université PARIS-SACLAY

M2
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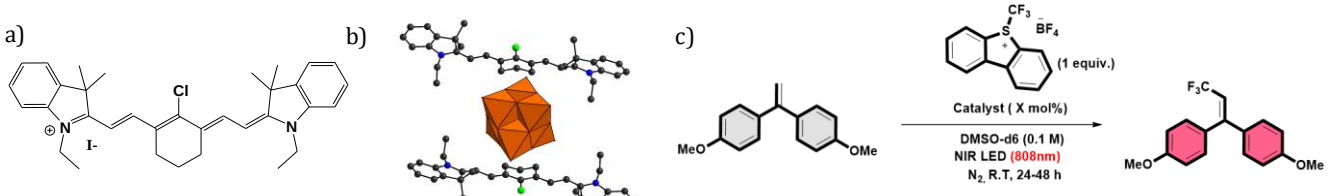
Covalent POM-Cyanine hybrids as photocatalyst operating in the NIR range

In the global context of the energy crisis caused by excessive consumption of polluting fossil fuels, **the use of solar energy appears to be an ideal solution** as this energy source is non-toxic and available in limitless quantities. In organic and polymer chemistry, the use of light for triggering reactions has thus been widely developed and numerous photoactive systems operating under UV or visible irradiation have been developed. However, these photocatalytic species have some limitations: using high energy UV-light is risky for the operator, the low light penetration depth prevents their use on a large scale and these systems **do not use all of the solar energy** (5% and 46% of the solar spectrum in the UV and visible regions, respectively, with 45% corresponding to the near infrared (NIR) and 4% to the infrared (IR)). To overcome these limitations, **researchers have thus developed photocatalysts that also absorb in the NIR range** (780-2500 nm).[1]

Our group has worked in the field of photocatalysis for several years[2] and has recently developed novel ionic assemblies combining **cationic cyanines with anionic polyoxometalates** (POMs), POMs being molecular oxides containing metals in high oxidation states (primarily W, Mo, and V). Some of these compounds have demonstrated effectiveness under **NIR irradiation** (808 nm) either as **photoinitiators** for radical polymerization (**W_6-Cya_2**) or as **photocatalysts** (**Mo_6-Cya_2**) for alkene trifluoromethylation reactions (unpublished results, see figure below). These promising preliminary results are partly attributable to the significantly enhanced stability of the photosensitizer (cyanine) in the presence of the POM.



Cyanine — **Mo_6-Cya_2**

With Cyanine (5 mol%), conversion **35%**
With **Mo_6-Cya_2** (2,5 mol%), conversion **80%**

Consequently, as part of a Master's (M2) internship, we now aim to expand this family of compounds **by synthesizing unprecedented covalent POM cyanine organic-inorganic hybrids**. The organic (functionalized cyanines) and inorganic (functionalized POMs) as well as the organic-inorganic targeted hybrids will be synthesized and characterized using complementary techniques (NMR, IR, UV, mass spectrometry, TGA, X-Ray diffraction…), and their photocatalytic efficiency under 808 nm irradiation will be evaluated via ^{1}H NMR measurements. In addition, their activity as photoinitiators for radical polymerization will be studied in collaboration with the team of Pr. Davy-Louis Versace (UPEC).

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Keywords: **Polyoxometalates • Cyanines • Photocatalytic applications under NIR light**

(1) S. K. Pagire *et al.*, *Angew. Chem. Int. Ed.* **2026**, *65*, e26147; (2) a) Y. Benseghir *et al.*, *J. Am. Chem. Soc.* **2020**, *142* (20), 9428, b) K. Talbi *et al.*, *Appl. Catal. B: Environ.* **2025**, *378*, 125644.