

Highlighting photophysical properties of a new negative photochromic class

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Various “negative”* photochromic molecules have been recently studied, compared to “positive” photochromes, and they have already proved to be interesting for various applications (security devices, biological probes or drugs, solar energy storage etc).^{[1], [2]} A new negative photochromic family, based on nitrile-rich acceptors (**NRA**), have gained attention these past few years due to their attractive properties.^[3] Nevertheless, their photophysical properties remain relatively unexplored. In this work, we investigate the behavior of NRA compounds in different conditions. First, the synthesis and spectroscopic properties of a series of three NRA-based photochromic molecules are described. By studying the influence of solvent, temperature and pH^[4] on their photophysical and photochemical properties, we show that absorption, fluorescence and photoswitching kinetics can be drastically tuned (Figure 1). Nanosecond transient absorption and DFT calculations provide useful information to understand these specific behaviors.

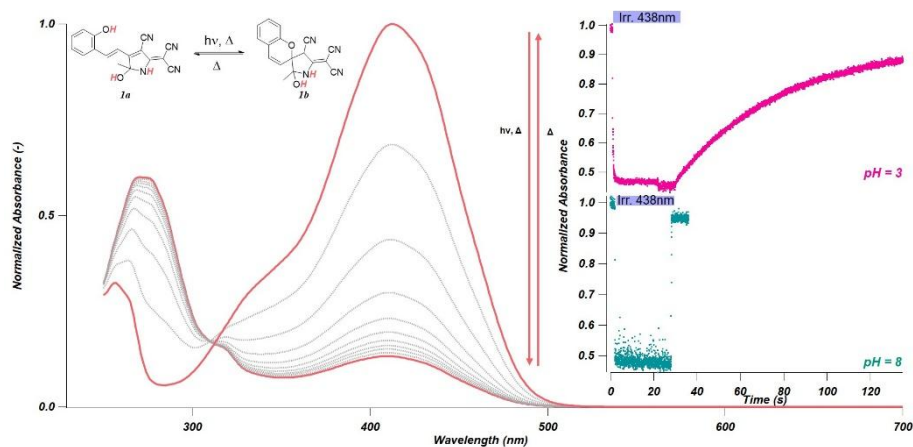


Figure 1. (Left) Absorption spectra of molecule **1** collected during an irradiation at 438 nm, in CH₃CN. (Right) Absorbance at 430 nm of molecule **1** followed during an irradiation at 438 nm (35.5 mW), in a CH₃CN:H₂O medium at 2 different pH (**1a**: colored form, **1b**: colorless form).

* Contrarily to “positive” photochromes, the colored form is the stable isomer in “negative” ones.

[1] K. Nakatani, J. Piard, P. Yu, R. Métivier, “Introduction: Organic Photochromic Molecules” in *Photochromic Materials: Preparation, Properties and Applications*, **2016**, Tian H., Zhang J. (eds.), Wiley-VCH, pp. 1-45

[2] S. Aiken, R. J. L. Edgar, C. D. Gabbutt, B. M. Heron, P. A. Hobson, *Dyes Pigm.* **2018**, *149*, 92-121.

[3] M. Y. Belikov, M. Y. Levlev, S. V. Fedoseev, O. V. Ershov, *Res. Chem. Intermed.* **2020**, *46*, 3477-3490.

[4] C. Yang, T. Khalil, Y. Liao, *RSC Adv.* **2016**, *6*, 85420-85426.