

## Towards an efficient and sustainable photocatalytic reduction of CO<sub>2</sub> by molecular systems

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Photocatalytic CO<sub>2</sub> reduction into chemical feedstocks is considered a promising strategy to achieve an energy sustainable society. From a practical viewpoint, CO<sub>2</sub> reduction must be coupled with water oxidation in order to use the electrons and protons obtained in this process.<sup>1</sup> However, the presence of water promotes the hydrogen evolution reaction, which is thermodynamically and kinetically more favored than the CO<sub>2</sub> reduction reaction. Therefore it is mandatory to develop catalytic systems capable to selectively and efficiently reduce CO<sub>2</sub> in fully aqueous media under visible light irradiation. Despite the progress done so far, photocatalytic systems showing high activity while retaining high selectivity versus hydrogen production are rare and predominantly noble metal-based.

In this seminar we will show that cobalt porphyrins are excellent catalysts for the reduction of CO<sub>2</sub> to CO *in fully aqueous media* not only due to the unprecedented activities attained for CO production (TON<sub>CO</sub> = 4000, TOF<sub>CO</sub> = 2400 h<sup>-1</sup>) but also due to their ability to retain a high selectivity for CO production (up to 90%).<sup>2-4</sup> Mechanistic studies based on kinetic, spectroscopic, electrochemical analyses and DFT calculations show that the first electron-transfer step of the photocatalytic mechanism involve a reductive quenching of the excited state of the chromophore (PS) by the sacrificial electron donor followed by an electron transfer from PS<sup>-</sup> to the Co<sup>II</sup>TPPS catalyst forming [Co<sup>I</sup>TPPS]<sup>-</sup>. The latter species can be further reduced to give a porphyrin-reduced intermediate [Co<sup>I</sup>(TPPS<sup>-</sup>)]<sup>2-</sup> which can react with CO<sub>2</sub> forming the CO<sub>2</sub>-binding [Co<sup>III</sup>(TPPS<sup>-</sup>)(CO<sub>2</sub><sup>2-</sup>)]<sup>2-</sup> species. The subsequent C-O cleavage coupled with protonation and water elimination affords the generation of CO and the recovery of the initial Co<sup>II</sup>TPPS species. In this work we have demonstrated that cobalt porphyrins are promising catalytic systems towards the efficient and selective CO<sub>2</sub>-to-CO photoconversion in *fully aqueous media*.

### References

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