

PHD OFFER

SUPRAMOLECULAR ASSEMBLIES OF POLYOXOMETALATE-DITHIENYLETHENE WITH PHOTO-MODULABLE LUMINESCENCE

Keywords: hybrid organic-inorganic materials, polyoxometalates, dithienylethenes, chirality, photochromism, photoluminescence.

Supervision: Julien BOIXEL (ISCR, Rennes) & Rémi DESSAPT (IMN, Nantes)

Context: Photo-activatable luminescent molecular materials, capable of reversibly modifying their emission properties in response to a light stimulus, play a key role in innovative optical technologies^{1,2} such as optoelectronics,³ information storage,⁴ bioimaging, biomedical applications,⁵ as well as defense and anti-counterfeiting technologies.⁶

A promising approach to develop such materials involves assembling photochromic organic molecules with luminescent inorganic clusters.^{7,8} However, several criteria need improvement, such as the speed and contrast of photo-switching in the solid state, the range of emission wavelengths (visible, near IR), or the fatigue resistance. Therefore, new assembly strategies are needed. Moreover, a current major challenge is to introduce chirality into materials to enable the photo-control of chiroptical properties (circularly polarized luminescence: CPL, circular dichroism: CD),⁹ thus facilitating exploration of emerging research areas such as chirality-induced spin selectivity¹⁰ and excitonic materials.¹¹ However, there are significant gaps in the understanding of photo-activatable chiroptical materials that need to be addressed for these materials to be integrated into effective photo-active devices.

Position: This thesis project aims to develop a new family of molecular materials with photo-modulable luminescence combining photochromic dithienylethenes (DTEs) with luminescent polyoxometalates (POMs) which are anionic nano-sized molecular oxides of transition metal ions (W, Mo). This project is part of a collaboration between Dr. Julien BOIXEL (organic synthesis, DTEs, photochromism: ISCR, Rennes) and Dr. Rémi DESSAPT (inorganic and hybrid organic-inorganic synthesis, photoactive POMs: IMN, Nantes), who have recently demonstrated the effectiveness of the photochromism property in materials combining DTEs and non-luminescent POMs.^{12,13}

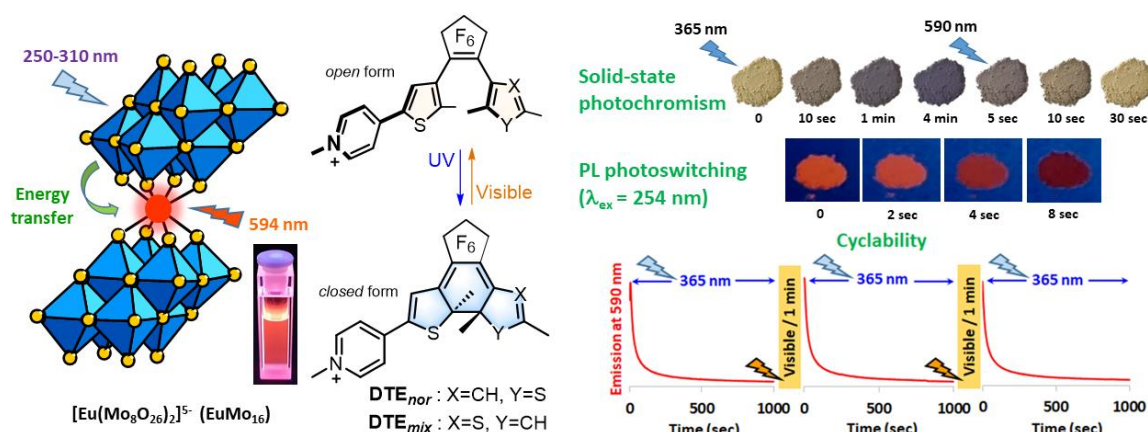


Fig. 1 Solid-state photochromic and photoswitchable luminescent properties of new supramolecular Ln-POMs/DTEs assemblies (unpublished results).

Very recently, the two collaborators achieved a new proof of concept by preparing the very first ionic supramolecular assemblies combining cationic DTEs and luminescent lanthanide-based POMs anions (Ln-POMs) (Fig. 1). These materials exhibit excellent reversible photoluminescence modulation in the solid state, with DTEs acting as optical switches to enable (in the open form) or quench (in the closed form) the emission of Ln-POM entities (unpublished results). The mechanism of photoluminescence modulation relies on Förster resonance energy transfer (FRET), which requires precise matching between the emission energy of Ln-POM and the absorption energy of DTE in its closed form.

Approach: The development and study of new Ln-POM/DTE assemblies, endowed with solid-state photoluminescence modulation properties, as well as the introduction of chirality into these assemblies, are divided into three interdependent axes:

Axis 1: Optimization of photoluminescence modulation: This involves the development of Ln-POM/DTE assemblies with luminescence properties extending from visible to near-infrared (NIR) wavelengths, where the emission wavelength of Ln-POMs $[\text{Ln}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ (LnMo_{16}) and $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ (LnW_{10}) can be adapted depending on the lanthanide ion used (Terbium, Tb^{3+} : 550 nm, Europium, Eu^{3+} : 650 nm, Ytterbium, Yb^{3+} : 980 nm). Building upon recent preliminary results, new materials will be synthesized and characterized. In particular, X-ray diffraction analyses will be performed to determine their crystal structures, while photophysical and spectroscopic methods will evaluate their photochromism and luminescence properties.

Axis 2: Development of chiral Ln-POM and DTE entities: Chiral versions of Ln-POMs and DTEs will be prepared. LnMo_{16} entities exhibit intrinsic chirality (Fig. 2). However, the Δ and Λ enantiomers crystallize in a racemic ratio with the achiral tetra-*n*-butylammonium salt. To obtain enantiopure crystals, LnMo_{16} entities will be crystallized with a chiral cation, such as N,N,N'-butylethylpentylpropylammonium (BEPPA) (Fig. 2).

Chirality introduction within the DTEs will be achieved through atropisomerism. This approach, proven for the preparation of structurally simple DTEs devoid of functional groups, prevents racemization during the photoisomerization reaction. In this PhD, new chiral DTEs will be synthesized, possessing both the structural requirements for atropisomerism and a pyridinium group essential for assembly with Ln-POMs (Fig. 2). Enantiomeric DTEs will be separated on chiral HPLC columns, and chiroptical properties (CPL, CD) will be measured.

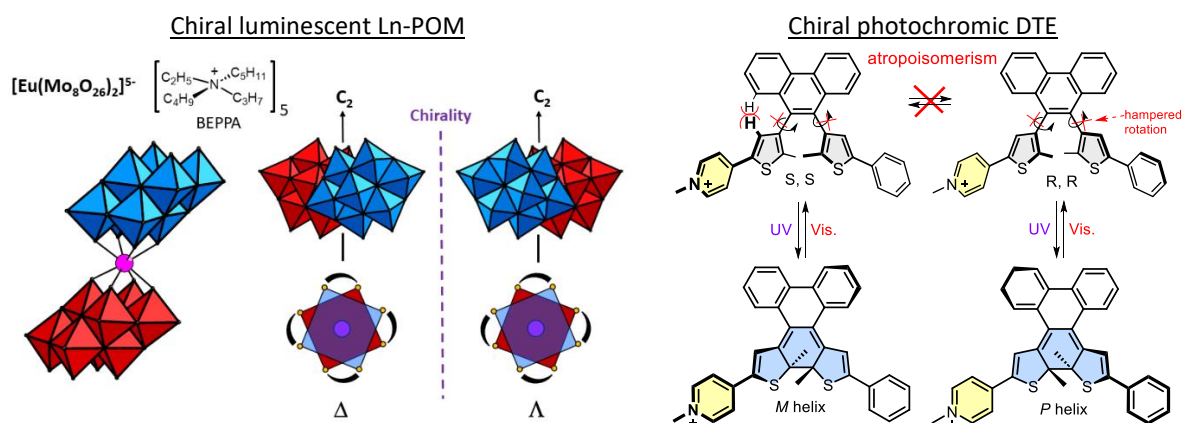


Fig. 2 Representation of the chiral $[\text{Eu}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ (EuMo_{16}) Ln-POM, and an atropisomeric DTE.

Axis 3: Development of chiral supramolecular assemblies: New chiral Ln-POM/DTE assemblies will be realized according to several possible combinations $\text{Ln-POM}_{\text{achiral}}/\text{DTE}_{\text{chiral}}$, $\text{Ln-POM}_{\text{chiral}}/\text{DTE}_{\text{achiral}}$ or $\text{Ln-POM}_{\text{chiral}}/\text{DTE}_{\text{chiral}}$, and their photophysical properties (photochromism, CPL luminescence) will be characterized. This unprecedented possibility of assemblies with controlled chirality will allow for finely determining the structure/property relationships governing chiroptical activity, thus filling the gaps in our understanding of photo-activatable chiroptical materials.



Environment: To ensure the appropriate environment and success of this project funded by the **EUR LUMOMAT** (<https://www.lumomat.fr/>), the candidate will conduct their research activities in the two partner laboratories: the **Institut des Matériaux de Nantes Jean Rouxel (IMN)** et the **Institut des Sciences Chimiques de Rennes (ISCR)**, which possess complementary expertise. This multidisciplinary research topic involves organic chemistry for the preparation of DTEs and inorganic chemistry for the synthesis of Ln-POMs and targeted supramolecular assemblies. It also includes an opening towards physical chemistry with the characterization of photophysical properties. Additionally, the candidate will have the opportunity to gain experience in a wide variety of characterization techniques: single-crystal and powder X-ray diffraction analyses, NMR spectroscopy, vibrational (IR, Raman) and optical (absorption, steady-state and time-resolved photoluminescence, and CPL) spectroscopies, thermal analyses, scanning electron microscopy (SEM) and transmission electron (TEM) microscopy. Furthermore, several opportunities to present results at national and international conferences will be possible during the PhD.

Candidate profile: The profile sought is that of a young scientist holding or in the process of obtaining a Master's degree (or equivalent), extremely motivated by exploratory synthesis, and possessing a strong interest in interdisciplinary subjects (molecular chemistry, photophysics, materials science). Expected and necessary skills include experience in organic synthesis (M1 and/or M2 internship), proficiency with common tools for molecular chemistry characterizations, and familiarity with photophysical characterization (absorption, emission).

Start of PhD: October 2024

The application package (Curriculum Vitae, transcripts of Master 1 and 2 degrees (or equivalents), and a letter of motivation) should be sent to both PhD supervisors, **deadline: June 30, 2024.**

PhD supervision:

Dr. Julien BOIXEL, ISCR, Rennes, Phone : +33 (0)2 23 23 31 67 (julien.boixel@univ-rennes.fr).

Dr. Rémi DESSAPT, IMN, Nantes, Phone : +33 (0)2 40 37 39 53 (remi.dessapt@cnsr-immn.fr).

References:

- (1) Luo, W.; Wang, G. *Adv. Opt. Mater.* **2020**, *8* (24), 2001362. doi/10.1002/adom.202001362.
- (2) Gonzalez, A.; Kengmana, E. S.; Fonseca, M. V.; Han, G. G. D. *Mater. Today Adv.* **2020**, *6*, 100058. doi/10.1016/j.mtadv.2020.100058.
- (3) Zhao, J.-L.; Li, M.-H.; Cheng, Y.-M.; Zhao, X.-W.; Xu, Y.; Cao, Z.-Y.; You, M.-H.; Lin, M.-J. *Coord. Chem. Rev.* **2023**, *475*, 214918. doi/10.1016/j.ccr.2022.214918.
- (4) Yanling Zhuang; Xiuli Ren; Xueting Che; Shujuan Liu; Wei Huang; Qiang Zhao. *Adv. Photonics* **2020**, *3* (1), 014001. doi/10.1117/1.AP.3.1.014001.
- (5) Sun, J.; Li, H.; Gu, X.; Tang, B. Z. *Adv. Healthcare Mater.* **2021**, *10* (24), 2101177. doi/10.1002/adhm.202101177.
- (6) Li, Z.; Wang, G.; Ye, Y.; Li, B.; Li, H.; Chen, B. *Angew. Chem. Int. Ed.* **2019**, *58* (50), 18025–18031. doi/10.1002/anie.201910467.
- (7) Mokhtar, A.; Morinaga, R.; Akaishi, Y.; Shimoyoshi, M.; Kim, S.; Kurihara, S.; Kida, T.; Fukaminato, T. *ACS Materials Lett.* **2020**, *2* (7), 727–735. doi/10.1021/acsmaterialslett.0c00131.
- (8) Rice, A. M.; Martin, C. R.; Galitskiy, V. A.; Berseneva, A. A.; Leith, G. A.; Shustova, N. B. *Chem. Rev.* **2020**, *120* (16), 8790–8813. doi/10.1021/acs.chemrev.9b00350.
- (9) Zhang, L.; Wang, H.-X.; Li, S.; Liu, M. *Chem. Soc. Rev.* **2020**, *49* (24), 9095–9120. doi/10.1039/D0CS00191K.
- (10) Abendroth, J. M.; Stemer, D. M.; Bloom, B. P.; Roy, P.; Naaman, R.; Waldeck, D. H.; Weiss, P. S.; Mondal, P. C. *ACS Nano* **2019**, *13* (5), 4928–4946. doi/10.1021/acsnano.9b01876.
- (11) Li, G.; Fei, X.; Liu, H.; Gao, J.; Nie, J.; Wang, Y.; Tian, Z.; He, C.; Wang, J.-L.; Ji, C.; Oron, D.; Yang, G. *ACS Nano* **2020**, *14* (4), 4196–4205. doi/10.1021/acsnano.9b09101.
- (12) Bolle, P.; Menet, C.; Puget, M.; Serier-Brault, H.; Katao, S.; Guerchais, V.; Boucher, F.; Kawai, T.; Boixel, J.; Dessapt, R. *J. Mater. Chem. C* **2021**, *9* (38), 13072–13076. doi/10.1039/D1TC02947A.
- (13) Stetsiuk, O.; Bolle, P.; Cordier, M.; Boixel, J.; Dessapt, R. *J. Mater. Chem. C* **2022**, *10* (3), 899–907. doi/10.1039/D1TC04561J.
- (14) Albrecht, N.; Amiaud, T.; Humbert, B.; Faulques, E.; Dessapt, R.; Serier-Brault, H.; Bolle, P. *Inorg. Chem.* **2019**, *58* (24), 16322–16325. doi/10.1021/acs.inorgchem.9b02941.
- (15) Walko, M.; Feringa, B. L. *Chem. Comm.* **2007**, 1745–1747. doi/10.1039/B702264F.