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Electrocatalytic CO2 reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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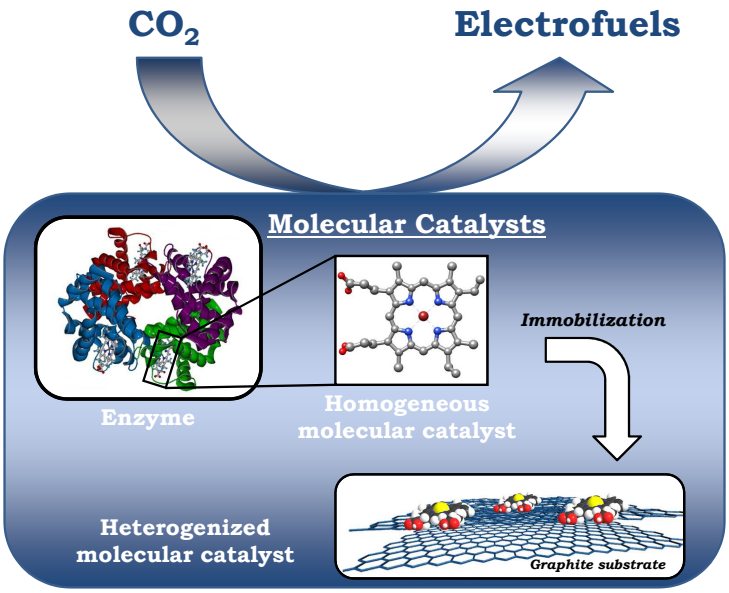
CHAPTER 4

Molecular catalysis of CO_2 reduction



4.1 Introduction

Molecular catalysis of electrochemical reactions is carried out by electrochemically generated species, which are able to oxidize or reduce the reactant molecule, using multiple (proton-coupled) electron transfer steps. The catalytic cycle is closed by regeneration of the initial molecular catalyst. Activation of small molecules such as H_2, O_2 and CO_2 by molecular catalysts has been widely studied, especially in an attempt to address the challenges described in chapter 1.[1,2]

In the case of carbon dioxide, seminal work performed by Vol'pin et al. showed that the CO_2 molecule can be activated by coordination to a transition metal center.[3,4] Fundamental knowledge on the coordination chemistry of CO_2, and on the relevance for catalysis has been acquired throughout the years.[5–7] Molecular catalysis of CO_2 reduction is mostly carried out by (transition-)metal complexes. The molecular approaches are interesting, since they generally allow for high selectivity, high activity and fine-tuning of the catalyst e.g. to mimic efficient enzymes. Consequently, they are able to provide important mechanistic insight.[8,9] Moreover, from a practical perspective, it is straightforward and relatively simple to employ the molecular catalyst by dissolving it in the supporting electrolyte solution. Unfortunately, molecular catalysts are usually less durable than heterogeneous electrocatalysts, and the formation of species beyond 2-electron transfer products (carbon monoxide, formate, oxalate) is scarce.[10,11] Additionally, one may run into solubility issues, especially when working in aqueous media.

4.2 Overview of molecular catalysts for CO_2 electroreduction

Depending on the type of ligands, the homogeneous molecular catalysts for CO_2 reduction can be roughly categorized in:[12]

1. Macrocyclic metal complexes e.g. porphyrins, phthalocyanines, corroles and cyclams.

2. Polypyridyl metal complexes containing e.g. 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) or 2,2'; 6',2"-terpyridine (tpy) ligands.

3. Phosphine metal complexes containing e.g. 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine (PPh3) ligands.

Examples of the backbone of macrocyclic complexes often used as molecular CO_2 reduction catalysts are shown in Figure 4.1a-d. Examples of ligands related to polypyridyl- and phosphine complexes are shown in respectively Figure 4.1e-f and Figure 4.1h,i. For a more complete list of different ligands and metal complexes, the reader is referred to excellent reviews in the field.[1,10,12,13]

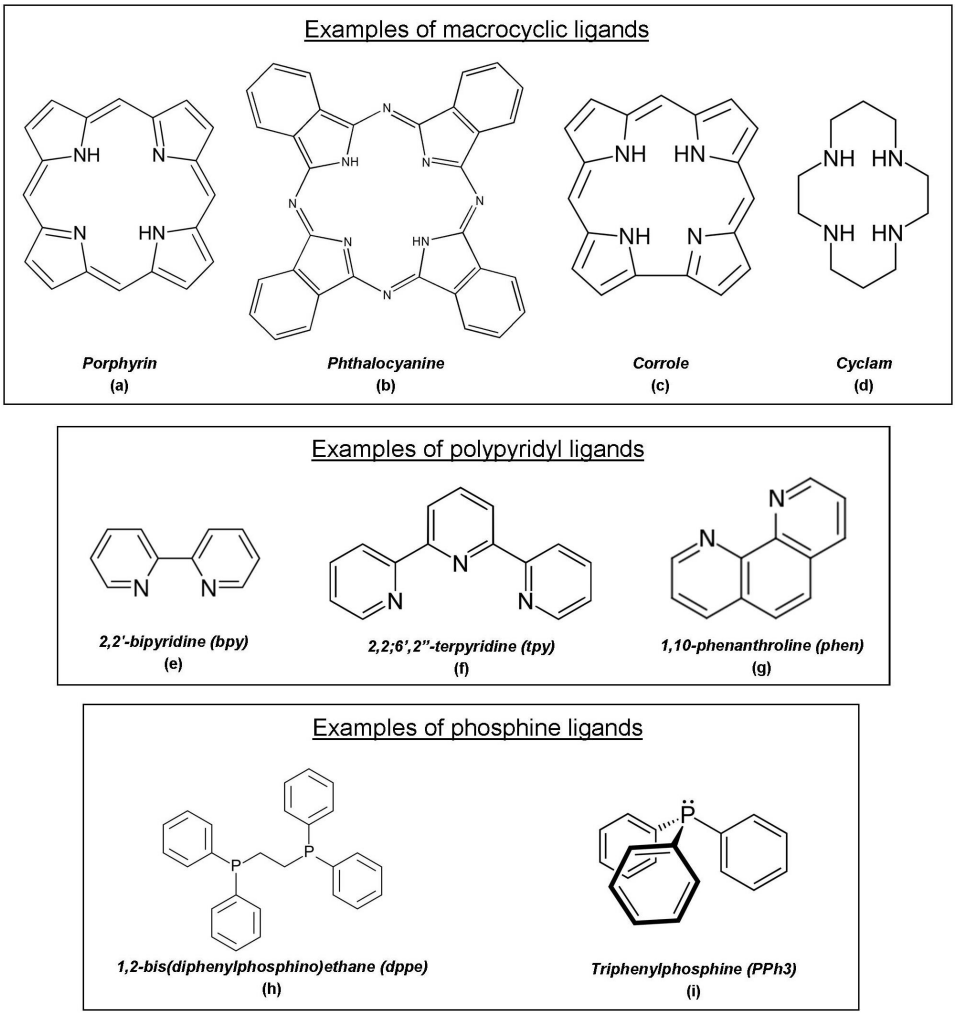


Figure 4.1 Examples of unsubstituted ligands often observed in metal complexes for CO_2 electroreduction: (a-d) macrocyclic ligands, (e-g) polypyridyl ligands and (h,i) phosphine ligands.

In the remainder of this thesis, we will focus on metalloporphyrins. This planar macrocyle has a versatile chemistry and broad range of applications, due to its stability, and variety of possible properties, which can be obtained by modification of peripheral substituents and metal centers. Examples of important metalloporphyrins in nature are heme in the red blood cells (iron porphyrin), and chlorophyll in plants (porphyrin with Mg center). Due to the planarity of the macrocycle, interaction

with the metal center is possible from both sides of the plane. Extensive work on porphyrin (electro)chemistry in general has been summarized in the literature.[14–16]

With respect to the electrocatalytic CO_2 reduction by metalloporphyrins, Fe and Co metal centers have received considerable attention. Savéant and coworkers investigated iron porphyrins to gain insight in the mechanism of CO_2 reduction toward CO.[17] They found that addition of Lewis- and Brønsted acids significantly improves the selectivity toward CO, and the stability of the catalyst.[18–21] Furthermore, modification of the metal center was shown to change the dominant product from CO to HCOOH.[22] Additionally, they report on substituent effects of the catalyst.[23–25] The investigation of CO_2 reduction on these porphyrins started mainly under homogeneous conditions in non-aqueous electrolytes, but more recently shifted toward aqueous electrolytes.[26,27]

4.3 Heterogenization of molecular catalysts

Heterogenization of molecular catalysts can be considered as the bridge between homogeneous- and heterogeneous catalysis, where the catalyst is immobilized on a preferably inert surface. Heterogenization of molecular catalysts is attractive, since much less catalyst is required compared to homogeneous conditions, and the catalyst can be used even when it is not soluble in the supporting electrolyte. Moreover, there are more attractive prospects for industrial scale-up purposes such as generally better robustness and durability of the heterogenized catalyst, and the ability to circumvent product-catalyst separation.[13]

After adsorption, the porphyrin is usually oriented with the macrocycle parallel to the surface.[16] There are several ways of immobilizing the (molecular) catalyst on a surface, *viz.* covalent- or non-covalent adsorption, electropolymerization on the surface, and dispersion in polymer films.[28–30] Studies have been performed on several molecular catalysts, immobilized on different substrates, and by various methods.[13]

Although interesting systems, showing high selectivity and activity for CO_2 reduction, have been reported for heterogenized molecular catalysts, we still lack detailed fundamental insight in order to efficiently produce electrofuels, with high stability. Therefore, it is very important to perform systematic studies to obtain insight beyond the empirical level, especially because of the many variables which may influence the system, as will be discussed in more detail in the subsequent chapters.

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