Tailored Ru-Complex Grafted Nanofilms for Light-Voltage Driven Systems

Sara Helis[†] **and Tony Breton**

MOLTECH-Anjou –UMR 6200 CNRS, Université d'Angers, 2 Boulevard Lavoisier,
49045 Angers Cedex, France
† corresponding author's email: sara.helis@univ-angers.fr

Photocatalysis and photoelectrocatalysis offer promising routes for solar energy conversion and sustainable chemical transformations. However, in most cases, the catalyst is in homogeneous phase (solution), limiting its recyclability, stability, and integration into devices. Developing robust, surface-bound alternatives is essential for enabling more durable and scalable light-driven systems. In this context, constructing well-defined photoelectrocatalytic interfaces remains a major challenge, particularly when precise control over film structure and composition is required to maximize the catalyst efficiency (increasing TurnOver and minimizing overvoltage).

Polypyridine Ruthenium complexes exhibit remarkable photophysical and redox properties, making them prime candidates for light-voltage-driven applications[1].

In this work, we demonstrate an innovative approach to design photoelectrocatalytic interfaces through the electrografting of bis-terpyridine ruthenium complex $[Ru(tpy)(tpy\text{-}ph\text{-}N_2^+)]^{3+}$ onto carbon surfaces. Through mono- or co-grafting of diazonium salts we achieve fine-tuning of the film's thickness, composition, and chemical architecture at the molecular level. This approach offers a powerful means to tailor the electronic, steric, and conformational properties of the resulting films.

To achieve a more comprehensive picture of the film organization and to understand the precise structure-property relationships, we employe a multi-technique investigation. The dynamic of the layer grafting is investigated by Electrochemical quartz crystal microbalance (EQCM) whereas Atomic Force Microscopy (AFM) revealed its morphology (roughness and thickness). UV-vis spectroelctrochemistry[2] is used to monitor the optical changes of the Ru complex film associated to its redox activity, enabling a better understanding of the interfacial reactivity. While this work is still under investigation, preliminary results indicate that the optical properties of the films are strongly influenced by the density and distribution of the grafted moieties. Modulating such properties will lead to a control over the photoelectrocatalytic performance of the surface.[4] This study contributes to advancing molecular-level engineering of light-sensitive interfaces, paving the way for future applications in sustainable catalysis.

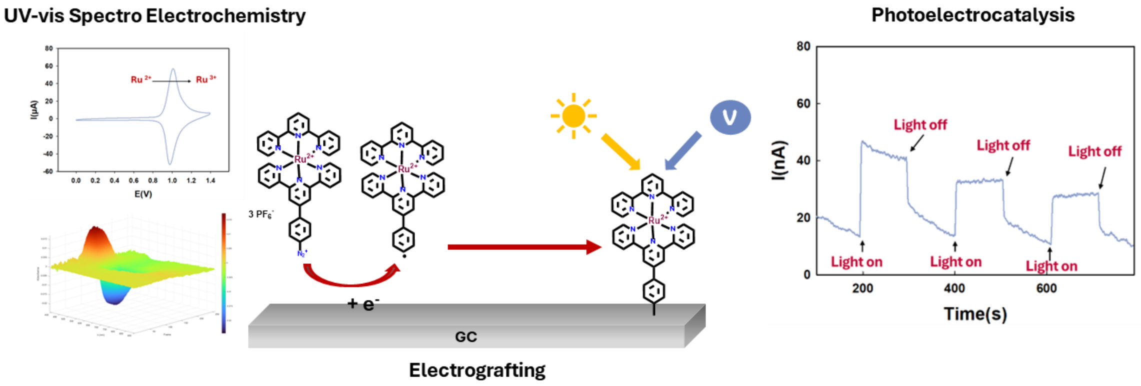

Figure 1: Overview of the multi-technique approach used to investigate the photoelectrocatalytic behavior of the organic nanofilms

References

[1] J. J. Concepcion, M.-K. Tsai, J. T. Muckerman, et T. J. Meyer, *J. Am. Chem.* 132, 1545-1557, **2010**.

[2] L. Pichereau, C. Gautier, et T. Breton, *J. Mater. Chem. C*, 10, 7111-7118, **2022**.

[3] J. D. Knoll, B. A. Albani, et C. Turro, *Acc. Chem. Res.*, 48, 2280-2287, **2015**

[4] N. Kaveevivitchai, L. Kohler, R. Zong, M. El Ojaimi, N. Mehta, et R. P. Thummel, *Inorg. Chem.*, 52, 10615-10622, **2013**.