Thin Films and Interfaces
Group Seminar

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Strategies for Artificial Photosynthesis: Molecular vs. Heterogeneous Water Oxidation Catalysts

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Technological implementations of artificial photosynthesis require the development of efficient water oxidation catalysts (WOCs).[1] Whereas molecular WOCs are excellent model systems to study water oxidation mechanisms, their heterogeneous counterparts do not require further immobilization strategies.[2,3] Our previous work brought forward bio-inspired molecular Co(II)-cubane WOCs along the lines of nature's photosystem II.[4,5]

Recently, we introduced $[Co^{II}_4(dpy\{OH\}O)_4(OAc)_2(H_2O)_2](ClO_4)_2$ (dpk = di(2-pyridyl)ketone; **Co_4O_4-dpk**)[6] as the first molecular catalyst that links both WOC classes through its $\{H_2O\text{-}Co_2(OR)_2\text{-}OH_2\}$ edge-site motif. This moiety has been identified as a *sine qua non* for cobalt oxide-based WOCs,[4] and Co_4O_4-dpk presents the unique opportunity to study it within a stable molecular environment. **Co_4O_4-dpk** displays high photocatalytic activity, and its stability under catalytic conditions was underscored with a wide range of analytical techniques (such as FT-IR and ^{1}H NMR spectroscopy, EXAFS/XANES, and DLS).[6] The presence of an intact cubane core in solution was supported by XAS measurements and DFT-MD simulations. Time-dependent EXAFS monitoring indicates that the Co(II) centers of **Co_4O_4-dpk** are readily oxidized to Co(III) and recover rather slowly. However, chemical oxidation experiments with $[Ru(bpy)_3]^{3+}$ point out that quantitative oxidation of all Co(II) centers may not be a prerequisite for water oxidation.

We furthermore synthesized the first Co/Ni mixed cubane WOC series, $[Co^{II}_xNi_{4-x}(dpy\{OH\}O)_4(OAc)_2(H_2O)_2](ClO_4)_2$ (**$Co_xNi_{4-x}O_4$-dpk**).[6] These heterometallic 3d-3d metal cubanes open up the opportunity to test solid the implementation of state WOC design principles in molecular catalysts and vice versa. Our molecular WOC development is complemented by systematic studies on Co-containing heterogeneous WOCs, such as CoNCN or the $La_{1-x}Sr_xBO_3$ perovskite series (B = Fe, Co, Ni, or Mn).[3] Their structure-activity relationships will be presented, followed by a disussion of comprehensive design perspectives through knowledge transfer between molecular and solid state WOC research.

[1]] J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev*. **2015**, *115*, 12974.
[2] J. Li, R. Güttinger, R. Moré, F. Song, W. Wan, G. R. Patzke, *Chem. Soc. Rev*. **2017**, doi: 10.1039/c7cs00306d.
[3] H. Liu, R. Moré, H. Grundmann, C. Cui, R. Erni, G. R. Patzke, *J. Am. Chem. Soc*. **2016**, *138*, 1527.
[4] F. Evangelisti, R. Güttinger, R. More, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2013**, *135*, 18734.
[5] F. Evangelisti, R. More, F. Hodel, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2015**, *137*, 11076.
[6] F. Song, R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Luber, G. R. Patzke, *J. Am Chem. Soc*. **2017**, DOI: 10.1021/jacs.7b07361.