Functionalization of a Metal-Organic Framework Semiconductor for Tuned Band Structure and Catalytic Activity

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This study presents two strategies to modify the thermally stable crystalline UiO-66(Zr) metal-organic framework (MOF) structure, in which the organic struts have been functionalized to modulate the electronic band structure and the catalytic activity toward selective oxidation of benzyl alcohol to benzaldehyde. The two strategies include the functionalization of the organic struts with branched ligands and manually creating structural defects with unsaturated organic linkers. The computational and experimental results show that functional groups such as -NH₂ and -NO₂ attached to the main organic strut modify the electronic environment of the photoactive aromatic carbon and thereby reduce the optical bandgap by 1 eV, improving the photocatalytic activity. Whereas the introduction of structural defects by the organic linker desaturation provides a shift in the highest occupied molecular orbital (HOMO), resulting from a decrease in the strut coordination with the inorganic knots, modulating the catalytic activity without light illumination.

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Thanks to the high surface area and the permanent porosity, Metal-Organic Frameworks (MOFs) also build up an ideal platform for developing a new generation of heterogeneous catalysts. 1–3,9 The commonly employed approaches to control the catalytic activity in the porous materials like traditional porous zeolite are to engineer the surface functions and manipulate the structure defects that may bare variable functional active sites like Lewis Acid and/or Lewis Base. 6,10 Over the traditional porous materials, MOFs exhibit the superior exceptionality on the chemical variability by introducing the molecular catalysts for desired catalytic reactions. These catalytically active molecules can be directly incorporated into MOFs during the synthesis process by being pre-linked on the organic linkers or post-grafted on the framework after the formation of MOFs. Theoretically, both approaches ensure the completely isolated and homogeneous dispersion of these molecular catalysts across the entire frameworks with the extreme accessibility for each functional moiety, which prevents their aggregation and related deactivation. Furthermore, this approach limits the solubility concern that always disturbs the molecular homogeneous catalysis systems. 6,11,12 The versatility of molecular catalysts imparts the possibility to better control the selectivity and targeted catalytic reactions over MOF-based catalysts.

Alternatively, the catalytic activity originating from the molecular moieties, many MOFs materials demonstrated superior catalytic activity from the metal ions at the inorganic nodes that could be made catalytically active by removal of the solvent ligands resulting in the coordinately unsaturated metal ion sites as the catalytic centers. 13–15 Similar activity is evident in zeolite materials. Unfortunately, a fundamental understanding of the nature of such active sites in MOFs is at its early stages, and it still remains unclear how to sterically define and experimentally modify these sites, or how the sites’ activity can be further tailored and improved. 6 It is the approach of the following paper to use a combination of experimental and theoretical investigation to aid in the understanding the structural modification on the MOFs’ properties.

An alternative approach to exploit the metal nodes’ catalytic activity in MOFs does not require the open metal ions to act as a photocenter under light illumination. In such a case, the organic linkers function as the photoactive sites and inject electrons along the linkers into the metal nodes where catalytic reactions happen. 6,10

Zr-based MOFs have been proven to have photocatalytic activity for organic dye degradation, water splitting for H₂ generation and CO₂ reduction. 16–19 MOFs, as a new kind of photocatalyst, offer significant advantages over the conventional metal oxide photocatalysts: (i) high surface area and uniform pores facilitate the diffusion and adsorption of substrates; (ii) the redox center is highly exposed, leading to increased reaction rates; and (iii) organic functionalization provides the flexibility for tailoring the electronic structure. However, most of these photoactive MOFs always fall in the ultraviolet light absorption range and suffer from low thermal stability. 5,9 Therefore, it remains a challenge to harvest majority of the solar spectrum with thermally stable MOF materials.

All these attributes enable MOFs to be combinations of heterogeneous and homogeneous catalysts, 6,12 which makes MOFs very sensitive to the modifications of the organic linkers and inorganic knots that critically determines the final activity on the catalytic reactions. Herein we combine the theoretical prediction and experimental results to show these effects originating from the commonly used preparation processes, (i) organic linker modification by varying the side groups and (ii) unsaturated organic linker defects that are commonly observed with very small change in the preparation parameters.

Experimental

Synthesis of UiO-66-R MOFs.—The synthesis of UiO-66-R MOFs follows the literature. 10,20 Briefly, the same molar concentrations of ZrCl₄ and the organic linker BDC-R were dissolved in DMF (1,4-benzenedicarboxylic acid for H₂, 2-amino-1,4-benzenedicarboxylic acid for NH₂ and 2-nitro-1,4-benzenedicarboxylic acid for NO₂, respectively). The resulting solution was transferred into a Teflon-lined autoclave for 48 hours at 120 °C. The precipitant was collected using a centrifuge and washed with DMF and methanol, and then re-dispersed in methanol for three days with gentle stirring. After that, the solid was collected and dried at 120 °C under vacuum.

Synthesis of organic linker unsaturated UiO-66 MOFs.—The synthesis of these kinds of UiO-66 MOFs followed the procedure developed by Hupp group by adding concentrated HCl (35–38% w/w). Representatively, the proper amount of ZrCl₄ was first dissolved in concentrated HCl aqueous solution, while the organic linker BDC-R (R=H, NO₂, and NH₂) were dissolved in DMF. Thereafter, the two solutions were mixed with ultrasonication to yield a clear solution.
The resultant mixture was placed in an oven at 80 °C overnight. The precipitants were collected by centrifuge and washed with DMF twice and redispersed in methanol for one day. Finally, the powders were collected and dried under vacuum at 120 °C overnight. It was estimated that at least three organic linkers (struts) are lost in each unit cell. This loss of coordination resulted in further modulation of the MOF’s properties.

**Characterizations.**—The UV-Vis absorption spectra of the as-prepared MOF materials were recorded on a Shimadzu 2550 UV-Vis spectrometer under the diffuse-reflection model using an integrating sphere (UV 2401/2, Shimadzu) coated with BaSO₄.

**Catalytic organic transformation testing.**—The organic transformation catalysis testing was carried out in a flask containing 5 mL of DMF, 200 μL of benzene alcohol, and 100 mg of UiO-66 MOF catalysts with stirring. All the reactions were conducted at room temperature with the constant O₂ bubbling as an oxygen source. The reaction solution was sampled with a regular time interval and then analyzed with Shimadzu 2550 GC equipped with a FID detector and a non-polar CP-Sil 5CB column. For the photocatalytic activity, the reaction was conducted in a light box equipped with lamps with a visible light spectrum centered at 420 nm. Whereas the other reactions conditions keep constant.

**Computational**

To aid in understanding how the change in structure influences the MOFs’ electronic properties, a series of ground state density functional theory (DFT) predictions were carried out following the approach described in previous studies. DFT calculations used the functional form of the ultra-soft (US) pseudo-wave function that was based on the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function with a cutoff wave function kinetic energy of 816 eV (60 Ry). The potential cutoff energy was specified to be ten times the kinetic cutoff energy. The accuracy and stability of the specified unit cell was confirmed prior to simulation. A Monkhorst-Pack k-point mesh sampling 4 × 4 × 4 grid. A dispersion correction term was incorporated to account for Van der Waals interactions to accurately account for hydrogen interactions. Dispersion scaling parameters were specified to be 0.7 and cutoff radius for the dispersion interaction was 900 Å. All unit cells were relaxed to a pressure less than 0.5 kPa. A non-self-consistent calculation was used to sample the density of states with a k-point mesh and trapezoidal integration with an 8 × 8 × 8 grid.

**Results and Discussion**

In this study, Zr-based UiO-66 MOFs have been selected as the target MOF structure because of their exceptional chemical stability in strong acid aqueous solutions, high thermal stability up to 300–400 °C, as well as their demonstrated catalytic activity as Lewis Acid catalysts and photocatalytic activity for chemical fuel generation. The goal of this study is to understand what physical mechanisms influence the electrical and catalytic properties of a UiO-66 MOF. This understanding will permit the optimization of the proposed MOF material design of potentially new MOFs.

UiO-66(Zr) MOFs, with a nominal chemical formula [Zr₆O₈(OH)₄][C₆H₄(COO)₂]₆, are built up with inorganic Zr₆O₈(OH)₄ oxocluster knots bridged with 12 1,4-benzenedicarboxylate organic struts to form a face-centered cubic network (Figs. 1a and 1b). It is the Zr₆ inorganic unit that imparts the robust UiO-66(Zr) with its inherent chemical, mechanical and thermal stability. UiO-66(Zr) MOFs are one typical representative for their photocatalytic activity that originates from the conjugated electronic structure of the organic linker. More specifically, the sp² bonded carbon in the aromatic ring of the strut is photoactive with a UV bandgap and efficient photoexcited charge separation. Because of this UV sensitivity, most photoactive MOFs have a bandgap larger than 3.4 eV. For example, UiO-66(Zr), has an estimated bandgap based on UV-VIS light absorption spectrum of approximately 3.64 eV corresponding to the absorption cutoff edge at around 340 nm (Fig. 1c). The organic linkers can be lengthened to reduce the bandgap energy, but this changes the lifetime of photoexcited carriers and conductivity of linkers. Moreover, these longer linkers typically rely on the non-commercial organic linker precursors.

In addition to changing the length of the linker, the metal ion can also be exchanged to modulate the MOF’s properties. However, the stability and the redox level requirements limit the selection of metal cores for photoactive MOFs. A more favorable route to reduce the bandgap and to modulate the electronic structure in MOFs is the substitution of the side groups onto the main organic linker.
conjugated π electron structure in the organic linker is extremely sensitive to substitutions, which provides a simple yet effective modification procedure.31-35 Despite the pre-existing knowledge available from organic dyes, few studies have been conducted to investigate the effects of substituted linkers on the electronic band structure of MOFs. Few reports have given insight into the electronic band structure of MOFs. It remains a significant challenge to design and synthesize MOFs with tunable light capture capability for driving photocatalytic reactions.

Bandgap modulation of MOF.—To realize the modulation of the electronic structure, organic linkers with different branched groups, i.e. H, NO2, and NH2, corresponding to BDC, NO2-BDC and NH2-BDC, respectively, were used during the solvothermal synthesis process, which one-step yielded the UiO-66(Zr) MOFs materials with corresponding side functionalities, as shown in the inset in Fig. 1C. The unchanged X-ray diffraction (XRD) patterns (Fig. 2) indicate that the substituted side groups did not alter the original cubic crystal structure of UiO-66(Zr) MOFs. An apparent color changes for these three UiO-66(Zr) MOFs was visually confirmed. To quantitatively evaluate the absorption edge, we performed the UV-VIS absorption spectrum measurements, as shown in Fig. 1C. As expected, the substitution of side groups results in the broadening of light absorption into the visible light region. H-Uio-66 has an absorption edge cutoff at 340 nm, corresponding to a bandgap of 3.64 eV in the deep UV region. NO2 could significantly increase the light harvesting capability up to 425 nm with a bandgap of 2.92 eV. NH2 shows the maximum leading to a bandgap decrease. A considerable bandgap modulation was achieved through functionalization and found to be sensitive to substitutions, which provides a simple yet effective modification procedure.

### Table I. Experimental and DFT prediction of the bandgap for both the fully saturated (FS) and unsaturated (US) MOF designs. There is not a significant change in the bandgap for the US case.

| Configuration          | UV-Vis Cutting Edge (nm) | UV-Vis Bandgap (eV) | DFT (eV) |
|------------------------|--------------------------|---------------------|----------|
| H-Uio-66(Zr) (FS)      | 340                      | 3.64                | 2.50     |
| NO2-Uio-66(Zr) (FS)    | 425                      | 2.92                | 2.10     |
| NH2-Uio-66(Zr) (FS)    | 450                      | 2.76                | 1.80     |
| H-Uio-66(Zr) (US)      | -                        | -                   | 2.30     |
| NO2-Uio-66(Zr) (US)    | -                        | -                   | 2.00     |
| NH2-Uio-66(Zr) (US)    | -                        | -                   | 1.85     |

As determined in other studies, the conjugated π electron structure in the aromatic ring is extremely sensitive to metal substitutions and functionalization, which act on the photosensitive carbon region of the linker. Both modifications subsequently affect the bandgap structure of MOFs. To understand the influence of the bonding between the aromatic ring and the coordination of the metal clusters, a ground state density functional theory calculation was carried out to investigate the projected density of states and the origins of the modulation. Computational results validated that the bandgap decreases in both NH2- and NO2-MOFs are prominently related to the sp2 hybridization between N atoms in functional groups (NO2 and NH2) and carbon atoms in aromatic rings.20,36 For NH2 group, a complementary π-bond with the carbon atoms in the aromatic ring, the nitrogen atoms also form σ-orbital hydrogen type bonding with the outlying pair of hydrogen on the functional group resulting in a mid-gap donor site, which contributes a valence state and results in a decrease in the bandgap when compared to the non-functionalized BDC linker.20 Whereas for NO2 configuration, the N-O bond are ready to accept p-orbital electrons from the sp2 hybridized carbon atoms in aromatic ring, most likely functioning as an acceptor when comparing BDC-NO2 to BDC. This leads to a slight modification of the p-orbitals, and then the combination contributes a valence state near the valence band maximum leading to a bandgap decrease. A considerable bandgap modulation was achieved through functionalization and found to be highly influenced by the bonding nature of the functional group with the aromatic carbon ring.

Table I is a summary of the experimental and DFT predicted band gaps for each of the structures investigated in this study in both an unsaturated and a fully saturated configuration. Both the experimental and DFT results convey the trend of decreasing bandgap when the MOF linker coordination decreases and with the addition of functionalization. The reader should note that the DFT predictions are underpredicted due to the inherent assumption of DFT; however, the trends are similar. While there are computational methods to provide better estimates of the band gaps such as hybrid functionals, these functionals often introduce a degree of empiricism that distracts from the first principle nature of the calculation.

### Testing catalytic activity.—To test the catalytic activity of the MOF materials, a model reaction for benzyl alcohol to benzaldehyde (Fig. 3a) was used to test the catalytic activity of UiO-66 MOF materials under the visible light shining centered at 420nm. 0.2 g of UiO-66 powder was dispersed in 5 mL of DMF with 200 μL of substrate benzyl alcohol. The catalytic reaction was performed under the light illumination when oxygen is bubbled into the solution. The reaction cell used for this experiment is shown in Fig. 3b. After 12 hours of reactions, the product was detected with Shimadzu GC-2014. As demonstrated in a previous study,19 the sole product, benzaldehyde, was detected indicating 100% selectivity of UiO-MOF upon this reaction. As expected, NH2-MOF and NO2-MOF display the organic transformation efficiency of 3.0% and 0.9%, while H-MOF has negligible activity for this reaction under visible light with wavelength centered at 420 nm. This result confirms that the catalytic activity for such organic transformation comes from photocatalysis. Therefore, it is reasonable that NH2 functionalized MOFs has maximum
conversion efficiency due to its lower bandgap and ability to utilize more of photons. Furthermore, the bald-BDC MOFs display zero activity because of the inability to readily absorb visible light. It should be noted that the relative lower efficiency was mainly due to the lower light power density of the light source used for the experiment. By increasing the light intensity or the number of photons absorbing at the surface, it is assumed the conversion rate should increase. When the photons have energies much larger than the bandgap of MOFs, the photogenerated charge carriers activate the molecular oxygens to create the reactive radicals that finally drive the organic transformation reactions.

Metal cluster coordination modification.—The UiO-66 MOFs materials were prepared in a mild solvothermal process where organic linkers and inorganic knot precursors are dissolved in DMF and start self-assembly under solvothermal conditions. In this case, as discussed above, each Zr6 oxoclusters should be fully coordinated and surrounded with 12 BDC- R organic linkers. Such UiO-66 MOF materials as shown in Fig. 3 do not show catalytic activity for the benzaldehyde reaction in dark, which indicates fully-coordinated UiO-66 MOFs crystals formed. However, when some extra coordinators like acetic acid and benzoic acid were added, there are systematically missing organic linkers for real materials, see Figure 4a compared to Figure 4b. Such linker deficiency allows coordinative unsaturated sites on Zr to be identified as the superior active sites for Lewis Acid based reactions. However, it remains a great challenge to precisely control the reaction activity and the distribution of these active sites and acidity by varying the synthesis and post-treatment process. Recently, a facile synthesis protocol to prepare UiO MOFs materials has been proposed by adding a concentrated HCl acid. Different to other acid coordinators that would help slow down the reaction rate and enhance the crystallinity of MOFs materials, the presence of HCl speeds up the formation of UiO-66 materials more quickly by aiding in dissociating linkers from nodes. Through theoretical calculation and experimental results, it was assumed that four of 12 node linkers missing compared to the regular UiO-66 MOFs family materials, which would generate linker unsaturation defects and allow for more inorganic knots exposed, as compared in Fig. 5.

There was an apparent change in the MOF powder color when processing included the HCl acid, which supports a modification of the linkers. The appearance decolorized the structure compared to the regular UiO-66 MOFs materials. However, the face-centered-cubic crystal structure remained with decreased diffraction intensity. To confirm the possible catalytic activity from the exposed Zr ions acting as Lewis Acid sites, we conducted the same organic transformation reaction (benzyl alcohol to benzaldehyde) with the same conditions except for no light illumination. As stated before, the regular UiO-66-R MOFs materials demonstrated no activity in driving this reaction in the dark (Fig. 5). Surprisingly, the unsaturated UiO-66-HCl demonstrated the unprecedented activity for this reaction with an efficiency up to 21%. The product was detected to be pure benzaldehyde, demonstrating 100% selectivity. However, the unsaturated UiO-66-NH2 and UiO-66-NO2 exhibit almost same but very low activity for...
Figure 5. Conversion efficiency and selectivity for coordinatively unsaturated UiO-66 MOF materials in dark. The reactions were conducted under the same conditions except for the light illumination.

Figure 6. Plots of the elemental projected density of states for both the unsaturated and saturated cases. (a) is the H-Uio-66(Zr)-66, (b) is the NH₂ case, and (c) is the NO₂ case. Unsaturating the structure results in a decrease coordination of oxygen and change in the valance states and ultimately a change in the Lewis Acid sites.

Acid sites to activate this reaction. The dramatically suppressed activity with side NO₂ and NH₂ functionalities should be attributed to the electronic structure modulation that negatively affects the activity of these exposed Zr ions. In this process, molecular O₂ are mandatorily present for generating active radicals to initiate the reaction. The interactions between O₂ and Zr ions in unsaturated UiO-66-R MOFs materials were calculated with DFT theory to elucidate the effect of the electronic modulation of the Lewis Acid sites’ activity.

To understand how the electronic structure is influenced by unsaturating the MOF structure, a series of DFT calculations were employed to determine the projected density of states (PDOS). Fig. 6 is an illustration of the PDOS for all three cases in both unsaturated and saturated (regular) MOF designs. For all the cases in Fig. 6 the Fermi energy is aligned to provide a relative comparison amongst all cases. All the states below the Fermi energy are filled states and associated with the bonding of the MOF structure. All states above the Fermi energy are assumed unfilled or unoccupied. If we focus on the HOMO states below the Fermi energy and compare the density of states values for each species, an understanding of the type of bonder can be ascertained. As the density of states is derived from the expectation value of the electronic wavefunctions, if there are complimentary peaks in the elemental projected density of states, there is some certainty that these are covalent type states. This can be confirmed by the interaction and overlapping peaks in the density of states for both oxygen and carbon. This is a direct result of the classic sigma bonds that these two elements form the organic linker structure. More interesting is what unsaturating the structures does to the band structure. As is illustrated in Fig. 6a and 6b there is a shifting of the oxygen density of states as the structure is unsaturated. Recall the oxygen atoms are situated at the intersection of the linker and the metalloid. In the unsaturated case...
the oxygen’s coordination is decreased. This shift in band structure is a result of a shift in the Fermi energy, which results in a change in the Lewis Acid sites. The decreased coordination of the oxygen results in the addition of valence states that influence the LUMO states. This can be further confirmed in all the cases of Fig. 6 by a change in the curvature of the LUMO levels from the introduction of several additional valence states.

As noted from the PDOS plot of Fig. 6 and tabulated in Table I, there is not a significant change in the bandgap when the MOF is unsaturated. This is confirmed experimentally by noting that the UV-Vis is not discernible between the fully-saturated and unsaturated cases. This supports the claim that by unsaturating the MOF the increased activity is a not a result of increased light absorption by increased selectivity at the exposed Zr sites. Future studies, will confirm this claim by investigating and predicting the Gibbs energy of the reaction using DFT.

Conclusions

This research demonstrated that catalytic activity of MOFs materials was very sensitive to the electronic structure modulation even with very tiny structural variations due to the presence molecular catalytic moiety. This approach offers another method to systematically tailor the catalytic activity and selectivity of the MOFs. The theoretical and experimental approaches confirmed that the HCl treatment modified the MOF structure by saturating the metal while maintaining the MOF’s crystallinity. By decreasing the coordination of the metal clusters, the exposed Zr ions increased their active catalytic activity. This was reasoned to be synonymous to modification of the Lewis Acid sites by exposing Zr. It was confirmed by the DFT calculations that there was significant shift in the Fermi energy that confirms a change in the Lewis Acid site. Overall, this modification demonstrates additional promise for tailoring MOF structures for photocatalysis based applications.

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