A panchromatic modification of Metal-Organic Frameworks’ light absorption spectra.
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1 - Experimental

1.1 - Synthesis
Light yellow UiO-66-NH₂ was synthesized as reported by Schaate et al.¹ using a H₂O:Zr-10:1 ratio. The reaction was carried out in closed glass bottles at 120°C for 12 hs. The solids were isolated and washed twice with DMF and CH₂Cl₂. After this, the MOF postfunctionalization by a diazotization reaction was performed using acetic acid solutions of N,N-dimethylaniline, α-naphtol, β-naphtol, diphenylamine, cresile blue, basic fuscine, malachite green and crystal violet, as coupling agents following the procedure reported by Nasalevich et al.² The formula of UiO-66-NH₂ was assumed to be
[Zr$_{24}$O$_{120}$C$_{192}$H$_{144}$N$_{24}$] g/mol) with 24 NH$_2$ groups per mole and 7% solvent content (TGA based). A solution of NaNO$_2$ with six times the equivalent amount to NH$_2$ groups was cooled down to 0°C with ice and the UiO-66-NH$_2$ was suspended in it. A solution 0.03molL$^{-1}$ was added to the yellowish suspension until a 3 fold excess of HCl respect to nitrite was achieved. The suspension was stirred 10 minutes until a change of colour from pale yellow to brownish orange is observed. The diazo coupling agents were added dropwise with a twofold excess respect to nitrite. The suspension exhibited a fast colour change once the first drops were added. The suspension was kept in an ice bath and left to warm up overnight. The solids were isolated by centrifugation, washed with acetic acid 3 times and twice with acetone. The solid were dried at room temperature.

To determine the specific reaction with –NH$_2$ groups at the MOF structure, the reaction was repeated in the above mentioned conditions with 1-naphthol and UiO-66. No colour was developed.

### 1.2 - Characterization

#### 1.2.1 - X-Ray diffraction

X-Ray diffraction (XRD) measurements were performed in a Panalytical Diffractometer, Model Empyrean with PIXCEL3D detector for non-postfunctionalized samples (UiO-66 and UiO-66-NH$_2$) using Cu Kα radiation ($\lambda_{Cu}$ = 1.54056Å) and a PW 3710 Phillips diffractometer for postfunctionalized using Co Kα radiation ($\lambda_{Co}$ = 1.78901Å). All measurements were performed in Bragg-Brentano configuration and normalized to Co Kα radiation.

#### 1.2.2 - Nitrogen adsorption–desorption isotherms

Nitrogen adsorption–desorption isotherms were obtained at 77 K for all samples using a Micromeritics ASAP 2460. Prior to the measurements all the samples were degassed at 180 °C overnight under a pressure of 0.02 Pa.

#### 1.2.3 – Diffuse reflectance spectroscopy - DRS

Reflectance spectra were measured using a UV-visible scanning spectrophotometer (SHIMADZU UV-2101PC) attached to an integrating sphere. Sample powders were mounted into the integrating sphere using a quartz slide. Reflectance was transformed to absorbance using the Kubelka—Munk model.

#### 1.2.4 - Fourier Transform Infrared - FTIR

Fourier Transform Infrared (FTIR) spectroscopy was carried out in a Nicolet Magna 760 FTIR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA) in single attenuated total reflectance (ATR) mode.

#### 1.2.5 - Raman

Raman spectra were collected with a Renishaw InVia Confocal Raman microscope. UiO-66 sample was excited with a 785nm to avoid fluorescence. Coloured samples were measured in resonant Raman with a 488nm laser.

The raw data (dots) is shown together with a smoothed data (line) for guidance in the peaks position. Data was smoothed with a Savitzky-Golay filtering algorithm and the background removed.
1.2.6 - Thermogravimetric analysis - TGA

Thermogravimetric analysis (TGA) was used for successfully functionalized samples to quantify the solvent residual amount, average molecular mass of the MOFs and the diazo coupling yield. The experiments were performed with a NETZSCH STA 409 CD thermobalance. Approximately 25 mg of each MOF was heated in an alumina crucible with 5°C min⁻¹ up to 950 °C in synthetic air (20.5 % O₂ in N₂) flow of 50 mL min⁻¹. Additionally, to check the gas species released at each temperature, a NETZSCH QMS 403C Aeolos quadrupole mass spectrometer (MS) was used.

1.2.7 – Photocatalytic tests

For the photocatalytic test, a stock solution of 2mM of Methylene Blue (MB) was prepared dissolving 0.0639 g of MB in 100mL of distilled water. Dilution 1:10 were performed in order to get 0.2mM of MB. 15 mg of each MOF was placed in a Pyrex glass test tube with a magnetic stirrer and 10 mL of 0.2mM MB was added. TiO₂ (Titanium (IV) oxide, anatase, 99.9% (metals basis), Alfa Aesar. 45m²/g) was also tested as a positive test for photocatalysis. Suspensions were stirred in dark conditions in order to quantify the adsorption of MB onto the solids. After 1 hour, aliquots of 3 mL were filtered with 20µm nylon filters and absorbance at 664nm was measured. A Xenon Lamp was used as light source for photocatalysis, and the remaining suspensions were irradiated for 1.5 hs under continuous stirring. At which time, aliquots of 3 mL were filtered with 20 µm nylon filters and absorbance at 664 nm was measured.

2 – Obtained structures

Fig SI-2.1 - UiO-66-NH₂ crystal structure.
Fig SI-2.2 - Zr₆O₄(OH)₄ clusters linked by terephthalic acid and photograph of the solid.

Fig SI-2.3 - Zr₆O₄(OH)₄ clusters linked by 2-aminoterephthalic acid and photograph of the solid.

Fig SI-2.4 - UiO-66-NH₂ diazo coupled with N,N-Dimethylaniline and photograph of the obtained solid.

Fig SI-2.5 - UiO-66-NH₂ diazo coupled with 1-naphtol and photograph of the obtained solid.
Fig SI-2.6- UiO-66-NH₂ diazo coupled with diphenylamine and photograph of the obtained solid.

3 – FTIR

The FTIR of UiO-66-NH₂ samples exhibits a N-H bending at 1655 cm⁻¹ which is absent in the rest of the samples. Also a C-N stretching at 1257 cm⁻¹ is observed.

Fig SI-3- FTIR spectra of 1) UiO-66, 2) UiO-66-NH₂ and UiO-66-NH₂ coupled with 3) N,N-dimethylaniline, 4) 1-Naphthol, 5) 2-Naphthol and 6) Diphenylamine.
4 - Raman

4.1 - UiO-66

Fig SI-4.1 - Raman spectra of UiO-66

4.2 - UiO-66-NH$_2$

Fig SI-4.2 - Raman spectra of UiO-66-NH$_2$
4.3 - UiO-66-NH2 diazo coupled with N,N-Dimethylaniline

![Graph showing Raman spectra of UiO-66-NH2 coupled with N,N-dimethylaniline. Peak assignment according to Ref 3.]

Fig SI-4.3a- Raman spectra of UiO-66-NH₂ coupled with N,N-dimethylaniline. Peak assignment according to Ref 3.

![Diagram showing azo-quinonoid tautomeric equilibrium in UiO-66-NH₂ coupled with N,N-dimethylaniline. Equilibrium species according to Ref 3.]

Fig SI-4.3b- Azo-quinonoid tautomeric equilibrium in UiO-66-NH₂ coupled with N,N-dimethylaniline. Equilibrium species according to Ref 3.
4.4 - UiO-66-NH$_2$ diazo coupled with 1-Naphthol

Fig SI-4.4a- Raman spectra of UiO-66-NH$_2$ coupled with 1-Naphthol. Peak assignment according to Ref 4.

Fig SI-4.4b- Azo-hydrazone tautomer equilibrium in UiO-66-NH$_2$ coupled with 1-Naphthol. Equilibrium species according to Ref 5.
4.5 - UiO-66-NH₂ diazo coupled with 2-Naphthol

Fig SI-4.5a- Raman spectra of UiO-66-NH₂ coupled with 2-Naphthol. Peak assignation according to Ref 4.

Fig SI-4.5b- Azo-hydrazone tautomeric equilibrium in UiO-66-NH₂ coupled with 2-Naphthol. Equilibrium species according to Ref 6.
4.6 - UiO-66-NH₂ diazo coupled with Diphenylamine

Fig SI-4.6a- Raman spectra of UiO-66-NH₂ coupled with Diphenylamine. Peak assignment according to Ref 7.

Fig SI-4.6b- Protonation equilibrium in UiO-66-NH₂ coupled with Diphenylamine. Equilibrium species according to Ref 8.
5 - TGA–MS measurements

5.1 - UiO-66

Fig SI-5.1 - TGA of UiO-66 sample and MS for H$_2$O and CO$_2$ channels
5.2 - UiO-66-NH$_2$

Fig SI-5.2 - TGA of UiO-66-NH$_2$ sample and MS for H$_2$O and CO$_2$ channels
5.3 - UiO-66-NH2 diazo coupled with N,N-Dimethylaniline

Fig SI-5.3- TGA of UiO-66-NH₂ diazo coupled with N,N-Dimethylaniline sample and MS for H₂O and CO₂ channels
5.4 - UiO-66-NH$_2$ diazo coupled with 1-Naphthol

Fig S1-5.4- TGA of UiO-66-NH$_2$ diazo coupled with 1-Naphthol sample and MS for H$_2$O and CO$_2$ channels
5.5 - UiO-66-NH$_2$ diazo coupled with 2-Naphthol

Fig SI-5.5 - TGA of UiO-66-NH$_2$ diazo coupled with 2-Naphthol sample and MS for H$_2$O and CO$_2$ channels
5.6 - UiO-66-NH₂ diazo coupled with Diphenylamine

Fig SI-5.6- TGA of UiO-66-NH₂ diazo coupled with diphenylamine and MS for H₂O and CO₂ channels.
6 – Nitrogen sorption isotherms

Fig SI-6- Isotherms of UiO-66-NH$_2$ coupled with N,N-dimethylaniline, 1-Naphtol, 2-Naphthol and Diphenylamine

7 – Photocatalysis

Fig SI-7- Correlation between band gap and Methylene Blue degradation performance.
8 - TGA Calculations

The TGA measurements were used to obtain the solvent adsorbed in the pores, the average molar mass and the diazo coupling shield.

The variables used for these determinations were:

First mass loss step % = \( m_1 \)

Second mass loss step % = \( m_2 \)

Final mass % = \( m_f \)

To identify the steps, MS spectra was used to follow the m/z=18 and m/z=44 which corresponds to water and carbon dioxide respectively. The first mass loss step was attributed to solvent loss, principally water. The second mass loss step corresponds to organic matter destruction. In this step of the TGA, all the MOF structure is converted to ZrO\(_2\) and combustion products. This mass loss can be corrected by subtracting the solvent loss.

\[
\% Mass\ loss_{corrected} = m_3 = \frac{m_2}{100\% - m_1} \cdot 100\% = \frac{m_2}{(m_2 + m_f)} \cdot 100\%
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA solvent loss (%)</th>
<th>TGA final mass (%)</th>
<th>Normalized mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>13.6</td>
<td>38.4</td>
<td>44.5</td>
</tr>
<tr>
<td>UiO-66-NH(_2)</td>
<td>6.5</td>
<td>38.5</td>
<td>41.1</td>
</tr>
<tr>
<td>UiO-66-OH</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>N,N-dimethylaniline</td>
<td>9.8</td>
<td>37.4</td>
<td>41.4</td>
</tr>
<tr>
<td>1-naphtol</td>
<td>10.5</td>
<td>38.2</td>
<td>38.3</td>
</tr>
<tr>
<td>2-naphtol</td>
<td>7.9</td>
<td>36.5</td>
<td>39.6</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>7.1</td>
<td>38.8</td>
<td>41.7</td>
</tr>
</tbody>
</table>

Table SI-1 – TGA results

The decomposition path for UiO-66 should be:

\[
\text{Zr}_{24}\text{O}_{120}\text{C}_{192}\text{H}_{96} + x \text{O}_2 \rightarrow 24 \text{ZrO}_2 + \text{combustion products}
\]

According to this equation, the ideal mass loss should be:

\[
\% Mass\ loss_{ideal} = \frac{24 \cdot M_r\text{ZrO}_2}{M_r\text{UiO-66}} \cdot 100\%
\]

\[
M_{rav} = \frac{24 \cdot M_r\text{ZrO}_2 \cdot (100 - m_1)}{m_f}
\]

The same calculation can be performed for the rest of substituted UiO-66. Necessary information is placed in Table SI-1

The molecular masses obtained from TGA measurements show several differences from the molecular mass calculated from the molecular formula. The average molecular formula is a weighted average between the successfully diazo coupled MOF and the hydrolysis product of the diazonium salt, which corresponds to its transformation into an OH group with a molecular formula: \( \text{Zr}_{24}\text{O}_{144}\text{C}_{192}\text{H}_{96} \).
\[ Mr_{av} = x_1 \cdot Mr_1 + x_2 \cdot Mr_2 = x_1 \cdot Mr_1 + (1 - x_1) \cdot Mr_2 \]

Where \( Mr_1 \) corresponds to the successfully diazo coupled MOF, \( Mr_2 \) to the hydrolysis product of the diazonium salt and, \( x_1 \) and \( x_2 \) the corresponding weighting factors, according to this model, \( x_1 \) would be the diazo coupling shield.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOF molecular formula</th>
<th>MOF molecular mass (g/mol)</th>
<th>Ideal mass loss (%)</th>
<th>Average molecular mass-TGA (g/mol)</th>
<th>Diazo coupling yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>Zr_{24}O_{120}C_{192}H_{96}</td>
<td>6509</td>
<td>45.4</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>UiO-66-NH_2</td>
<td>Zr_{24}O_{120}C_{192}H_{144}N_{24}</td>
<td>6869</td>
<td>43.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>UiO-66-OH</td>
<td>Zr_{24}O_{144}C_{192}H_{96}</td>
<td>6893</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>N,N-dimethylaniline</td>
<td>Zr_{24}O_{120}C_{384}H_{288}N_{72}</td>
<td>10013</td>
<td>29.5</td>
<td>7138</td>
<td>7.8</td>
</tr>
<tr>
<td>1-naphtol</td>
<td>Zr_{24}O_{144}C_{332}H_{240}N_{48}</td>
<td>10589</td>
<td>27.9</td>
<td>7725</td>
<td>22.5</td>
</tr>
<tr>
<td>2-naphtol</td>
<td>Zr_{24}O_{144}C_{332}H_{240}N_{48}</td>
<td>10589</td>
<td>27.9</td>
<td>7465</td>
<td>15.4</td>
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<tr>
<td>Diphenylamine</td>
<td>Zr_{24}O_{144}C_{332}H_{312}N_{72}</td>
<td>11573</td>
<td>25.6</td>
<td>7084</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table SI-2 – TGA calculations

9 – References


