An Introduction to Electrocatalysis: Hydrogen Evolution from Mono and Binuclear Cobalt Complexes

Begin by reading the attached paper by Valdez *et al.* (*PNAS*, [DOI:10.1073/pnas.1118329109](http://dx.doi.org/10.1073/pnas.1118329109)), then consider the following questions related to the manuscript.

1. The authors discuss the importance of reducing protons to dihydrogen in a solar water splitting scheme. In order to understand the relationship between these reactions, write an overall balanced equation for the water-splitting reaction and find ΔG° (in kJ/mol) for splitting one equivalent of water. Then construct two balanced half reactions for the overall water splitting. Why is light required to drive this reaction?
2. This paper investigates cobalt-catalyzed reduction of protons to hydrogen. How does the presence of a catalyst change ΔG° for the water-splitting reaction?
3. Draw the structure of CoII(dmgBF2)(dpgBF2)(CH3CN)2 (the product obtained from reducing complex **3**). Why is this complex used as a model for **2** rather than the previously reported CoII(dmgBF2)2(CH3CN)2 or CoII(dpgBF2)2(CH3CN)2?
4. Provide a valence electron count for CoII(dmgBF2)(dpgBF2)(CH3CN)2? Does this count make sense for a stable complex? Why or why not?
5. The paper discusses two possible pathways for hydrogen generation: homolytic and heterolytic. Why are they named this way? Sketch out the mechanism for each pathway.
6. The paper describes the synthesis of tethered complexes containing two cobalt centers. Which pathway would be most strongly affected by using a bimetallic instead of a monometallic catalyst? Why?
7. Define cyclic voltammetry.
8. What is overpotential? Why is it important for an electrocatalyst to operate at a low overpotential?
9. Rationalize the shapes of the electrochemical traces in the paper (Figure 1). Why does the normal "duck" shape of the cyclic voltammetric wave for CoII/I disappear in the presence of added acid?
10. Examine Table 1 and explain any trends that you find for redox potentials and/or catalytic rates.
11. Think more broadly about the features that we might want in an electrocatalyst for proton reduction in a working photocatalytic device. List as many of these as you can (they can be related to cost/availability, operating conditions/solvent, electrochemical properties and operating potential, catalytic performance, etc.). Judging by these criteria, how well do the catalysts in this paper stack up? Where is there room for improvement?