

# FROM CO<sub>2</sub> TO FUELS: BIOINSPIRED METAL CATALYSTS

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While developed in a number of directions, bioinspired molecular catalysis has been explored only very recently for CO<sub>2</sub> reduction, a challenging reaction, of prime importance in the context of the energetic transition to be built up. This approach is particularly relevant as Nature teaches us that CO<sub>2</sub> reduction is possible, at low overpotentials, high rates and large selectivity, and gives us unique clues to design and discover new interesting molecular catalysts. Indeed, based on our relatively advanced understanding of the structures and mechanisms of the active sites of fascinating metalloenzymes such as formate dehydrogenases and CO dehydrogenases, it is possible to design original, active, selective and stable, molecular catalysts. This novel class of catalysts consists of mononuclear Mo, W and Ni and as well as dinuclear Mo-Cu and Ni-Fe complexes, in which the metal ions are coordinated by sulfur ligands, more specifically dithiolene chelates mimicking the natural molybdopterin (MPT) cofactor. (Figure 1) This research is multidisciplinary as it implies detailed biochemical, functional and structural characterization of the inspiring enzymes together with synthetic organic and organometallic chemistry. The most important achievements in this direction, starting from the first report of a catalytically active biomimetic bis-dithiolene-Mo complex in 2015, are discussed in this lecture [1-5].

In addition, bioinspired catalysis can expand to active and selective solid catalytic materials, in which single metal sites can be assembled on a heterogenous surface in a configuration mimicking biological mononuclear metal sites, as reported recently [6-10].

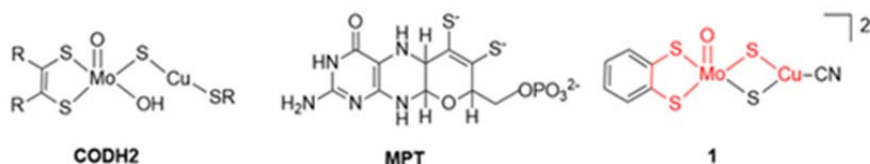


Fig. 1: Active site of Carbon Monoxide Dehydrogenase (CODH<sub>2</sub>), molybdopterin (MPT) and an active bioinspired catalyst, [(bdt)Mo(O)S<sub>2</sub>CuCN]<sup>2-</sup> (complex 1).

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