Electronic Supporting Information

Enhancing optical absorption of Metal-Organic Frameworks for improved visible light photocatalysis

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1. Experimental section

1.1. Materials and reagents

All chemicals were purchased from Sigma-Aldrich and were used without further purification. Methanol and dimethylformamide (DMF) were additionally dried over molecular sieves (zeolite 5Å).

1.2. Synthesis details

Synthesis of MIL-125(Ti). This material was synthesized according to the method reported previously [1]. In a typical experiment 3.53 g of terephthalic acid and 56 mL of anhydrous DMF were mixed and placed in a round bottom flask. The mixture was then heated at 105^0 C for 1 hour to dissolve the acid and remove the water residuals. Keeping the temperature of the solution at 105^0 C 14 mL of anhydrous methanol was added and a reflux condenser was applied. The solution was boiled under stirring for 1 hour longer. After that 4.2 mL of titanium isopropoxide was added. The resulting mixture was kept under stirring and refluxed for 72 hour at 100^0 C. After cooling down to room temperature and filtering the mixture a white solid was isolated. It was washed with DMF for 24 hours at 155^0 C and then methanol at 100^0 C. The white product was dried in air at 100^0 C to remove methanol from the pores.

Synthesis of NH_2-MIL-125(Ti). Similar to the synthesis described above with the only difference of using 2-aminoterephtalic acid (ATA) instead of the terephthalic acid. Keeping the quantities of the other reagents constant one should use 3.85 g of ATA.

Synthesis of MR-MIL-125(Ti). For the synthesis of methyl red-MIL-125(Ti) 200 mg of NH_2-MIL-125(Ti) was suspended in 90 mL of water. Taking into account the molecular formula of NH_2-MIL-125(Ti) [$Ti_8O_8(OH)_4(C_6H_3C_2O_4NH_2)_6$] and the solvent content determined by TGA (~13%) this amount corresponds to 110 µmol. Thus the amount of NH_2 groups is 6 times as large and is 660 µmol. 45.5 mg of $NaNO_2$ (660 µmol) was dissolved in the water suspension of the MOF. The mixture is then cooled down to 0^0 C under continuous stirring and 60 mL 0.03 M HCl (3 fold excess with respect to the nitrite) was added dropwise keeping the temperature around 0^0 C. While stirring the suspension vigorously a colour change from yellow to almost white was observed within the first 10 minutes of the reaction. After 2 hours of reaction 197 mg of diethylaniline was dissolved in 30 mL of acetic acid (2 fold excess with respect to the nitrite) and added dropwise to the cold reaction mixture. At this stage the colour of the suspension was changing from white to orange. The mixture was allowed to warm up to room temperature within an hour and stirred for 2 hours longer in order to complete the transformation. The orange solid was filtered off, washed with acetic acid, acetone and dried at 100^0 C.

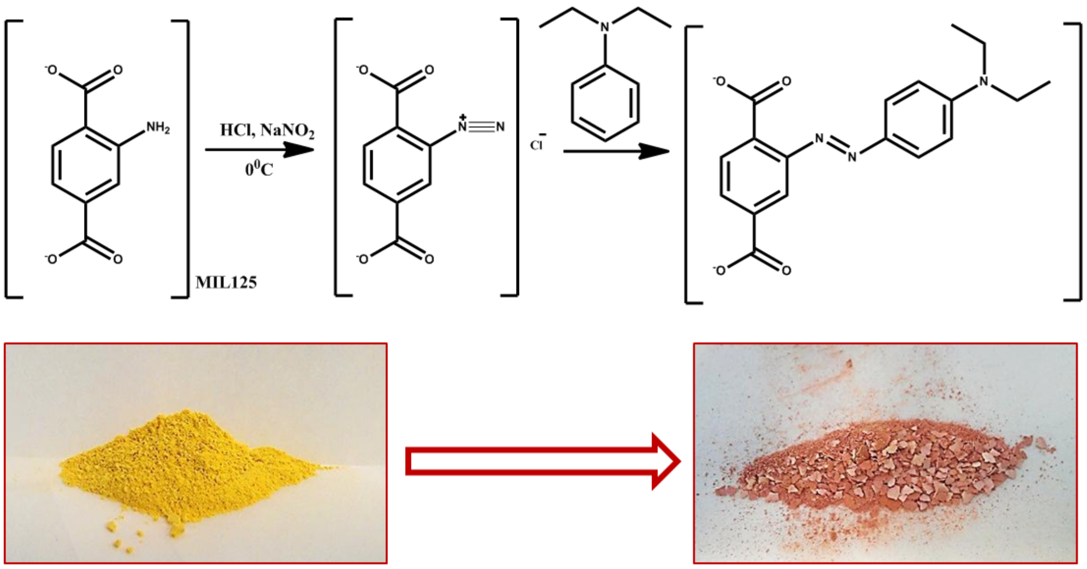


Figure S1. Post-synthetic modification scheme.

The reaction scheme is summarized in Figure S1. At the first stage the aminoterephthalates of the NH_2-MIL-125 framework are reacted with acidic solution of $NaNO_2$. Once the diazonium salt is formed it is further converted to the MR-MIL-125 material by the addition of diethylaniline. The change of the optical absorption is evident.

1.3. Photocatalytic tests

All the photocatalytic investigations were carried out in a home-built reactor. It consists of a standard 20 mL Perkin-Elmer scintillation vial capped with a Teflon lead. The lead is equipped with a Pyrex window at the top and two side ports for gas purging and sampling (Figure S2)

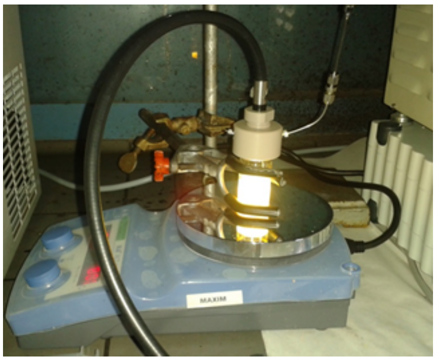


Figure S2. Photocatalytic reactor at work

APEX fiber illuminator (71225) serves as a light source (New Port, the USA). The model we used is equipped with 150W Xe lamp and there is a possibility of applying optical filters. The filter used in this work was S904200 (ESCO products, the USA). It cuts on the light of the 420 – 720 nm wavelength. Light intensity was measured with AvaSpec-3648-2-USB2 (Avantes, the Netherlands). The incident light power as a function of wavelength at the gas-liquid interface distance is plotted in Figure S3:

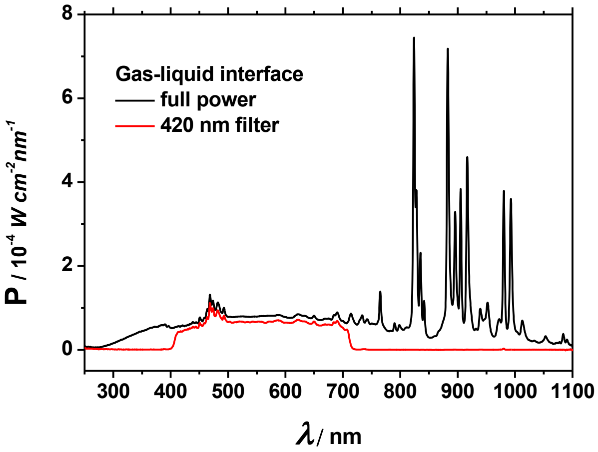


Figure S3. Incident photon power of the Xe lamp used in the photocatalytic experiments with (red) and without (black) 420 nm optical filter

In a typical experiment the reactor was loaded with 12 mL of CH_3CN, 200 µL of benzyl alcohol, 12/18 mg of a catalyst and purged with 30 mL/min air flow for 30 minutes. The mixture was sampled before and after the saturation of the solution with oxygen. The suspension was continuously stirred at the rate of 800 min^{-1}. After the saturation the illumination was started. The reaction mixture was periodically sampled with a filter-capped syringe. The volume of every probe was around 0.2 mL. The samples were analysed with 6890 gas chromatograph (Agilent) run isothermally. Benzaldehyde was found to be the only product of the reaction when the liquid phase was analysed. Blank experiments carried out in the dark didn't yield any appreciable changes of the benzaldehyde concentration. The blank experiment shown in the main text of the manuscript was performed in the absence of the catalysts.

In order to quantify the fraction of incident light that could be absorbed by the catalysts the diffuse reflectance UV/Vis data were transformed to $F(R)$ using the Kubelka-Munk function. The spectra were then normalized with respect to the most intense absorption bands. After obtaining the relative $F(R)$ spectra (in the form of the fractions of unity) and multiplying them by the measured incident photon power the following graph can be obtained:

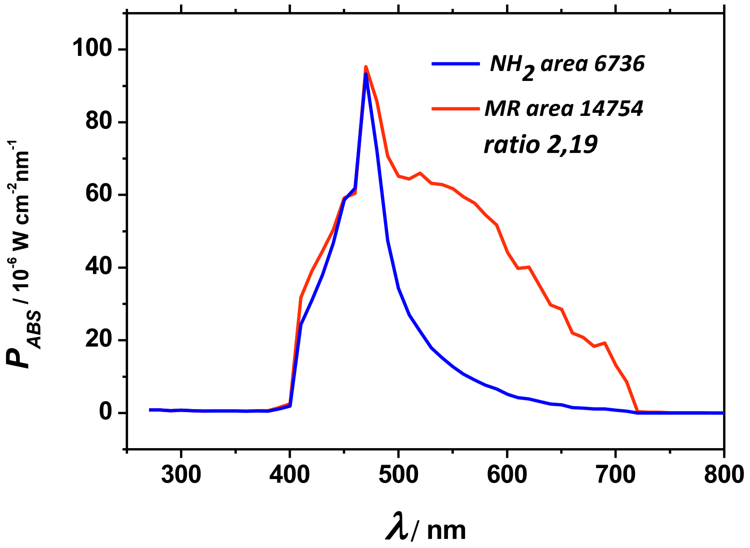


Figure S4. The incident light power that could be potentially absorbed by NH_2-MIL-125(Ti) (blue) and MR-MIL-125(Ti) (red)

Integration of the curves results in a total incident photon power corrected for the optical absorption of the two photocatalysts.

Turn-over frequency (*TOF*) of the different catalysts were calculated based on the formation of mol benzaldehyde per unit time and per mol of titanium present, extrapolated to the start of the experiment:

$$TOF = \frac{N_{benzaldehyde}}{N_{sites} \cdot t}$$

The number of sites N_{sites} was assumed to be equal to the number of titanium atoms:

$m_{NH2\text{-}MIL\text{-}125} = 12$ mg * 0.87 (water loss as determined by TGA) = 0.01044 g

$N_{NH2\text{-}MIL\text{-}125} = 0.01044$ g /1583.2 g/mol = $6.594*10^{-6}$ mol

$N_{Ti} = 8N_{NH2\text{-}MIL\text{-}125} = 8*6.594*10^{-6}$ mol = $5.275*10^{-5}$ mol

The C [mol/L] vs t [min] data in the case of NH_2-MIL-125(Ti) were correlated by a linear relation:

$C(t) = 7.762*10^{-8}\, t + 1.17*10^{-6}$ [mol/L].

The $7.762*10^{-8}$ slope is in [mol/(L min)] units and has to be corrected for the reactor volume of 12 mL to obtain a rate:

$$(7.762*10^{-8}\ \mathrm{mol/(L*min)})*0.012\ \mathrm{L} = 9.313*10^{-10}\ \mathrm{mol/min}$$

$$TOF_{NH_2-MIL-125} = \frac{9.313\cdot 10^{-10}}{5.275\cdot 10^{-5}} = 1.766\cdot 10^{-5}\min^{-1} = 0.00106h^{-1}$$

The same relation was used for the calculations of *TOF*s of the catalysts reported in literature.

The TGA from [2] did not reveal a significant weight loss while heating the sample up to 120 ^{0}C. Therefore the material was considered guest-free for the calculations. Since there was no TGA reported in [3] the catalyst was assumed to be guest-free.

However the loadings of the two catalysts were different: 12 mg in the case of NH_2-MIL-125(Ti) and 18 mg of MR-MIL-125(Ti). Taking into account the degree of functionalization determined by NMR one can calculate the activity enhancement in the case of the modified framework:

- 12 mg of NH_2-MIL-125(Ti) exhibited the BA formation rate of 0.931 nmol/min
- 18 mg of MR-MIL-125(Ti) produced 1.56 nmol/min
- According to the NMR analysis only 30% of the methyl red framework was functionalized. Therefore, 18 mg can be divided into 12.6 mg of NH_2-MIL-125(Ti) (70%) and 5.4 mg of MR-MIL-125(Ti). The latter is valid
- 12 mg of NH_2-MIL-125(Ti) gives an activity contribution of 0.931 nmol/min, then 12.6 mg of NH_2-MIL-125(Ti) corresponds to 9.776 nmol/min. Noteworthy, this is valid under the assumption that the catalyst activity linearly depends of the catalyst mass in this catalyst concentration regime.
- Thus 5.4 mg of MR-MIL-125(Ti) is responsible for the residual reaction rate contribution:
  (15.6 – 9.776) = 5.825 nmol/min
- If now one calculates the mass/activity ratios for the frameworks:
  MR: $\frac{m}{A} = \frac{5.4}{5.825} = 0.927$ NH_2: $\frac{m}{A} = \frac{12}{9.31} = 1.289$

The ratio of these two reveals the activity gain in the case of the modified structure: 1.289/0.927 = 1.4 ~ 40% gain.

In the main text this value is compared against the increase of the optical absorption (2.2 fold). The comparison is reasonable since the absorption enhancement originates from the modified fraction of the framework (30%) while 70% which is, in fact, NH_2-MIL-125(Ti) should have the same optical absorption as in the case of the pure non-modified framework.

1.4. Recyclability test

In order to prove the stability of the catalyst a recyclability test was carried out. In this experiment 21 mg of MR-MIL-125(Ti) was suspended in 12 mL of CH_3CN, 200 µL of benzyl alcohol was added. Then an air flow of 30 mL/min was applied for 30 minutes. After saturating the preparation with oxygen and taking the first sample, the reaction mixture was exposed to the visible light of the same light source as described above. The reaction was sampled every 6 hours and analysed with the GC. After completion of the first 24 hours of the reaction the catalyst was filtered off, washed on a filter with CH_3CN and dried in air at room temperature. The spent catalyst was used for the second cycle following the same procedure. The results of the test are depicted in Figure S5:

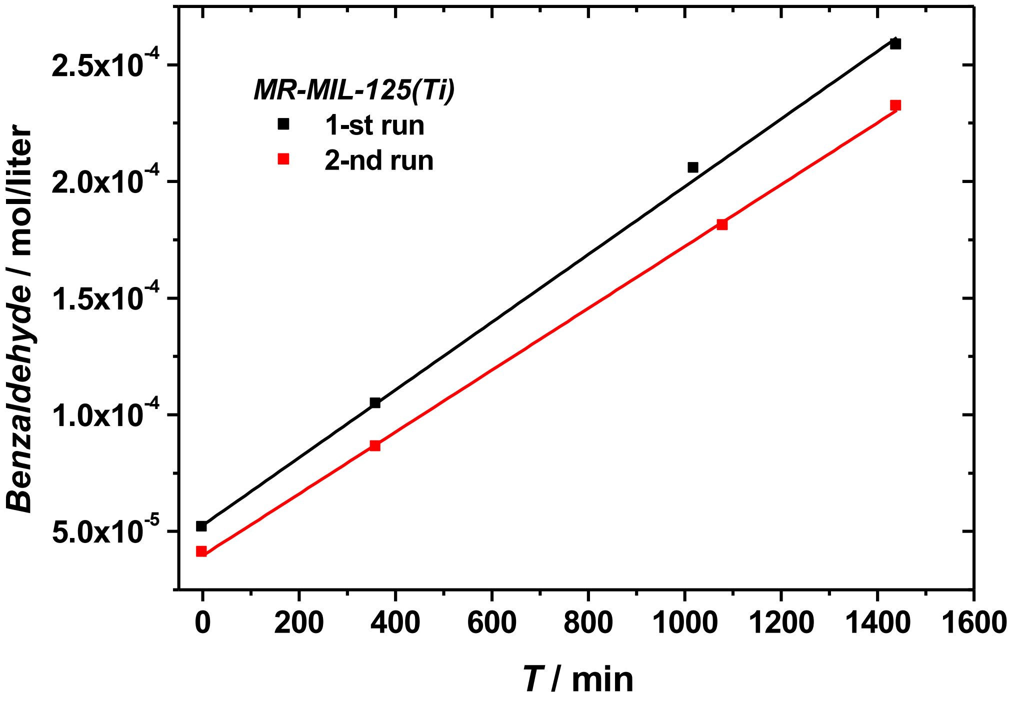


Figure S5. The recyclability test. The catalyst can be recycled without losses of its photocatalytic activity.

As is evident from the plot the activity of the catalyst remains constant after recycling. The fitting of the kinetic curves linear equations resulted into the following rates:

$1.451*10^{-7}$ [mol/(L min)] in the first run and $1.325*10^{-7}$ [mol/(L min)] in the second. These rates correspond to the activities of 82.9 [nmol/(g min)] and 79.5 [nmol/(g min)] respectively which are well in line with the value found previously (86.7 [nmol/(g min)]). These results clearly indicate that the catalyst can be recycled without significant loss of activity. Moreover, no catalyst deactivation is observed after 24 hours of illumination suggesting the excellent stability of this photocatalytic system.

1.5. Characterization and Methods

X-Ray diffraction patterns were measured using Bruker-AXS D5005 with CuKa radiation.

N_2-physisorption experiments were carried out at 77K in Quantachrome Autosorb-6B unit gas adsorption analyser. Prior to the measurements the samples were degassed at 423K under vacuum for 16 hours. The BET surface areas were calculated using intervals allowing positive BET constants. The total pore volumes were calculated at 0.95 relative pressure.

DRIFT studies were performed with a standard IFS66 spectrometer (Bruker), equipped with a high-temperature cell with CaF_2 windows and a 633 nm laser. The spectra were collected with a resolution of 4 cm^{-1}. KBr was used as a background. Before the spectra were taken the samples were heated at 120 ^0C in a 10 mL/min He flow.

NMR investigations: The ^1H NMR was performed at Varian-Inova spectrometer at 25^oC, operating at 300 MHz. 20 mg of MR-MIL-125(Ti) was dissolved in concentrated KOH and then placed in a 5 mm NMR tube and 10% (vol.) of D_2O was added. The chemical shift was related to an external standard *t*-BuOH (1.2 ppm).

Photoluminescence studies: Steady-state emission spectra were acquired using a QuantaMaster QM-1 (PTI). 100 W Xenon arc lamp (200-900 nm) was used as a light source equipped with 121A excitation double monochromators. Model MP-1 sample compartment, 101A emission monochromator, Model 710 photon counting detector PMT (185-900 nm) completed the experimental setup.

Scanning Electron Microscopy was carried out with a Philips XL 20 (tungsten) microscope. The microscope can be operated at voltages 1 – 30 kV with a resolution of 6 – 9 nm. Gold on carbon was used as a test-sample.

Diffuse reflectance UV/Vis spectra were recorded using Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating sphere (‘‘Labsphere”) in the 200–800 nm range. $BaSO_4$ was used as a white standard.

Time Resolved Microwave Conductivity (TRMC)

TRMC probes a change in conductance induced by light. This change represents the product of charge generation yield and the charge carriers’ mobility. In a typical experiment a sample is excited with a laser pulse and mobile charge carriers are probed with microwaves. These experiments were performed at a dedicated home-built setup. For a complete description one is referred to [4]. Excitation of the sample was achieved by 340 nm laser light pulses of a Q-switched Nd:YAG laser (“Infinity 15-30”, Coherent). The laser was employed to pump an optical parametric oscillator (OPO) yielding 3 ns fwhm pulses. The experiments were carried out at the full light intensity of $2.024*10^{14}$ incident photons/cm^2.

2. Results

2.1. X-Ray diffraction

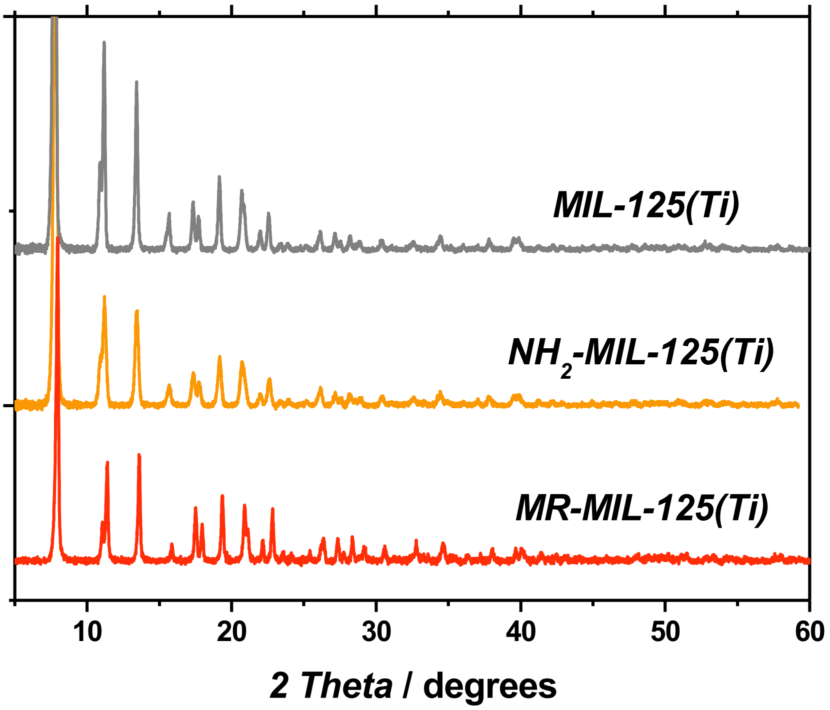


Figure S6. PXRD patterns of the X-MIL-125(Ti) series catalysts:

MIL-125(Ti) (gray), NH$_2$-MIL-125(Ti) (orange) and MR-MIL-125(Ti) (red). Both structures show a P1(1)-triclinic lattice (a = b = 18.67 Å, c=18.14 Å, α = β = γ = 90.00°)

2.2. Nitrogen physisorption

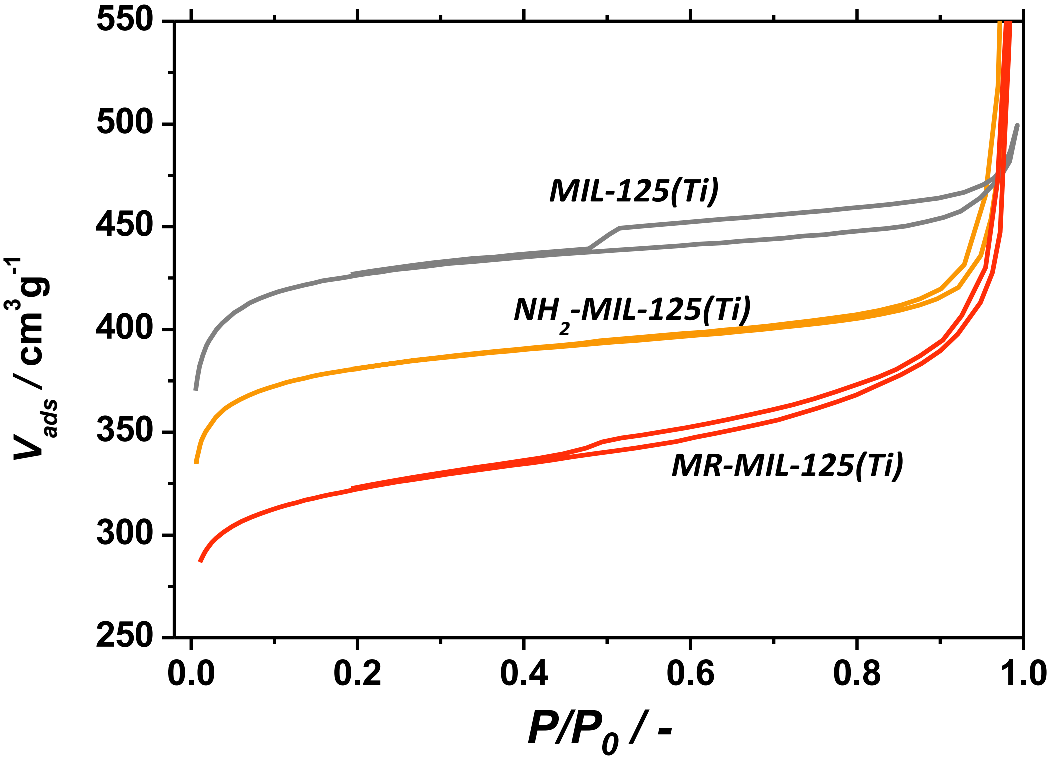


Figure S7. Nitrogen adsorption isotherms

Catalyst	S_{BET} m^2/g	**Range of relative pressures used for BET calculation**	V_p mL/g
MIL-125(Ti)	1710	(5.4 – 30.3) ***10^{-3}**	0.72
NH$_2$-MIL-125(Ti)	1500	(6.1 – 69.3) ***10^{-3}**	0.67
MR-MIL-125(Ti)	1250	(11 – 72.5) ***10^{-3}**	0.64

Table S1. Textural properties of the three catalysts investigated in the study

2.3. DRIFT analysis

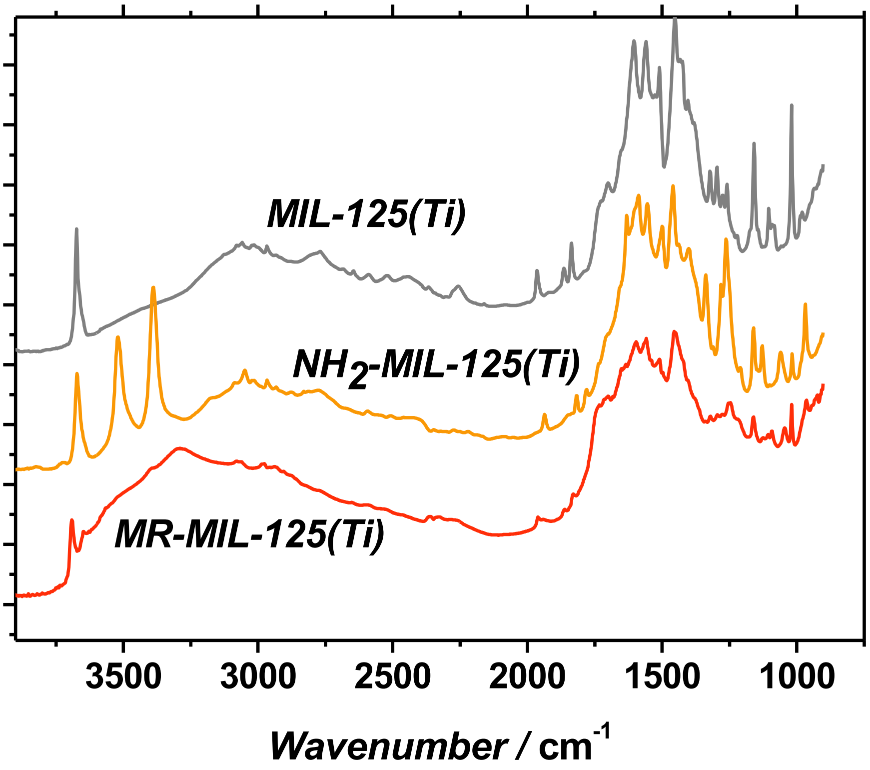


Figure S8. Diffuse Reflectance Fourier-Transform spectroscopy of the three catalysts: MIL-125(Ti) (gray), NH_2-MIL-125(Ti) (orange) and MR-MIL-125(Ti) (red).

2.4. Nuclear Magnetic Resonance analysis

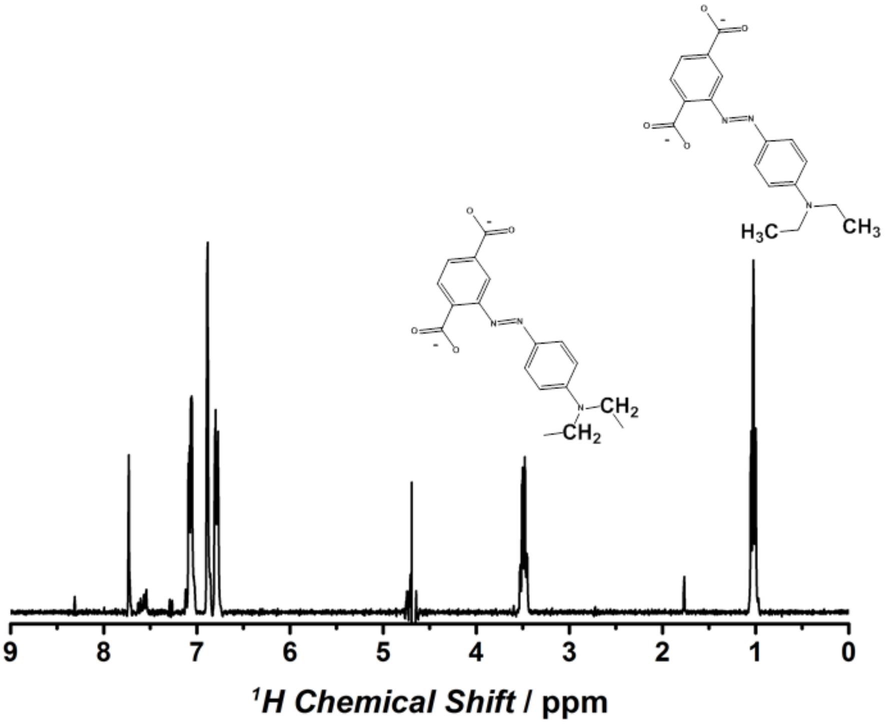
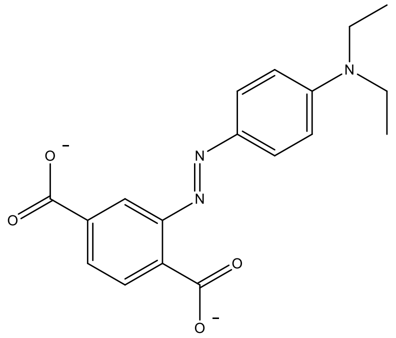


Figure S9. 1H-NMR of the dissolved in NaOH methyl red-MIL-125(Ti). The two alkyl signals can be seen at around 1 and 3.5 ppm.

Quantitative NMR analysis



Because the imine bond is cleaved by dissolution in KOH, it is difficult to say whether the aromatic resonances originate from the MOF linker or from the diethyl aniline functionality. It is therefore safer to perform quantitative analysis integrating over the complete aromatic region, and establish the following expected ratios:

$$R_1 = \frac{3+4\alpha}{4\alpha}$$

$$R_2 = \frac{3+4\alpha}{6\alpha}$$

R_1 is the ratio between aromatic protons and methylene protons from the functionality, R_2 the ratio between aromatic protons and methyl protons, α is a value between 0 and 1, which is the degree of functionalization. Each aniline functionality brings four aromatic protons, four methylene protons and six methyl protons – which leads to these ratios. From integration of the NMR spectra of the dissolved MOF samples we obtain:

R_1=3.93 and R_2=2.341 which lead to $\alpha = 0.256$ and $\alpha = 0.299$. This therefore suggests that the degree of functionalization lies between 25.6% and 29.9%.

2.5. Photoluminescence studies

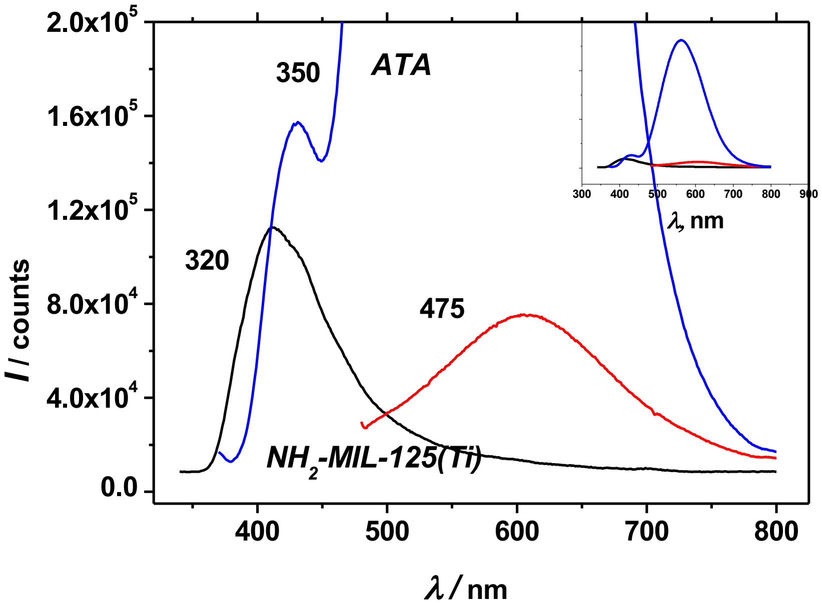


Figure S10. Steady-state emission spectra of NH_2-MIL-125(Ti) and aminoterephtalic acid (ATA) obtained with a slit of 10 and 2 nm respectively. NH_2-MIL-125(Ti): excitation at 320 nm (black) – 380 nm filter, excitation at 450 nm (red) – 475 nm filter. ATA: excitation at 350 nm (blue) – 380 nm filter. The inset shows the difference in emission magnitudes for the two materials.

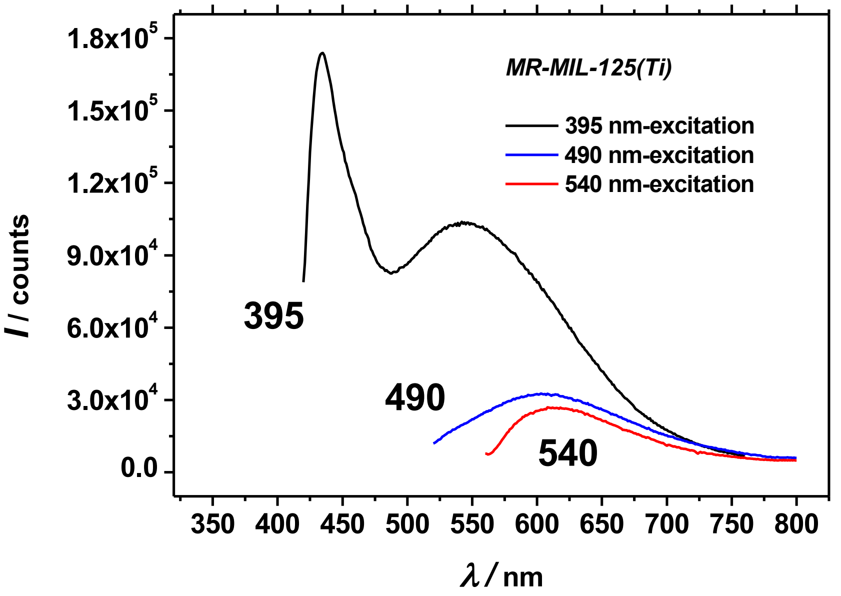


Figure S11. Steady-state emission spectra of MR-MIL-125(Ti) obtained with a slit of 10 nm: excitation at 395 nm (black) – 420 nm filter, excitation at 490 nm (blue) – 515 nm filter, excitation at 540 nm (red) – 570 nm filter.

The materials utilized in the current study have been subjected to photoluminescence spectroscopic investigations. Figure S10 displays steady-state emission spectra of NH_2-MIL-125(Ti) and the corresponding linker, aminoterephtalic acid, measured at different excitation wavelengths. One should note that the measurements were carried out at different slits: 2 nm for ATA and 10 nm for NH_2-MIL-125(Ti). The larger the slit the more light a sample receives. The two different slits were used in order to compensate for the dramatic difference in the emission intensities for the two materials and to avoid the oversaturation of the detector. This result clearly shows that the massive radiative decay of the free linker (ATA) originating from the local excitation of the molecule [5] is barely detectable in the case of NH_2-MIL-125(Ti). It suggests that most of the light absorbed by the MOF can be further used for photocatalytic transformations. However, the non-radiative relaxation mechanisms have to be taken into account.

Figure S11 demonstrates steady-state emission spectra of MR-MIL-125(Ti). As is evident from the figure, upon excitation at 395 nm the MR-MIL-125(Ti) exhibits two distinct emission band centred at 435 and 545 nm. The band at 435 nm can originate from the 70% of NH_2-MIL-125(Ti) found in the modified framework as revealed by the NMR analysis. Indeed, the emission of non-functionalized NH_2-MIL-125(Ti) demonstrates a similar band centred at 415 nm. The red-shift of the emission band in the case of the modified framework can be a sign of an interaction between the two components of the MR-MIL-125(Ti) framework. A more detailed investigation of the electronic properties of the materials is needed in order to provide a comprehensive interpretation of the emission spectra.

2.6. Scanning Electron Miscroscopy

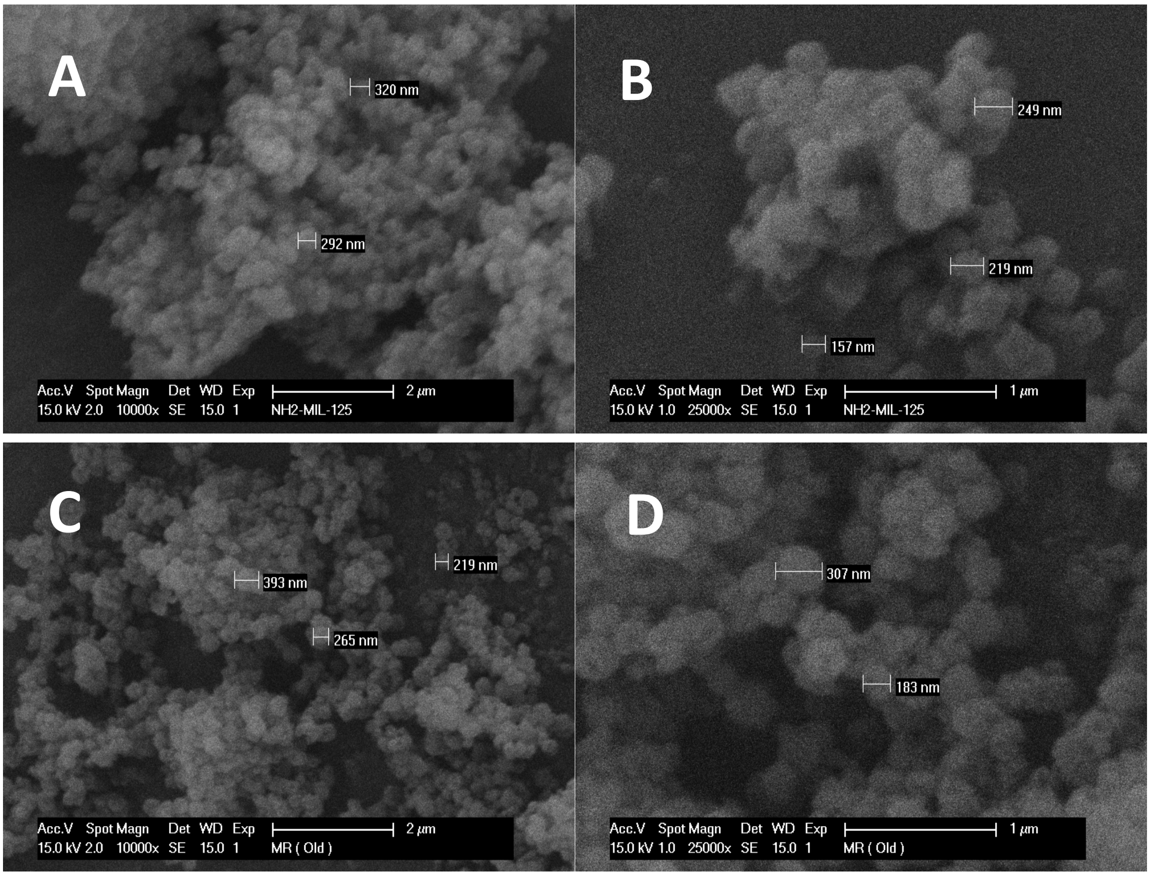


Figure S12. SEM images of NH_2-MIL-125(Ti) (A, B) and MR-MIL-125(Ti) (C, D)

Figure S12 shows SEM images of NH_2-MIL-125(Ti) and MR-MIL-125(Ti) recorded at two different magnifications. One can see that the crystal shape and the crystal size are preserved during the post-functionalization.

2.7. Diffuse Reflectance UV/Vis Spectroscopy

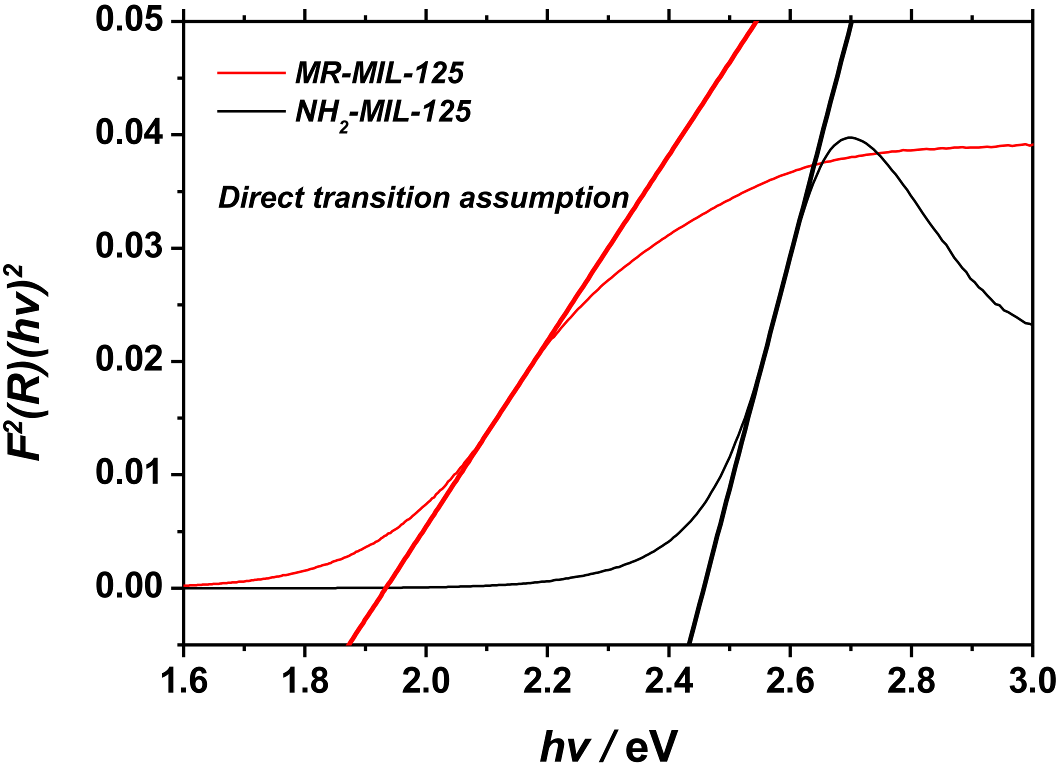


Figure S13. Tauc plot for the two photocatalysts: NH_2-MIL-125(Ti) (black) and MR-MIL-125(Ti) (red).

A Tauc plot was used in order to calculate "band gaps" of the solids. The Kubelka-Munk functions, *F(R)*, were taken for the calculation instead of absorption coefficients used in a classical model. Noteworthy, the degree of *F(R)*, i.e. square, indicates that the transitions are believed to be direct. The band gap energies determined by linearization of the Tauc curves were found to be 2.46 and 1.93 eV for NH_2-MIL-125(Ti) and MR-MIL-125(Ti) respectively. We should emphasise that the band gap energies are reported for the sake of convenience while such a characteristic is not applicable for the MIL-125(Ti) in a view of the current study.

2.8. Time Resolved Microwave Conductivity

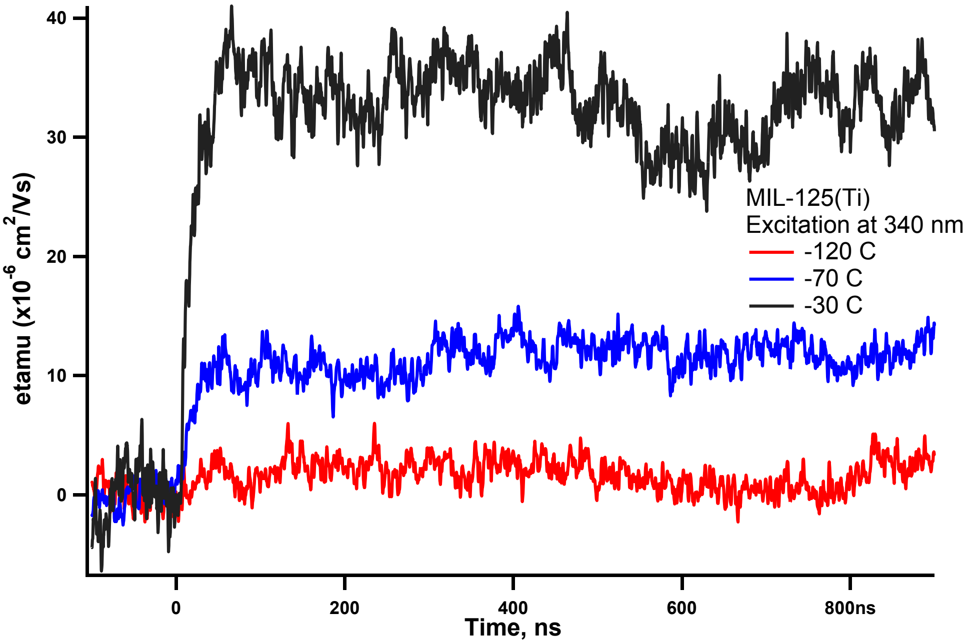


Figure S14. Time-resolved microwave conductivity traces for MIL-125(Ti). The experiments were carried out at the excitation wavelength 340 nm and at 3 different temperatures: -120 °C (red), -70 °C (blue) and -30 °C (black).

TRMC probes a change of conductance which is a product of charge generation yield and charge carriers mobility. In order to distinguish between the two physical parameters additional transient absorption spectroscopic studies are needed. However, assuming a charge generation yield of 100% then this results in a poor conductance of ~10^{-5} $cm^2V^{-1}s^{-1}$ for MIL-125(Ti) As a matter of comparison the mobility of TiO_2 is ~1 $cm^2V^{-1}s^{-1}$ [6]

As is evident from Figure S14 the change of conductance is strongly dependent on temperature in contrast to the typical semiconductor behaviour. Our observations suggest tunnelling as the main pathway for charge carrier mobility.

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