# Supporting Information for:

# The Role of Leached Zr in the Photocatalytic Reduction of CO<sub>2</sub> to Formate by Derivatives of UiO-66 Metal Organic Frameworks

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# **1. Reagents and General Considerations**

All chemicals were used as received without further purification unless indicated. Polyvinylpyrrolidone (PVP, average  $M_w \sim 55,000$ ), terephthalic acid (98%, 1.4benzenedicarboxylic acid, BDC), 2-aminoterephthalic acid (99%, NH2-BDC) and sodium formate (99.9%) were purchased from Sigma-Aldrich. 2-bromoterephthalic acid (97%) was purchased from Alfa Aesar. Monosodium 2-sulfoterephthalic acid (98%, SO<sub>3</sub>Na-BDC) was purchased from TCI America. 2-methylterephthalonitrile (97%) was purchased from Ark Pharm. Zirconium tetrachloride (99.5%, ZrCl<sub>4</sub>) was purchased from Oakwood Chemicals. A 1000 ppm Zr standard was purchased from Inorganic Ventures to construct a calibration curve. ACS reagent grade N, N'-dimethylformamide (DMF), N, N'-dimethylacetamide (DMA), concentrated hydrochloric acid (HCl, 36-38%), formic acid, glacial acetic acid, hydrofluoric acid (48 wt% in water, HF), methanol (MeOH) and 190 proof ethanol (EtOH) were obtained from Fischer Chemicals. Hexadeutero dimethyl sulfoxide (99.9%, DMSO-d<sub>6</sub>) was purchased from Cambridge Isotope Laboratories. Dry acetonitrile (MeCN, 9.0 ppm water content, calculated from Karl Fisher titration) was obtained from a solvent system installed by Pure Process Chemicals, LLC. A carbon dioxide (CO<sub>2</sub>, 99.9%, 10 ppm water) tank was used in all experiments. 2-hydroxyterephthalic acid<sup>1</sup> (OH-BDC) and 2,5dimercapto-1,4-benzenedicarboxylic acid<sup>2-4</sup> ((SH)<sub>2</sub>-BDC) and 2-methylterephthalic acid<sup>5</sup> (CH<sub>3</sub>-BDC) were synthesized as described previously. Triethylamine (TEA) was dried over potassium hydroxide (KOH), distilled under vacuum, and stored in a Schlenk tube in the glovebox. Triethanolamine (TEOA) and diethylamine (DEA) were distilled under vacuum and stored in a Schlenk tube in the glovebox.

Glassware was oven-dried for 24 hours prior to use. Unless otherwise noted, all the MOFs were synthesized under air and they were synthesized in the dark for UiO-66-NH<sub>2</sub>/SO<sub>3</sub>H/(SH)<sub>2</sub> by wrapping the round bottom flask with an aluminum (Al) foil. They were also stored in an amber vial in air for further use. A nitrogen filled glovebox was used for air-sensitive procedures.

# 2. Physical Measurements

Powder X-ray diffractions (PXRD) were taken using Bruker AXS D8 Advance X-ray powder diffractometer equipped with Bruker NaI(Tl) scintillation detector. Samples were scanned at 40 kV and 40 mA, using Cu K $\alpha$  radiation ( $\lambda = 1.54$ ), a step size of  $2\theta = 0.02^{\circ}$  (1 s/step) over a  $2\theta$  range of 5 to 40°. Zero-background discs were used to minimize background scattering. PXRD diffraction patterns were processed using the Bruker Diffrac Plus EVA software.

The TGA analysis was performed on a Hi-Res 2950 TGA V5.3C. About 10 mg of activated MOF samples were placed on alumina pans and heated at a rate of 10 °C/min from 25-800 °C under 100 mL/min nitrogen flow.

The SEM imaging was recorded on samples loaded on a carbon tape and coated with Au/Pd with a thickness of 5 nm to improve with the electronic conductivity as well as beam damage on FEI Quanta 600 FEG SEM and Zeiss FIB-SEM instruments.

An iCAP 6300 Duo ICP-OES from Thermo Scientific was used to quantify leaching of zirconium (Zr) metals from the MOFs into the organic phase. After catalysis, an aliquot of the supernatant solution was filtered through a plug of celite and 100  $\mu$ L of the sample was diluted up to 10 mL with de-ionized water and used for subsequent analyses. A calibration curve (**Figure S1**) was obtained by using various dilution of a 1000 ppm Zr standard in aqueous solution.



Figure S1. Calibration curve for concentration of the Zr.

All <sup>1</sup>H NMR spectra were recorded on a Varian Unity-class 300 MHz spectrometer and referenced with respect to the respective deuterated solvents. All spectral analysis was done using MestReNova 14.1.0 software.

Formate production was quantified using a Thermo Scientific Dionex Integrion, equipped with a Dionex Ionpac AS23 (4×250 mm) column. A combination of 4.5 mM sodium carbonate and 0.8 mM sodium bicarbonate solution in 18 m $\Omega$  water was used as the eluent. After the reaction, an aliquot of the suspension was passed through a plug of celite and 0.5 – 1 mL sample was injected to quantify formate. A calibration curve (**Figure S2**) was constructed by injecting 1 -200 ppm of aqueous sodium formate solution into the instrument.



**Figure S2**. Calibration curve for formate (HCOO<sup>-</sup>). S = Siemens, measures the ionic conductivity of the formate ions.

#### 3. Synthesis of MOFs

All the MOFs (except PVP assisted UiO-66-NH<sub>2</sub> and UiO-66-CH<sub>3</sub>) used in this work were synthesized in 5-10 g scale to avoid variations in catalytic performances owing to structural changes from multi-batch syntheses. While there are reported procedures in the literature to synthesize multigram scale UiO-66-H<sup>6</sup> and UiO-66-NH<sub>2</sub><sup>7</sup>, analogous MOFs are not synthesized in such a scale. The table below lists all different modulators probed to synthesize the UiO-66-X (X= OH, SO<sub>3</sub>H and (SH)<sub>2</sub>) MOFs in less than 500 mg scale. The modulator affording better crystallinity as well as overall yield was chosen to carry out the scale-up synthesis.

**Table S1.** List of various modulators probed to synthesize UiO-66-X.(The bolded modulators were chosen for the scale-up syntheses)

MOF	Modulator	Notes		
UiO-66-H	none	Obtained crystalline solids in small scale following a		
		reported synthesis. <sup>8</sup>		
	HCl	Obtained crystalline solids both in small and large scale		
		following a reported synthesis. <sup>9</sup>		
	$H_2O$	Obtained crystalline solids following a reported		
		synthesis.' Successfully employed to make large scale		
		crystalline solids.		
UiO-66-NH <sub>2</sub>	HCl	Obtained crystalline product following a reported method		
		both in small and large scale. <sup>9</sup>		
	$H_2O$	Obtained crystalline product following a reported method $\frac{7}{7}$		
		in large scale.'		
UiO-66-OH	formic acid	Obtained crystalline product following a reported method		
(Figure S4)		in small scale in DMA solvent and $ZrCl_4$ instead of		
		ZrOCl <sub>2</sub> as the precursor. <sup>15</sup>		
	acetic acid	Obtained crystalline product in better yield following a		
		reported method in large scale. Chosen for the scale-up		
	ШО	Synthesis.		
	H <sub>2</sub> O	Obtained amorphous product following a reported method		
	formia acid	III Siliali Scale.		
(100%)	Torrine actu	in small scale in DMA solvent and ZrCl, instead of		
(100%)		In small scale in DiviA solvent and $\Sigma IC14$ instead of $Z_{\rm rOC}$ is the precursor <sup>10</sup> However, the MOE lost its		
(Figure 55)		crystallinity upon activation under vacuum as reported		
		nreviously		
	acetic acid	Obtained very little amorphous product following a		
		reported method. <sup>11</sup>		
H <sub>2</sub> O		Obtained amorphous product following a reported		
		method. <sup>7</sup>		
UiO-66-	acetic acid	Obtained crystalline product that retained its crystallinity		
H0.89SO3H0.11		upon activation under vacuum, following a reported		
(Figure S5)		method. <sup>11</sup> Chosen for the scale-up synthesis.		
UiO-66- (SH)2	acetic acid	Obtained solids of inferior crystallinity following a		
(Figure S6)		reported method. <sup>12</sup>		
	formic acid	Obtained solids of inferior crystallinity following a		
1		reported method in DMA solvent and ZrCl4 instead of		
		$ZrOCl_2$ as the precursor used. <sup>10</sup>		
	H <sub>2</sub> O Obtained solids of inferior crystallinity for			
	reported method. <sup>7</sup>			
HCl Obtained crystalline solids		Obtained crystalline solids following a reported method. <sup>9</sup>		
		Chosen for the scale-up synthesis.		

#### 3.1 Synthesis of UiO-66-H

The synthesis was carried out following the literature procedure reported for UiO-66-NH<sub>2</sub> with the exception that a round bottom flask under refluxing conditions was used instead of a glass reactor in the autoclave.<sup>7</sup> ZrCl<sub>4</sub> (12.1 g, 0.0519 mol) and water (3.00 mL, 0.167 mol) were added to 800 mL N, N'-dimethylformamide (DMF) in a 2 L round bottom flask fitted with a stir bar. The suspension was stirred at 50 °C until ZrCl<sub>4</sub> was fully dissolved. BDC (8.61 g, 0.0518 mol) was added to the solution and stirred until fully dissolved. The solution was further stirred at 500 rpm and held at 120 °C for 24 hours during which a solid precipitated. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed with DMF. The solid was soaked in 300 mL EtOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period the solvent phase was replaced with fresh EtOH each day. Finally, the soaked solid was filtered and subsequently heated to 85 °C for 4 hours, then at 150 °C for 18 hours under vacuum to remove any residual solvent and fully activate the pores. The final yield was 13.8 g (97.2%) with respect to ZrCl<sub>4</sub>, based on the molecular formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OOC-C<sub>6</sub>H<sub>4</sub>-COO)<sub>6</sub>. The TGA and PXRD shown in *Figure S7* corroborate well with the literature report.<sup>8</sup>

#### 3.2 Synthesis of UiO-66-NH<sub>2</sub>

A previously reported literature procedure was followed to synthesize UiO-66-NH<sub>2</sub> with the similar exception of the reaction vessel mentioned above.<sup>7</sup> ZrCl<sub>4</sub> (12.0 g, 0.0515 mol) and water (3.00 mL, 0.167 mol) were added to 800 mL DMF in a 2 L round bottom flask fitted with a stir bar wrapped in foil. The suspension was stirred at 50 °C until ZrCl<sub>4</sub> was fully dissolved. NH<sub>2</sub>-BDC (9.43 g, 0.0521 mol) was added to the solution and stirred until fully dissolved. The solution was further stirred at 500 rpm and held at 120 °C for 24 hours during which a pale-yellow solid was formed. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed with DMF. The solid was soaked in 300 mL EtOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period the solvent phase was replaced with fresh EtOH each day. Finally, the soaked solid was filtered and subsequently heated to 85 °C for 4 hours, then at 150 °C for 18 hours under vacuum to remove any residual solvent and fully activate the pores. The final yield was 12.0 g (79.5%) with respect to ZrCl<sub>4</sub>, based on the molecular formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OOC-C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)-COO)<sub>6</sub>. The MOF was stored in an amber vial in air for further use. The TGA and PXRD shown in *Figure S8* corroborate well with the literature report.<sup>7</sup>

#### 3.2.1 UiO-66-NH<sub>2</sub> of various particle size

A PVP-assisted synthesis reported previously in the literature was followed to systematically tune the particle size of UiO-66-NH<sub>2</sub>.<sup>13</sup> However, this method was not reproducible in affording the same particle size in multiple runs with the same amount of PVP. Hence, three trials affording uniform distribution of a single particle size (observed by SEM imaging) were chosen even though those trials were not reproducible. The scale used to synthesize these three categories of MOF was twice what was reported previously.

8.5 *mM PVP UiO-66-NH*<sub>2</sub>: NH<sub>2</sub>-BDC (0.218 g, 1.20 mmol), TEA (20.0 μL, 0.144 mmol), acetic acid (40.0 mL, 0.720 mol), and a 60.0 mM ZrCl<sub>4</sub> (0.279 g, 1.20 mmol) solution in DMF were

added sequentially to a 260 mL DMF solution containing PVP (0.284 g, 2.55 mmol) in a 1 L round bottom flask fitted with a stir bar wrapped in foil. The final concentration of PVP was 8.5 mM in 300 mL DMF. The resulting suspension was then heated at 120 °C under 600 rpm stirring. After one minute, the stirring was stopped, and the mixture was allowed to react statically at 120 °C for 8 hours. Afterwards, the yellowish solid was filtered through 0.45 micron filter paper and washed with DMF and further soaked in 50 mL MeOH over 3 days. During this period, the solvent phase was replaced with fresh MeOH each day. Finally, the soaked solid was filtered and subsequently heated under vacuum at 120 °C overnight. The final yield was 0.118 g (33.5%) based on ZrCl4.

4.25 mM PVP UiO-66-NH<sub>2</sub>: An analogous procedure to that described above was followed with the final concentration of PVP of 4.25 mM in 300 mL DMF. The final yields were 0.210 g (59.6%) based on ZrCl<sub>4</sub>.

0 mM PVP UiO-66-NH<sub>2</sub>: An analogous procedure to that described above was followed with the final concentration of PVP of 0 mM in 300 mL DMF to synthesize UiO-66-NH<sub>2</sub>. The final yields were 0.250 g (70.9%) based on ZrCl<sub>4</sub>.

### 3.3 Synthesis of UiO-66-OH

ZrCl<sub>4</sub> (7.22 g, 0.031 mol) was added to 540 mL DMF and acetic acid (60.0 mL, 1.05 mol) in a 2 L round bottom flask fitted with a stir bar. The suspension was stirred at 50 °C until the ZrCl<sub>4</sub> was fully dissolved. To help in dissolution, the mixture was further sonicated. Afterwards, OH-BDC (5.53 g, 0.030 mol) was added to the solution and stirred until fully dissolved. The solution was further stirred at 500 rpm and held at 120 °C for 24 hours during which a solid precipitated. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed with DMF. Then it was soaked in 300 mL EtOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period, the solvent phase was replaced with fresh EtOH each day. Finally, the soaked solid was filtered and subsequently heated to 120 °C for 3 hours under vacuum to remove any residual solvent and fully activate the pores. The final yield was 9.00 g (99.0%) with respect to ZrCl<sub>4</sub>, based on the molecular formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OOC-C<sub>6</sub>H<sub>3</sub>(OH)-COO)<sub>6</sub>. The TGA and PXRD shown in *Figure S12* corroborate well with the literature report.<sup>9</sup>

### 3.4 Synthesis of UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub>

A ~130 fold scale up was carried out following a previously reported method in literature.<sup>11</sup> ZrCl<sub>4</sub> (7.05 g, 0.030 mol) was added to 540 mL N,N-dimethylformamide (DMF), and 60.0 mL (1.05 mol) acetic acid in a 2 L round bottom flask fitted with a stir bar wrapped in foil. The suspension was stirred at 50 °C until the ZrCl<sub>4</sub> was fully dissolved. To help in dissolution the mixture was further sonicated for 20 minutes. Afterwards, BDC (4.17 g, 0.0251 mol) and SO<sub>3</sub>Na-BDC (1.42 g, 0.00529 mol) were added to the solution and stirred until fully dissolved. The solution was further stirred at 500 rpm and held at 120 °C for 24 hours during which a very pale-yellow solid was formed. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed with DMF. Then it was soaked in 300 mL MeOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period, the solvent phase was replaced with fresh MeOH each day. Finally, the soaked solid was filtered and subsequently heated to 120 °C for 3 hours under vacuum to remove any residual solvent and fully activate the pores.

To quantify the % of SO<sub>3</sub>H functionality incorporation in the framework, 10 mg of the activated MOF was digested in 570  $\mu$ L of DMSO-d<sub>6</sub> and 30 $\mu$ L of 48 wt% HF (aq) and sonicated for 10 min to ensure complete dissolution before measuring <sup>1</sup>H NMR spectrum. The relative ratio of areas under the two sets of peaks (**Figure S3**) corresponding to the BDC and SO<sub>3</sub>H-BDC was 8.23:1, i.e., ~11% incorporation. The TGA and PXRD shown in *Figure S13* corroborate well with the literature report.<sup>11</sup>

Hence, the final yield was calculated to be 8.13 g (93.9%) with respect to ZrCl<sub>4</sub>, based on the molecular formula of  $Zr_6O_4(OH)_4(SO_3H-BDC)_{0.66}(BDC)_{5.34}$ . The MOF was stored in an amber vial in air for further use.



**Figure S3**. <sup>1</sup>H NMR spectrum (300 MHz, DMSO-d<sub>6</sub>) showing the linkers in the digested UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub>.

#### 3.5 Synthesis of UiO-66-(SH)<sub>2</sub>

ZrCl<sub>4</sub> (4.01 g, 16.9 mmol) was added to 31.0 mL 36.5-38% concentrated HCl and 220 mL DMF in a 1 L round bottom flask fitted with a stir bar and wrapped in foil. The suspension was sonicated for 30 min for better dispersion. Afterwards, (SH)<sub>2</sub>-BDC (4.74 g, 19.9 mmol) was added to the solution and stirred until fully dissolved. The solution was heated 80 °C for 24 hours with no stirring during which a pale orange solid precipitated at the bottom of the flask. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed

with DMF. Then it was soaked in 300 mL EtOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period the solvent phase was replaced with fresh EtOH each day. Finally, the soaked solid was filtered and subsequently heated to 120 °C for 3 hours under vacuum to remove any residual solvent and fully activate the pores. The final yield was 5.61 g (95.1%) with respect to ZrCl4, based on the molecular formula of  $Zr_6O_4(OH)_4(OOC-C_6H_3(SH)_2-COO)_6$ . The MOF was stored in an amber vial in air for further use. The TGA and PXRD shown in *Figure S13* corroborate well with the literature report.<sup>12</sup>

#### 3.6 Synthesis of UiO-66-CH<sub>3</sub>

A previously reported procedure for synthesizing UiO-66-NH<sub>2</sub> was followed to make UiO-66-CH<sub>3</sub>.<sup>9</sup> ZrCl<sub>4</sub> (0.125 g, 0.536 mmol), 15 mL DMF and 1 mL concentrated HCl were combined in a 20 mL scintillation vial and sonicated for 20 minutes. Solid BDC-CH<sub>3</sub> (0.135 g, 0.746 mmol) was then added and the vial was capped and heated at 80 °C overnight with no stirring during which a white solid precipitated at the bottom of the flask. After cooling the suspension to room temperature, the solid was filtered through 0.45 micron filter paper and washed with DMF. It was then soaked in 50 mL EtOH for 3 days to exchange the DMF trapped inside the pores of the solid. During this period the solvent phase was replaced with fresh EtOH each day. Finally, the soaked solid was filtered and subsequently heated to 100 °C for 3 hours under vacuum to remove any residual solvent and fully activate the pores. The final yield was 0.111 g (71.0%) with respect to ZrCl<sub>4</sub>, based on the molecular formula of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OOC-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)-COO)<sub>6</sub>. The PXRD shown below corroborate well with the literature report.<sup>10</sup>

### 4. Photocatalytic Conditions

For photoreduction studies, a 66477-200HXF-R1 lamp system / LIK control from Newport was used. This provided constant light intensity over longer period of experimental time. It was attached to a Xe Arc 200 W lamp with no filter and the lamp was functional over UV-vis region. Before photolysis experiments, the Xe 200 W lamp was turned on and allowed to equilibrate for 30 minutes. The beam was focused to a ~3 cm circle ~16 cm away from the lamp.

Typically, ~25 mg of MOF was loaded into an oven-dried custom-made 44 mL Schlenk tube fitted with a Teflon valve under ambient air. 15 mL of a 5:1 MeCN:amine solution was then added to the MOF in air. The tube was sealed with the Teflon valve and put under N<sub>2</sub> in the Schlenk line briefly for sparging. The MOF suspension was then degassed by three freeze-pump-thaw cycles in the Schlenk line and backfilled with CO<sub>2</sub> for 20 minutes while stirring to ensure complete saturation of the solution. The Schlenk tube was next placed ~10 cm away from the lamp on a stir plate and stirred at 800 rpm for a set amount of time. To compare the effect of UV region light on the photocatalysis, a few trials with the UiO-66-NH<sub>2</sub> and UiO-66-(SH)<sub>2</sub> MOFs were carried out with a 320±5 nm bandpass filter (20CGA-320 from Newport), fitted onto the Xe lamp (**Table S6-7**). The formate generated during the photocatalysis was quantified using IC.

# 5. Leaching Study of UiO-66-NH<sub>2</sub> in TEOA and DEA

After the allotted time of photolysis of ~ 25 mg MOFs in a degassed 5:1 MeCN:amine solution, the 44 mL Schlenk tube, loaded with catalytic solution, was taken into the glovebox. The solution was centrifuged in 1.5 mL batches to separate the MOF from the supernatant solution. MOFs settled at the bottom of the centrifuged tubes were separated from the supernatant solution by decanting. These MOFs were further washed two times with fresh MeCN and then collected all together to make a suspension in a fresh 15 mL 5:1 MeCN:amine solution was preserved for checking formate production and leaching analyses. The rest of the solution was passed through a plug of celite to prevent any lingering solid particle going into the solution into an oven-dried, fresh 44 mL quartz Schlenk tube. These two quartz Schlenk tubes were capped with Teflon valve under glove-box atmosphere and taken outside. These tubes were next subjected to three freeze-pump-thaw cycles followed by backfilling with CO<sub>2</sub>. Finally, the suspensions were irradiated again for 24 hours before repeating the same separation procedure one more time.

## 6. Recycling Study of MOFs

To check the recyclability, ~ 25 mg of UiO-66-NH<sub>2</sub> and UiO-66-(SH)<sub>2</sub> MOFs were irradiated in 15 mL 5:1 MeCN:amine solutions for 3 hours. Afterwards, the formate production was checked following the method previously mentioned. At this point, the MOFs were filtered under air and washed with ~ 30 mL of fresh MeCN and air dried for 30 min. Next, the MOFs were combined with fresh amine solution and photolyzed further for 3 hours. Results are described in **Table S5**.

# 7. Time-Course Study of MOFs

~25 mg of MOF sample was loaded in 44 mL quartz Schlenk tube fitted with a stir bar and 15 mL of a 5:1 MeCN: amine solution was added. Afterwards, the suspension was subjected to three freeze-pump-thaw cycles followed by backfilling with  $CO_2$  for 20 minutes to ensure complete saturation. The tube was then irradiated for 3 hours at 800 rpm stirring rate. Next the aliquots at different time-points were taken out in 2 different pathways to test for formate generation, as explained below-

i. After allotted time of photolysis, the Schlenk tube containing MOF suspension was brought into the glovebox. 1 mL aliquot of the supernatant solution was taken out for IC analysis and replaced with 1 mL fresh 5:1 MeCN:amine solution. The suspension was taken outside the box and sparged with CO<sub>2</sub> for 20 min for complete saturation and then photolyzed further for next 3 hours before repeating the same procedure.

This prompted us to modify our method that will also reduce the time of work-up of the solution on between photolysis (associated with taking it inside the glovebox, opening it under  $N_2$ atmosphere and then re-saturating with CO<sub>2</sub>) and hence will be more time efficient. All results discussed make use of method ii.

ii. To overcome the above-mentioned issues, the Schlenk tube was not moved away from the lamp at any time during the modified procedure. In a typical experiment, after every

3 hours-time point, the outlet of the Schlenk tube was sparged with CO<sub>2</sub> by fitting a CO<sub>2</sub> filled balloon through a septum. The stirring was stopped 10 minutes before taking an aliquot out to let the MOFs settle. However, the MOFs in DEA and UiO-66-(SH)<sub>2</sub> MOF in both TEOA and DEA did not settle completely and remained dispersed in solution (owing to leaching). Next, under CO<sub>2</sub> atmosphere, the Teflon valve was briefly opened to take out 1 mL aliquot of the supernatant solution/suspension using a long needle. The valve was closed within 30 seconds after opening and stirring was resumed.

Discrepancies between formate produced at the 12 hours timepoint and in independent 12 hours runs may be due to the removal of leached material at every time point, and the inadvertent removal of solid MOF during the time-course analysis, as no centrifugation was done.

## 8. Hammett Analysis

Initial rate of formate production  $(k_x)$  after 3 hours (from the time-course study) for UiO-66-X (X=NH<sub>2</sub>, OH, SO<sub>3</sub>H, (SH)<sub>2</sub> and CH<sub>3</sub>) was calculated in both TEOA and DEA. The rate of formate production by UiO-66-H (k<sub>H</sub>) was used further to calculate  $k_x/k_H$ . Finally, the Hammett plots in TEOA and DEA were obtained by plotting Hammett parameters for each substituent, taken from ref <sup>14</sup> and log( $k_x/k_H$ ).



Figure S4. Hammett analysis of UiO-66-X MOFs in TEOA.



Figure S5. Hammett analysis of UiO-66-X MOFs in DEA.

# 9. PXRD Measurements



Figure S6. PXRD of as-synthesized UiO-66-OH with various modulators (water, formic acid, acetic acid).



**Figure S7**. PXRD of as-synthesized UiO-66-SO<sub>3</sub>H with various modulators; (above) PXRD of the mixed linker UiO-66-SO<sub>3</sub>H; (below) PXRD of pure UiO-66-SO<sub>3</sub>H.



Figure S8. PXRD of as-synthesized UiO-66-(SH)<sub>2</sub> with various modulators.



Figure S9. PXRD of activated UiO-66-H before and after catalysis.



Figure S10. PXRD of activated UiO-66-NH<sub>2</sub> before and after catalysis.



Figure S11. PXRD of activated 170-UiO-66-NH<sub>2</sub> before and after catalysis.



Figure S12. PXRD of activated 720-UiO-66-NH<sub>2</sub> before and after catalysis.



Figure S13. PXRD of activated 650-UiO-66-NH<sub>2</sub> before and after catalysis.



Figure S14. PXRD of activated UiO-66-OH before and after catalysis.



Figure S15. PXRD of activated UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub> before and after catalysis.



Figure 16. PXRD of activated UiO-66-(SH)<sub>2</sub> before and after catalysis.



Figure S17. PXRD of activated UiO-66-CH<sub>3</sub>.

# **10.TGA Analysis**



Figure S18. TGA analysis of UiO-66-X.



Figure S19. SEM image of UiO-66-H before catalysis. The red bar corresponds to the size indicated.



Figure S20. SEM image of UiO-66-H after 12 hours of catalysis in TEOA. The red bar corresponds to the size indicated.

# After catalysis in DEA

**Figure S21**. SEM image of UiO-66-H after 12 hours of catalysis in DEA. The red bar corresponds to the size indicated.



Figure S22. SEM image of UiO-66-NH $_2$  before catalysis. The red bar corresponds to the size indicated.

# After catalysis in TEOA



**Figure S23**. SEM image of UiO-66-NH<sub>2</sub> after 12 hours of catalysis in TEOA. The red bar corresponds to the size indicated.



Figure S24. SEM image of UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. The red bar corresponds to the size indicated.



Figure S25. SEM image of UiO-66-OH before catalysis. The red bar corresponds to the size indicated.



Figure S26. SEM image of UiO-66-OH after 12 hours of catalysis in TEOA. The red bar corresponds to the size indicated.

# HV HFW 5/25/2017 WD mag HI spot 5 µm 20.00 kV 25.6 µm 4:20:51 PM 10.8 mm 5 000 x 3.0 OH-DEA NOF

**Figure S27.** SEM image of UiO-66-OH after 12 hours of catalysis in DEA. The red bar corresponds to the size indicated.



**Figure S28**. SEM image of UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub> before catalysis. The red bar corresponds to the size indicated.



**Figure S29**. SEM image of UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub> after 12 hours of catalysis in TEOA. The red bar corresponds to the size indicated.



Figure S30. SEM image of UiO-66- $H_{0.89}$ SO<sub>3</sub> $H_{0.11}$  after 12 hours of catalysis in DEA. The red bar corresponds to the size indicated.



**Figure S31**. SEM image of UiO-66-(SH)<sub>2</sub> before catalysis. The red bar corresponds to the size indicated.



Figure S32. SEM image of UiO-66- $(SH)_2$  after 12 hours of catalysis in TEOA. The red bar corresponds to the size indicated.



Figure S33. SEM image of UiO-66- $(SH)_2$  after 12 hours of catalysis in DEA. The red bar corresponds to the size indicated.



**Figure S34**. SEM image of 170-UiO-66-NH<sub>2</sub> before catalysis. The edges of the octahedron are considered as their particle dimension. The blue bar corresponds to the size indicated.



**Figure S35**. SEM image of 170-UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. The edges of the octahedron, shown by the blue bar, are considered as their particle dimension.



**Figure S36**. SEM image of 720-UiO-66-NH<sub>2</sub> before catalysis. The edges of the octahedron, shown by the blue bar, are considered as their particle dimension.

# 4.25 mM PVP after catalysis in DEA



**Figure S37**. SEM image of 720-UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. The edges of the octahedron, shown by the blue bar, are considered as their particle dimension.



**Figure S38**. SEM image of 600-UiO-66-NH<sub>2</sub> before catalysis. The edges of the octahedron, shown by the blue bar, are considered as their particle dimension.

8.5 mM PVP after catalysis in DEA 🎽



**Figure S39**. SEM image of 600-UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. The edges of the octahedron, shown by the blue bar, are considered as their particle dimension.

MOF	Shape	Particle Dimension, $x (nm)^a$	Surface Area (nm <sup>2</sup> ) <sup>b</sup> (propagated	Volume (nm <sup>3</sup> ) <sup>c</sup> (propagated error)	Zr% in the surface volume <sup>d</sup>
	1	(error)	$\frac{\mathbf{error}}{725 \cdot 10^3}$	420105	2.20
U10-66-H	cube	35. ×10 <sup>4</sup>	/35×10 <sup>3</sup>	428×10 <sup>3</sup>	3.39
		(10)	(0.0326)	(0.0495)	
UiO-66-NH <sub>2</sub>	sphere	50. (5.0)	$78.5 \times 10^2$	$65.4 \times 10^3$	22.1
			(0.114)	(0.173)	
170-UiO-66-	octahedron	$17.\times10^{1}(10)$	$9.94 \times 10^{2}$	$23.2 \times 10^{5}$	6.89
NH <sub>2</sub>			(0.0671)	(0.102)	
720-UiO-66-	octahedron	72.×10 <sup>1</sup> (30)	$17.8 \times 10^{5}$	17.6×10 <sup>7</sup>	1.26
NH <sub>2</sub>			(0.0475)	(0.0547)	
650-UiO-66-	octahedron	65.×10 <sup>1</sup> (30)	$14.5 \times 10^{5}$	$12.9 \times 10^{7}$	1.84
NH <sub>2</sub>			(0.0527)	(0.0799)	
UiO-66-OH	sphere	40.(10)	$50.3 \times 10^{2}$	$33.5 \times 10^3$	27.1
			(0.285)	(0.433)	
UiO-66-	octahedron	$17.\times10^{1}(20)$	994×10 <sup>2</sup>	$23.2 \times 10^{5}$	6.89
H0.89SO3H0.11			(0.134)	(0.204)	
UiO-66-	sphere	60. (10)	$113 \times 10^{2}$	$11.3 \times 10^{4}$	17.4
$(SH)_2$			(0.190)	(0.289)	

**Table S2.** Particle size, surface area surface volume and %Zr present in the surface volume of UiO-66-X.

<sup>a</sup>Dimensions are defined by the edge of the cube and octahdron shaped MOFs, and diameter of the spherical ones, as recorded by SEM imaging. <sup>b</sup>Surface areas are defined as  $4\pi(0.5x)^2$  for spheres,  $6x^2$  for cubes and  $2\sqrt{3x^2}$  for octahedrons. <sup>c</sup>Volumes are defined by  $4/3\pi x^3$  for spheres,  $x^3$  for cubes and  $\sqrt{2/3x^3}$  for octahedrons. <sup>d</sup>The length of one linker connected to one node in UiO-66-H MOF crystal is 20Å.<sup>15</sup> The same is approximated for the other UiO-66-X MOFs as well. The % Zr present in the surface volume is calculated using (volume of the MOF- Volume of the inner core)/volume of the MOF\*100%. For UiO-66-H, % Zr =  $\frac{350^3 - 346^3}{350^3} \times 100\%$ .

# 12. Quantification of Defects in UiO-66-X MOFs

The quantification of defects in UiO-66-X was done by a previously reported method<sup>16</sup> by loading the defect sites with acetic acid (modulator) and quantifying the linker: modulator ratio. A higher value will indicate more defects present in the framework.

*UiO-66-H*: UiO-66-H was prepared by using water as the modulator. Therefore, the defect sites in these MOFs had free hydroxo moieties. 20.3 mg of this MOF was soaked in 1 mL 8% acetic acid solution in DMF at room temperature for 24 hours. Afterwards, the solid was filtered and soaked in DMF for 2 days. During this period, the solid was centrifuged, and the supernatant solvent phase was replaced with fresh DMF in every 12 hours. Next, the soaking process was repeated for 2 days with acetone. Finally, the solid was filtered through a 0.45 micron filter paper and washed with acetone. Next, the solid was subjected to drying at 100 °C under vacuum for 30 min before the <sup>1</sup>H NMR analysis.

UiO-66-X ( $X = NH_2$ ,  $(SH)_2$ ): ~ 20 mg of UiO-66-NH<sub>2</sub> and UiO-66-(SH)<sub>2</sub> were treated same way to substitute the defect sites with acetate as described above and subjected to digestion.

UiO-66-X (X = OH,  $SO_3H$ ): The UiO-66-OH and UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub> MOFs were synthesized using acetic acid, and hence the defect sites were already occupied by acetate moieties and so there was no need for linker exchange.

<sup>1</sup>*H* NMR analysis of the digested MOFs: 1 mg of each MOF was added to a solution of 40  $\mu$ L H<sub>2</sub>SO<sub>4</sub> and 700  $\mu$ L of DMSO-d<sub>6</sub> and sonicated for 20 minutes to complete the digestion. The <sup>1</sup>H NMR spectra were recorded and the ratio of the acetic acid to linker to was obtained by the relative integration.



**Figure S40**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>,) of the digested sample of UiO-66-H. \* DMF and acetone are indicated.





**Figure S42**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>,) of the digested sample of UiO-66-OH. \* DMF and **a**cetone are indicated.



**Figure S43**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) of the digested sample of UiO-66-H<sub>0.89</sub>SO<sub>3</sub>H<sub>0.11</sub>. \* DMF and  $\blacktriangle$  acetone are indicated.







hours of catalysis in DEA. \* DMF and  $\blacktriangle$  acetone are indicated.



**Figure S47**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) of the digested sample of 950-PVP UiO-66-NH<sub>2</sub>. \* DMF and  $\blacktriangle$  acetone are indicated.



4.25 mM PVP UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA

**Figure S48**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) of the digested sample of 950-UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. \* DMF and **a** acetone are indicated.



**Figure S49**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) of the digested sample of 650-PVP UiO-66-NH<sub>2</sub>. \* DMF and  $\blacktriangle$  acetone are indicated.



**Figure S50**. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) of the digested sample of 650-UiO-66-NH<sub>2</sub> after 12 hours of catalysis in DEA. \* DMF and **a** acetone are indicated.

**Table S3.** Defect quantification for UiO-66-X. MOF formula obtained from this defect quantification is represented by  $Zr_6O_4(OH)_4L_{(6-0.5x)}A_x$ .

where $x = \frac{6R}{1+0.5R}$ x = acid (A): linker (L) ratio.					
Quantification of	Acid: Linker (R)	x	6-0.5x		
Defects (modulator					
used during MOF					
synthesis)					
UiO-66-H (water)	0.323	1.66	5.17		
UiO-66-NH <sub>2</sub> (water)	0.427	2.28	4.86		
UiO-66-OH (acetic		0.89	5.56		
acid)	0.163				
UiO-66-H0.89SO <sub>3</sub> H0.11		0.99	5.51		
(acetic acid)	0.156				
UiO-66-(SH) <sub>2</sub> (HCl)	0.607	2.77	4.62		

**Table S4.** Defect quantification of UiO-66-NH<sub>2</sub> MOFs of various size before and after 12 hours of photocatalysis in 5:1 MeCN: DEA.

Particle Dimension (nm)	Time of Quantification	Acid: Linker (R)	x	6-0.5x
170	Before catalysis	0.067	0.389	5.81
	After catalysis	0.357	1.82	5.09
650	Before catalysis	0.390	1.96	5.02
	After catalysis	0.553	2.60	4.70
720	Before catalysis	0.180	0.991	5.50
	After catalysis	0.373	1.89	5.06

#### **13.Various Control Experiments**

**Table S4.** Catalysis by UiO-66-X in the dark. Conditions: 25 mg of MOF in 15 mL 5:1 MeCN:amine solution, that was saturated with 0.85 atm  $CO_2$  was stirred in a 44 mL glass Schlenk tube fitted with Teflon valve for 24 hours, wrapped in a foil. Each experiment was performed once. 24 h was chosen to represent an upper-limit to the background, as most experiments were done using 12 h of irradiation.

Amine	MOF	Formate (µmol)
TEOA	UiO-66-H	0.150
	UiO-66-NH <sub>2</sub>	5.14
	UiO-66-OH	0.150
	UiO-66-H0.89SO3H0.11	0.440
	UiO-66- (SH)2	3.67
DEA	UiO-66-H	0
	UiO-66-NH <sub>2</sub>	1.84
	UiO-66-OH	0.150
	UiO-66-H <sub>0.89</sub> SO <sub>3</sub> H <sub>0.11</sub>	2.57
	UiO-66- (SH) <sub>2</sub>	2.20
	170-UiO-66-NH <sub>2</sub>	<sup>a</sup> 2.50
	650-UiO-66-NH <sub>2</sub>	<sup>a</sup> 0.770
	950-UiO-66-NH <sub>2</sub>	<sup>a</sup> 0.867

<sup>a</sup> The reactions were carried out for 12 hours.

**Table S5.** Recycling Studies with MOFs in TEOA. Conditions: 25 mg of MOF in 15 mL 5:1 MeCN:TEOA solution, that was saturated with 0.85 atm CO<sub>2</sub>, was photolyzed in a 44 mL glass Schlenk tube fitted with Teflon valve for 3 hours (1<sup>st</sup> cycle). Then the MOFs were filtered in air and an aliquot of the filtrate was analyzed for formate. The MOF was washed with ~20 mL fresh MeCN and then added to a fresh amine solution, saturated with CO<sub>2</sub> and further photolyzed for another 3 hours (2<sup>nd</sup> cycle).

MOF	Formate (µmol)		
	1 <sup>st</sup> Cycle	2 <sup>nd</sup> Cycle	
UiO-66-NH <sub>2</sub>	8.07	2.93	
UiO-66-(SH)2	13.2	2.90	

**Table S6.** Effect of UV-cut filter on MOFs irradiated with amines. Conditions: 25 mg of MOF in 15 mL 5:1 MeCN:amine solution, that was saturated with 0.85 atm  $CO_2$  was stirred in a 44 mL glass or quartz Schlenk tube fitted with a Teflon valve with or without a 320 nm UV-cut filter, respectively.

MOF	Amine	Filter	Formate (µmol) (error)
UiO-66-NH <sub>2</sub>	DEA <sup>a</sup>	no	26.5 (1.5)
		yes	28.0 (3)
	<b>TEOA</b> <sup>a</sup>	no	7.30 (1.2)
		yes	7.30 (0.1)
UiO-66-	DEA <sup>b</sup>	no	5.80
(SH)2		yes	4.60
	TEOA <sup>a</sup>	no	13.0 (0.3)
		ves	13.1 (0.01)

<sup>a</sup>Photolysis was carried out for 24 hours and two trials were done. <sup>b</sup>Photolysis was carried out for 3 hours and only one trial was done.

**Table S7.** Effect of UV-cut filter on MOFs added to pre-irradiated amines. Conditions: 25 mg of MOF was added to a 15 mL 5:1 MeCN:amine solution, that was pre-irradiated with or without a 320 nm UV-cut filter for 24 hours under degassed condition, in a 44 mL glass Schlenk tube fitted with a Teflon valve. The tube was wrapped with a foil and saturated with 0.85 atm CO<sub>2</sub> and then left for stirring in the dark for another 24 hours.

MOF	Amine	Filter	Formate (µmol) (error)
UiO-66-NH <sub>2</sub>	DEA	no	39.0 (2)
		yes	34.0 (3)
UiO-66- (SH)2	DEA	no	5.40 (1)
		yes	4.40 <sup>a</sup>

<sup>a</sup>The experiment was done once.

**Table S8.** Reactivity of amines in light in the presence or absence of a 320 nm UV filter. Conditions: 15 mL of a 5:1 MeCN: amine solution was taken in a 44 mL Schlenk tube fitted with a Teflon valve and a stir bar. The solution was degassed by three freeze-pump-thaw cycles and saturated with 0.85 atm  $CO_2$  and then left for stirring for 24 hours in front of the lamp in the presence and absence of the 320 nm UV-cut filter. The amount of formate was quantified by IC.

Amine	Filter	Formate (µmol)
TEOA	yes	0.132
	по	0.396
TEA	yes	0.847
	по	239
DEA	yes	0.150
	no	0.100

**Table S9.** Photolysis of ZrCl<sub>4</sub> salt with BDC-NH<sub>2</sub> linker in TEOA and DEA.Conditions: ZrCl<sub>4</sub> (14.6 mg, 0.0626 mmol) and BDC-NH<sub>2</sub> (14.6 mg, 0.0800 mmol) were suspended in 15 mL of a 5:1 MeCN:amine solution in a 44 mL Schlenk tube fitted with a Teflon valve and a stir bar. The solution was degassed by three freeze-pump-thaw cycles and saturated with 0.85 atm CO<sub>2</sub> and then left for stirring for 24 hours in front of the lamp with no filter. The amount of formate was quantified by IC.

Amine	Formate (µmol) <sup>a</sup>
TEOA	2.93
DEA	0.661

<sup>a</sup>The experiment was done once.

#### 13.1 The effect of BDC-(SH)<sub>2</sub> linker on leached UiO-66-OH MOF solution.

To assess the effect of the linker identity on the overall photocatalysis, BDC-(SH)<sub>2</sub> linker was chosen since UiO-66-(SH)<sub>2</sub> was found to be the most effective photocatalyst. UiO-66-OH, on the other hand leached significantly over 24 hours under a typical photocatalytic condition in TEOA. Therefore 25.3 mg, 0.109 mmol of UiO-66-OH was taken in 15 mL of a 5:1 MeCN:TEOA solution in a 44 mL Schlenk tube. After degassing, the suspension was irradiated for 24 hours. Next the tube was taken into the glovebox where the solids were filtered through a plug of celite. A typical photoirradiation of UiO-66-OH MOF in CO<sub>2</sub> over 24 hours showed 2.4% leaching of the Zr metal. However, leaching in this case, in the absence of CO<sub>2</sub>, was found to be 1.48%. To this leached solution 16.9 mg, 0.0734 mmol of BDC-(SH)<sub>2</sub> (70 mol% of the MOF added initially) was added and after saturating the suspension with CO<sub>2</sub>, it was photo-irradiated for another 24 hours before checking for the formate generation.

#### 14. Unsuitability of photolyzing UiO-66-(SH)<sub>2</sub> in aqueous TEOA buffer.

In order to study the correlation of formate generation by UiO-66-(SH)<sub>2</sub> in various pH's, aqueous buffer solutions with TEOA were prepared with pH 7 and 8. However over 12 hours of photolysis

25.3 mg of UiO-66-(SH)<sub>2</sub> completely dissolved in 15 mL of these aq. TEOA solutions. The MOF seemed unstable even when photolyzed in 15 mL 1:1 water:MeCN solution of pH 7 and 8 containing TEOA. The MOFs were found to be stable only when the amount of water:MeCN was limited to 1:14 in a 15 mL buffer solution of pH 8.6 and 9.6.



# **15. Structure-Property Correlations.**

**Figure S51**. Correlation of the bandgap of various linkers<sup>17</sup> with the amount of formate generated with TEOA (grey) and DEA (red) by UiO-66-X MOFs, as shown in the main text (Figure 6).



**Figure S52**. Correlation of the bandgap<sup>18, 19</sup> of UiO-66-X MOFs with the amount of formate generated with TEOA (grey) and DEA (red).



**Figure S53**. Correlation of the dry Brønsted acidity<sup>20</sup> with the amount of formate generated with TEOA (grey) and DEA (red) by UiO-66-X MOFs.



**Figure S54**. Correlation of the wet Brønsted acidity<sup>20</sup> with the amount of formate generated with TEOA (grey) and DEA (red) by UiO-66-X MOFs.



**Figure S55**. Correlation among the crytal size, defects and amount of formate generated by x-UiO-66-NH<sub>2</sub> MOFs, *before* 12 hours of photocatalyses in 5:1 MeCN:DEA.



**Figure S55**. Correlation among the crytal size, defects and amount of formate generated by x-UiO-66-NH<sub>2</sub> MOFs, *after* 12 hours of photocatalyses in 5:1 MeCN:DEA.

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