

# Efficient and highly selective photocatalytic reduction of CO<sub>2</sub> to CO in water by cobalt porphyrins

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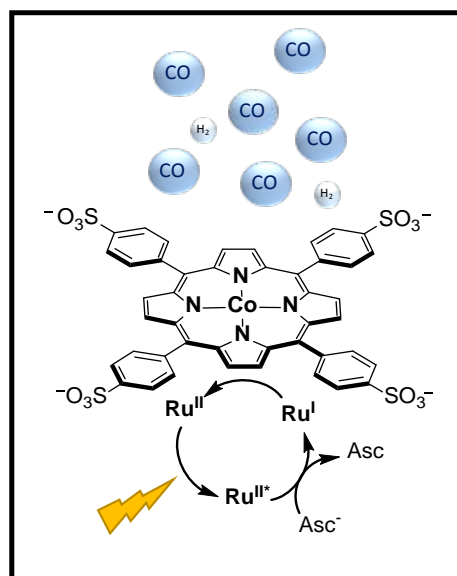
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The world energetic problem together with the global warming caused by CO<sub>2</sub> emissions are two well-known issues that are greatly threatening the sustainable development of mankind. Inspired by natural photosynthesis, a perfect approach to face these issues is the direct utilization of solar energy and water for the reduction of carbon dioxide into useful chemical fuels or chemical feedstock. However, the reduction of CO<sub>2</sub> is more complicated than the reduction of water to H<sub>2</sub>, since multiple products such as CO, methane, methanol or oxalate can be obtained. Furthermore, the reduction of CO<sub>2</sub> in aqueous media usually produce H<sub>2</sub> as main product. Therefore, the development of catalytic systems that can selectively and effectively reduce CO<sub>2</sub> into a single chemical fuel remains a great challenge, especially when using water as solvent.

In this regard, in the last years, considerable efforts have been performed towards the development of molecular systems for the selective reduction of CO<sub>2</sub> through the use of transition metals including Fe, Co, Ni and Mn. Despite the great progress achieved, most of the reported systems display selectivity in non-aqueous media, typically using DMF or CH<sub>3</sub>CN, in order to prevent the water reduction to H<sub>2</sub> pathway.

In this work, we present a family of water-soluble cobalt porphyrins for the selective photochemical reduction of CO<sub>2</sub> into CO in 100% aqueous solution. The catalytic system comprises the use of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as photoredox catalyst and ascorbate as sacrificial electron donor. Photochemical and electrochemical studies suggest a reductive quenching pathway by ascorbate forming the reduced Ru<sup>I</sup> species that can finally promote the generation of active Co intermediates species for the reduction of CO<sub>2</sub>. The exquisite selectivity towards CO production versus H<sub>2</sub> formation paves the way for the generation of efficient artificial photocatalytic devices (artificial leaf).



**Fig 1.** Reduction of CO<sub>2</sub> by water-soluble cobalt porphyrins.