

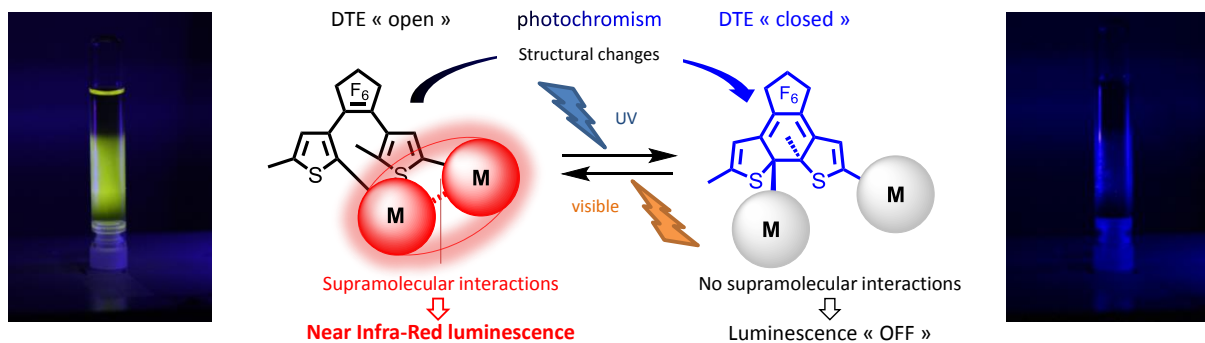
PhD offer

SYNTHESIS AND CHARACTERIZATION OF PHOTO-ACTUATOR MOLECULES: OPTICAL CONTROL OF SUPRAMOLECULAR INTERACTIONS

Chemistry / Molecular materials
Institut des Sciences Chimiques de Rennes

Keywords – Photochromism, luminescence, organic and organometallic synthesis, supramolecular interactions.

Context – Luminescent molecular systems constitute a particularly active area of research as they offer many applications in various fields such as in biology (bio-imaging), optoelectronic devices (storage of molecular data) or electroluminescent devices (OLED, LEEC...). In all these domains, the luminescence is used as output signal for sensitivity and resolution reasons. Particularly, low energy luminescence (near infra-red NIR) and long luminescence life-time (microsecond range) are appealing criteria because they can reduce the photo-bleaching (degradation) and eliminate the auto-fluorescence of biological media.[1] In this highly competitive context, we will go one step further by controlling the luminescence property by an external stimuli, that will open new routes toward multifunctional systems. We are particularly well positioned in this research field, based on our expertise on the control of the optical properties of photochromic platinum complexes.



Project – The systems that will be developed during this thesis will raise the challenge of controlling low energy luminescence. The PhD student will synthesize and study new photo-active organometallic architectures. Light will be used as external stimulus to control the optical properties of the new molecular objects (all-optical control). The design of the new chromophores will involve a diarylethene (DTE) backbone and the synthesis strategy will combine our know-how in organic and organometallic chemistry through the use of metallo-catalyzed cross-coupling reactions (Sonogashira, Stille, Suzuki-Miyaura...) and cyclometallation. All the syntheses will be carried out under argon atmosphere and using Schlenk techniques, vacuum ramp and glove box. The photochromic behavior (*i.e.*, the photo-isomerization between a non-conjugated "open" form and a the conjugated "closed" form) will trigger structural modification of the molecular structure



allowing or not, the formation of supramolecular interactions between chromophores. The near infra-red luminescence of these systems will come from these supramolecular interactions between chromophores, entirely driven by photochromism at the molecular level. The target systems will also present an axial chirality that will enlarge the properties to circularly polarized luminescence (CPL). The new compounds will be fully characterized using multi-core NMR (^1H , ^{13}C , ^{19}F ...), high mass resolution (HRMS), elemental analysis (EA), electrochemistry and diffraction spectroscopy techniques. The optical properties of the new compounds will be measured by UV-visible absorption spectroscopy. The properties of photochromism and luminescence will be evaluated, notably by determining quantum yields and photoluminescence lifetime.

Conditions / environment – In addition to the synthesis aspect, the PhD student will perform the photophysical characterizations in Rennes (photochromism, luminescence, absorption). The low-energy luminescence measurements will be carried out in collaboration with Dr. Keith Man-Chung Wong from the University of Shenzhen (China). **Short stays in the group of Dr. Keith M.-C. Wong will be possible during the thesis.**

The PhD student will benefit from a stimulating scientific environment and will benefit from solid training in organic/ organometallic synthesis and photophysics through the expertise of the group. This project is part of the "molecular materials" axis of the team which benefits from strong collaborations at national and international level allowing the PhD student, if he / she wish, to perform a stay of 1 to 3 months in another university. The PhD student will also have the opportunity to present his work at national or international conferences.

The 3-year thesis contract will start in October 2019. The candidate must be motivated, have a real interest for the organic and organometallic synthesis and the associated optical properties.

Application – Curriculum Vitae, academic records of the tow last years, a cover letter.

Contact – Julien Boixel  02 23 23 31 67  julien.boixel@univ-rennes1.fr

➤ <https://iscr.univ-rennes1.fr/omc/dr-julien-boixel>

- (a) Wong, K. M.-C.; Yam, V. W.-W., *Acc. Chem. Res.*, **2011**, *44*, 424-434; (b) Tanaka, Y.; Man-Chung Wong, K.; Wing-Wah Yam, V., *Chem. Sci.*, **2012**, *3*, 1185-1191; (c) Yeung, M. C.-L.; Yam, V. W.-W., *Chem. Sci.*, **2013**, *4*, 2928-2935.
- (a) Boixel, J.; Guerchais, V.; Le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekkine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; Righetto, S.; De Angelis, R., *J. Am. Chem. Soc.*, **2014**, *136*, 5367-5375; (b) Boixel, J.; Guerchais, V.; Le Bozec, H.; Chantzis, A.; Jacquemin, D.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D., *Chem. Comm.*, **2015**, *51*, 7805-7808; (c) Boixel, J.; Zhu, Y.; Le Bozec, H.; Benmensour, M. A.; Boucekkine, A.; Wong, K. M.-C.; Colombo, A.; Roberto, D.; Guerchais, V.; Jacquemin, D., *Chem. Comm.*, **2016**, *52*, 9833-9836.