Catalyst Design in Hybrid Photocatalytic Systems for the Reduction of CO_2

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Introduction

Hybrid photocatalytic systems have been used and studied extensively for CO_2 reduction and other environmentally relevant processes. However, the effect of the linking unit which connects the molecular catalyst to the semiconducting surface hasn't been explored to a significant degree. Using systems which have been shown previously to facilitate photocatalytic reduction of CO_2 (Co/Cu cyclams and TiO_2/C_3N_4 nanoparticles), it is possible to study what effect linkers with variable length, flexibility, and bend angle have on the electron transfer from the surface to the catalyst. By measuring catalytic activity and rates of electrons transfer through electron paramagnetic resonance (EPR), it will be possible to identify which properties of linkers help promote efficient electron transfer.

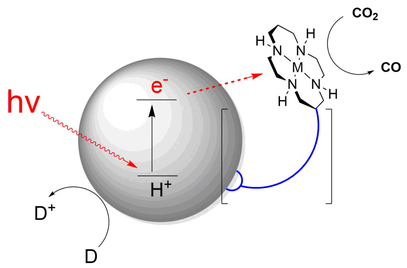


Figure 1: (Left) Example hybrid photocatalytic system with the linkage between molecular catalyst and nanoparticle highlighted in brackets

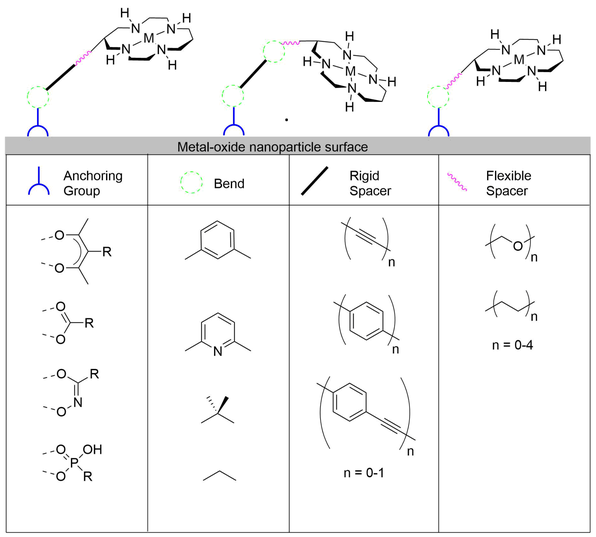
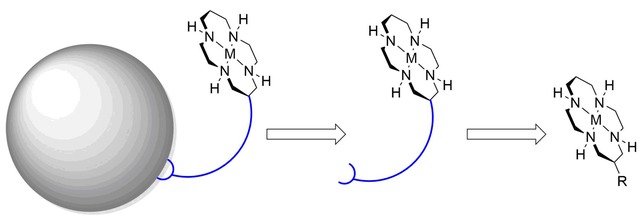


Figure 2: (Above) Planned linker components. **Figure 3:** (Below) Ideal retrosynthetic pathway towards the efficient generation of a series of hybrid photocatalytic systems.



Experimental

In order to efficiently study the linkages in these hybrid photocatalytic systems it is first necessary to produce molecular catalysts (cyclams) with functional groups capable of coupling to the linkers. These functionalization's must be attached through the *C*-position of the cyclam in order to prevent the linkers from altering the electronics of the catalyst. However the synthesis of *C*-functionalized cyclams has proven to be a time-consuming, inefficient and unsuccessful process (**Figure 4**), making the discovery of an effective synthetic route towards *C*-functionalized cyclams the first goal of this project.

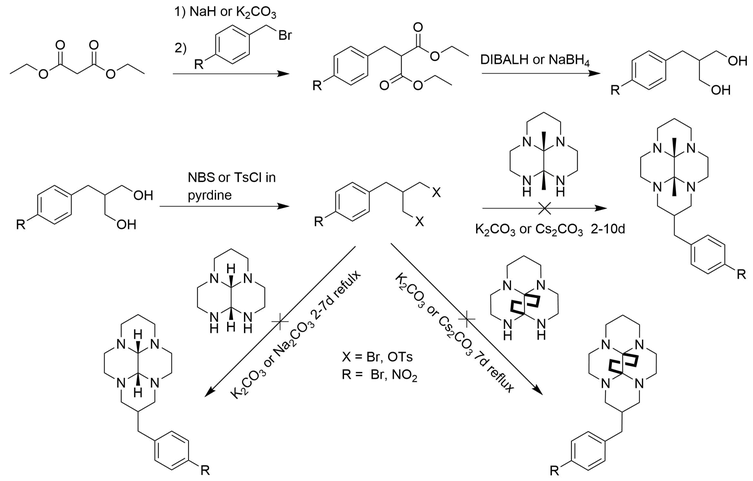
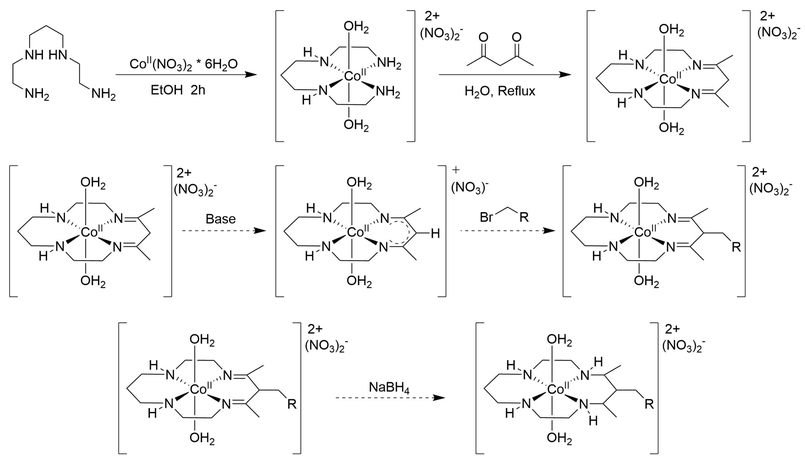


Figure 4: (Above) Original synthetic pathway towards *C*-functionalized cyclams which was abandoned after multiple failed attempts.

Figure 5: (Below) Synthetic route to generation of *C*-functionalized cyclams via nucleophilic attack by stable dienato complex. R = Linker unit to be attached.



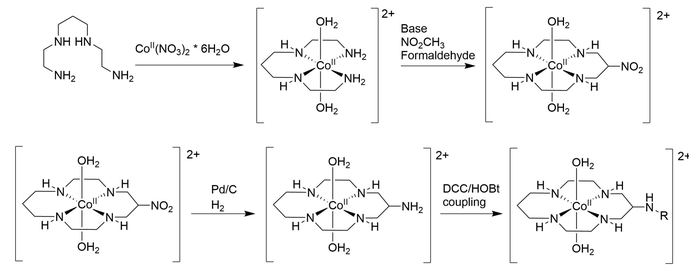


Figure 6: Metal templating route towards the generation of amine-functionalized cyclams. R = Linker unit to be attached.

Results & Future Work

The current synthetic routes utilizing a series of metal templating reactions however, have produced multiple metal complexes in a relatively short period of time. Once these pathways are fully optimized, they will be capable of producing *C*-functionalized cyclams on multi-gram scales in a matter of days using inexpensive reagents. These synthetic routes will be the only of their kind in the current literature.

After the completion of the first series of C-functionalized cyclam molecular catalysts, the synthetic focus will shift towards the synthesis of various linkers. These linkages will contain variations in length, bend angles, and flexibility (**Figure 2**) while also having the functional groups necessary for coupling to the molecular catalyst and an anchoring group. Following this, the catalysts-linker will be attached to a semiconducting nanoparticle surface and its catalytic activity will be evaluated using a solar light simulator and measuring the amount of CO produced. Using this information, alongside data collected from other electrochemical experiments such as bulk electrolysis, cyclic voltammetry and EPR spectroscopy, the beneficial aspects of the connection between a catalyst and a semiconductor surface will be evaluated. Leading to a better understanding of hybrid photocatalytic systems for the reduction of CO_2.

References & Funding

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