

Photochemical CO₂ Reduction Using Rhenium(I) Tricarbonyl Complexes with Bipyridyl-Type Ligands with and without Second Coordination Sphere Effects



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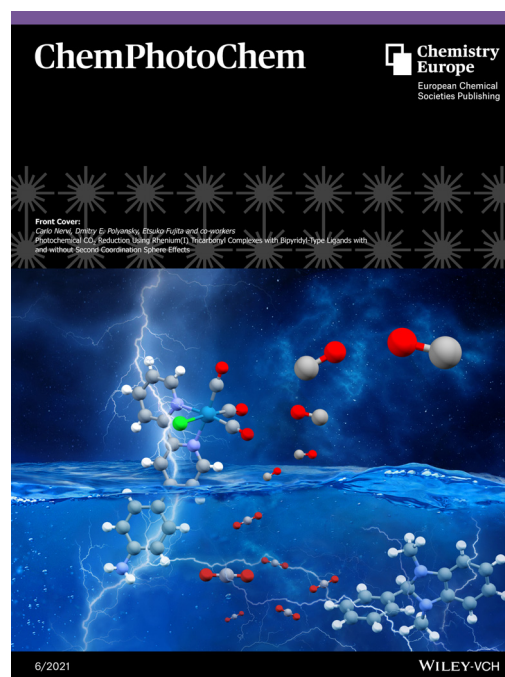


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The front cover artwork is provided by Elena Amadio, University of Torino (Italy). The image shows the photocatalytic reduction of CO₂ to CO by an aniline-substituted Re-bpy catalyst in the presence of a strong electron donor (BIH). Read the full text of the Article at [10.1002/cptc.2020000307](https://doi.org/10.1002/cptc.2020000307).

What prompted you to investigate this topic/problem?

Because the increase in the anthropogenic CO₂ concentration is believed to cause global warming and is closely related to the use of fossil fuels, recycling CO₂ with environmentally sustainable approaches is among the most important priorities to avoid catastrophic climate changes. Mimicking natural photosynthesis and producing solar fuels or precursors to fuels from CO₂ and water using solar irradiation will help in mitigating negative effects of CO₂ emission and disclose a renewable chemical feedstock of carbon-based chemicals. In particular, this paper elucidates the structure–activity relationship for photocatalytic CO₂ reduction with a series of Re-bpy complexes using an integrated computational and experimental approach, making comparisons with previous investigations of electrochemical CO₂ reduction. While rhenium complexes do not absorb a large part of the solar spectrum, they offer the advantage of being self-sensitized, i.e., in addition to being catalysts, they can simultaneously act as photosensitizers owing to their relatively long-lived excited states, which trigger their reaction with a sacrificial reductant to initiate catalysis. Specifically, an aniline-substituted Re-bpy photocatalyst ab-



sorbs visible light intensely compared to related catalysts, and the presence of the aniline moiety has a beneficial effect on the photocatalytic activity for CO₂ reduction to CO in *N,N*-dimethylacetamide. In the case of a Ph-OH group in the second coordination sphere, these complexes are active for photochemical CO₂ reduction, despite the formation of a stable, six-coordinate Re-OPh intermediate via reductive deprotonation, as previously observed.

How did the collaboration on this project start?

The collaboration started naturally because of common research interests, and similar views on the necessity of detailed mechanistic and kinetic investigations for the rational design of effective catalysts. The group at the University of Torino has much experience and knowledge about electrochemical CO₂ reduction with Re catalysts. The Brookhaven National Laboratory (BNL) group has a long history of mechanistic and kinetic investigations in photochemical CO₂ reduction using a variety of spectroscopic tools (photochemical and radiation-induced reactions using time-resolved UV-vis-IR detection, and use of a synchrotron light source). Laura Rotundo (University of Torino) successfully carried out a part of her PhD studies at BNL, resulting in a synergistic collaboration between the two research teams. The success of the collaboration will be enhanced soon when Laura joins BNL as a postdoctoral research associate.

What are the main challenges in the broad area of your research?

We believe that photocatalytic processes, i.e., so-called artificial photosynthesis, are among the best approaches for harvesting sunlight as an energy source for cleaner and more efficient processes of CO₂ utilization/recycling. Nature has optimized these processes to satisfy environmental needs. Human demands dramatically grew in a very short time (relative to the evolution of Nature). Therefore, it is mandatory to find a more efficient solution compatible with our ecosystem, without compromising the rapidly evolving lifestyle of new generations. The main challenges are the search for earth-abundant, effective, and durable catalysts to harvest and store intermittent solar energy as chemical energy using water and CO₂. To avoid the use of sacrificial reagents, the water oxidation reaction must be coupled with CO₂ reduction. Furthermore, CO₂ reduction beyond CO towards liquid fuels is another formidable challenge.

Acknowledgements

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