orio; S. Delbaere, J Am Chem Soc 2019, 141 (48), 19151.

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