



Fabricating Earth-Abundant Molecular Systems Enabling Efficient Photocatalytic CO₂ Reduction in Water

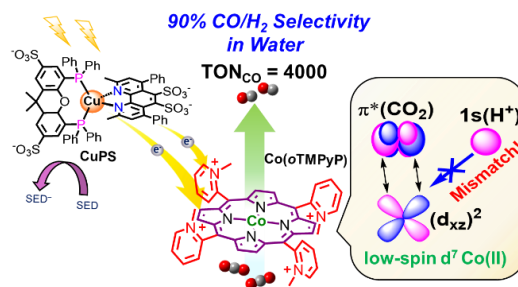
Kyushu University Xian Zhang

In this newsletter, I would like to briefly share our recent progress on developing photocatalytic systems for CO₂ reduction in aqueous media. To mitigate global warming and undesirable climate changes, substantial efforts have been devoted to dramatically suppress the CO₂ emission. One of the most promising strategies is the light-driven conversion of CO₂ into value-added chemicals and fuels. While many homogeneous molecular systems have been developed for photocatalytic CO₂ reduction,¹ the pursuit of environmentally friendly as well as earth-abundant systems operating in fully aqueous media remains a critical challenge.

We first invented a water-soluble heteroleptic copper(I) complex (**CuPS**) tethered to four hydrophilic sulfonate groups and reported on its photophysical and electrochemical properties.² Due to the steric hindrance surrounding the Cu center, **CuPS** preserves the long-lived emission property even in fully aqueous media. Employing this **CuPS** as a photosensitizer in combination with a multi-electron chargeable cobalt porphyrin catalyst, we demonstrated that **Co(σ TMPyP)** achieves 90% selectivity for CO₂-to-CO conversion with a TON_{CO} of 4000 under visible light irradiation.³ Computational analysis revealed that this high selectivity arises from the efficient suppression of the competing H₂ evolution pathway. This inhibition was attributed to the fact that the active intermediate of **Co(σ TMPyP)**, which triggers CO₂ binding, possesses an unusual configuration in its low-spin d⁷ Co(II) center, leading to disfavor the proton reduction due to the mismatch in making MO association with the H⁺ 1s orbital. Remarkably, this system represents the first example of a molecular catalyst that avoids the conventional activation pathway involving a filled d_{z2} orbital for CO₂ binding. Instead, the reaction proceeds via the combined use of π - and σ -type associations, in which two degenerate $\pi^*(\text{CO}_2)$ orbitals form association with a filled d_{xz} and a half-filled d_{z2} orbital, respectively. The strategy sheds a new light

on the rational control of reaction rates and pathways through frontier MO engineering.

To address the gradual photodegradation of **CuPS**, we further introduced a hydrophobic wrapping strategy using polycationic alkylammonium ions.⁴ This supramolecular protection effectively enhanced photoinduced electron transfer, providing a novel platform for improving the durability and performance of water-soluble photosensitizers in aqueous media. These results offer valuable insights into the design of photostable, earth-abundant systems for CO₂ reduction reaction and broader solar fuel applications.



We believe the development of water-soluble hybrid molecular systems based on earth-abundant elements still remains a central theme. Our results contribute are in line with this vision by offering fundamental design principles for fabricating useful catalysts and photosensitizers.

“Go ahead and never give up!”, often said by my PhD supervisor, Prof. Ken Sakai. It reflects the spirit that influenced my research journey. It was under his mentorship that I first encountered the world of photocatalysis, a field that is now central to my research. Though I didn’t always have a well-defined destination, only a sense of excitement guided me from one experiment to the next. In retrospect, each experiment conducted, each challenge tackled, and each insight gained have gradually shaped a clear path toward my passion for artificial photosynthesis.

References

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2. *ACS Catal.* **2019**, *9*, 11263–11273.
3. *ACS Catal.* **2021**, *11*, 10436–10449.
4. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217807.