Robust, Catalytic Metal-Organic Framework with Open 2,2'-Bipyridine Sites

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Supporting Information

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General Methods

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (\(^1\)H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS.

Experimental Procedures

*General.* All bpydc-containing MOFs described were isolated and stored as dried solids. However, upon extended storage (~3 d) without special precautions (e.g. simple storage at ambient conditions) the MOFs began to decompose as gauged by PXRD and SEM.

*Synthesis of UiO-67.* ZrCl\(_4\) (24.5 mg, 0.105 mmol), glacial acetic acid (210 mg, 3.5 mmol), and H\(_2\)bpydc (4,4’-biphenyl-dicarboxylic acid) (26 mg, 0.105 mmol) were placed in a scintillation vial with 4 mL dimethylformamide (DMF). The solids were dispersed via sonication for ~10 mins, followed by incubation at 120 °C for 24 h. After cooling, solids were collected by centrifugation at 6500 rpm for 15 min in a fixed angle rotor, and the solvent was decanted. The solids were washed with DMF (2 × 10 mL), followed by soaking in methanol (MeOH) for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum (yield: 35 mg, 94 % based on Zr).

*Synthesis of UiO-67-bpydc.* ZrCl\(_4\) (24.5 mg, 0.105 mmol), glacial acetic acid (189 mg, 3.15 mmol), and H\(_2\)bpydc (2,2’-bipyridine-5,5’-dicarboxylic acid) (26 mg,
0.105 mmol) were placed in a scintillation vial with 4 mL DMF. The solids were dispersed via sonication for ~10 mins, followed by incubation at 120 °C for 24 h. After cooling, solids were collected by centrifugation and the solvent was decanted. The solids were washed with DMF (2 × 10 mL), followed by soaking in methanol (MeOH) for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum (yield: 33 mg, 88 % based on Zr).

**Synthesis of UiO-67-bpydcₓ/bpdc₁₋ₓ.** Synthesis of mixed UiO-67-bpydcₓ/bpdc₁₋ₓ was synthesized with the same concentration (i.e. 0.105 mmol of ZrCl₄ and 0.105 mmol of the total amount of organic ligands) and condition as UiO-67-bpydc, using an reactant solution with a molar ratio of x:(1-x):1:30 for H₂bpydc/H₂bpdc/ZrCl₄/acetic acid in a scintillation vial with 4 mL DMF (Table S2). The solids were dispersed via sonication for ~10 mins, followed by incubation at 120 °C for 24 h. After cooling, solids were collected by centrifugation and the solvent was decanted. The solids were washed with DMF (2 × 10 mL), followed by soaking in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum (yield: 35 mg, 94 % based on Zr).

**Using PSE to prepare UiO-67-bpydc₀.₃₆/bpdc₀.₆₄.** 25 mg (0.1 mmol) H₂bpydc was dissolved in 2 mL 4 % KOH solution, then titrated with minimal amount of 1 M HCl to pH=8 before adding in 0.5 mL DMF. 36 mg UiO-67 (0.1 mmol eq. of bpdc) was introduced into this solution, followed by incubation at room temperature for 24 h. Then, solids were collected by centrifugation and the solvent was decanted. The solids were washed with copious amount of MeOH (3 x 10 mL), then left to soak in MeOH for 3 d,
and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

**Using PSE to prepare UiO-67-bpydc**. 125 mg (0.5 mmol) H₂bpydc was dissolved in 2 mL 4% KOH solution, then titrated with minimal amount of 1 M HCl to pH=8 before adding in 0.5 mL DMF. 36 mg UiO-67 (0.1 mmol eq. of bpdc) was introduced into this solution, followed by incubation at 85 °C for 24 h. Then, solids were collected by centrifugation and the solvent was decanted. The solids were washed with copious amount of MeOH (3 x 10 mL), then left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

**Metalation with Pd(II) of UiO-67-bpydc**. PdCl₂(CH₃CN)₂ (14 mg, 0.055 mmol) was dissolved in 2 mL acetonitrile. Then UiO-67-bpydc (18 mg, 0.05 mmol equiv. bpydc) was placed into Pd-based solution. The solids were dispersed *via* sonication for ~10 mins, then incubated at 65 °C for 24 hours. After 24 h at 65 °C, the supernatant was decanted by centrifugation and the solids were washed profusely with acetonitrile (3 x 10 mL) and MeOH (4 x 10 mL), until the supernatant was colorless. The solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

**Metalation with Pd(II) of UiO-67-bpydco.5/bpdc0.5**. PdCl₂(CH₃CN)₂ (7 mg, 0.0275 mmol) was dissolved in 2 mL acetonitrile. Then UiO-67-bpydco.5/bpdc0.5 (18 mg, 0.025 mmol equiv. bpydc) was placed into Pd-based solution. The solids were dispersed *via* sonication for ~10 mins, then incubated at 65 °C for 24 hours. After 24 h at 65 °C, the supernatant was decanted by centrifugation and the solids were washed profusely
with acetonitrile (3 × 10 mL) and MeOH (4 × 10 mL), until the supernatant was colorless. The solids were left to soak in MeOH for 3 d, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 d of soaking, the solids were collected via centrifugation and dried under vacuum.

**Suzuki-Miyaura Coupling Reaction Catalyzed by UiO-67-Pdbpydc\(_{0.5}\)/bpdc\(_{0.5}\).** 4-bromo-toluene (171 mg, 1 mmol, 123 µL), phenylboronic acid (183 mg, 1.5 mmol), and K\(_2\)CO\(_3\) (276 mg, 2 mmol) were subsequently introduced and mixed in a vial containing 4 mL toluene. UiO-67-Pdbpydc\(_{0.5}\)/bpdc\(_{0.5}\) (23 mg, ca. 0.025 mmol Pd) was then transferred to the solution. The vial was incubated at 95 °C for 16 h, followed by centrifugation to separate the solids from the solution. 60 µL of the supernatant was diluted in 1 mL acetone and analyzed by GC-MS. The catalyst was recovered by washing with water (3 × 15 mL) to separate from undissolved K\(_2\)CO\(_3\). During washing, the aqueous solution was titrated with 1M HCl to pH~7. Finally, the solids were washed with MeOH (2×15 mL), then soaked in fresh MeOH (10 mL) for over 6 h, before the catalyst was dried under vacuum for reuse.

**Powder X-ray Diffraction (PXRD) Analysis.** ~20-30 mg of UiO-67 derivative samples were dried under vacuum prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu K\(\alpha\) (\(\lambda=1.5418 \text{ Å}\)), with a scan speed of 1 sec/step, a step size of 0.02° in 2\(\theta\), and a 2\(\theta\) range of ~5 to 45° (sample dependent). The experimental backgrounds were corrected using Jade 5.0 software package.
Digestion and Analysis by $^1$H NMR. Approximately 10 mg of UiO-67 material was dried under vacuum and digested with sonication in 590 µL DMSO-$d_6$ and 10 µL of 40% HF.

Digestion and Analysis by ESI-MS. ESI-MS was performed using a ThermoFinnigan LCQ-DECA mass spectrometer, and the data was analyzed using the Xcalibur software suite. Samples for analysis by ESI-MS were prepared by 10 µL of digested $^1$H NMR solution diluted in ~0.5-1 mL of MeOH.

BET Surface Area Analysis. ~50 mg of UiO-67 sample was evacuated on a vacuum line overnight at room temperature. The sample was then transferred to a pre-weighed sample tube and degassed at 105 °C on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mm Hg. The sample tube was re-weighed to obtain a consistent mass for the degassed exchanged MOF. BET surface area (m$^2$/g) measurements were collected at 77 K by N$_2$ on a Micromeritics ASAP 2020 Adsorption Analyzer using the volumetric technique, and the surface area of each material was averaged by three independent samples analysis.

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy. ~2-5 mg of activated UiO-67 materials was transferred to conductive carbon tape on a sample holder disk, and coated using a Cr-sputter coating for 8 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum. Oxford EDX and Inca software are attached to determine elemental mapping of particle surfaces at a working distance at 10 mm. Around 19000× magnification images are collected.
Gas Chromatography-Mass Spectroscopy. GC-MS was performed using a Thermo Traceplus GC-MS spectrometer, equipped with an autosampler, and the data was analyzed using the Xcalibur software suite. The GC-MS sample was prepared by diluting Suzuki coupling reaction solution to ~1 mL acetone.
Table S1. EDX results of Pd metallated UiO-67-bpydc_x/bpdc_{1-x}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% bpydc(^a)</th>
<th>Atomic Ratio of Metals(^b)</th>
<th>% Metal(^c)</th>
<th>Overall Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-67-bpydc(<em>{0.5})/bpdc(</em>{0.5})</td>
<td>50 %</td>
<td>Zr:Pd:Cl 1:(0.52±0.02):(1.01±0.03)</td>
<td>100 %</td>
<td>Zr(_6)O(_4)(OH)(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(PdCl(_2)bpydc)(_3) (bpdc)(_3)</td>
</tr>
<tr>
<td>UiO-67-bpydc</td>
<td>100%</td>
<td>Zr:Pd:Cl 1:(0.94±0.04):(1.86±0.07)</td>
<td>94 %</td>
<td>Zr(_6)O(_4)(OH)(_4) (PdCl(_2)bpydc)(_5.6) (bpdc)(_0.4)</td>
</tr>
</tbody>
</table>

\(^a\) Value based on \(^1\)H NMR study of digested MOF as well as ligand % in solvothermal solution.

\(^b\) Based on an average of three independent samples, the value in the parentheses is the error of each atomic ratio.

\(^c\) % Metalation is (no. of metalated bpydc sites)/(no. of bpydc sites)

Table S2. Direct solvothermal synthesis condition of UiO-67-bpydc\(_x\)/bpdc\(_{1-x}\).\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZrCl(_4) (mmol)</th>
<th>H(_2)bpydc (mmol)</th>
<th>H(_2)bpdc (mmol)</th>
<th>acetic acid (mmol)</th>
<th>Overall Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-67</td>
<td>0.105</td>
<td>0</td>
<td>0.105</td>
<td>3.15</td>
<td>Zr(_6)O(_4)(OH)(_4)(bpdc)(_6)</td>
</tr>
<tr>
<td>UiO-67-bpydc(<em>{0.25})/bpdc(</em>{0.75})</td>
<td>0.105</td>
<td>0.026</td>
<td>0.078</td>
<td>3.15</td>
<td>Zr(_6)O(_4)(OH)(_4)(bpydc)(_1.5)(bpdc)(_4.5)</td>
</tr>
<tr>
<td>UiO-67-bpydc(<em>{0.5})/bpdc(</em>{0.5})</td>
<td>0.105</td>
<td>0.052</td>
<td>0.052</td>
<td>3.15</td>
<td>Zr(_6)O(_4)(OH)(_4)(bpydc)(_3)(bpdc)(_3)</td>
</tr>
<tr>
<td>UiO-67-bpydc(<em>{0.75})/bpdc(</em>{0.25})</td>
<td>0.105</td>
<td>0.078</td>
<td>0.026</td>
<td>3.15</td>
<td>Zr(_6)O(_4)(OH)(_4)(bpydc)(_4.5)(bpdc)(_1.5)</td>
</tr>
<tr>
<td>UiO-67-bpydc</td>
<td>0.105</td>
<td>0.105</td>
<td>0</td>
<td>3.15</td>
<td>Zr(_6)O(_4)(OH)(_4)(bpydc)(_6)</td>
</tr>
</tbody>
</table>

\(^a\) All the reactions are carried out using a 20 mL scintillation vial with 4 mL DMF at 120 °C for 24 h.
**Figure S1.** $^1$H NMR of HF/$d^6$-DMSO digested UiO-67-bpydc with labels of each peak.

**Figure S2.** SEM of UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$ (left) and UiO-67-bpydc (right). Scale bar is 1 µm on the left, and 5 µm on the right.
Figure S3. $^1$H NMR of HF/d$_6$-DMSO digested UiO-67 (before and after PSE with H$_2$bpdc).

Figure S4. PXRD of UiO-67 before and after PSE with H$_2$bpdc.
Figure S5. EDX of UiO-67-Pdpydc$_{0.5}$/bpdc$_{0.5}$, suggested an 1:0.52:1.01 atomic ratio of Zr:Pd:Cl.

Figure S6. PXRD of UiO-67-Pdpydc$_{0.5}$/bpdc$_{0.5}$ and UiO-67-Pdpydc.
Figure S7. SEM and EDX elemental mapping of UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$.

Figure S8. GC-MS trace of reaction solution of Suzuki coupling after 16 h with: (a) UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$; (b) PdCl$_2$; (c) 10% Pd/C; and (d) UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$. Each peak is labeled with the appropriate chemical structure.
Figure S9. PXRD of UiO-67-Pdbpydc<sub>0.5</sub>/bpdc<sub>0.5</sub>: (a) before catalysis; (b) after one cycle of catalysis; (c) and after three cycles of catalysis.

Figure S10. SEM of post-catalysis (after one cycle) UiO-67-Pdbpydc<sub>0.5</sub>/bpdc<sub>0.5</sub>. 