Utilizing mixed-linker zirconium based metal-organic frameworks to enhance the visible light photocatalytic oxidation of alcohol

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Abstract

A series of mixed-linker zirconium-based metal-organic frameworks (Zr-MOFs) have been synthesized in one-pot reactions. The Zr-MOFs, containing 2-amino-1,4-benzenedicarboxylate (NH₂-BDC) as the primary linker and 2-X-1,4-benzenedicarboxylate (X-BDC, X = H, F, Cl, Br) as a secondary linker, have been used as visible light photocatalysts. The incorporation of multi-functional groups into the catalysts was characterized by PXRD, STEM, NMR, N₂ physisorption diffuse reflectance FTIR, and diffuse reflectance UV-Vis. The effects of different linkers on the photocatalytic property of the Zr-MOFs were evaluated in the oxidation of benzyl alcohol. The photocatalytic oxidation reaction was performed using a 26 W helical bulb as the visible light source, and the temperature of the reaction was kept at 80 °C. The Zr-MOF containing mixed NH₂-BDC and F-BDC linkers gives five times more conversion in the oxidation of benzyl alcohol compared to the Zr-MOF made of mixed NH₂-BDC and H-BDC linkers. We only observed partial oxidation product, benzaldehyde, from the photocatalytic oxidation reaction.

Graphical Abstract

Keywords

UiO-66, visible light, photocatalysis, heterogeneous, selective oxidation of alcohol

1. Introduction

Since the discovery of ultraviolet (UV) light-irradiated, photocatalytically active TiO_2 by Honda and Fujishima in 1972,¹ immense efforts have been directed to improve the efficiency of this semiconductor.² This led to a spurt of research towards utilizing light as an effective source of energy for many important chemical transformations. By applying molecular orbital theory, significant advances have been made in the design of these photocatalysts owing to an improved understanding of the utilization of light energy by molecules.³ Traditional semiconductors, quantum dots,⁴ and supramolecular ensembles⁵ have also been engineered to efficiently execute photocatalytic reactions. A new class of materials, a hybridized organic-inorganic structural motif known as metal-organic frameworks (MOFs) has emerged as an interesting multi-purpose platform. MOFs have found considerable applications in gas storage,⁶ heterogeneous catalysis,^{7,8} separations,⁹ drug delivery,¹⁰ and chemical sensing.¹¹ Interestingly, due to the inherent ability to control the functionality of the organic linkers and the inorganic secondary building units during their synthesis,¹² these materials have shown considerable promise for photocatalysis.

Application of MOFs in photocatalysis was first rationalized in the MOF-5 system due to its semiconductivity.^{13,14} However, MOF-5 is only active as a catalytic system upon UV light irradiation. To tune the band gap of MOFs to absorb visible light, Fu et al.¹⁵ and other groups^{16,17} modified the type of organic bridging linkers and produced visible light active catalysts. However, the catalytically active sites that reside at the inorganic building blocks of these MOFs yield relatively low activity.¹⁸ In comparison, MOF-based photocatalysts synthesized by Lin et al. through linker coordination with redox metal complexes show significantly enhanced photocatalytic activity in water oxidation, CO_2 reduction, and organic transformations.¹⁹

We hypothesized that incorporating different linkers of appropriate functionalities into a single framework could affect its catalytic property which provides a new opportunity for designing improved catalysts. In literature, the incorporation of different functionalized linkers into a single MOF has been demonstrated by Burrows and coworkers through post-synthetic modification (PSM).²⁰ Starting with aldehyde-functionalized MOF-5, comprised of ZnO_4 clusters connected by aldehyde-functionalized benzenedicarboxylate linkers, Burrows intended to chemically modify the aldehyde group to other useful groups. However, the aldehyde group was only modified partially, resulting in a mixed-linker MOF system. Using a bottom-up approach, Deng and co-workers,²¹ incorporated up to six linkers with different functional groups into MOF-5. This MOF was synthesized by a one-pot synthesis approach, where the different linkers were added at the beginning of the synthesis. Besides MOF-5 system, Marx and coworkers introduced mixed linkers into MIL-53(Al).²² Lin's group produced mixed-linker MIL-101(Fe) for drug delivery applications.²³

In this report, we synthesized task-specific mixed linker Zr-MOFs using bottom-up approach in one-pot, aiming to improved activity in visible light photocatalytic reactions. We utilized 2-amino-1,4-benzenedicarboxylic acid ($\text{NH}_2\text{-BDC}$) as a primary linker to shift the absorption wavelength of the parent UiO-66 which comprise of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters and 1,4-benzenedicarboxylate (BDC) linker²⁴ to the visible light regime, and a secondary linker, 2-X-1,4-benzenedicarboxylic acid (X-BDC, where X = H, F, Cl, Br) was incorporated in the same MOF to adjust the local environment and electronic properties around the active sites and thus their activity. Their

catalytic performance was evaluated their in the visible light photocatalytic oxidation of benzyl alcohol. The as-synthesized mixed-linker UiO-66 MOFs containing halogen functional groups showed enhanced catalytic activity compared to the UiO-66-NH₂ and UiO-66-NH₂-H MOFs.

2. Experimental

2.1. Catalyst preparation

Anhydrous zirconium tetrachloride (ZrCl₄, 98%), and 2-amino-1,4-benzenedicarboxylic acid were purchased from Acros Organics. 2-bromo-1,4-benzendicarboxylic acid and was purchased from Alfa Aesar and benzenedicarboxylic acid was purchased from Sigma Aldrich. All chemicals were used without further purification. 2-chloro-1,4-benzenedicarboxylic, 2-fluoro-1,4-benzenedicarboxylic acid, and 2-iodo-1,4-benzenedicarboxylic acid were synthesized according to a reported procedure in literature.^{25,26}

For the synthesis of 2-iodo-1,4-benzenedicarboxylic acid and 2-fluoro-1,4-benzenedicarboxylic acid, the respective functionalized dimethyl terephthalate was used. In general, 0.5 g (2.36 mmol) of dimethyl-2-fluoroterephthalate was dissolved in 20 mL of aqueous sodium hydroxide (1.0 M aqueous NaOH, 1.0 M) at 353 K for 30 minutes with continuous stirring. After 30 minutes, the clear solution was cooled down to room temperature. Concentrated hydrochloric acid (HCl, assay 37%) were added dropwise to the solution while stirring until the pH reaches 1. The resultant white precipitate was recovered by vacuum filtration, and wash with copious amount of water to remove the excess acid. The white powder was vacuum dried overnight at room temperature.

For the synthesis of 2-chloro-1,4-benzenedicarboxylic acid, 0.5 g (3.25 mmol) and 1.6 g (9.8 mmol) were dissolved in 20 mL aqueous potassium hydroxide solution (KOH, 2 M). The solution was set to refluxed overnight. The solution was allowed to cool to room temperature and acidified with concentrated hydrochloric acid to pH 1. The precipitate was collected by vacuum filtration and rinse with copious amount of water. The precipitate was dried in vacuum at room temperature to obtained 2-chloro-1,4-benzenedicarboxylic acid.

UiO-66-NH₂ was synthesized according to a process reported in literature.²⁷ In a typical synthesis, 1.7 mmol of zirconium tetrachloride (ZrCl₄) was dissolved in 100 mL of dimethylformamide (DMF) in a Teflon PFA wide mouth jar. An equimolar amount of the linker, 2-amino-1,4-benzenedicarboxylic acid (1.7 mmol), was dissolved into the clear solution with the aid of sonication for about 5 minutes. The tightly capped Teflon jar was then transferred into a 120 °C pre-heated oven. The Teflon jar was maintained under static conditions for 24 hours. After 24 hours, the suspension was cooled to room temperature and the precipitate was isolated by centrifugation at 8000 rpm for 15 minutes. The isolated precipitate was washed with 40 mL DMF thrice to remove any unreacted substrates. The precipitate was further washed with methanol to allow the exchange of DMF trapped in the framework with a lower boiling point solvent. During each wash, the suspension was kept at room temperature for 12 hours before being centrifuged. Finally, the precipitate was dried at 150 °C under dynamic vacuum overnight to remove the trapped solvent.

For the synthesis of mixed-linker Zr-MOFs (Scheme 1), 1.7 mmol of zirconium tetrachloride was dissolved in 100 mL DMF in a Teflon PFA wide mouth jar. The primary linker 2-amino-1,4-benzenedicarboxylic acid (0.85 mmol) and the second organic linker 2-X-1,4-benzendicarboxylic acid (0.85 mmol, X = H, F, Cl, Br)

were dissolved into the solution by sonication. The Teflon jar was sealed and transferred into a 120 °C preheated oven. After 24 hours, the precipitate was isolated, purified and dried following the same procedure used for UiO-66-NH₂. The as-synthesized mixed-linker UiO-66 MOFs were denoted as UiO-66-NH₂-X (X = H, F, Cl, Br).

Scheme 1. Synthesis of the mixed-linker Zr-MOFs. Equimolar quantities of primary linker 2-amino-1,4-benzenedicarboxylic acid and secondary linker 2-X-benzene-1,4-dicarboxylic acid (X = H, F, Cl, Br).

2.2. Catalyst characterization

The powder X-ray diffraction (PXRD) patterns were collected at room temperature using a STOE Stadi P powder diffractometer equipped with an image plate and a Cu K α radiation source (40 kV, 40 mA, $\lambda=1.5405$ Å).

For nuclear magnetic resonance (NMR) characterization, about 10 mg of catalyst was digested in 580 μ L of DMSO-d₆ and 20 μ L of HF. After complete dissolution of the catalyst by sonication, the solution was used to collect a ¹H NMR spectrum. ¹H NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400.39 MHz.

The size and morphology of the Zr-MOF was investigated using scanning transmission electron microscopy (STEM). Energy-dispersive X-ray (EDX) analysis was used to identify the elements present in the mixed linkers in the Zr-MOF crystal. Scanning transmission electron microscopy (STEM) images was recorded on a Tecnai G² F20 electron microscope equipped with an EDX detector (Oxford INCA EDS).

Pore volume and surface area measurements using high purity nitrogen were performed using Micromeritics 3Flex Surface Characterization Analyzer. Prior to nitrogen adsorption and desorption measurements, the catalysts were degassed at 423 K for 6 hours. All nitrogen adsorption and desorption was measured at 77 K. Surface areas were determined by the Brunauer-Emmett-Teller (BET) equation in the range between 0.01 to 0.1 relative pressure so that the value of the y-intercept is positive.²⁸

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using Agilent Cary 670 FTIR equipped with a linearized Mercury-Cadmium-Telluride (MCT) detector, a Harrick diffuse reflectance accessory, and a Praying Mantis high temperature reaction chamber. Zr-MOFs were packed in the sample cup, followed by an activation process under high vacuum (10⁻⁶ torr) at 200 °C for 1 hour to remove any absorbed water. Heating for a longer time does not show any further changes in the IR spectrum. After the sample was cooled down to room temperature, the spectra were recorded at 1 cm⁻¹ resolution within the range of 4000–700 cm⁻¹. Kubelka–Munk correction was applied to generate the spectra for qualitative analysis. UV-Visible absorbance was measured using a Stellar Solid Diffuse-Reflectance Probe.

2.3. Catalytic performance test

The reaction was carried out in a sealed 6-dram glass vial (22.2 mL) with a magnetic stirrer. In a typical reaction, 0.10 mmol of catalyst (based on Zr content) was evacuated at 150 °C under vacuum to remove any absorbed species. The vial was then saturated with O₂ and 3 mL of toluene was injected into the vial. The suspension was sonicated for 5 mins, to homogenously disperse the catalyst. Mesitylene (13.91 µL, 0.10 mmol), and benzyl alcohol (26.0 µL, 0.25 mmol) were injected into the reaction vial. The suspension was stirred for 30 mins in the dark to achieve equilibrium. 0.1 mL of the solution was then collected as initial reference. An O₂ balloon was used to ensure the atmospheric O₂ pressure was maintained at 0.1 MPa. The reaction vial was then placed in a 80 °C oil bath and irradiated with a 26 W Helical bulb for 24 hours.

The conversion was calculated using the following expression:

$$\% = 100 \times \frac{C_0 - C_i}{C_0}$$

Where X is the conversion, C_0 and C_i are the molar concentrations of substrates before and after the photocatalytic reaction, respectively.

The turnover frequency (TOF) was calculated by the following expression:

$$\text{TOF} = \frac{\mu\text{mol of converted benzyl alcohol}}{\text{reaction time in minutes} \times \text{mass of Zr in gram}}$$

The TOF is calculated based on per mass of Zr instead of per unit of the catalyst mass because the molar mass of the catalyst changes with different functionalized linker.

3. Results and discussion

The powder X-ray diffraction (PXRD) patterns (Fig. 1) show that the Zr-MOFs synthesized with mixed bridging linkers are crystalline and isorecticular to the parent Zr-MOF, UiO-66.²⁴

Fig. 1. PXRD patterns of (a) simulated UiO-66 and as-synthesized Zr-MOFs (b) UiO-66-NH₂, (c) UiO-66-NH₂-F, (d) UiO-66-NH₂-Cl, (e) UiO-66-NH₂-Br.

The porosity of the Zr-MOFs was evaluated by nitrogen adsorption and desorption isotherm (Fig. 2). The BET surface area of UiO-66-NH₂-H that consists of mixed linkers of BDC-H and BDC-NH₂ is 885 m²/g. When the BDC-H linker is replaced by halide functionalized BDC, the BET surface area decreases. BET surface area for UiO-66-NH₂-F, UiO-66-NH₂-Cl and UiO-66-NH₂-Br are 871, 798, and 689 m²/g respectively. The decrease in

surface area indicates the incorporation of the halide-functionalized linkers in the Zr-MOF crystal. As the functional group gets bulkier, the total surface area decreases. However, the decrease in surface area of the Zr-MOFs made of mixed linkers cannot assure that each Zr-MOF crystal consisted of different linkers and not a physical mixture of two different functionalized Zr-MOFs.

Fig. 2. Nitrogen adsorption (left) and desorption (right) isotherm of different Zr-MOFs at 77 K: (aqua) UiO-66-NH₂-H, (blue) UiO-66-NH₂-F, (red) UiO-66-NH₂-Cl, (black) UiO-66-NH₂-Br.

By utilizing two different linkers during the synthesis of Zr-MOF, it is possible to form two kinds of Zr-MOF crystals with pure linkers. This will result in a physical mixture of NH₂-functionalized Zr-MOFs and halide-functionalized Zr-MOFs. To investigate the distribution of the functionalized-linker, STEM and EDX analysis were done on UiO-66-NH₂-F. EDX analysis was performed on a selected area (Box 1) from the STEM (Fig. 3) which represents a single Zr-MOF crystal. The intensity at 0.39 keV and 0.68 keV in the EDX spectrum (Fig. 4) correspond to the *K*-edge of nitrogen and fluorine respectively. This indicates that both the fluorine- and amine-functionalized linkers are in fact present in a single Zr-MOF crystal.

Fig. 3. STEM image of mixed linker Zr-MOF, UiO-66-NH₂-F. Box 1 is a selected area representing a single Zr-MOF crystal.

Fig. 4. EDX spectrum of UiO-66-NH₂-F collected from area 1 as shown in the STEM image.

Scheme 2. Idealized molecular representation of mixed-linker Zr-MOF. Aqua polyhedrons represent the Zr-oxo cluster. Black, red, blue and brown represent carbon, oxygen, nitrogen and halides respectively. Hydrogen atoms omitted for clarity.

The mixed-linker UiO-66 MOFs were synthesized using a 1:1 molar ratio of 2-amino-1,4-benzenedicarboxylic acid and 2-X-1,4-benzenedicarboxylic acid (X = F, Cl, Br). Idealized molecular representation of mixed-linker Zr-MOF is shown in Scheme 2. To quantify the actual composition of the mixed linkers in these Zr-MOFs, we digested the Zr-MOFs in DMSO-d₆ and HF by sonication. The digested Zr-MOFs were analyzed by ¹H NMR (Fig. 5). Molar percentages of the different linkers are calculated from the integration of their appropriate proton peaks (δ = 7.38 for BDC-NH₂, δ = 7.96 for BDC-Br, δ = 7.34 for BDC-Cl and δ = 7.70 for BDC-F) are shown in Table 1. From the NMR analysis of these digested Zr-MOFs, we found that the composition of the mixed-functional linkers in these Zr-MOFs is close to the theoretical value. Among the three amino-halide mixed-linker Zr-MOFs, F-BDC linkers show the highest incorporation efficiency into the UiO-66 frameworks compared to the Cl- and Br-BDC linkers, which could be due to the relatively higher pK_a values of the carboxylate groups on the F-BDC linkers.²⁹

Fig. 5. ^1H NMR spectrum of digested Zr-MOFs. (a) UiO-66- $\text{NH}_2\text{-F}$, (b) UiO-66- $\text{NH}_2\text{-Cl}$, (c) UiO-66- $\text{NH}_2\text{-Br}$. Highlighted peaks correspond to the aromatic protons on BDC- NH_2 . Peaks at $\delta = 8.1$ correspond to proton from DMF solvents.

Table 1: BDC-X linker composition in Zr-MOFs measured by ^1H NMR.

Entry	Catalyst	$-\text{NH}_2$ (mol %) ^[a]	$-\text{X}$ (mol %) ^[a]	pK_a X-BDC ^[b]
1	UiO-66-NH ₂ -F	43.1	56.9	2.86
2	UiO-66-NH ₂ -Cl	46.9	53.1	2.45
3	UiO-66-NH ₂ -Br	47.2	52.8	2.44

^[a] Calculated by peak area of NH₂-BDC to X-BDC linkers (X = F, Cl, Br)

^[b] pK_a values are obtained from SciFinder database.

The presence of multi-functionalities in the Zr-MOFs was also confirmed by DRIFTS (Fig. 6). The presence of amino group in all samples was clearly evident by the vibrations at ~ 3380 and $\sim 3510\text{ cm}^{-1}$, corresponding to the aromatic N-H stretching modes.³⁰ The presence of the halogen functional groups in UiO-66-NH₂-X (X= F, Cl, Br) is indirectly supported by the vibration at the $1000 - 1150\text{ cm}^{-1}$ region. This vibration corresponds to the enhanced in-plane C-H bending mode of the aromatic ring with substituted halogen groups.³⁰

Fig.6. DRIFTS spectrum of as-synthesized Zr-MOFs. (a) UiO-66-NH₂, (b) UiO-66-NH₂-F, (c) UiO-66-NH₂-Cl, (d) UiO-66-NH₂-Br.

Each Zr-MOFs show a strong absorbance peak circa 420 nm that is within the visible light absorbance spectrum (Fig. 6). This absorbance is due to the presence of amino group on the benzene ring that acts as an auxochromic and bathochromic group.³¹ The lone pair of electrons on the amino group donates electron density to the lowest unoccupied molecular orbital (LUMO) of the benzene ring (an anti-bonding orbital).³² This significantly shifts the highest occupied molecular orbital (HOMO) to a higher energy, which causes the decrease in band gap energy, E_g of the linker. Since the optical response of MOFs is ligand-to-metal charge transfer (LCMT) in character, the band gap shift of the linker influence the optical response of the MOF.^{33,34} The band gap of all the catalysts was calculated based on the formula $E_g = 1240/\lambda$. All Zr-MOFs show a similar band gap of 2.75 eV with similar peak intensity (Figure 7). As predicted by Hendon and coworkers,³⁴ introduction of strong electron-donating functional group such as amine will significantly reduce the band gap of the MOFs. Considering that aromatic halide can either be weakly electron-withdrawing or weak electron-donating, the overall effects in the mixed-linker Zr-MOFs is imperceptible and couldn't be resolved by our instrument.

Fig. 7. UV-visible diffuse reflectance spectra of Zr-MOFs. (aqua) UiO-66-NH₂, (blue) UiO-66-NH₂-F, (red) UiO-66-NH₂-Cl, (black) UiO-66-NH₂-Br.

The visible light photocatalytic activity of these Zr-MOFs was evaluated in benzyl alcohol oxidation utilizing a 26 W helical light bulb as the visible light source. The spectrum of the light source was measured (Fig. 8). The irradiation peaks from 400 nm to 700 nm are within the visible-light region. All the catalysts showed high selectivity towards benzaldehyde (>99%), no over-oxidized product was observed (Entries 4-8). In the absence of either the catalysts (entry 1) or the visible light (entry 9), less than 1% conversion was observed for the benzyl alcohol oxidation. Control experiments performed with UiO-66 (Table 2, Entry 2) and UiO-66-F (Table 2, Entry 3) in the presence of visible light showed no significant activity, indicating the importance of NH₂-BDC linkers as visible light antennae.

Table 2: Benzyl alcohol oxidation catalyzed by Zr-MOFs.^[a]

Entry	Catalyst	MOF ^[b] (mmol)	Conv. ^[c] (%)	TOF ^[e] ($\mu\text{mol min}^{-1} \text{g}^{-1}$)
1	Blank	-	<1	-
2	UiO-66	0.10	<1	-
3	UiO-66-F	0.10	<1	-
4	UiO-66-NH ₂	0.10	18.4	140
5	UiO-66-NH ₂ -H	0.10	11.7	89
6	UiO-66-NH ₂ -F	0.10	53.9	410
7	UiO-66-NH ₂ -Cl	0.10	38.2	290
8	UiO-66-NH ₂ -Br	0.10	43.4	330
9 ^[d]	UiO-66-NH ₂ -Br	0.10	<1	-

^[a] Reaction conditions: 0.25 mmol Benzyl alcohol, 0.1 mmol mesitylene in 3 mL toluene, 0.1 MPa O₂, heated at 80 °C for 24 h, irradiated with 26 W helical light bulb.

^[b] Based on Zr content.

^[c] Conversion as determined by GC using mesitylene as the internal standard. The selectivity to benzaldehyde is > 99%.

^[d] Reaction was performed in the absence of light.

^[e] Average turnover frequencies.

The conversion of benzyl alcohol using UiO-66-NH₂ (Table 2, Entry 4) as the catalyst is 18.4% in 24 hours. When the concentration of NH₂-BDC linkers was reduced by half as in UiO-66-NH₂-H (which only contains 45% NH₂-BDC, the remaining 55% of the linker is H-BDC), the conversion of benzyl alcohol decreased by almost half to 11.7% (Table 2, Entry 5). Considering the amount of Zr is the same in both cases (Table 2, Entry 4-5), the decreased conversion in UiO-66-NH₂-H indicates NH₂-BDC plays an important role in the visible light photo-excitation of electrons. Electron paramagnetic resonance (EPR) studies done by Long et. al¹⁶ indicated that upon visible light irradiation, the electrons from the HOMO (O, C and N 2p orbitals) of the amine-functionalized Zr-MOFs were excited and transferred to the O₂ molecules absorbed on the Zr³⁺ sites to form •O₂⁻ radicals. The •O₂⁻ radicals could further react with the benzylic cations that form upon reaction of benzyl alcohols with the photo-generated holes on the amino groups on the BDC linkers.

Fig. 8. Spectrum of the 26W helical light bulb used in the photocatalytic reaction.

To improve the catalytic activity of Zr-MOFs in the oxidation of benzyl alcohol, we introduced secondary linker during the synthesis of Zr-MOFs as depicted in Scheme 1. Noteworthy, in all these mixed-linker UiO-66 MOFs, is that the locations of the different linkers are randomly allocated because the Zr-MOFs are solid-solutions.³⁵ However, all the secondary linkers introduced into these Zr-MOFs do not absorb visible light. These Zr-MOF catalysts with mixed linkers show marked increase in the conversion of benzyl alcohol as noted in Table 2 (Entry 6-8).

Upon the replacement of H-BDC linkers with halogenated linkers (X-BDC, X=F, Cl, Br), the benzyl alcohol oxidation activity of the Zr-MOFs showed a four- to five-fold enhancement in comparison to UiO-66-NH₂-H. This could be due to the stabilization of the $\bullet\text{O}_2^-$ radical on the Zr^{3+} by the halogenated linkers, which decreases the recombination rate of the photogenerated electrons and holes. This enhancement in catalytic activity could also be related to the preferential interaction of the halogen groups with benzyl alcohol molecules that drives the equilibrium of the reaction to benzaldehyde. Molecular modeling studies carried out by Vermoortele et al. showed that different linkers with different electronic properties incorporated into Zr-MOFs could stabilize the reactants and intermediates, which led to the high conversion in the cyclization of citronellal.²⁵

4. Conclusion

In conclusion, we successfully developed mixed-linker Zr-MOF photocatalysts with enhanced activity in benzyl alcohol oxidation. The crystallinity of the as-synthesized Zr-MOFs which is isorecticular to UiO-66 was confirmed by powder X-ray diffraction. All the Zr-MOFs have high surface area and porosity. The surface area decreases as the size of the functional group increases. EDX analysis indicates that a single UiO-66-NH₂-F crystal contained both N and F atoms which indicates the presence of both NH₂-BDC and F-BDC linkers in a single Zr-MOF crystal. This excludes the possibility that the as-synthesized Zr-MOFs are physical mixture. The NMR studies of the digested Zr-MOFs show that the composition of the linkers is close to 1:1 molar ratio. The presence of different functional groups in the Zr-MOFs was further confirmed by diffuse reflectance infrared spectroscopy analysis through the specific vibration of each functional group. Partial substitution of the primary NH₂-BDC by electron-withdrawing halogenated BDC linkers enhanced the photocatalytic activity of the Zr-MOFs. We demonstrated that using mixed linkers with different functionalities to facilitate the design of efficient MOF catalysts is a promising direction. Further studies to understand the enhanced conversion with isorecticular UiO-66 MOFs of mixed linkers and to further improve their performance are underway.

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