Light Harvesting Artificial Reaction Centers: Exploring The Synthesis Of Reaction Center Mimics For Photocatalytic Proton Reduction
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Abstract

The storage of solar power into a chemical fuel is a promising alternative to fossil fuel and chemists are inspired by efficient natural photosynthesis. Artificial photosynthetic mimics have been produced, but lack in efficiency due to charge recombination and instability of reactive intermediates. Biology transcended these problems by i.) making use of multichromophoric arrays (antenna systems), ii.) the generation of fast, long-lived-charge-separated states through multi-step electron transfer and iii.) a confined space funneling redox equivalents into a reaction center that stabilizes reactive intermediates. This research is aimed at new designs for artificial light-harvesting reaction centers by synthesizing newly designed supramolecular cages. The research question is: what is the best synthetic route towards a multi-component artificial reaction center for the purpose of photocatalytic proton reduction? This work explores the synthesis via the following sub-questions. Zn(II)carboxylate connections bind in various ways, thus; can a supramolecular cage be synthesized via Zn(II)-carboxylate connections? Since these cages are small; how can the internal cage cavity volume be tuned via expansion of the ligand? Finally, given that steric crowding is a reasonable possibility; how can a small supramolecular cage be functionalized endohedrally? Supramolecular cages containing Zn(II)carboxylate connections were formed and characterized by DOSY. Ligands could be expanded via Pd- catalyzed cross-coupling. Endohedral functionalization via a microwave assisted condensation and a subsequent Pd-catalyzed Sonogashira coupling was successful. In doing so, the most promising synthetic route towards artificial reaction centers was determined. The Zn4L4-cage ligands were expanded in two dimensions, with a sterically demanding electronically active moiety attached endohedrally. Light-harvesting artificial reaction centers and their individual molecular components should be characterized by spectroscopic techniques like cyclic voltammetry (CV), (transient) UV-Vis and (transient) FT-IR in the future. In turn, resulting in a deeper understanding of photosynthesis and providing an alternative strategy towards solar-to- fuel devices.