Synthetically Modified Titanium Dioxide Nanoparticles for Photocatalysis

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Introduction

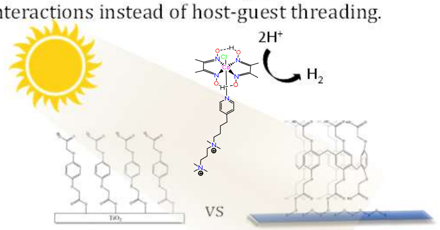
Solar photocatalysis is a growing field focused on the generation of energy in the form of fuels that can be utilized to reduce carbon emissions generated by the burning of fossil fuels. One example of a clean fuel is hydrogen, which can be burned to generate energy without generating carbon dioxide. Catalytic systems that generate hydrogen using water and solar power would be highly beneficial. One such example of these processes involves interacting a transition metal complex with a light-absorbing material.

Within the Caputo group, we focus on functionalizing TiO_2 (semi-conducting nanoparticle), a light-absorbing material with a host molecule Pillar[5]arene (P[5]) to enable host-guest self-assembly with a guest functionalized hydrogen-generation catalyst. P[5] is a macrocyclic compound consisting of 5 hydroquinone units linked by methylene bridges. The carboxylate functionalized variant of this compound (WP[5]) has been anchored on TiO_2 and successfully used as a host molecule. The catalyst is a cobaloxime coordination compound that is a well-known proton reduction catalyst. Previously, this compound has been functionalized with an ammonium-tail that can act as a guest compound. If the host and guest compounds associate, we can use cobalt to harvest electrons generated on the TiO_2 surface via solar irradiation.

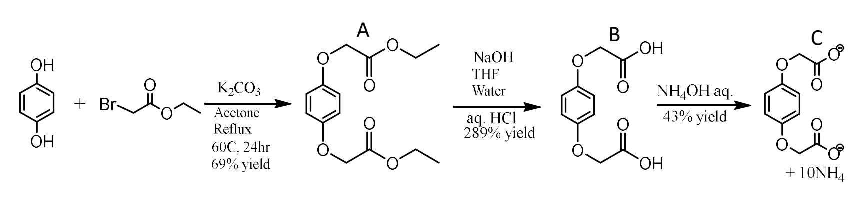
Research Question: Is the guest associating by electrostatics or by host-guest threading?

Project Goals

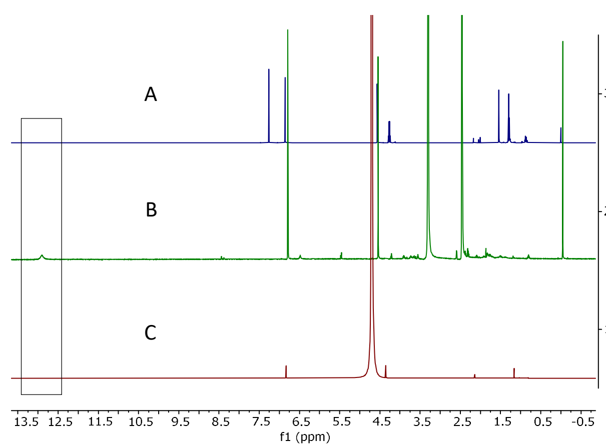
Formally, the goal of this project is to synthesize the monomeric precursor to Pillar[5]arene compound 2,2'-[1,4-Phenylenebis(oxy)]diacetate (referred to as $\mathbf{M}^{CO_2\,NH_4}$). This compound will then be loaded onto TiO_2 nanoparticles via carboxylate anchoring. This allows us to test whether the catalyst's cationic guest moiety can interact with the monomer functionalized TiO_2 by electrostatic interactions instead of host-guest threading.



Synthetic Scheme



^{1}H NMR Spectroscopic Characterization

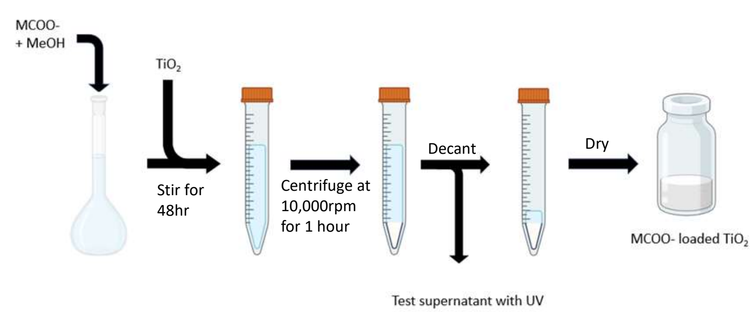


Analysis

1) In spectrum A, the ethyl ester peaks are present at 4.26ppm and 1.29ppm
2) In spectrum B, the ethyl ester peaks are gone, and the carboxylic acid peak is gained at 12.9 ppm
3) In spectrum C, the carboxylic acid peak is lost, signifying the formation of the carboxylate

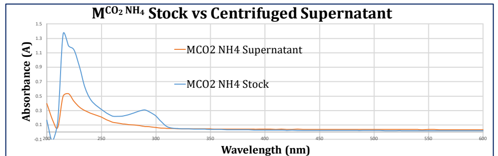
^{1}H NMR Spectrum for Structures A, B and C in $CDCl_3$ d_6DMSO and D_2O

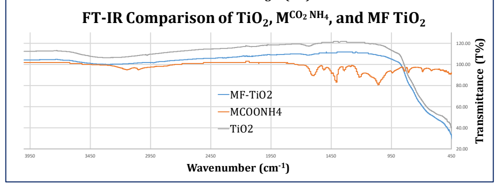
TiO_2 Loading Scheme



Scheme depicting the process of combining $M^{CO_2\,NH_4}$ and TiO_2 via centrifuge and collecting a dry product

UV-Vis and FT-IR Characterization





Conclusions and Future Work

- Successfully synthesized 2,2'-[1,4-Phenylenebis(oxy)]diacetate as confirmed by NMR spectroscopy
- Form calibration curve of MF-TiO_2 to quantify loading amounts and optimize accordingly
- Photocatalytic analysis of functionalized compound
- Repeat synthetic process at higher yields and larger scales
- Perform additional characterization (XPS) to confirm surface functionalization

Acknowledgements

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References

1. Tomoki Ogoshi*, Masayoshi Hashizume, Tada-aki Yamagishi and Yoshiaki Nakamoto*. Synthesis, Conformational and Host-Guest Properties of Water-Soluble Pillar[5]arene" *Chem. Commun.* **2010**, *46*, 3708-3710.
2. Qiang Jia, Xu-Sheng Du, Chun-Yu Wang, Kamel Meguellati "A one-pot synthesis of a self-included bisester-functionalized copillar[5]arene" *Chin. Chem. Lett.* **2019**, *30*, 721-724.