CO_2 conversion to valuable chemicals: electro- and photo-reduction using bipyridyl carbonyl complexes as molecular catalysts.

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Transformation and utilization of carbon dioxide are today greatly considered as they could both reduce CO_2 environmental impact (greenhouse gas effect) and create valuable chemicals like raw materials or energy rich compounds, which are not derived from fossil sources. For instance, formic acid, which is one of most simplest products from the two-electron two-proton CO_2 reduction, is a convenient liquid compound for both, H_2-storage and direct formic acid fuel cells to produce electrical energy. Nevertheless, CO_2 reduction still remains challenging since CO_2 is very stable. The CO_2 reduction reaction requires both a source of energy and a catalyst. If a renewable carbon-free primary energy source is used to power this reaction in water, and if the catalysts are based on metals abundant in the earth's crust the CO_2 reduction can be regarded as a sustainable viable solution which uses a waste product (CO_2) as a renewable raw material.

Among various methodologies, ElectroCatalytic Reduction (ECR) shows promise in converting CO_2. It is well-known that this electrochemically-driven reaction can be accomplished on bulk metallic cathodes but also, on molecular catalysts including systems based on Re, Ru and Os bipyridyl carbonyl complexes. It should be noted that, to date, only a few molecular electro-catalysts based on abundant metals have so far been reported.

Meanwhile, as solar light is an attractive renewable source of energy, which can be used directly, research towards PhotoCatalytic Reduction (PCR) of CO_2 with metallic bipyridyl carbonyl catalysts has been growing. Nevertheless efficient PC systems are scarce.

Herein we present the context and the state of the art of CO_2 electro- and photo-catalytic reduction across a few published examples and, in more detail, through our own results concerning: (i) $[Mn(L)(CO)_3Br]$ (L = bipyridyl derivatives) complexes for their efficient, selective and stable electrocatalytic properties;[1] (ii) $[Os(L)(CO)_2Cl_2]$ type complexes for their ability to act as photocatalysts for the two-electron reduction of CO_2.[2]

1. M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, *Angew. Chem. Int. Ed.* **2011***, 50,* 9903; (b) M. Bourrez, M. Orio, F. Molton, H. Vezin, C. Duboc, A. Deronzier, S. Chardon-Noblat, *Angew. Chem. Int. Ed.* **2014***, 53*, 240 and references cited therein.
2. J. Chauvin, F. Lafolet, S. Chardon-Noblat, A. Deronzier, M. Jakonen, M. Haukka, *Chem. Eur. J.* **2011***, 17*, 4313 and references cited therein.