Title	**Development of hydrogen-bonded organic frameworks for ammonia photocatalytic production**

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Project description:

Photocatalytic systems have attracted research interest as a clean approach to generate energy from abundant sunlight. In this context, developing efficient and robust photocatalytic structures is crucial. Recently, self-assembled organic chromophores have entered the stage as alternatives to both molecular systems and (in)organic semiconductors. Nanostructures made of self-assembled π-conjugated dyes offer molecular customizability to tune their optoelectronic properties and activities, while also providing benefits from heterogeneous catalysis (including ease of separation, recyclability and improved photophysical properties).

This project aims to develop hydrogen-bonded organic frameworks (HOFs), which unique properties can be exploited in photocatalytic production of valuable commodity chemicals, such as ammonia. Organic chromophores, which carry complementary hydrogen-bonding recognition motifs, will be used to prepare supramolecular frameworks. The prepared HOFs will take advantage of (*i*) π-π stacking between the chromophores which can greatly enhance photogenerated exciton migration; (*ii*) one-dimensional channel micropores beneficial for accelerated mass transfer and increased reaction sites; and (*iii*) the carboxylic acid groups involved in H-bonding can also participate as proton donors as active hydrogens. The porous channels will be then decorated with inorganic complexes that act as (electro)catalysts for production of chemicals with high energy content. In this way, it is envisioned that the photogenerated excitons will migrate to the inner surface of the pores to dissociate and efficiently drive redox reactions.

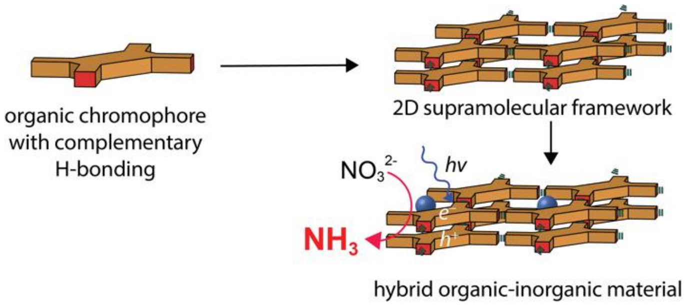

Fig. 1. Graphical summary of the proposed research project.

The prepared materials will be applied in heterogeneous catalysis, more specifically in ammonia production. Ammonia is currently produced mostly through Haber-Bosch process, which accounts for 1.5% of total worldwide energy production and greatly contributes to global greenhouse emissions. Developing alternative NH_3 production methods, which include “green” electrons from sunlight, is imperative for developing novel, sustainable, and environmentally-friendly systems. In addition to N_2 as nitrogen source for ammonia production, also nitrate (NO_3^-) will be tested. Due to the inert nature of N_2 and its low solubility in water, poor efficiencies and low NH_3 yields are to be expected. Nitrate, on the other hand, does not require the dissociation of high-energy bonds, and can achieve faster NH_3 production rates. Nitrate is also an abudant nitrogen source and is particularly present in polluted groundwater and industrial wastewater.

Related publications: (1) *J. Am. Chem. Soc.* **2022**, 144, 7, 3127–3136; (2) *J. Am. Chem. Soc.* **2021**, 143, 43, 18131–18138; (3) *J. Am. Chem. Soc.* **2021**, 143, 21, 8000–8010; (4) Nat. Chem. **2022**, 14, 1007–1012.