

Luminescent mechanoresponsive nanocomposite

Doctoral contract of three years financed by the French National Agency of Research (ANR) Keywords: chemistry, molecular chemistry, material chemistry, polymer, luminescence Starting in Sept-Oct 2024 Main location: Institut des Sciences Chimiques de Rennes (ISCR), University of Rennes, France Doctoral school S3M : https://ed-s3m.doctorat-bretagne.fr/en/doctoral-school-0

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The direct translation of a mechanical force into an easily readable luminescence signal opens up new perspectives in the field of materials and mechanical stress detection. To date, these functional materials are mainly based on the integration of emissive organic mechanophores. However, these compounds are limited by their photobleaching problems, lack of sensitivity and synthesis costs.

The aim of this PhD is to explore a new detection concept by developing low cost, mechanoresponsive luminescent (MRL) copolymers incorporating two complementary emitters: 3-oxindole derivatives and octahedral molybdenum clusters (Mo_6), and study their emission behavior under mechanical stress. Mo_6 are red phosphorescent with high quantum yields, have excellent photostability and are very sensitive to O_2 . Derivatives of 3-oxindoles are blue-green luminescent and can be easily functionalized to copolymerize and interact with Mo_6 (Figure 1).

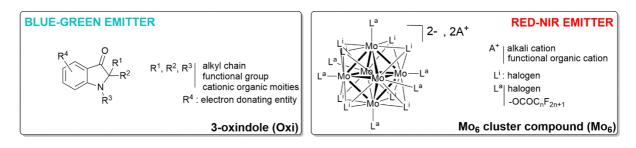


Figure 1. Representation of Oxi and Mo6 emitters.

This project brings together 2 fundamental concepts in a single material: i) the quenching of phosphorescence by O_2 , which destroys the O_2 molecules by producing singlet oxygen, ii) the variation of O_2 permeability under mechanical stress of semi-crystalline polymers. As described in Figure 2, such changes should modify the emission color of the nanocomposite containing the two emitters, thus allowing the direct visualization of a mechanical stress.

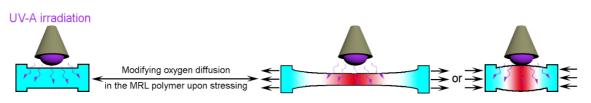


Figure 2. Mechanical stress detection principle under UV-A irradiation.

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This pluridisciplinary project is organized in several phases combining molecular and macromolecular synthesis, pure and in-operando photophysical studies (coupled with mechanical sensing). The person recruited will benefit from a threefold training in synthesis and characterization of hybrid polymers in the OMC (M. Achard) and CSM (M. Amela-Cortes, Y. Molard) teams at ISCR, in photophysical measurements (Caphter UAR ScanMAT platform) and in the characterization of mechanical behavior with and without UV-2A irradiation (IPR, QI2M team).

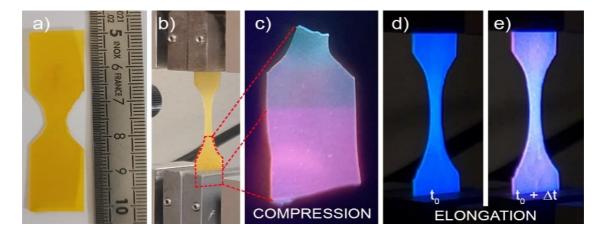


Figure 3. Proof of concept copolymer sample under normal light (a, b) and under UV-A irradiation (c, d, e); c) bottom part showing the compressed and elongated parts after break; sample during stretching: d)at the beginning (t0), and e) at the end (t0 + Δ t) of the irradiation.

This PhD project is part of the ANR "Everyone" research project (2024-2028). The successful candidate will have a profile as a molecular chemist with recognized skills in organic synthesis and ideally skills in optical spectroscopy (absorption, emission). Due to the interdisciplinary nature of the project, the ideal candidate will show a high degree of initiative and willingness to advance the topic in its entirety: from organic synthesis to mechanical testing. He/she must be able to work in a team in an international environment (fluency in English is mandatory).

Related publications:

S. Khlifi, J. Bigeon, M. Amela-Cortes, N. Dumait, H. Akdas-Kiliç, G. Taupier, S. Freslon, S. Cordier, S. Derien, M. Achard, G. h. Loas, Y. Molard, J. Mater. Chem. C 2021, 9, 7094-70102, 10.1039/D1TC01229K

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Robin, M.; Dumait, N.; Amela-Cortes, M.; Roiland, C.; Harnois, M.; Jacques, E.; Folliot, H.; Molard, Y., Direct Integration of Red-NIR Emissive Ceramic-like AnM6Xi8Xa6 Metal Cluster Salts in Organic Copolymers Using Supramolecular Interactions. *Chem. Eur. J.* **2018**, 24 (19), 4825-4829.

Amela-Cortes, M.; Paofai, S.; Cordier, S.; Folliot, H.; Molard, Y., Tuned Red NIR phosphorescence of polyurethane hybrid composites embedding metallic nanoclusters for oxygen sensing. *Chem. Commun.* **2015**, 51, 8177-8180.

