Porous Macroligands for Heterogenized Photocatalytic Solar Fuel Production

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Significance and Relevance

These findings highlight the promise of developing fully heterogeneous photosystems that use solar light as the sole energy source to convert CO_2, a major greenhouse gas, into valuable solar fuel. Recent efforts have focused on applying insights from molecular science to design heterogenized photosystems that leverage the structured framework of porous materials, including plasticity in a device-oriented perspective. With collaborative advances from both molecular and materials science, breakthrough photosystems using porous macroligands for heterogenized molecular catalysis for efficient carbon-based solar fuel production are likely to emerge in the near future.

Preferred and 2nd choice for the topic:

1. Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
2. CO2 utilization and recycling

Preferred presentation: Oral preferred

Introduction and Motivations

Photocatalytic CO_2 reduction reactions have gained enormous interest, as they offer sustainable routes to provide renewable fuels and small building blocks for chemicals. However, efficient, selective and long-term active photocatalysts and well-understood molecular structures of the active sites are still scarce. A fruitful strategy in the design of molecularly-defined heterogeneous catalysts is to immobilize isolated active sites within a hosting framework.

The integration of the catalytically active centers into a solid support without loss of performance compared to the homogeneous analog is still a major challenge.

To change the paradigm of molecular catalytic processes for fine chemical synthesis and green fuel production, we introduced recently the concept of solid porous macroligand for heterogenized molecular catalysis.[1] Having molecularly-defined active sites, porous macroligands have been found to drive the activity and the selectivity of heterogenized catalytic processes on a similar way as molecular ligands but with the advantage of the structuration in a three-dimensional framework and the confinement within a porous nanospace.[2]

Results and Discussion

Heterogeneous catalysis brings various advantages compared to homogeneous catalysis such as recyclability and easy separation of the product from the catalyst. Heterogenization of molecular catalyst can be performed using solids acting as macroligands for site-isolated molecular complex. We already demonstrated that fully heterogenous systems based on porous organic polymer macroligand POP displayed high productivity and stability over the time for the CO2 to formic acid photoreduction (Figure 1).

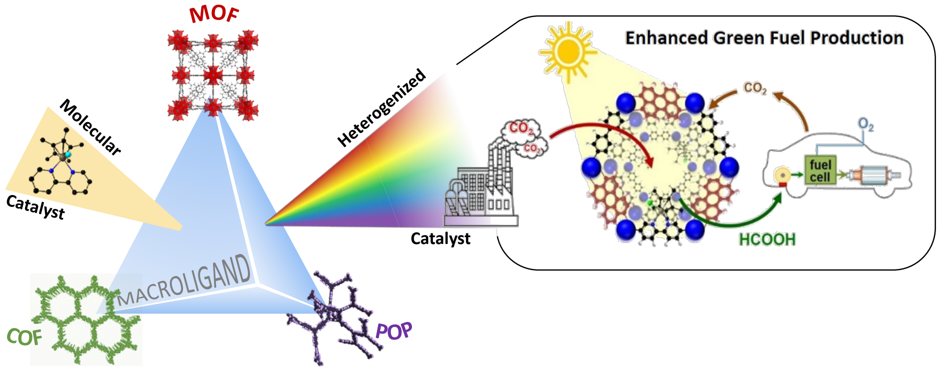

Figure 1 Porous hybrid solids as macroligands for the photocatalytic CO_2 conversion.

Aiming at increasing the sustainability of the photocatalysts synthesis, we moved from the previously reported palladium catalyzed macroligand synthesis to radical polymerization. Starting from vinylated monomers, this new synthetic strategy would bring flexibility into the POP macroligand along with new optical and electronic properties. The goal would be to build full heterogeneous systems, based on the same composition as the previous POP generation,[3,4] with PS and coordination site, acting as macroligands for the catalyst.

Preliminary tests were conducted on the Rh catalyst heterogenized within N-POP material and used with an external photosensitizer.[5]

In this work, an organic photosensitizer is successfully integrated within a porous organic polymer (POP) structure, preserving its photophysical and photocatalytic properties. This innovation aims to create all-in-one heterogeneous photocatalysts with both organic dyes and a molecular Rh catalyst as single sites in a non-conjugated porous matrix. The POP, constructed around perylene or polythiophene units, efficiently supports light harvesting and electron-hole generation. The inclusion of bipyridine co-monomers enables the coordination of organometallic active site as isolated single-site molecular catalysts for CO_2 reduction, producing formic acid as the sole carbon-based product. This highlights the synthetic versatility of POPs as porous macroligands, opening pathways for more sustainable molecular catalytic processes and solar fuel production. The results presented remain so far unpublished.

References

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