When Molecules Meet Materials: Heterogenised Molecular Systems for CO_2 Reduction and H_2 Evolution Reaction

Souvik Roy

School of Chemistry, University of Lincoln, UK

Conversion of CO_2 and water into fuels and value-added chemicals using renewable electrical or solar energy offers a promising route to mitigate anthropogenic carbon footprint and reduce our reliance on fossil fuels and petroleum industry. However, the challenge lies to develop suitable catalysts that can lower the kinetic barriers for water splitting and CO_2 activation, and drive the fuel synthesis selectively toward the desired product(s). Natural enzymatic systems offer inspirations for designing synthetic catalysts due to the excellent catalytic performance of the enzymes (Figure 1). In particular, molecular synthetic catalysts fascinate synthetic chemists the most due to their tuneability, which allows us to tailor the structure to fine-tune their intrinsic properties. However, these molecular systems are somewhat disadvantaged by practical consideration because they often function in homogeneous solution and displays limited long-term stability. Having an effective scaffold to mount the catalyst on, representing 'heterogenisation' of the molecule, is a key part of building a practical system that brings together the benefits of homogeneous and heterogeneous catalysis. In this talk, I will first explore molecular design of CO_2-reduction catalysts,[1] and subsequently discuss two approaches towards fabricating hybrid electro- and photo-catalytic solid materials (1) utilisation of molecular catalysts as building blocks for synthesis of modular porous materials,[2] and (2) direct immobilisation of molecular complexes onto semiconducting materials for solar-driven transformations.[3,4] Final part of the talk will focus on demonstrating how the fuel-forming cathodic half-reaction (CO_2 reduction) can be applied in a coupled electrolyser to produce value-added chemicals at the anode via organic electrooxidation.[5]

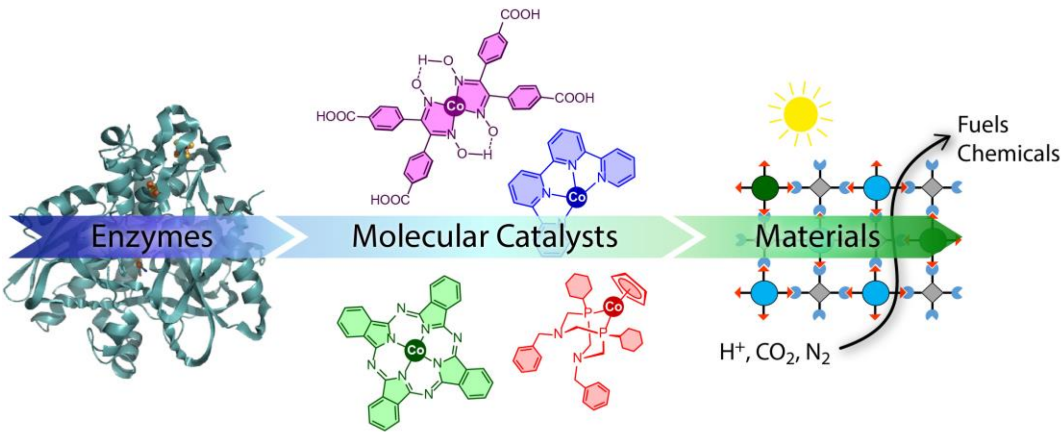

Figure 1. Strategy towards molecular design of bio-inspired catalysts and materials

References: 1) Roy *et al*, *J. Am. Chem. Soc.* **2017**, *139*, 3685. 2) Roy & Huang *et al*, *J. Am. Chem. Soc.* **2019**, *141*, 15942. 3) Roy *et al*, E. Reisner; *Angew. Chem. Int. Ed.* **2019**, *58*, 12180. 4) Roy *et al*, *ACS Catal.* **2021**, *11*, 1868. 5) Bajada & Roy *et al*, *Angew. Chem. Int. Ed.* **2020**, *59*, 15633.