Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

A panchromatic modification of Metal-Organic Frameworks' light absorption spectra.

Eugenio Otal*, Manuela Kim, Mauricio Calvo, Lassi Karvonen, Ismael Fábregas, Cesar Sierra, Juan Hinestroza

Content

1 - Experimental

1.1 - Synthesis

Light yellow UiO-66-NH_2 was synthesized as reported by Schaate *et al.* [1] using a H_2O: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 CH_2Cl_2. 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 fucsine, malachite green and crystal violet, as coupling agents following the procedure reported by Nasalevich *et al.* [2]. The formula of UiO-66-NH_2 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 ($K_{\alpha1}$ = 1.54056Å) and a PW 3710 Phillips diffractometer for postfunctionalized using Co Kα radiation ($K_{\alpha1}$ = 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 % O_2 in N_2) 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. TiO_2 (Titanium (IV) oxide, anatase, 99.9% (metals basis), Alfa Aesar. 45m^2/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

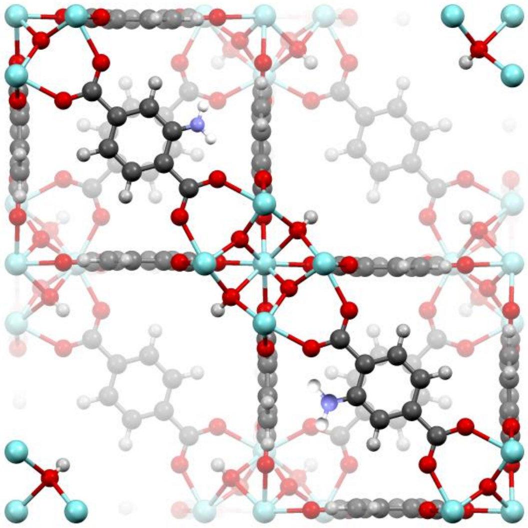


Fig SI-2.1 - UiO-66-NH_2 crystal structure.

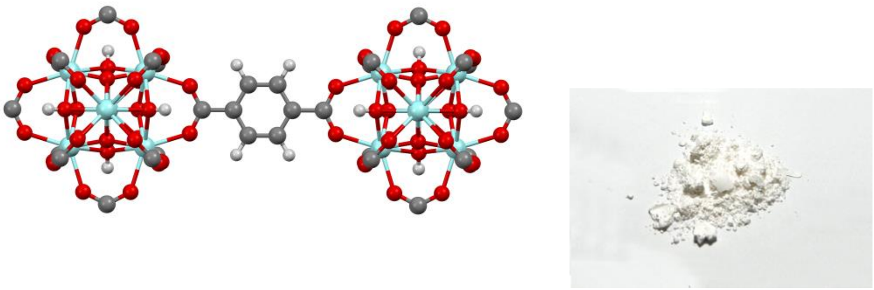


Fig SI-2.2 - $Zr_6O_4(OH)_4$ clusters linked by terephthalic acid and photograph of the solid.

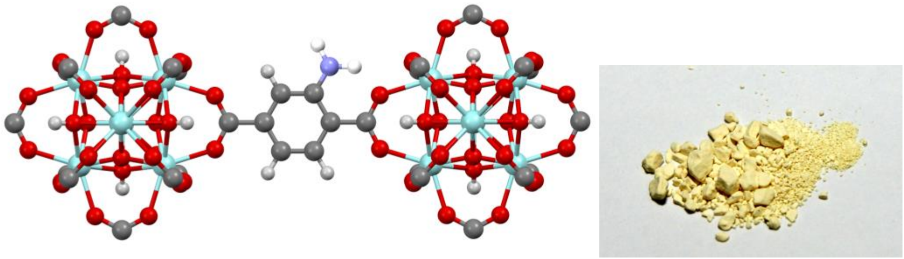


Fig SI-2.3- $Zr_6O_4(OH)_4$ clusters linked by 2-aminoterephthalic acid and photograph of the solid.

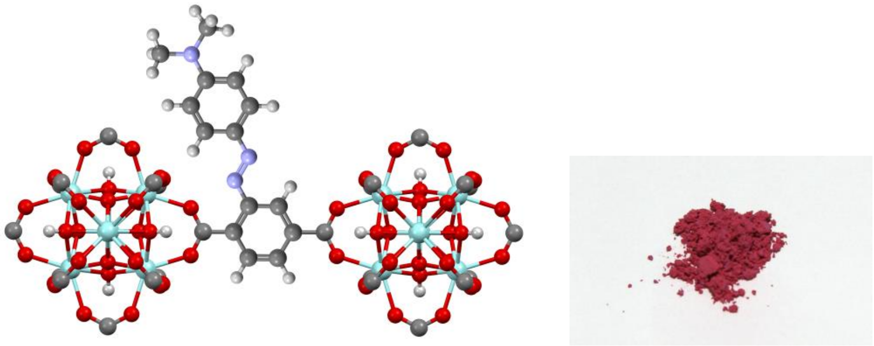


Fig SI-2.4- UiO-66-NH_2 diazo coupled with N,N-Dimethylaniline and photograph of the obtained solid.

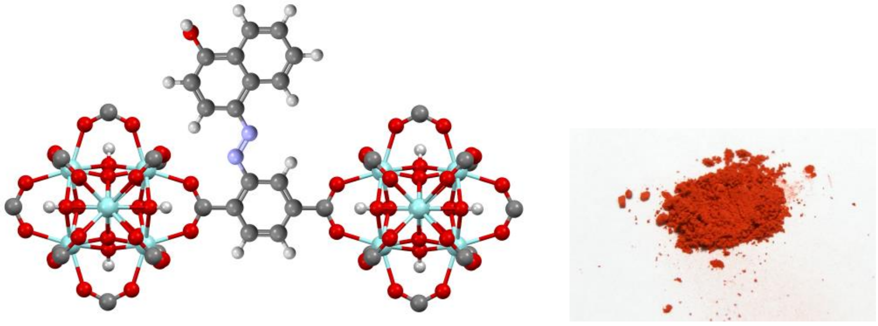


Fig SI-2.5- UiO-66-NH_2 diazo coupled with 1-naphtol and photograph of the obtained solid.

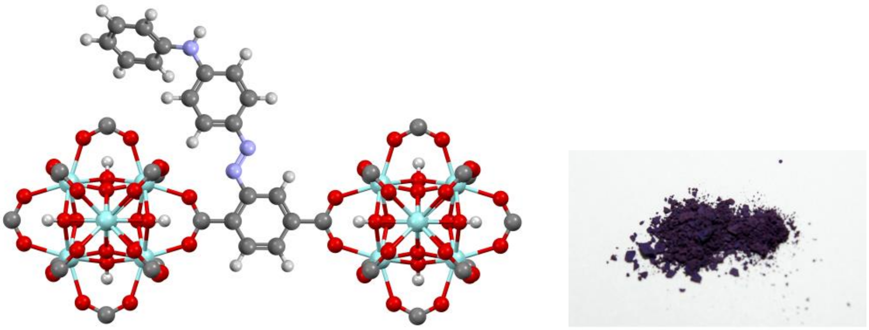


Fig SI-2.6- UiO-66-NH$_2$ diazo coupled with diphenylamine and photograph of the obtained solid.

3 – FTIR

The FTIR of UiO-66-NH$_2$ 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 1257cm^{-1} is observed

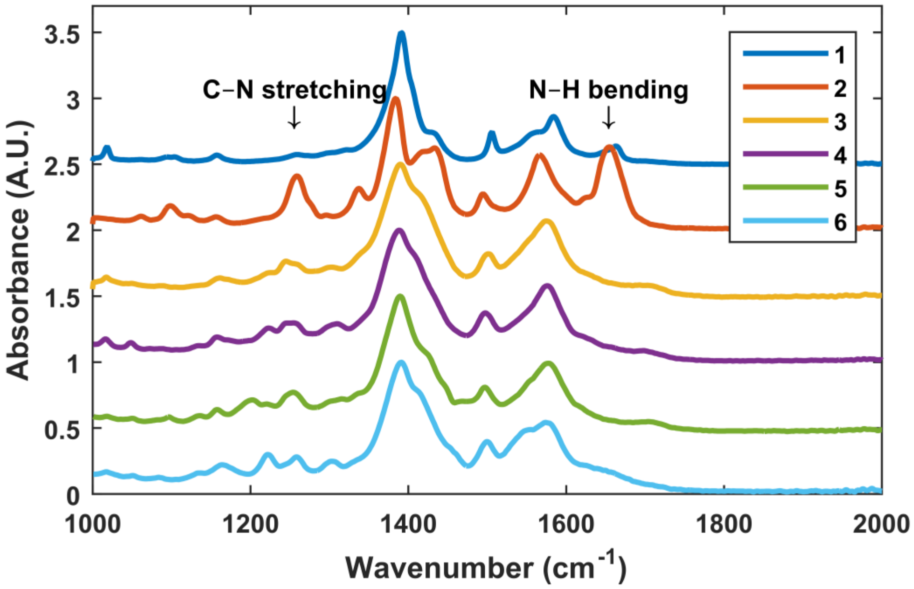


Fig SI-3- FTIR spectra of 1) UiO-66, 2) UiO-66-NH$_2$ and UiO-66-NH$_2$ coupled with 3) N,N-dimethylaniline,4) 1-Naphthol, 5) 2-Naphthol and 6) Diphenylamine

4 – Raman

4.1 - UiO-66

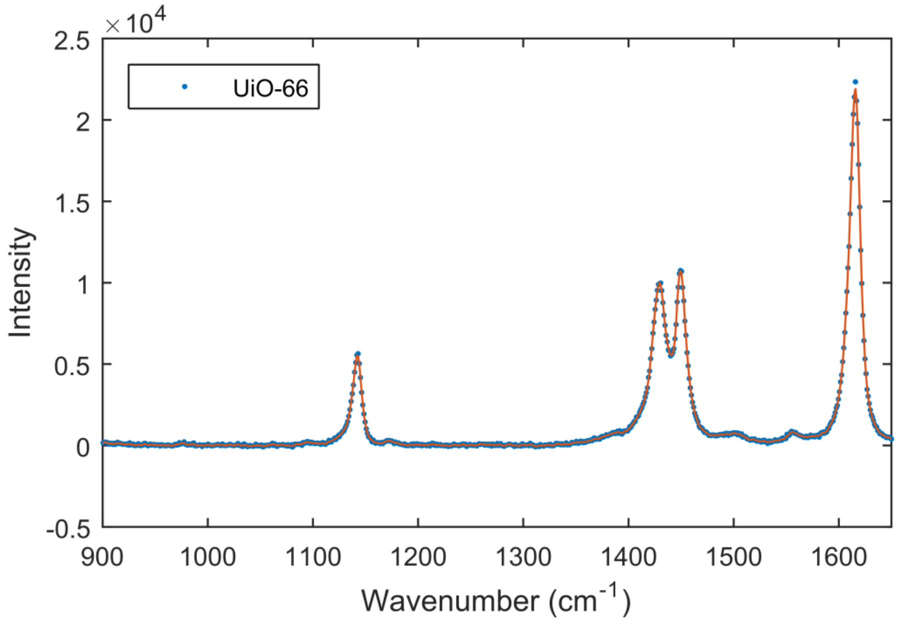


Fig SI-4.1- Raman spectra of UiO-66

4.2 - UiO-66-NH$_2$

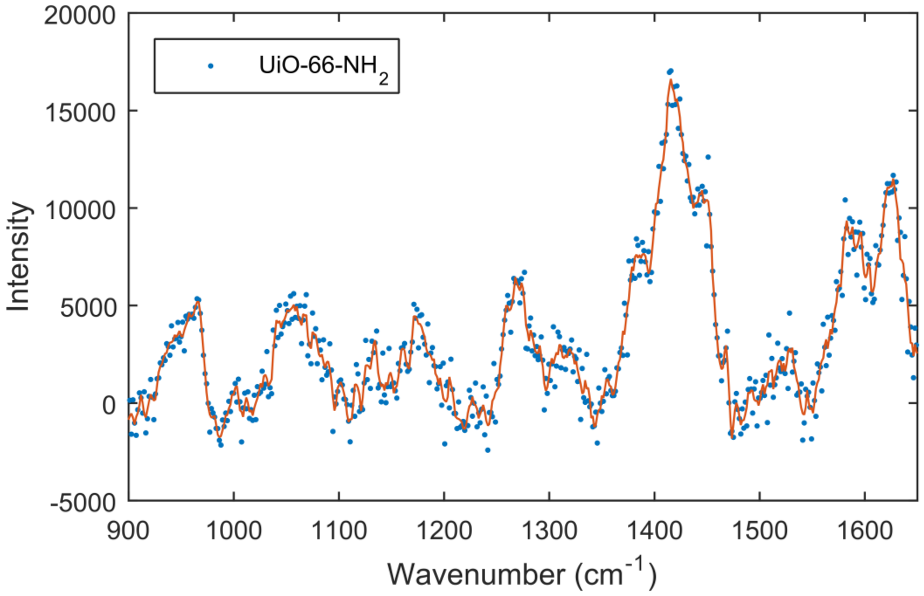


Fig SI-4.2- Raman spectra of UiO-66-NH$_2$

4.3 - UiO-66-NH2 diazo coupled with N,N-Dimethylaniline

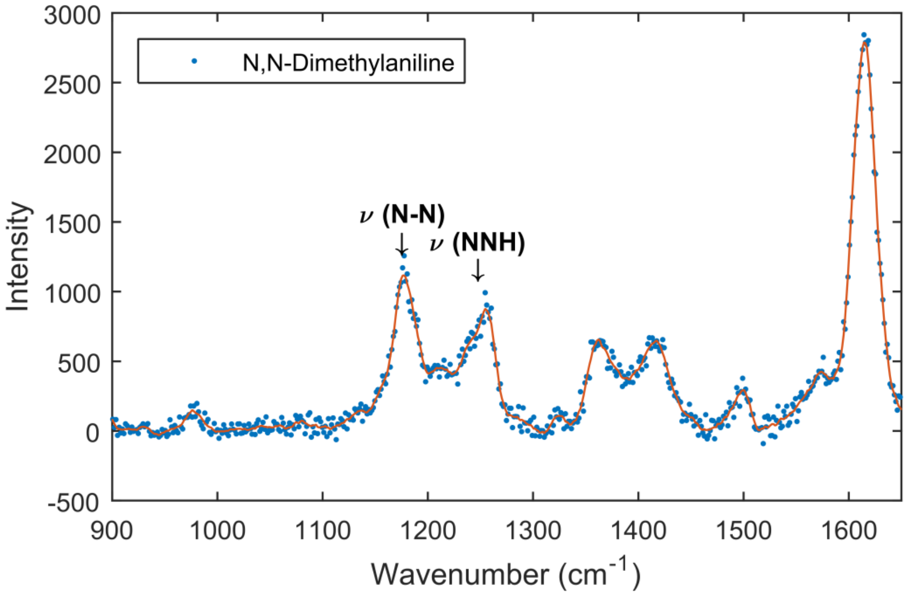


Fig SI-4.3a- Raman spectra of UiO-66-NH_2 coupled with N,N-dimethylaniline. Peak assignation according to Ref 3.

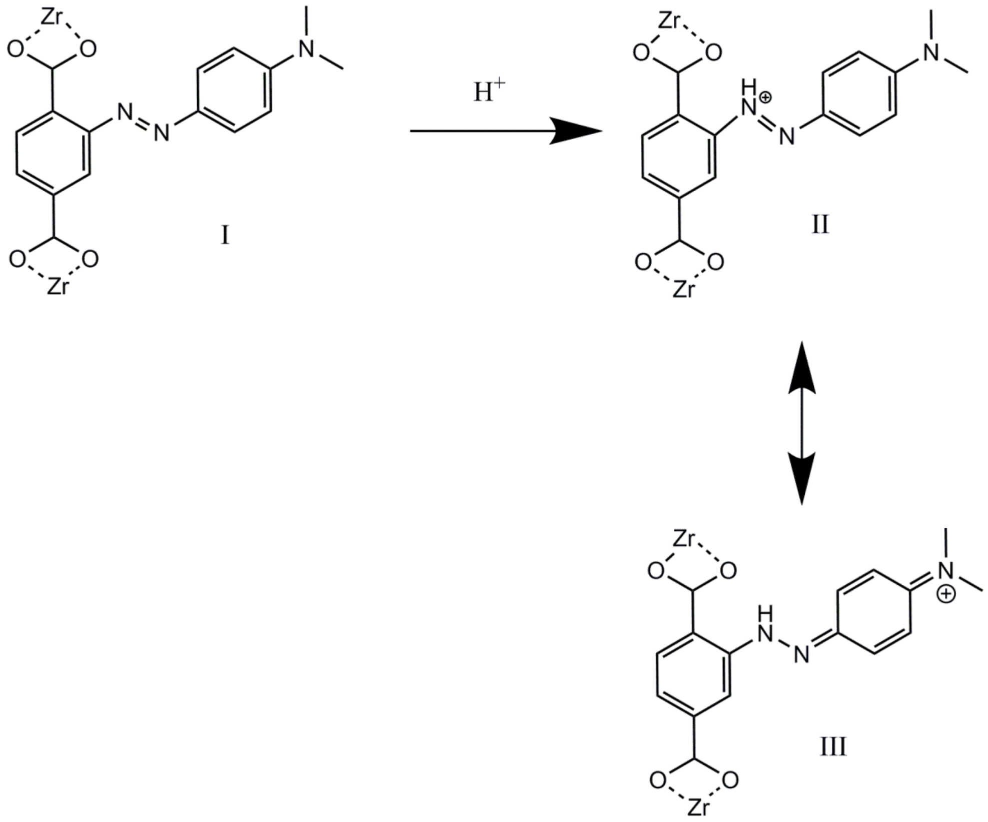


Fig SI-4.3b- Azo-quinonoid tautomeric equilibrium in UiO-66-NH_2 coupled with N,N-dimethylaniline. Equilibrium species according to Ref 3.

4.4 - UiO-66-NH_2 diazo coupled with 1-Naphthol

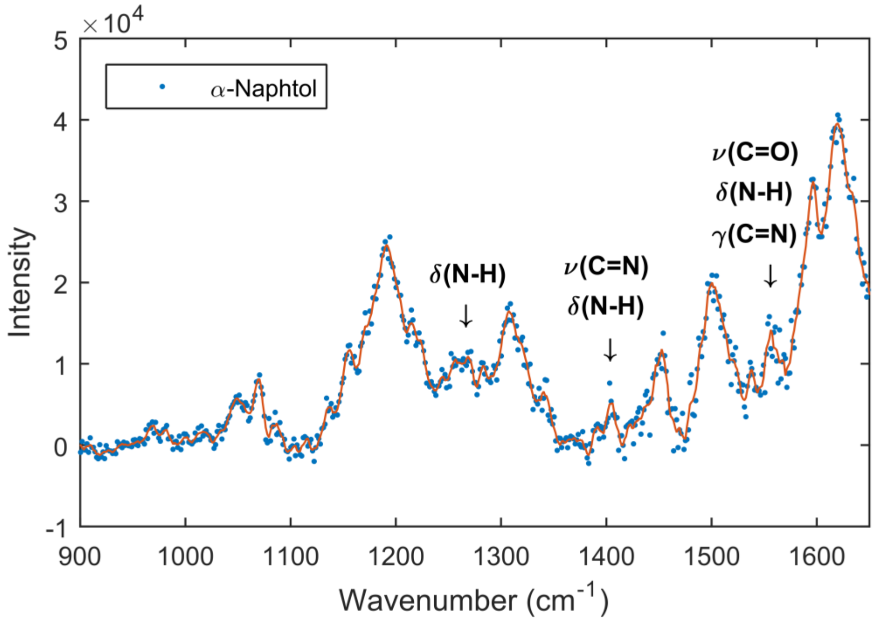
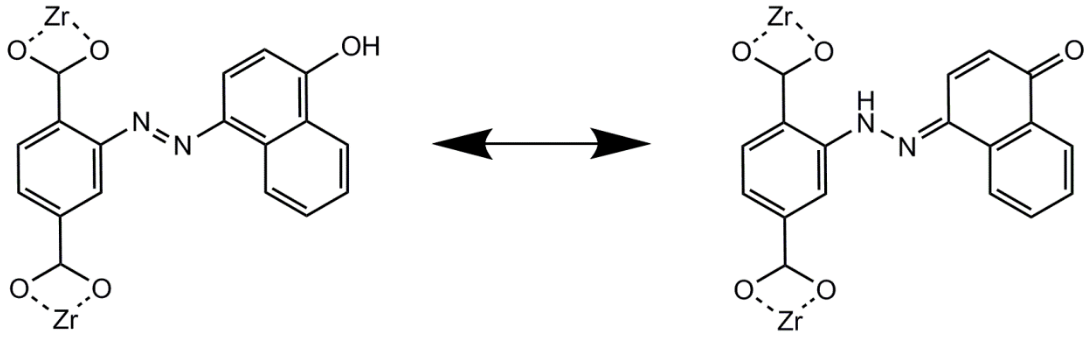


Fig SI-4.4a- Raman spectra of UiO-66-NH_2 coupled with 1-Naphthol. Peak assignation according to Ref 4.

.



I

II

Fig SI-4.4b- Azo-hydrazone tautomeric equilibrium in UiO-66-NH_2 coupled with 1-Naphthol. Equilibrium species according to Ref 5.

4.5 - UiO-66-NH$_2$ diazo coupled with 2-Naphthol

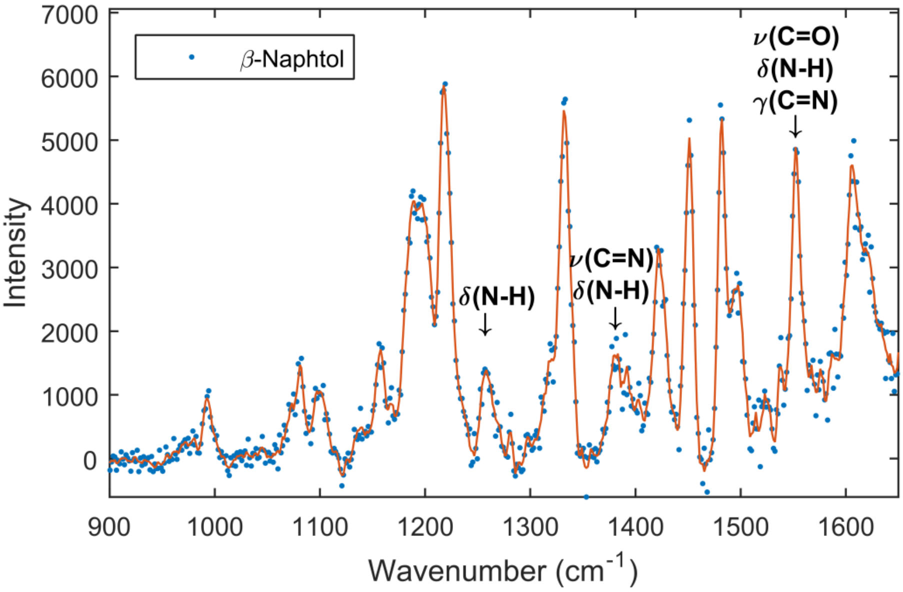
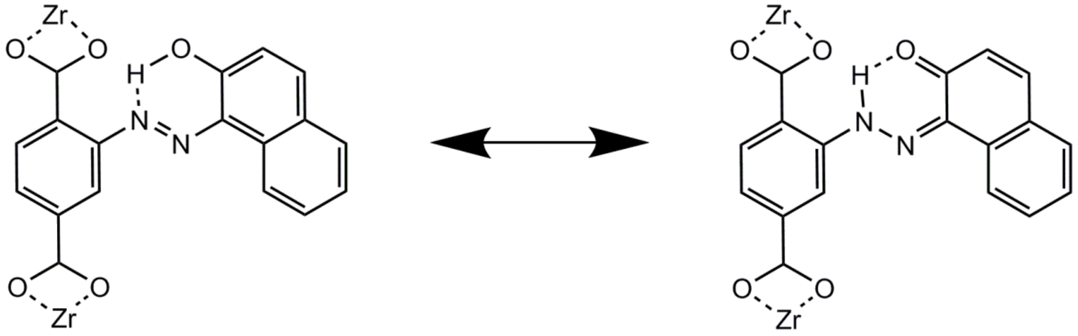


Fig SI-4.5a- Raman spectra of UiO-66-NH$_2$ coupled with 2-Naphthol. Peak assignation according to Ref 4.



I

II

Fig SI-4.5b- Azo-hydrazone tautomeric equilibrium in UiO-66-NH$_2$ coupled with 2-Naphthol. Equilibrium species according to Ref 6.

4.6 - UiO-66-NH_2 diazo coupled with Diphenylamine

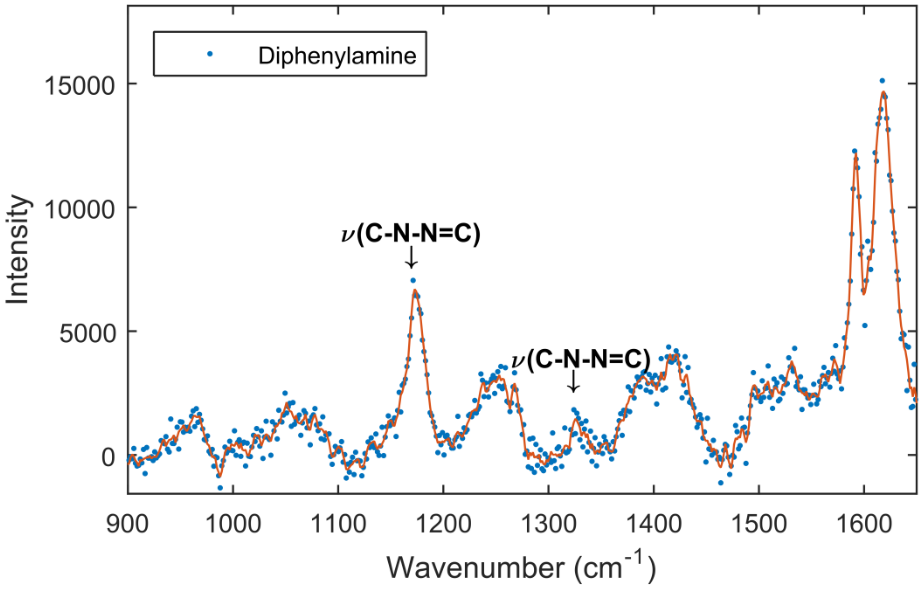


Fig SI-4.6a- Raman spectra of UiO-66-NH_2 coupled with Diphenylamine. Peak assignation according to Ref 7.

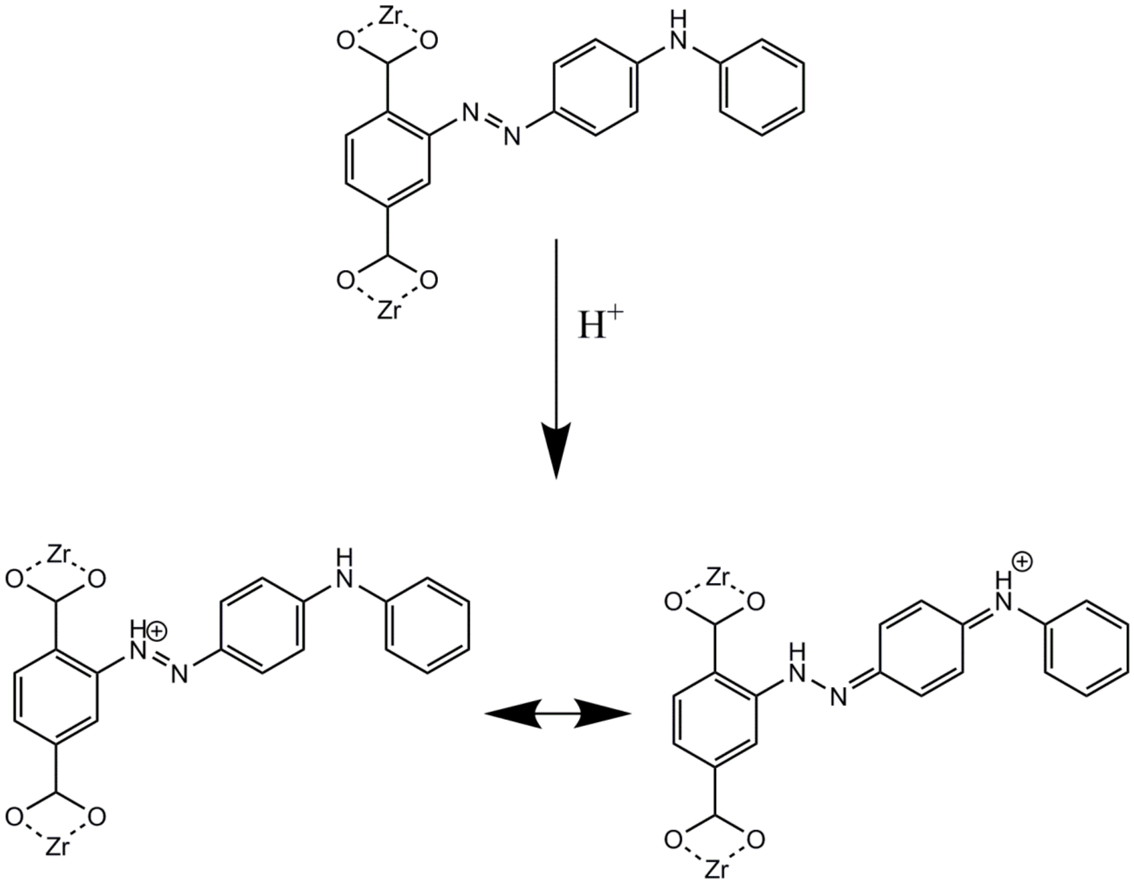


Fig SI-4.6b- Protonation equilibrium in UiO-66-NH_2 coupled with Diphenylamine. Equilibrium species according to Ref 8.

5 – TGA–MS measurements

5.1 - UiO-66

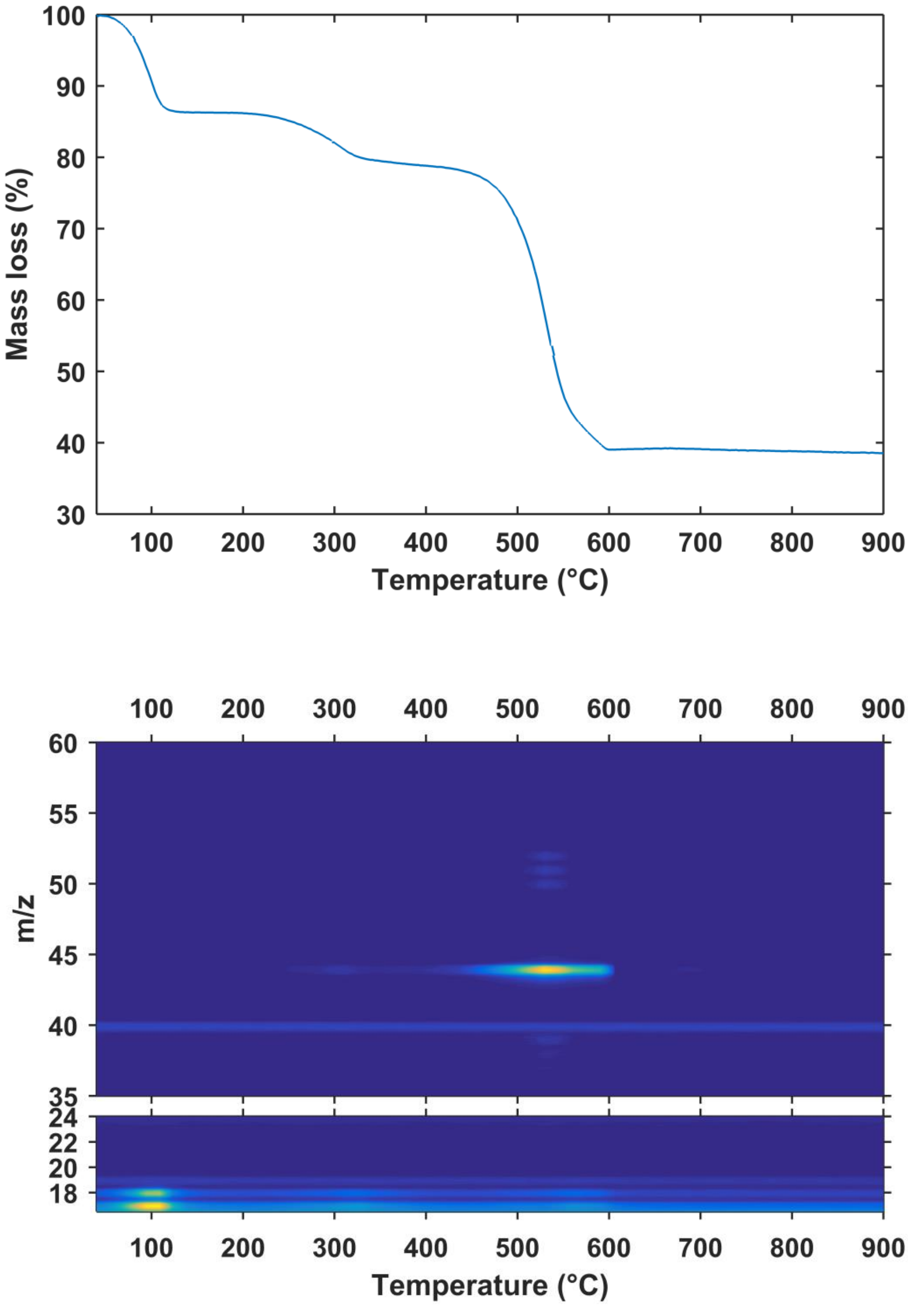


Fig SI-5.1 - TGA of UiO-66 sample and MS for H_2O and CO_2 channels

5.2 - UiO-66-NH$_2$

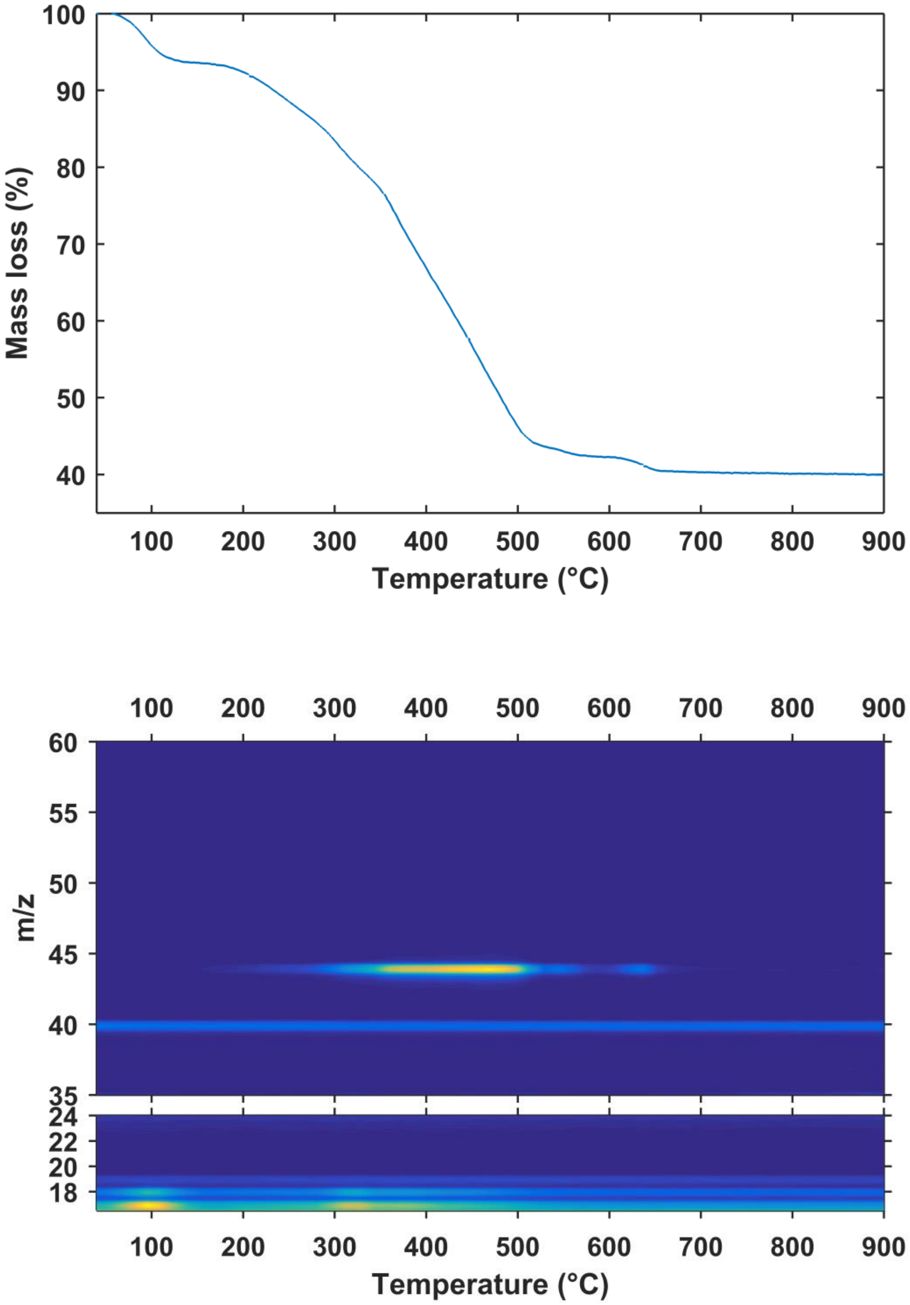


Fig SI-5.2- TGA of UiO-66-NH$_2$ sample and MS for H$_2$O and CO$_2$ channels

5.3 - UiO-66-NH2 diazo coupled with N,N-Dimethylaniline

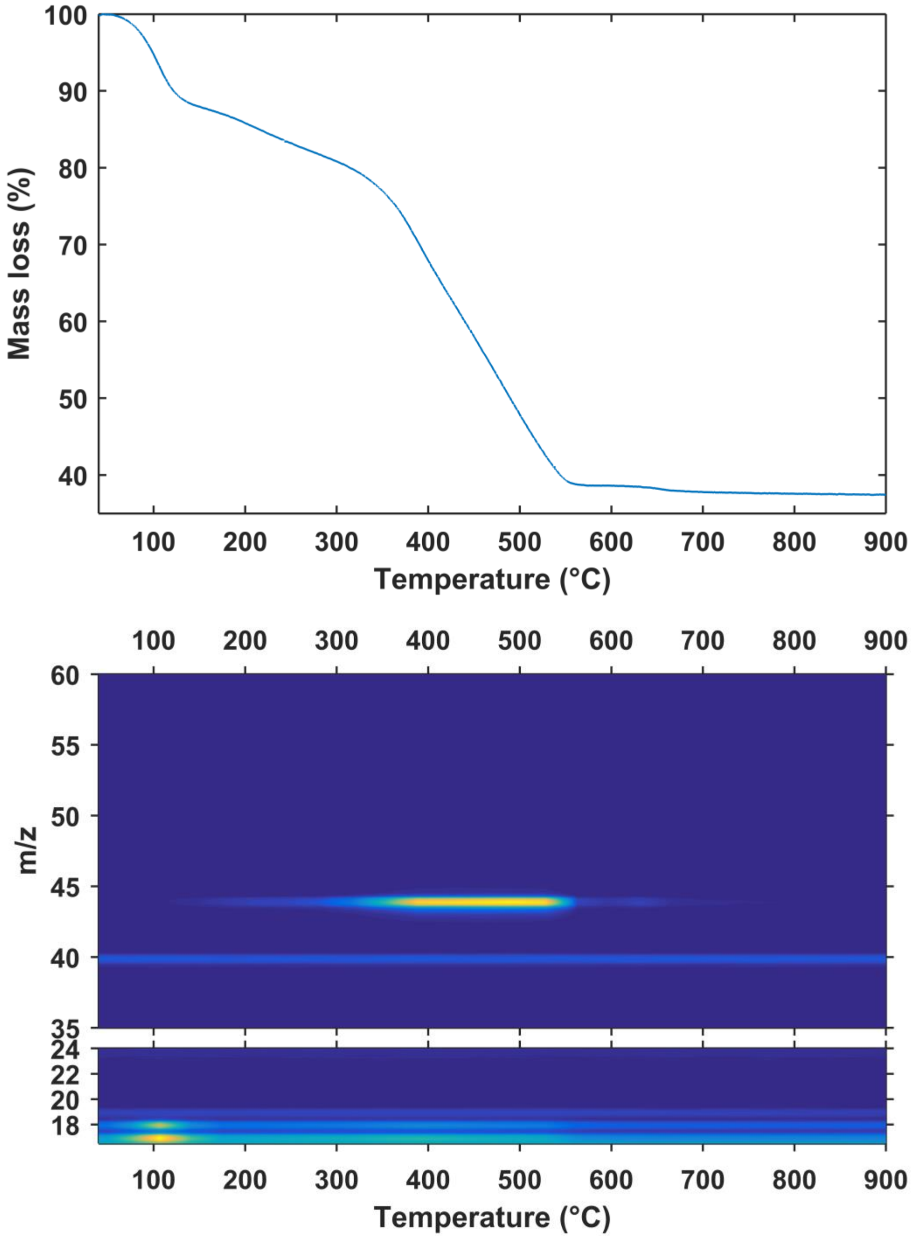


Fig SI-5.3- TGA of UiO-66-NH$_2$ diazo coupled with N,N-Dimethylaniline sample and MS for H_2O and CO_2 channels

5.4 - UiO-66-NH_2 diazo coupled with 1-Naphthol

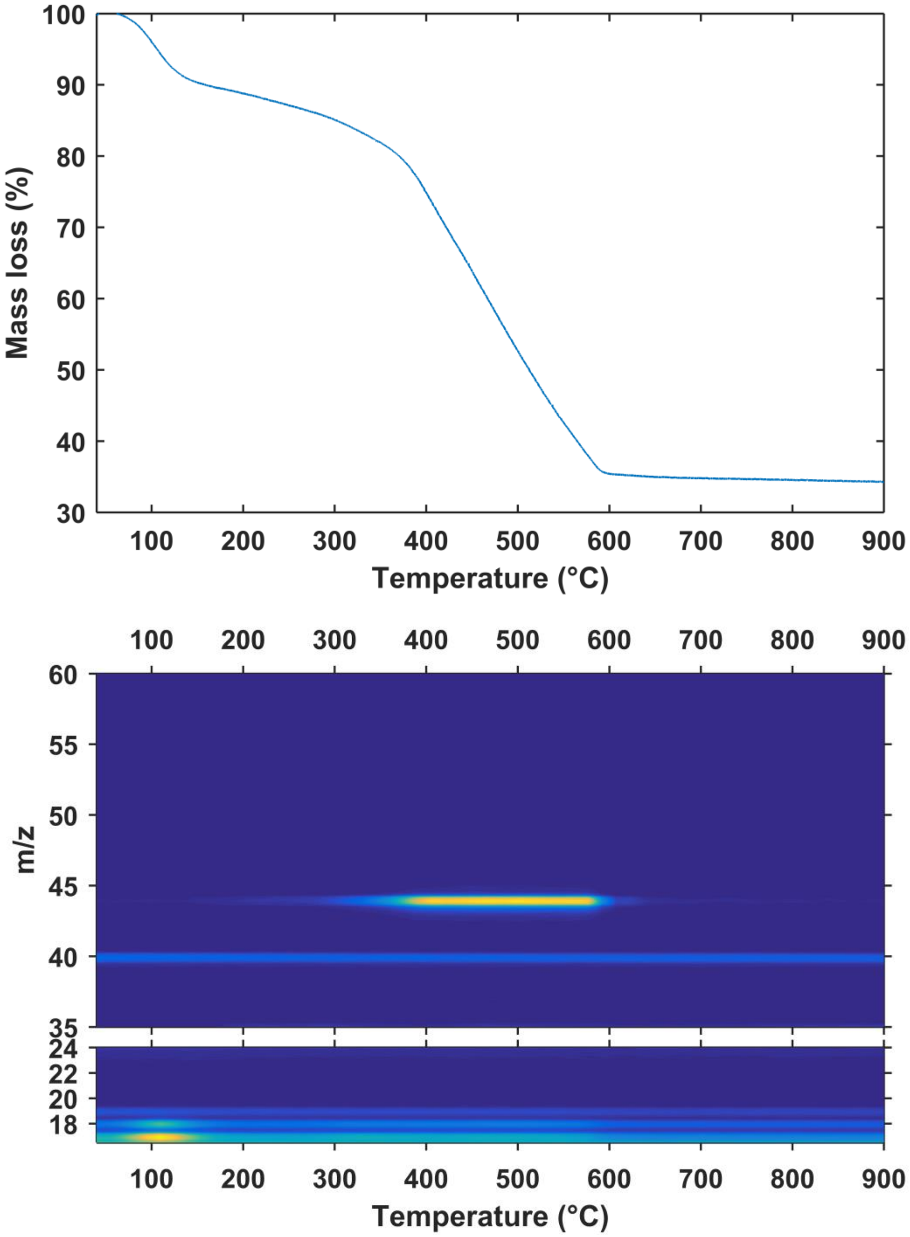


Fig SI-5.4- TGA of UiO-66-NH_2 diazo coupled with 1-Naphthol sample and MS for H_2O and CO_2 channels

5.5 - UiO-66-NH_2 diazo coupled with 2-Naphthol

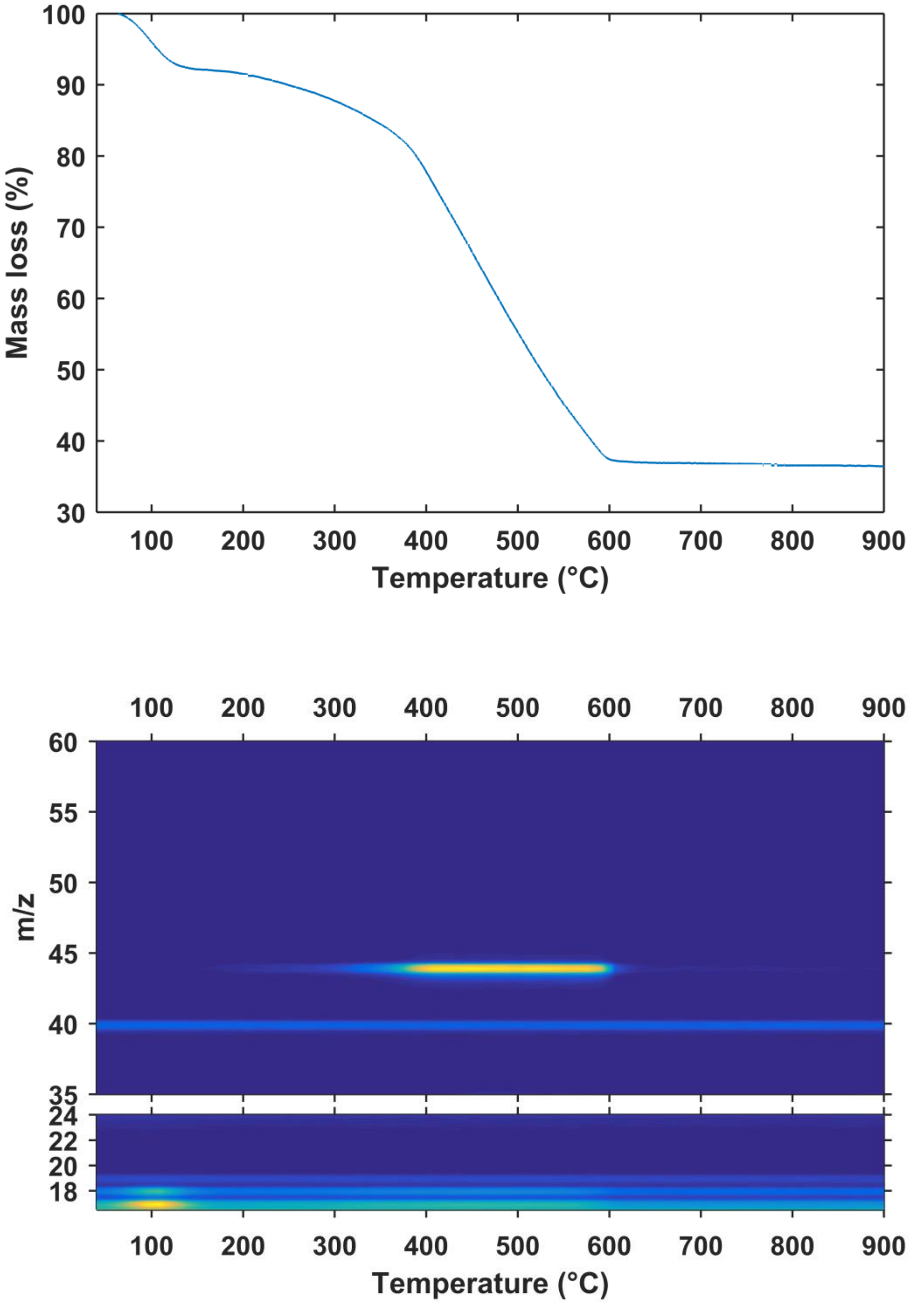


Fig SI-5.5- TGA of UiO-66-NH_2 diazo coupled with 2-Naphthol sample and MS for H_2O and CO_2 channels

5.6 - UiO-66-NH_2 diazo coupled with Diphenylamine

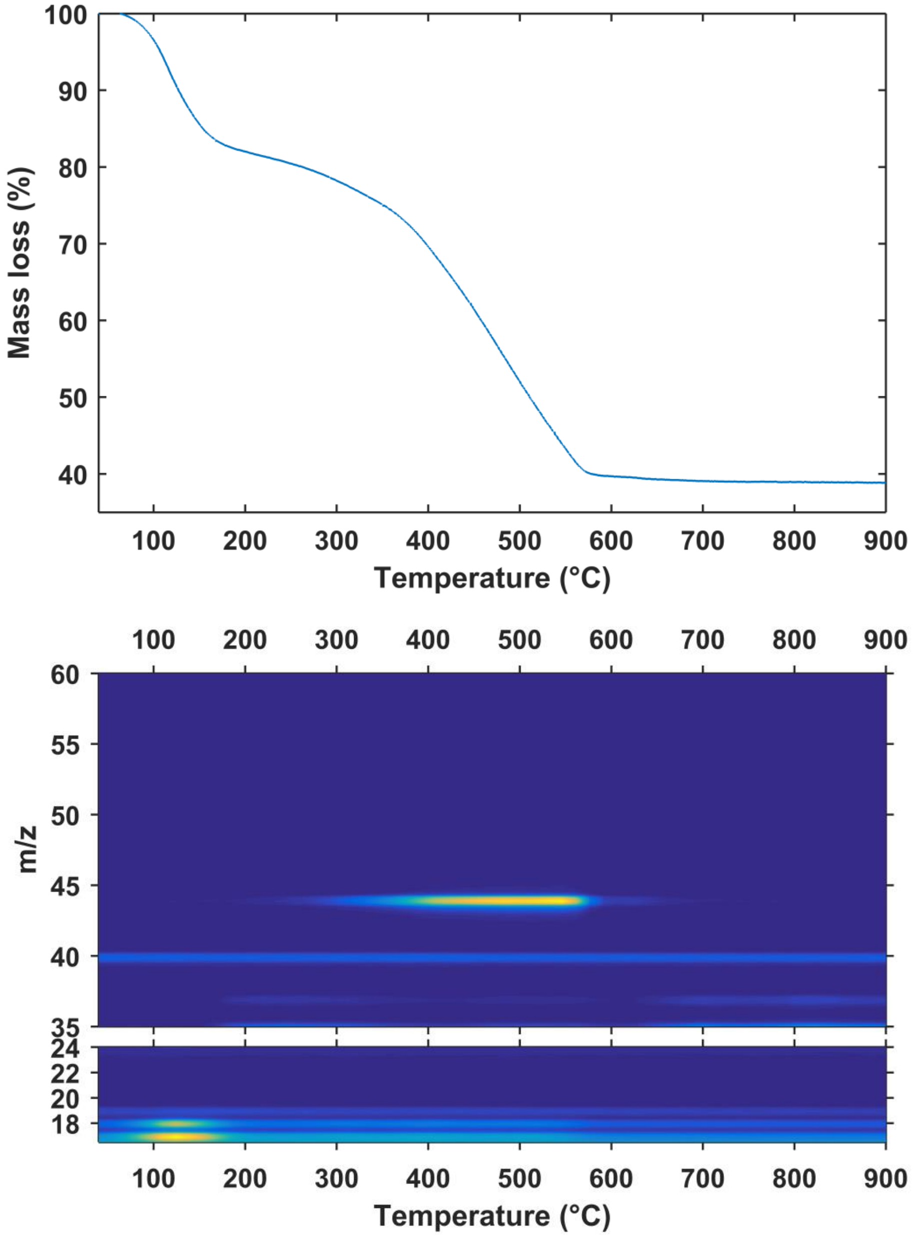


Fig SI-5.6- TGA of UiO-66-NH_2 diazo coupled with diphenylamine and MS for H_2O and CO_2 channels.

6 – Nitrogen sorption isotherms

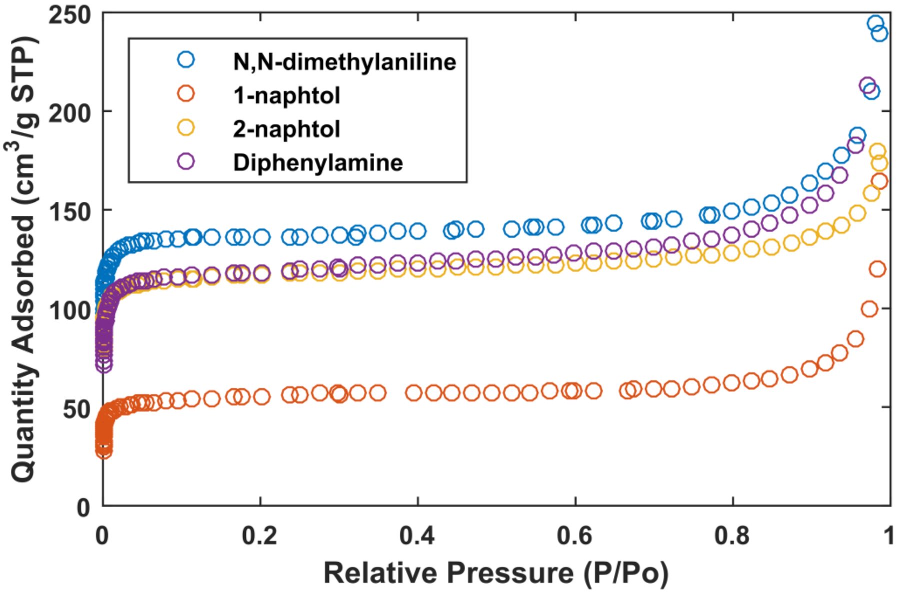


Fig SI-6- Isotherms of UiO-66-NH_2 coupled with N,N-dimethylaniline, 1-Naphthol, 2-Naphthol and Diphenylamine

7 – Photocatalysis

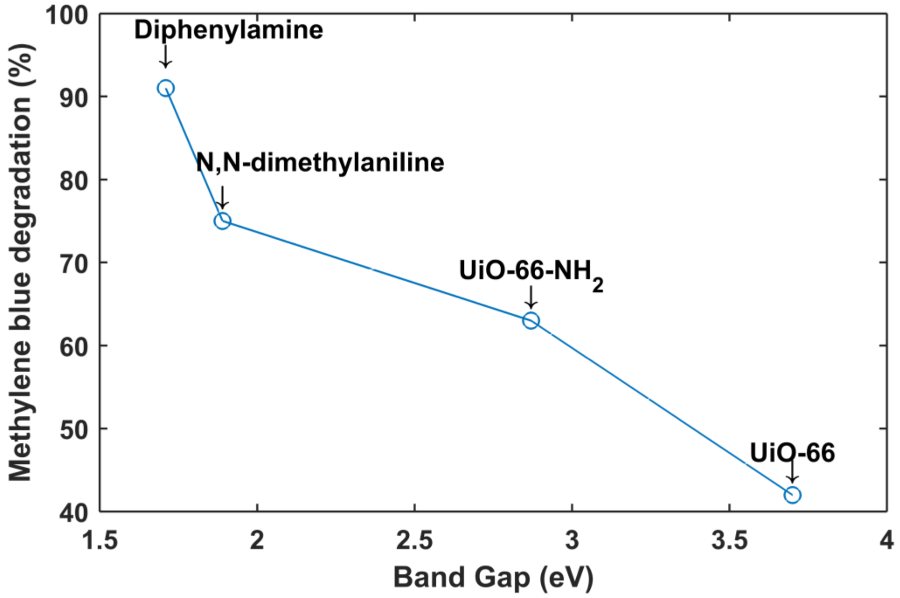


Fig SI-7- Correlation between band gap and Methylene Blue degradation performance.

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.

$$\%Mass\ loss_{corrected} = m_3 = {m_2}/{100\% - m_1} \cdot 100\% = {m_2}/{(m_2 + m_f)} \cdot 100\%$$

Sample	TGA solvent loss (%) m_1	TGA final mass (%) m_f	Normalized mass loss (%) m_3
UiO-66	13,6	38.4	44.5
UiO-66-NH_2	6,5	38.5	41.1
UiO-66-OH	N/A	N/A	N/A
N,N-dimethylaniline	9,8	37.4	41.4
1-naphtol	10,5	38.2	38.3
2-naphtol	7,9	36.5	39.6
Diphenylamine	7,1	38.8	41.7

Table SI-1 – TGA results

The decomposition path for UiO-66 should be:

$$Zr_{24}O_{120}C_{192}H_{96} + x\ O_2 \rightarrow 24\ ZrO_2 + \text{combustion products}$$

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

$$\%Mass\ loss_{ideal} = {24.Mr_{ZrO_2}}/{Mr_{\text{UiO}-66}} \cdot 100\%$$

$$Mr_{av} = {24.Mr_{ZrO_2} \cdot (100 - m_1)}/{m_f}$$

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: $Zr_{24}O_{144}C_{192}H_{96}$.

$$Mr_{av} = x_1.Mr_1 + x_2.Mr_2 = x_1.Mr_1 + (1 - x_1).Mr_2$$

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.

Sample	MOF molecular formula	MOF molecular mass (g/mol)	Ideal mass loss (%)	Average molecular mass-TGA (g/mol)	Diazo coupling yield (%)
UiO-66	$Zr_{24}O_{120}C_{192}H_{96}$	6509	45.4	N/A	N/A
UiO-66-NH_2	$Zr_{24}O_{120}C_{192}H_{144}N_{24}$	6869	43.0	N/A	N/A
UiO-66-OH	$Zr_{24}O_{144}C_{192}H_{96}$	6893	N/A	N/A	N/A
N,N-dimethylaniline	$Zr_{24}O_{120}C_{384}H_{288}N_{72}$	10013	29.5	7138	7,8
1-naphtol	$Zr_{24}O_{144}C_{432}H_{240}N_{48}$	10589	27.9	7725	22,5
2-naphtol	$Zr_{24}O_{144}C_{432}H_{240}N_{48}$	10589	27.9	7465	15,4
Diphenylamine	$Zr_{24}O_{144}C_{480}H_{312}N_{72}$	11573	25.6	7084	4.2

Table SI-2 – TGA calculations

9 – References

1 A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. – Eur. J.*, 2011, **17**, 6643–6651.

2 M. A. Nasalevich, M. G. Goesten, T. J. Savenije, F. Kapteijn and J. Gascon, *Chem. Commun.*, 2013, **49**, 10575–10577.

3 A. Bisset and T. J. Dines, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 499–505.

4 G. R. Ferreira, H. C. Garcia, M. R. C. Couri, H. F. Dos Santos and L. F. C. de Oliveira, *J. Phys. Chem. A*, 2013, **117**, 642–649.

5 P. J. Trotter, *Appl. Spectrosc.*, 1977, **31**, 30–35.

6 A. J. Barnes, M. A. Majid, M. A. Stuckey, P. Gregory and C. V. Stead, *Spectrochim. Acta Part A. Mol. Spectrosc.*, 1985, **41**, 629–635.

7 A. Bisset and T. J. Dines, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 1629–1636.

8 T. J. Dines, L. D. MacGregor and C. H. Rochester, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4096–4104.