Supporting Information

Amine Assisted Top Down Delamination of the Two-Dimensional Metal-Organic Framework Cu$_2$(bdc)$_2$

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1. General methods, equipment and parameters

**Chemicals** were purchased from Sigma Aldrich, TCI, Acros Organics, AppliChem, and Riedel-de Haën and used without further purification. Solvents were purchased from Sigma Aldrich, Fischer Chemicals or Acros Organics and stored under argon. Delamination tests were performed under argon atmosphere in Schlenk tubes.

**Powder X-ray diffraction** (PXRD) patterns were collected using a Stoe StadiP system in transmission mode. Samples were prepared in flat base sample holders. 3° Step wide and 80 sec per step exposure time were used. For measurements Cu Kα1 radiation (λ=0.15405 nm) was applied.

**Scanning electron microscope** (SEM) analysis was performed on the SU8020 scanning electron microscope (HITACHI, Japan) with an accelerating voltage of 1-2 kV. Dried materials were sputtered with gold. Average particle size was estimated from 10-20 measurements.

For **nitrogen physisorption** experiments a Belsorp-max system from MicrotracBEL (Japan) was used. The samples were additionally activated at 150 °C for 18 hours prior to measurements. The analysis was performed at 77 K.

Solid state **infrared** (IR) spectroscopy was performed using the Vertex 70 instrumentation of Bruker in DRIFT-IR mode. Samples were mixed with dry KBr (0.5 mg MOF + 100 mg KBr) directly before measurements. The spectrum was recorded with 32 scans in the frequency range of 4000 - 400 cm⁻¹.

**Atomic force microscopy** (AFM) was performed with the Dimension D3100 instrumentation of the Digital Instruments Company. The samples were prepared on a mica sample holder by dropping the particle containing suspension on the substrate. For **transmission electron microscopy** (TEM) JEM-1400 Plus system (JOEL Company) was applied with an operating voltage of 120 kV. The samples were prepared on a carbon covered copper-grid by dropping particle containing suspension (3 x 10 µL) on the sample holder.

2. Synthesis and characterization

2.1 Synthesis of Cu₂(bdc)₂ bulk material

Synthesis was performed according to the procedure reported by Carson et al.2

Terephthalic acid (66.6 mg, 0.4 mmol) and Cu(NO₃)₂·3H₂O (96.8 mg, 0.4 mmol) were dissolved in 8 mL DMF (p.a.). The solution was placed into a glass tube and heated at 100 °C for 24 h. The bluish green precipitate was washed with fresh DMF several times. **Yield:** 45 mg (50% based on linker amount)

The activation was performed in 2 different ways:

1) Direct activation from DMF: The sample was dried in high vacuum at 220 °C for 24 h.
2) Activation from ethanol after solvent exchange: The DMF was exchanged to ethanol by soaking of crystals in EtOH for several days. Subsequently the sample was dried in high vacuum at 80 °C for 24 h.

The activated samples were stored under inert gas atmosphere until further handling.

**Figure S1** a) Powder X-ray diffraction patterns of the Cu$_2$(bdc)$_2$: as made and activated theoretical,\textsuperscript{1,2} as synthesized in DMF, activated from DMF at 220 °C, as synthesized in ethanol, activated from ethanol at 80 °C. b) SEM images of Cu$_2$(bdc)$_2$ after activation from DMF 220 °C and ethanol at 80 °C.

**Figure S2** a) Nitrogen physisorption isotherms of the Cu$_2$(bdc)$_2$ bulk materials activated from DMF at 220 °C and ethanol at 80 °C. b) IR spectra of Cu$_2$(bdc)$_2$ after activation from DMF and ethanol at respective temperature.

### 2.2 Delamination of Cu$_2$(bdc)$_2$ by various amines

Cu$_2$(bdc)$_2$ sample activated at 220 °C (20 mg, 0.09 mmol) was placed in a GC vial, which was positioned in a Schlenk tube. On top of the GC vial a triangular stirring bar was located, which had no direct contact to the powder. A corresponding amine (see Table S1) solved in 5 mL ethanol was added to the MOF sample. The batch was stirred at ambient temperature under argon atmosphere for 24 hours and the resulting solid was finally washed with ethanol for several times.
Table S1 Amine amounts applied in delamination tests with Cu$_2$(bdc)$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Volume / Mass</th>
<th>Amount [mmol]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>ethylamine</td>
<td>17.5 µL</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>diethylamine</td>
<td>23.0 µL</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>triethylamine</td>
<td>30.5 µL</td>
<td>0.22</td>
</tr>
<tr>
<td>4</td>
<td>octylamine</td>
<td>36.5 µL</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>oleylamine</td>
<td>68.9 µL</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>ABCO</td>
<td>55.6 mg</td>
<td>0.50</td>
</tr>
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</table>

2.3 Delamination of Cu$_2$(bdc)$_2$ with ethylamine and octylamine

<table>
<thead>
<tr>
<th>Figure S3</th>
<th>SEM images of Cu$_2$(bdc)$_2$ after delamination in ethanol with ethylamine or octylamine at 40, 60 and 80 °C, respectively. N–H stretch 3400-3250 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure S4</td>
<td>SEM images of Cu$_2$(bdc)$_2$ after delamination tests with octylamine at 80 °C and varying parameters: concentration, treatment time, solvent.</td>
</tr>
</tbody>
</table>
Figure S5  a) PXRD patterns of Cu$_2$(bdc)$_2$: theoretical (as synthesized and activated)$^{1,2}$, after ethylamine (EA) and octylamine (OA) assisted delamination in ethanol, and after activation at 220 °C. b) Nitrogen physisorption isotherms at 77K. c) IR spectra of Cu$_2$(bdc)$_2$ bulk and delaminated materials after activation at 220 °C.
2.4 PVP assisted synthesis of Cu$_2$(bdc)$_2$ and delamination with ethylamine

**Figure S6** AFM images (left) and height profiles (right), of the particles obtained from supernatant suspension after delamination with a) ethylamine and b) octylamine.

**Figure S7** SEM images of Cu$_2$(bdc)$_2$ obtained from direct synthesis with PVP using various PVP amounts in the synthesis.
Figure S8  a) Theoretical PXRD pattern of Cu₂(bdc)₂(DMF)₂ (Ref. 2) (dark blue), PXRD patterns of Cu₂(bdc)₂ obtained in the PVP-assisted synthesis (10 mol% PVP) (light blue) and Cu₂(bdc)₂ after delamination with ethylamine (green).  b) IR spectra of Cu₂(bdc)₂-PVP (blue) and EA-treated Cu₂(bdc)₂-PVP (green).

Figure S9  AFM image (left) and height profiles (right) of the particles obtained from supernatant suspension after delamination of Cu₂(bdc)₂-PVP with ethylamine.

References
