Orthogonal band gap engineering of UiO-66 frameworks through active control of defects

Kurt Lejaeghere[1]*, Arthur De Vos[1], Kevin Hendrickx[1,2], Sven M.J. Rogge[1], Pascal Van Der Voort[2], Veronique Van Speybroeck[1]*

[1]*Center for Molecular Modeling, Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium*
** Email:Kurt.Lejaeghere@UGent.be, Veronique.VanSpeybroeck@UGent.be, web site: http://molmod.ugent.be/*

[2]*Department of Inorganic and Physical Chemistry, Center for Ordered Materials, Organometallics and Catalysis, Ghent University, Krijgslaan 281-S3, BE-9000 Ghent, Belgium, web site: http://www.comoc.ugent.be/*

Metal-organic frameworks (MOFs) are porous, crystalline materials that consist of inorganic moieties (*nodes*) connected by organic ligands (*linkers*). Because these building blocks can be combined in a multitude of ways, MOFs are highly tunable and thus particularly attractive for many applications. UiO-66, for example, is a zirconium-based MOF characterized by an exceptionally high thermal and mechanical stability. By post-synthesis modification of its different building blocks, it may be engineered to serve as a photocatalyst: light is absorbed by the linkers, which act as antennas, and the generated charge is transferred to the catalytically active metal node (ligand-to-metal charge transfer, LMCT).

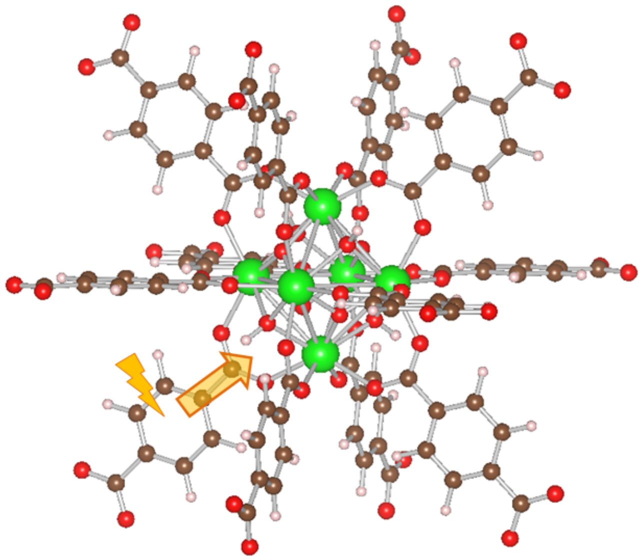

Fig1. Local environment of a Zr-based node in UiO-66. The charge generated by light absorption at a linker should be transferred to the metal site, where it acts as an active site for catalysis.

The use of UiO-66 in photocatalytic applications requires control over the band gap. The conduction band is of pronounced linker character, while for the valence band and for energy ranges considerably above the conduction band maximum, the electronic structure is determined by the node behaviour. In theory, both linker and node modifications are therefore able to tune the band gap. This talk will show that such modifications can be performed independently, making linker and node defects two orthogonal approaches to band gap engineering. The linkers are changed by increasing the linker length or by functionalizing them with electron-drawing or electron-donating groups. The nodes are changed by replacing Zr by isovalent metal atoms or by changing the local environment through linker removal. It is found that the generation of linker gap states reduces the effective band gap, and that node modifications may improve the LMCT capability.

1. K. Hendrickx, D.E.P. Vanpoucke, K. Leus, K. Lejaeghere, A. Van Yperen-De Deyne, V. Van Speybroeck, P. Van Der Voort and K. Hemelsoet, *Inorg. Chem.* **54**, 10701 (2015).
2. S.M.J. Rogge, J. Wieme, L. Vanduyfhuys, G. Maurin, T. Verstraelen, M. Waroquier and V. Van Speybroeck, submitted (2016).
3. A. De Vos *et al.*, in preparation (2016).

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