Understanding intrinsic light absorption properties of UiO-66 frameworks: A combined theoretical and experimental study

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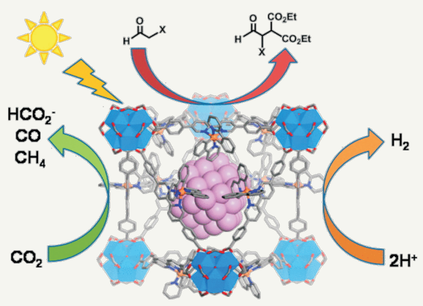
1. Introduction

Current needs in photocatalysis[1]:
- Efficiency
- Visible light activity
- Robustness

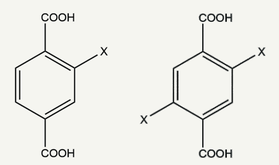
= Major challenges



Can Metal-Organic frameworks provide an answer?[2]

2. Scope

UiO-66-X and UiO-66-2,5X (X=OH, NH_2, SH)



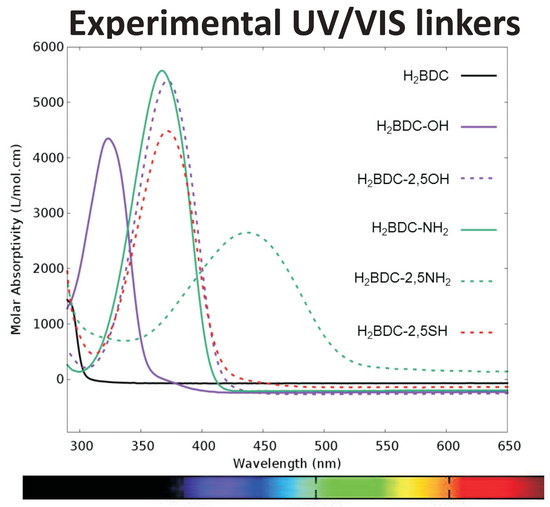
Three levels:
- Study of the separate linkers
- Clusters obtained from periodic structure
- Periodic Calculations

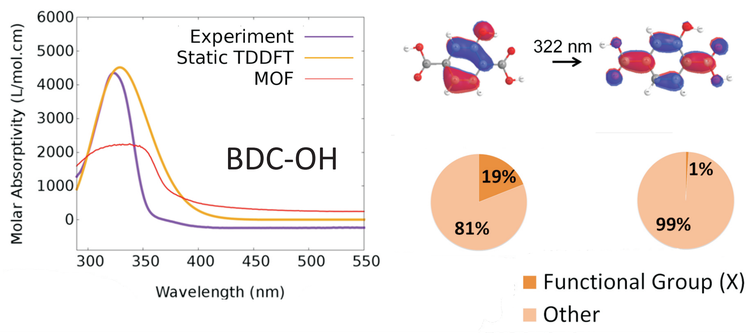
Get the complete picture of light absorption processes in UiO-66 frameworks

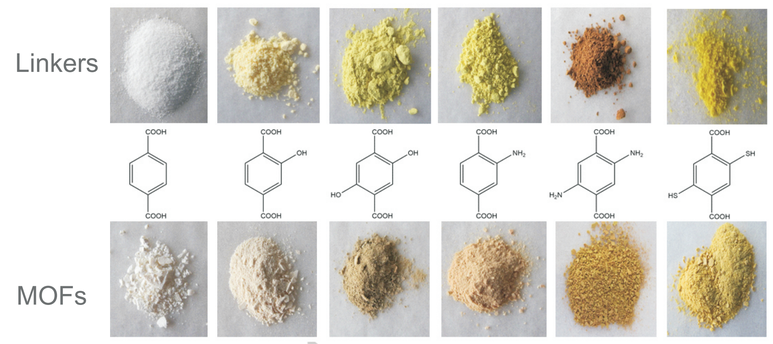
3. Linker Calculations

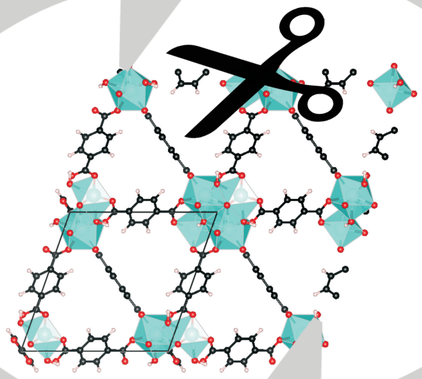
Exp.: Ref.[3]
Opt. and TDDFT: Gaussian09, B3LYP/6-311+G(d,p)

Experimental UV/VIS linkers



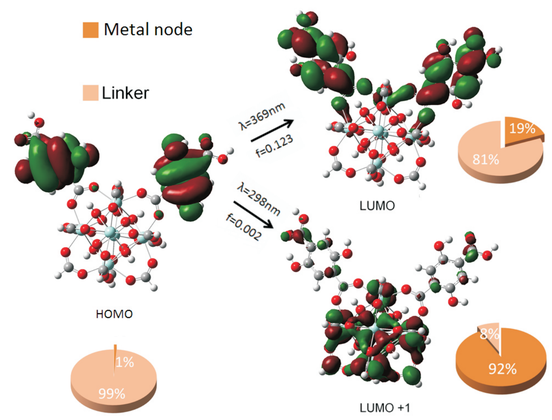


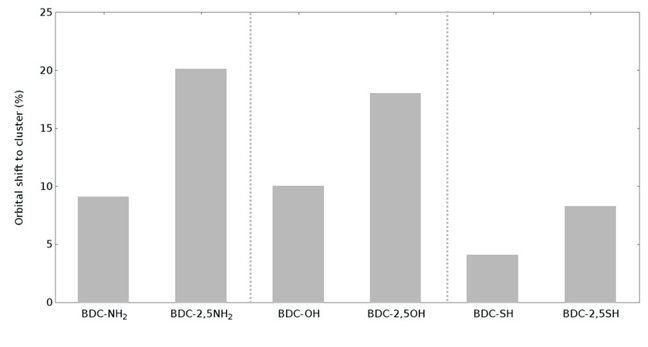




4. Cluster Calculations

Opt. and TDDFT: Gaussian09, B3LYP/DEF2TZVP

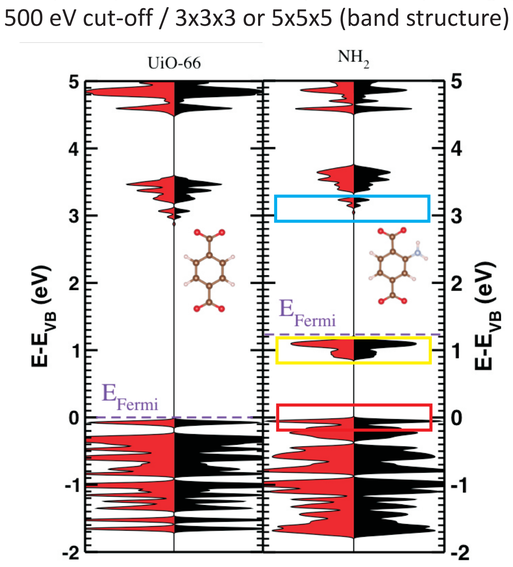


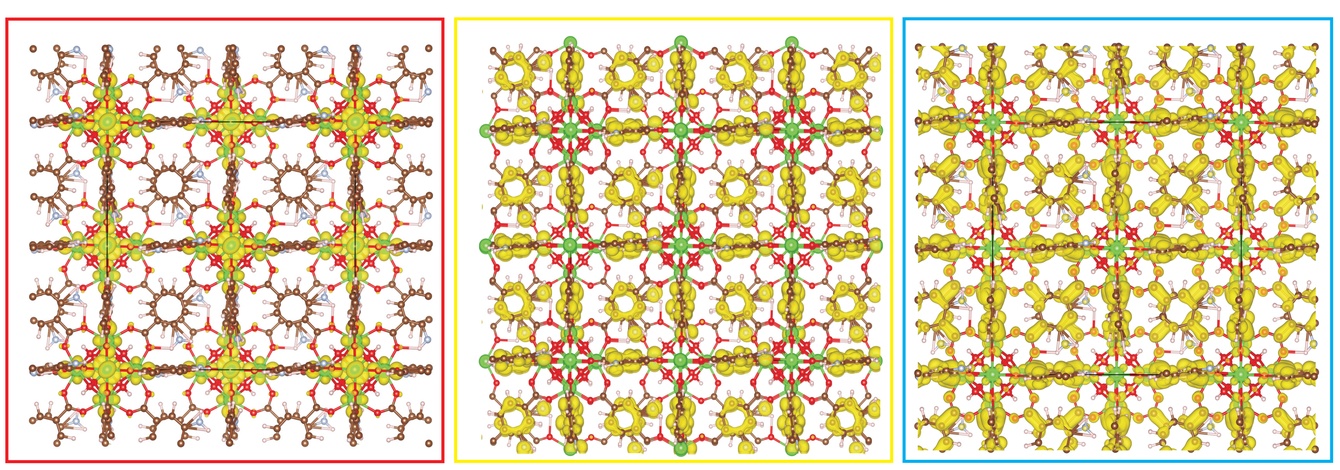


Ligand to Metal Charge Transfer (LMCT) shows to be not very efficient from orbital analysis, but depends on the functional group. This can explain the difference in catalytic activity [4]

5. Periodic calculations

VASP package
PBE (cell opt.,band structure) or HSE06 (band gap) functional
500 eV cut-off / 3x3x3 or 5x5x5 (band structure) k-point set





The analysis of the band structure shows the appearance of a filled gap state in the materials band gap, effectively lowering this in a range between 4.1-2.0 eV. From the P-DOS this band is mainly localized on the functional group. Moreover, the HOMO and LUMO are mostly linker based, which corroborates the findings of the cluster calculations.

Outlook

- Molecular dynamics simulation to improve the correspondence between experiment and theory
- Vibrational fingerprint
- Periodic TDDFT calculations

Conclusions

- Absorption properties can be tuned via linker functionalization
- LMCT is dependent on functionalization but not efficient in the visible range
- A functionalization-induced gap state effectively reduces the band gap

References

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