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A New Family of Polypyridyl Co(II) Complexes Based on Hexa- and Heptadentate Ligands for Photoinduced H_2 Production

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Hydrogen plays a primary role in the arduous challenge of replacing fossil fuels with renewable and clean sources of energy. Ideally, sunlight can drive processes such as the splitting of water, allowing the exploitation of the energy coming from the Sun through the formation of O_2 and H_2. In particular, the formation of H_2 through proton reduction requires the presence of a light-harvesting photosensitizer, an electron donor and a catalyst. Numerous complexes based on earth-abundant metals such as Ni, Fe and Co have been used as catalysts for electro- and photochemical hydrogen production. In particular, cobalt complexes based on tetra- or pentadentate polypyridyl ligands have shown high activity for H_2 production in water. However, the improvement of their efficiency and stability remains a great challenge. The research presented in this thesis aims at the development of cobalt catalysts with a new architecture presenting two bipyridines and one pyridine group connected to an aminoalkyl moiety. Different substituents are also introduced on the pyridyl or on the bipyridyl units to enable the investigation of structure-activity relationships.

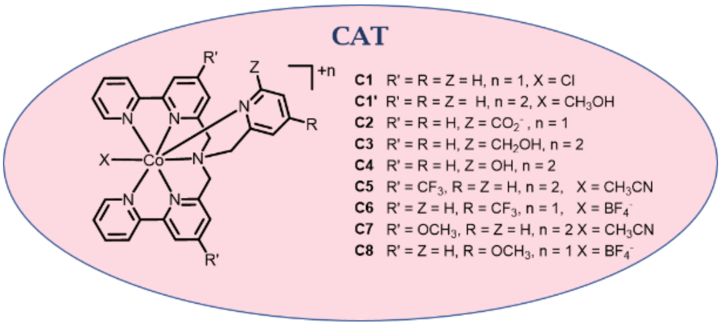

Figure 1. Chemical structures of the catalysts studied in this work.

More in detail, eight amino-polypyridyl cobalt complexes are synthesized and studied as catalysts for photoinduced hydrogen production in the presence of $Ru(bpy)_3^{2+}$ (where bpy : 2,2'-bipyridine) as photosensitizer and ascorbic acid as electron donor (Figure 1). The archetypical complex **C1** is the first example of a heptacoordinate cobalt catalyst based on a hexadentate ligand capable of producing H_2 in fully aqueous media. Under optimized conditions, a maximum turnover number (TON) of 16300 (mol H_2 (mol Cat.)$^{-1}$) is achieved by **C1** within 2 hours of irradiation. The catalytic mechanism of **C1** is further investigated combining evidences obtained by electrochemistry, transient absorption spectroscopy and quantum chemistry calculations. **C2**, **C3**, and **C4**, bearing substituents in peripheral position to promote intramolecular proton transfer, are studied as catalysts in water and organic solvents for photo- and electrochemical proton reduction, respectively. Under the same photochemical conditions, **C3** results slightly more efficient than **C1**. The introduction of electron withdrawing groups (i.e. $–CF_3$ in **C5** and **C6**) and of electron donating groups (i.e. $–OCH_3$ in **C7** and **C8**) strongly affects the catalytic properties of the complexes, with **C8** that outperforms the other catalysts in terms of TONs. The different activity of **C5**-**C8** is further discussed on the basis of transient absorption spectroscopy measurements and electrochemical studies. Overall, the results illustrate the potential of this new class of polypyridyl cobalt catalysts for light-driven proton reduction in fully aqueous conditions.

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