LABORATOIRE DE CHIMIE ENS DE LYON

ÉCOLE NORMALE SUPÉRIEURE DE LYON

PhD Thesis Proposal

Octa-β-phosphonate-substituted porphyrins for efficient and scalable visible light photocatalysis

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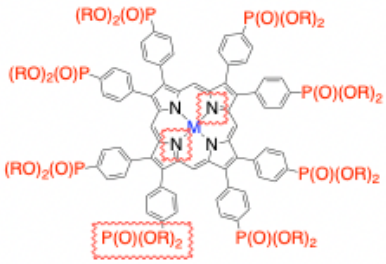
Porphyrins have been studied across various disciplines, including materials science, physics, biology, and medicine. Their growing popularity primarily results from the wide range of functions performed by naturally occurring tetrapyrrolic macrocycles. These compounds play crucial roles in photosynthesis, oxygen and electron transport, and various catalytic transformations. This functional versatility of porphyrinoids is possible due to subtle structural changes in the peripheral substituents and the complex biological environments in which they operate. The interaction between structure and function continues to captivate the scientific community. By modifying the structure of artificial porphyrins, we can gain insights into natural processes and harness porphyrins' properties to generate valuable research outcomes for society.

One notable application of these compounds is photocatalysis, which has experienced significant growth in the past two decades, thanks to the development of photoredox-catalyzed reactions.[1] Porphyrin photocatalysts already hold marked importance in oxidation reactions and photoredox-catalyzed C–C bond-forming reactions. The pivotal advantages of using porphyrins as red-light-excited photoredox catalysts were also recently demonstrated. However, their broader utilization in photocatalysis remains underdeveloped, primarily due to the challenges of their laborious synthesis and poor solubility in non-chlorinated solvents. This project aims to develop the next generation of porphyrin photocatalysts for reactions driven by visible light, with the goal of increasing the efficiency of photoreactions by reducing photocatalyst loading to ppm levels and preparing reusable photocatalysts.

Our strategy involves the investigation of metal complexes of readily available octa-β-phosphonate-substituted porphyrin 2HOPPP, which was recently synthesized in our group (Figure). These compounds are expected to exhibit exceptional solubility in non-chlorinated solvents and a minimal tendency to aggregate, even in aqueous environments. They are also suitable for the development of reusable photocatalysts.



MOPPP

M = 2H, Pd(II), Pt(II), In(III), Sni(IV)

R = H, Et

Fig. The structure of complexes proposed for investigation in this project.

Initially, Pt(II), Pd(II), In(III), and Sn(IV) complexes with 2HOPPP ligand will be prepared and characterized. Subsequently, we will conduct photocatalytic tests to explore their potential as photosensitizers, particularly for the oxidation of sulfides and alkenes using molecular oxygen. Additionally, we will evaluate their suitability as photoredox catalysts in reactions involving reductive quenching, such as the thiol-yne reaction and the decarboxylative alkylation of N-hydroxyphthalimine. Our emphasis will be on reducing catalyst loading and utilizing red light for irradiation. During this phase, we will establish correlations between photophysical properties of the complexes and their photocatalytic activity. Performing this study, we will identify the most promising complexes to develop reusable catalytic systems. Finally, the immobilization of these complexes in liquid or solid phases will be investigated to enhance reactivity and enable recycling.[3]

This multidisciplinary project offers the opportunity to acquire diverse skills in organic and inorganic synthesis, the development of molecular materials, spectroscopic characterization of molecules and materials, single X-ray analysis, and gain a profound understanding of photoredox catalysis, which plays a pivotal role in chemistry in this century.

References

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