Understanding Experiments: the Power of First Principle Simulations of Metal-Organic Frameworks

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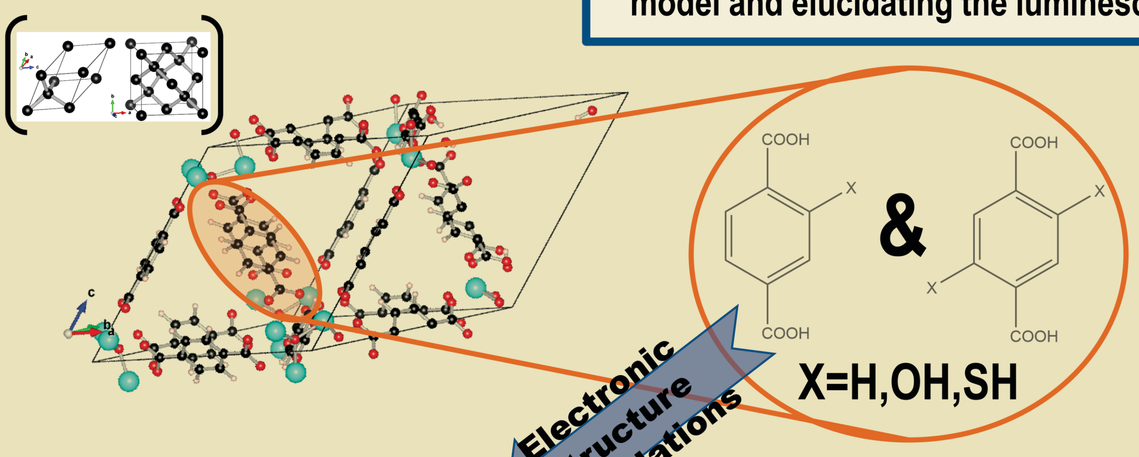
Abstract

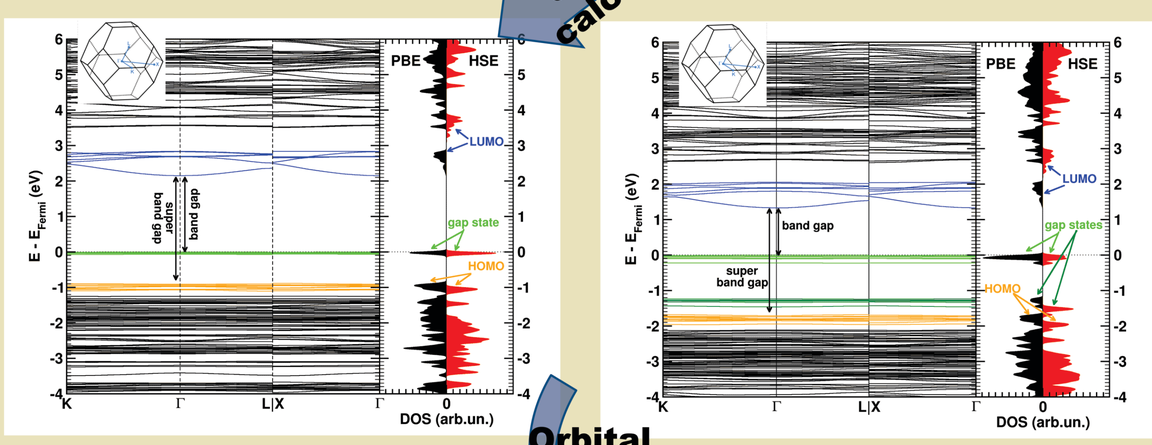
Metal-organic Frameworks (MOFs) are a versatile class of crystalline materials showing great promise in a wide range of applications. Recently light-based applications have become of interest with focus on luminescence and photocatalysis. Although new luminescent MOFs are readily synthesized, understanding of the underlying mechanisms in the electronic structure are often lacking.

First principle simulations of these MOFs can be used both for validating the model and elucidating the luminescent behavior.

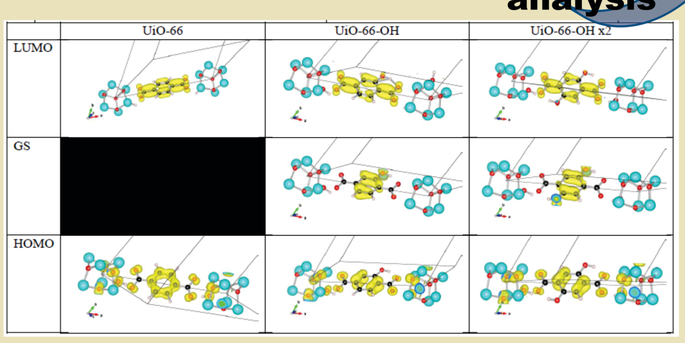
Old: UiO-66(Zr)-X

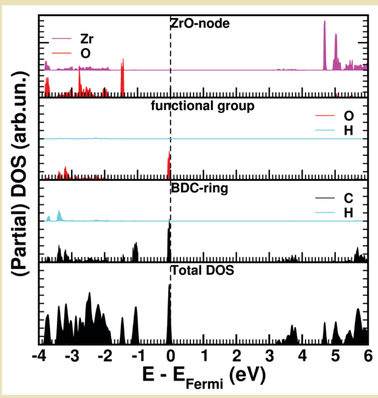


Electronic structure calculations



Orbital character analysis





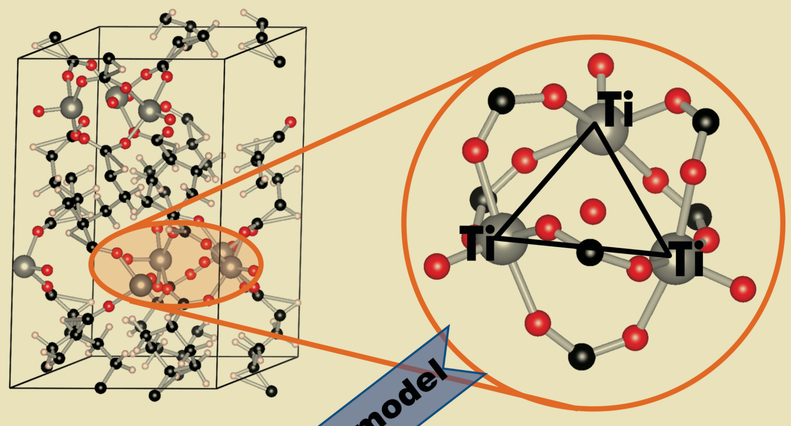
Experimental validation

	PBE		HSE06		Exp.
	Band gap (eV)	Gap state width (eV)	Band gap (eV)	Gap state width (eV)	Band gap (eV)
UiO-66	2.920	-	4.030	0.100	3.97
UiO-66-OH	2.150	0.070	3.010	0.200	3.21
UiO-66-OHx2	1.350	0.100	2.150	0.220	2.54
UiO-66-SH	1.850	0.220	2.661	0.350	2.63
UiO-66-SHx2	1.331	0.230 & 0.220	2.101	0.360 & 0.350	-

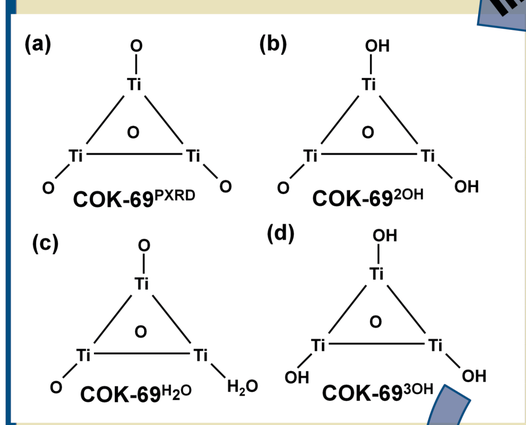
Conclusion

- Functional groups modify the electronic structure through the introduction of a gap-state.
- The later originates from the π-orbital of the linker.
- The calculated band gap shows perfect agreement with the experimentally determined one.

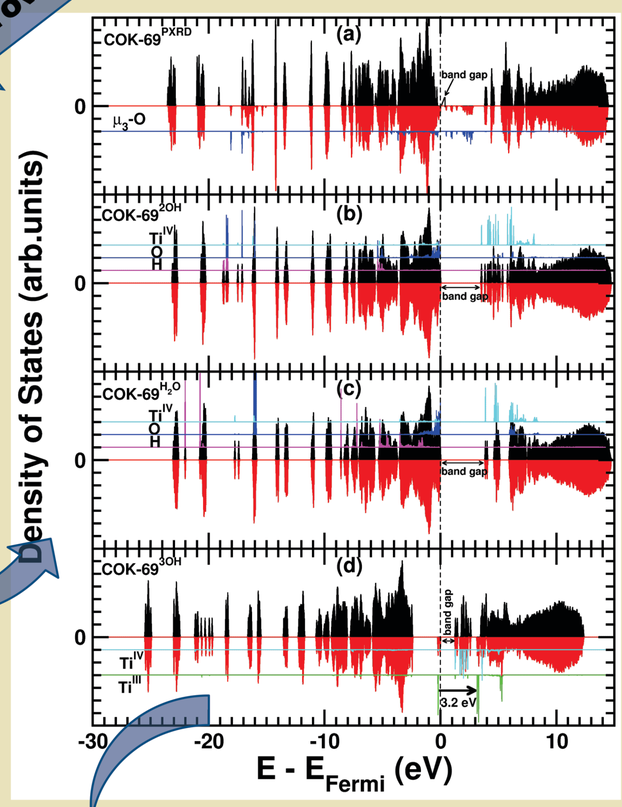
New: COK-69(Ti)



Improve model

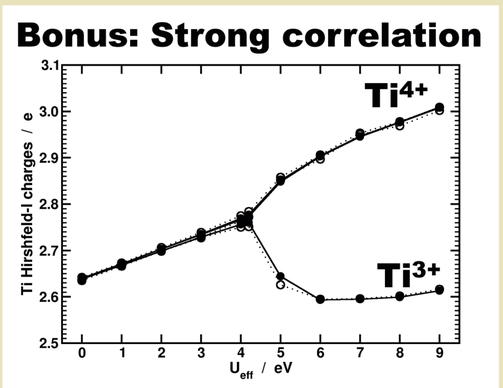


Check electronic structure



Experimental validation

Bonus: Strong correlation



Conclusion

- First principle simulations can be used to fine-tune the atomic scale model of the flexible photoactive MOFs like COK-69
- The blue color of the reduced COK-69 can directly be linked to the presence of Ti^{3+} species.
- To accurately describe the electronic structure of the COK-69 MOF one needs to go beyond DFT.

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References:

[1] "*Understanding intrinsic light absorption properties of UiO-66 frameworks*", K. Hendrickx, D.E.P. Vanpoucke, K.Leus, *et al.* Inorganic Chemistry, in revision

[2] "*A Flexible Photoactive Titanium MOF based on a [TiIV3(μ3-O)O2(COO)6]-Cluster*", B.Beuken, F.Vermoortele, D.E.P.Vanpoucke, et al. Angewandte Chemie, accepted

[3] D.E.P. Vanpoucke, P. Bultinck, and I. Van Driessche, *J. Comput. Chem.* **34** 405-417 (2013) & *j. Comput. Chem.* **34** 422-427 (2013)