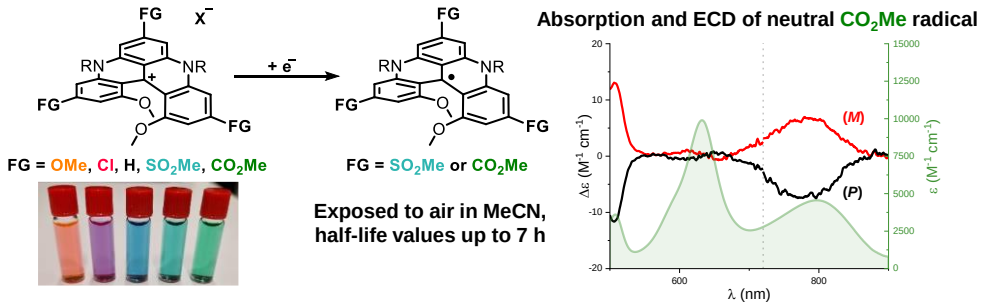
Electronic and Chiroptical properties of *para*-Functionalized Cations and Neutral Radicals of Diaza [4]Helicenes

Bibiana, Fabri

bibiana.fabri@unige.ch

Organic dyes offer extensive molecular control over optical and electronic properties allowing the design of stable carbocations and open-shell radicals, useful for many applications.[1] Accessing dyes with tuned absorption and emission of (circularly polarized) light in a wide spectral range is of practical value in (chir)optical applications.[2] Herein, a new family of poly-functionalized cationic [4]helicenes and their corresponding neutral radicals are presented. Thanks to Ir-catalyzed late-stage functionalization,[3] triple regioselective introduction of *para* electron-donating (EDGs) or electron-withdrawing groups (EWGs) was achieved on a dimethoxyquinacridinium scaffold.[4] Depending on their electronic nature, these newly introduced moieties strongly influence electrochemical and (chir)optical properties of the helical core: *i.e.*, redox potentials, energy band gap, Φ_f, lifetime, electronic circular dichroism (ECD) and circularly polarized luminescence (CPL) spectra. Additionally, EWGs allow the access to stable neutral radicals, easily prepared by mono electron reductions under electrochemical or chemical conditions. These radical helicenes present increased ECD at low energies compared to the parent helical cations with g_{abs} values above 10^{-3} ($\lambda \sim 700$-900 nm). The open-shell electronic nature of the radicals was further characterized by EPR revealing an important spin density delocalization that contributes to their persistence.[5]



References:

[1] a) D. A. Nicewicz, T. M. Nguyen, *ACS Catalysis* **2014**, *4*, 355-360; b) L. Ji, J. Shi, J. Wei, T. Yu, W. Huang, *Adv. Mater.* **2020**, *32*, 1908015; c) A. Abdurahman, T. J. H. Hele, Q. Gu, J. Zhang, Q. Peng, M. Zhang, R. H. Friend, F. Li, E. W. Evans, *Nat. Mater.* **2020**, *19*, 1224-1229.

[2] a) P. Mayorga Burrezo, V. G. Jiménez, D. Blasi, I. Ratera, A. G. Campaña, J. Veciana, *Angew. Chem. Int. Ed.* **2019**, *58*, 16282-16288. b) S. Kasemthaveechok, L. Abella, M. Jean, M. Cordier, T. Roisnel, N. Vanthuyne, T. Guizouarn, O. Cador, J. Autschbach, J. Crassous, L. Favereau, *J. Am. Chem. Soc.* **2020**, *142*, 20409-20418. c) R. Rodríguez, C. Naranjo, A. Kumar, P. Matozzo, T. K. Das, Q. Zhu, N.Vanthuyne, R. Gómez, R. Naaman, L. Sánchez, J. Crassous, *J. Am. Chem. Soc.* **2022**, 144, 7709-7719.

[3] L. Frédéric, B. Fabri, L. Guénée, F. Zinna, L. Di Bari, J. Lacour, *Chem. Eur. J.* **2022**, e202201853.

[4] J. Bosson, N. Bisballe, B. W. Laursen, J. Lacour, *Helicenes. Synthesis, Properties and Applications (Eds.: J. Crassous, I. G. Stara, I. Stary), Wiley-VCH*, **2022**, Chapter 4, p. 127-165.

[5] B. Fabri, T. Funaioli, L. Frédéric, C. Elsner, E. Bordignon, F. Zinna, L. Di Bari, G. Pescitelli, J. Lacour *submitted*.