

Supporting information

Textural properties were determined from N₂ adsorption/desorption isotherms measured at 77 K. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. Hydrogen sorption properties were determined by the Sievert's manometric method on outgassed samples at 473 K under dynamic vacuum. The excess sorption isotherms at 77 K (wt.% hydrogen excess amount over the initial dry mass of the sample) were measured with a good repeatability. Real equation of state from NIST package was used for hydrogen gas. The excess sorption isotherms display a type I trend typical for monolayer adsorption on microporous materials. The adsorption and desorption isotherms are completely reversible, whatever the solid.

Microcalorimetry experiments were carried out at 77 K. The calorimeter consists of two thermopiles of around 800 thermocouples each, mounted in electrical opposition. This system is immersed in a liquid nitrogen cryostat. Around 100 mg of sample is placed in a sample cell, which after outgassing during one night under a vacuum of 0.6 Pa, is attached to a simple manometric device coupled to the calorimeter. A continuous procedure of H₂ introduction is employed which is slow enough (around 2.9 cm³.h⁻¹) to be in *quasi-equilibrium* conditions. Once these conditions are verified, this procedure leads to a high resolution in both the isotherm and differential enthalpies of adsorption. Each experiment was repeated at least twice to ensure repeatability.

Evolution of the hydrogen sorption capacities as a function of the specific surface area is shown in Figure S1. A linear correlation (full line) has been refined from the data. However grafted MIL53(Fe)-(CF₃)₂ and non grafted UiO-66(Zr) with the largest heat of adsorption are clearly above the correlation line.

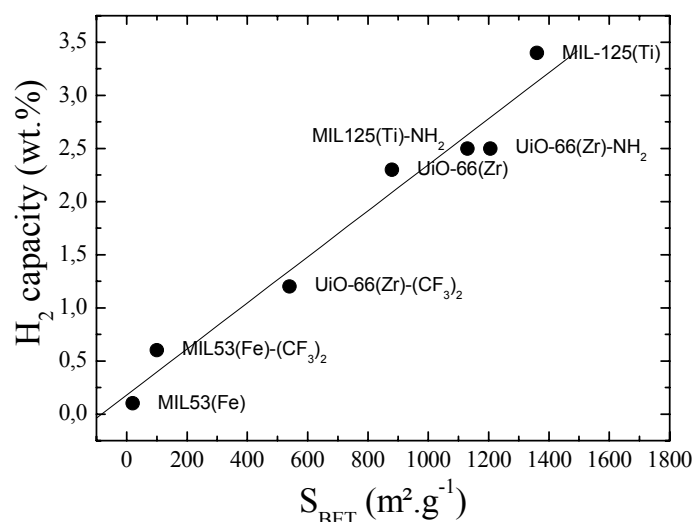


Figure S1: Evolution of the hydrogen capacity determined at 77K and 4 MPa as a function of the specific surface area.

Synthesis of MOF samples.

MIL-53(Fe) was prepared as described in Ref. 23. from a mixture of 10 mmol of terephthalic or 1,4 benzenedicarboxylic acid $\text{HO}_2\text{CC}_6\text{H}_4\text{-CO}_2\text{H}$ (Aldrich, 98%), 5 mmol of iron(III) chloride hexahydrate (Aldrich, 99%) in 50 mL of dimethylformamide (DMF) (Aldrich, 98%). The slurry is then introduced in a 125 ml Teflon liner further introduced in a metallic PAAR bomb. The system is then heated overnight (16 h) at 150°C . The resulting yellow product was filtered off. To exchange DMF remaining into the pores with water, the solid was suspended in deionized water under stirring for 16 h. X-Ray powder diffractogram (Bruker D5000, $\lambda_{\text{Cu}} \approx 1.5406 \text{ \AA}$) of the sample is in a very good agreement with the one calculated from the published structure (Figure S2).

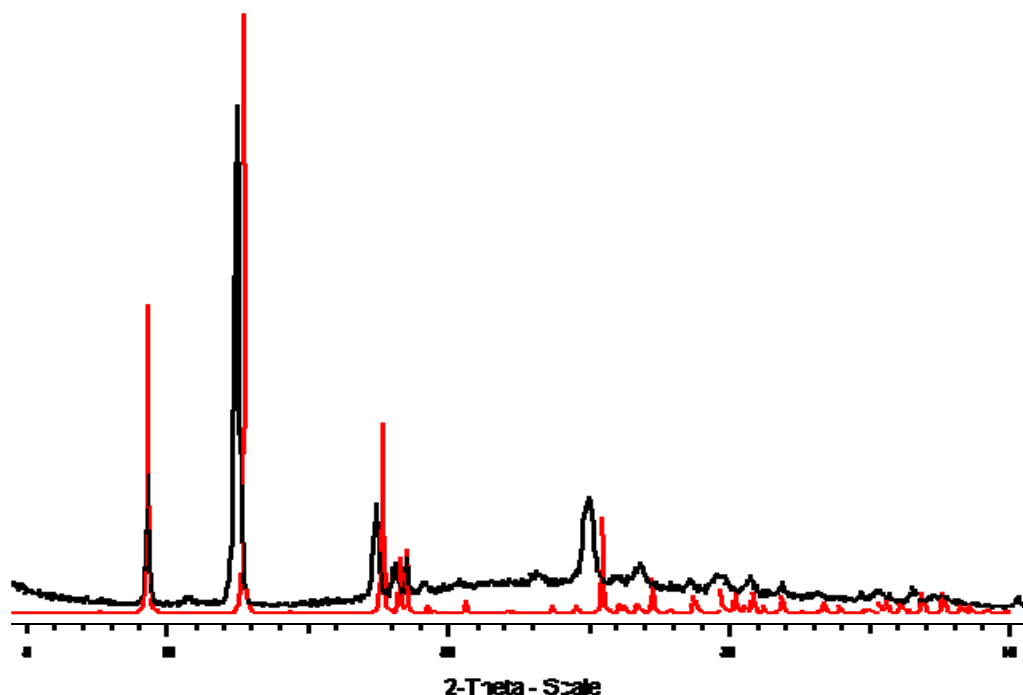


Figure S2. Comparison of the simulated XRD pattern of MIL-53(Fe) (red) with the experimental XRD pattern of MIL-53(Fe) (black).

MIL-53(Fe)-(CF₃)₂ was prepared as already described in Ref.18 from a mixture of 5 mmol of 2,5-diperfluoromethylterephthalic acid $\text{HO}_2\text{CC}_6\text{H}_2(\text{CF}_3)_2\text{-CO}_2\text{H}$, 5 mmol of iron(III) chloride hexahydrate (Aldrich, 99%) in 50 mL of deionized water. The slurry is then introduced in a 125 ml Teflon liner further introduced in a metallic PAAR bomb. The system is then heated overnight (16 h) at 100°C . The resulting yellow product is filtered off, washed with deionised water and then dried at room temperature. The sample is finally heated at 250°C under vacuum (5 mbar) for 2 days to remove the free linker from the framework. X-Ray powder pattern (Bruker D5000, $\lambda_{\text{Cu}} \approx 1.5406 \text{ \AA}$) of this flexible sample shows a mixture of two forms with different pore opening, similarly to previous reported structure. (Figure S3).

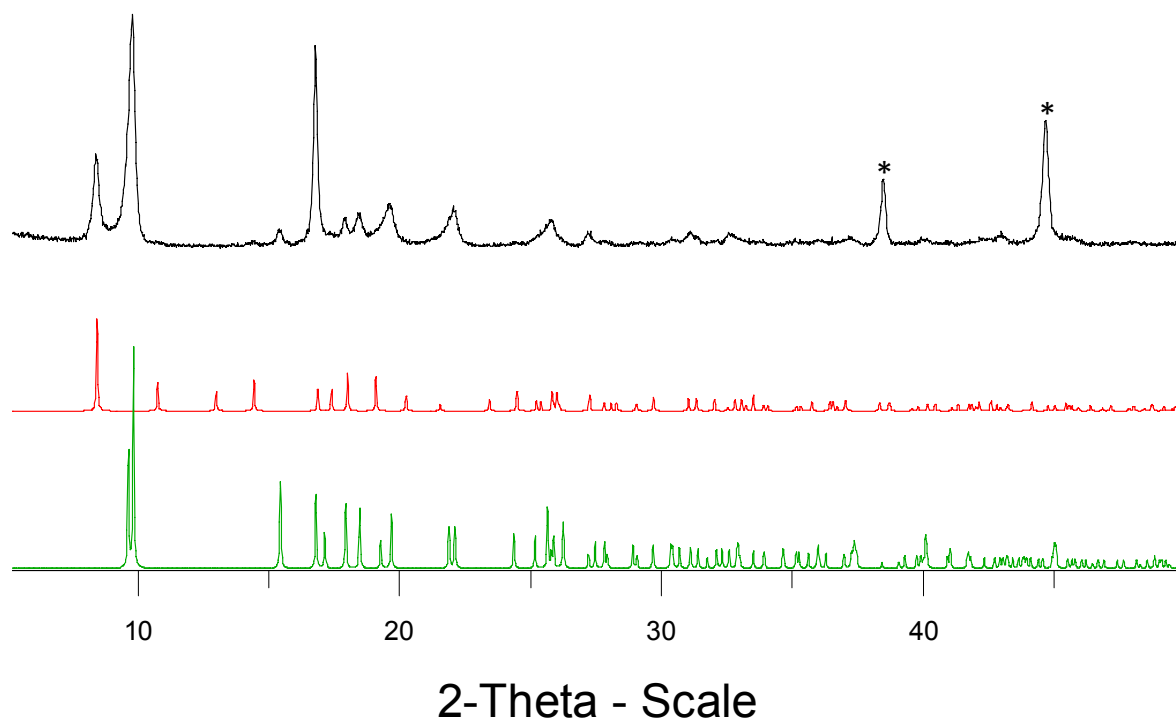


Figure S3. Comparison of the simulated XRD pattern of open (red) and close (green) form of MIL-53(Fe)-(CF₃)₂ with the experimental XRD pattern of MIL-53(Fe)-(CF₃)₂ (black). * : Al sample holder.

UiO-66(Zr) is prepared from a large scale mixture of zirconium tetrachloride ZrCl₄ (Aldrich, 99.9%), terephthalic acid or 1,4 benzenedicarboxylic acid HO₂CC₆H₄-CO₂H (Aldrich, 98%), hydrochloric acid (Aldrich, 37%) and DMF (Aldrich, 98%) in the 25 mmol : 50 mmol : 50 mmol : 150 mL ratio. The slurry is then introduced in a 750 ml Teflon liner further introduced in a metallic PAAR bomb. The system is then heated overnight (16 h) at 220°C. The resulting white product is filtered off, washed with DMF to remove the excess of unreacted terephthalic acid, then washed again with acetone and then dried at room temperature. The sample is finally heated at 250°C under vacuum (5 mbar) to remove the DMF from the framework. X-Ray powder diffractogram (Bruker D5000, $\lambda_{\text{Cu}} \approx 1.5406 \text{ \AA}$) of the sample is in a very good agreement with the one calculated from the published structure (Figure S4). Nitrogen sorption measurements (BelSorp Max apparatus) gave a BET surface area of 880(4) m².g⁻¹.

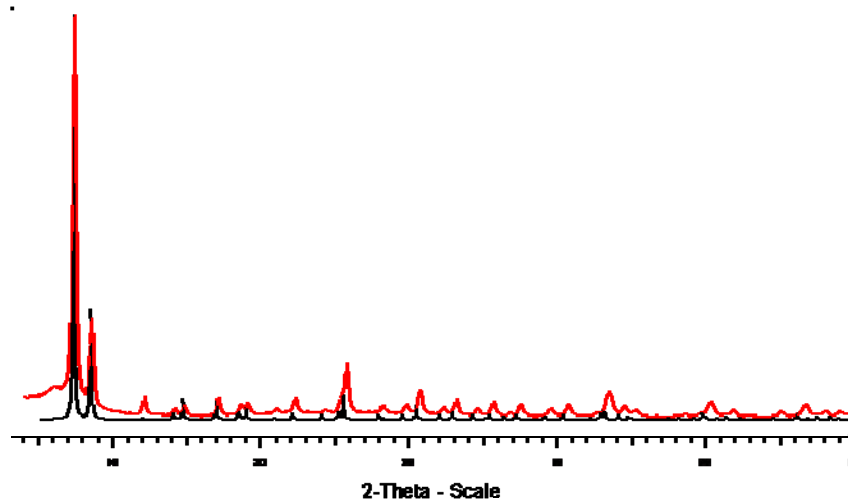


Figure S4. Comparison of the simulated XRD pattern of UiO-66 (black) with the experimental XRD pattern of UiO-66(Zr) (red).

UiO-66(Zr)-NH₂ A solution of 1 mmol of zirconium tetrachloride ZrCl₄ (Aldrich, 99.9%) and 1 mmol of 2-aminoterephthalic acid HO₂CC₆H₃NH₂-CO₂H (Aldrich, 99%) in 3.0 mL of DMF (Aldrich, 98%) was prepared and added to a 23 mL teflon liner. The reaction took place in a metallic PARR digestion bomb by heating to 100°C for 24 hours. After cooling to room temperature, the solid was recovered by filtration. The solid was further treated using DMF, the compound was then left overnight in large volumes of DMF. After a second filtration, the solid was washed with tetrahydrofuran (THF; Aldrich, 99.9%). A comparison between the simulated and experimental XRD patterns is shown in Figure S5.

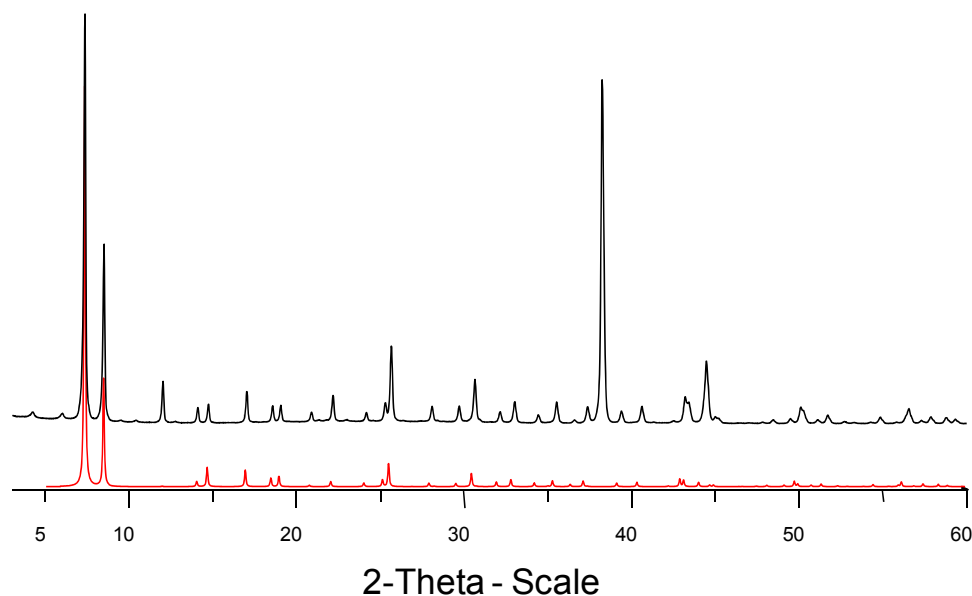


Figure S5. Comparison of the simulated XRD pattern of UiO-66(Zr)-NH₂ (black) with the experimental XRD pattern of UiO-66(Zr)-NH₂ (red).

UiO-66(Zr)-(CF₃)₂ was prepared for the first time from a large scale mixture of zirconium

tetrachloride $ZrCl_4$ (Aldrich, 99.9%), diperfluoromethyl terephthalic acid $HO_2CC_6H_2(CF_3)_2-CO_2H$ (synthesised as described in ref. 18), hydrochloric acid (Aldrich, 37%) and DMF (Aldrich, 98%) in the 2.5 mmol : 2.5 mmol : 2.5 mmol : 150 mL ratio. The slurry was then introduced in a 125 mL Teflon liner and further introduced in a metallic PARR bomb. The system was heated for a day (24 h) at 100 °C. The resulting white product was filtered off, washed with DMF to remove the excess of unreacted organic ligand, then washed again with THF to exchange DMF with THF (Aldrich, 99.9%), more volatile and easily removable by moderate heating. X-Ray powder diffractogram (Brüker D5000, $\lambda_{Cu} \approx 1.5406 \text{ \AA}$) of the sample is in a very good agreement with the one calculated from the non-functionalised published structure (see Figure S6). Nitrogen sorption measurements (BelSorp Mini apparatus) gave a BET surface area of 540(2) m^2/g . This lower surface area is in agreement with the effect of sterical hindrance and the heavier molecular weight of this unprecedented modified UiO-66(Zr).

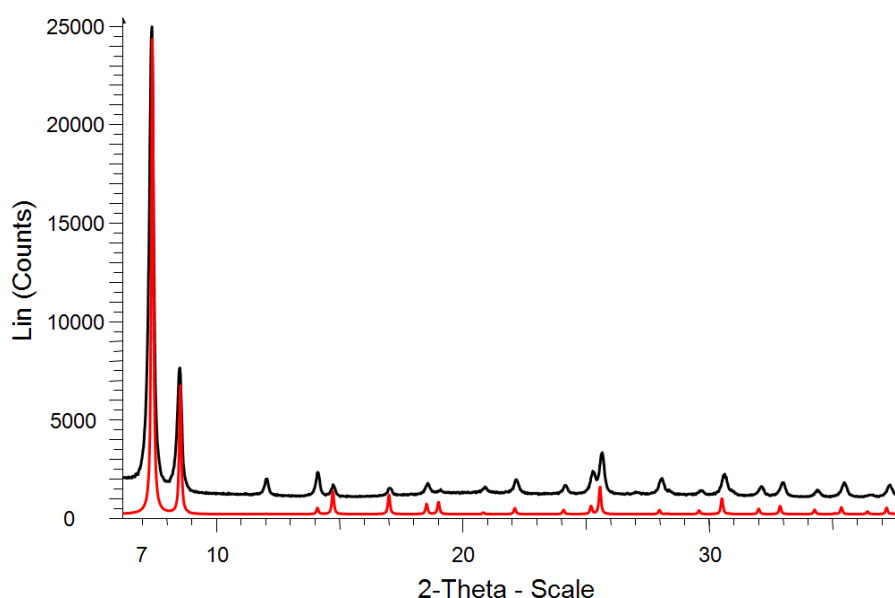


Figure S6. Comparison of the simulated XRD pattern of UiO-66 (red) with the experimental XRD pattern of UiO-66(Zr)-(CF₃)₂ (black).

MIL-125(Ti) or $Ti_8O_8(OH)_4[O_2C-C_6H_4-CO_2]_6$ was obtained as previously reported (Ref. 20) starting from 1.5 mmol of terephthalic acid (250 mg) (Aldrich, 98 %), 1 mmol of titanium isopropoxide $Ti(OiPr)_4$ (0.3 ml) (Acros Organics, 98%), introduced in a solution of 4.5 ml of DMF (Acros Organics, extra-dry) and 0.5 ml of dry methanol (Aldrich, 99.9%). The mixture was stirred gently during 5 minutes at room temperature and then further introduced in a 23 ml Teflon liner and then put into a metallic PAAR digestion bomb at 150°C during 15 hours. Back to room temperature, the white solid was recovered by filtration, washed twice with acetone and dried under air at room temperature. The resulting white product was filtered off, washed with DMF to remove the excess of unreacted organic ligand, then washed again with methanol to exchange

DMF with MeOH, more volatile and easily removable by moderate heating. Nitrogen sorption measurements (BelSorp Mini apparatus) gave a BET surface area of 1360(5) m²/g. A comparison between the simulated and experimental XRD patterns is shown in Figure S7.

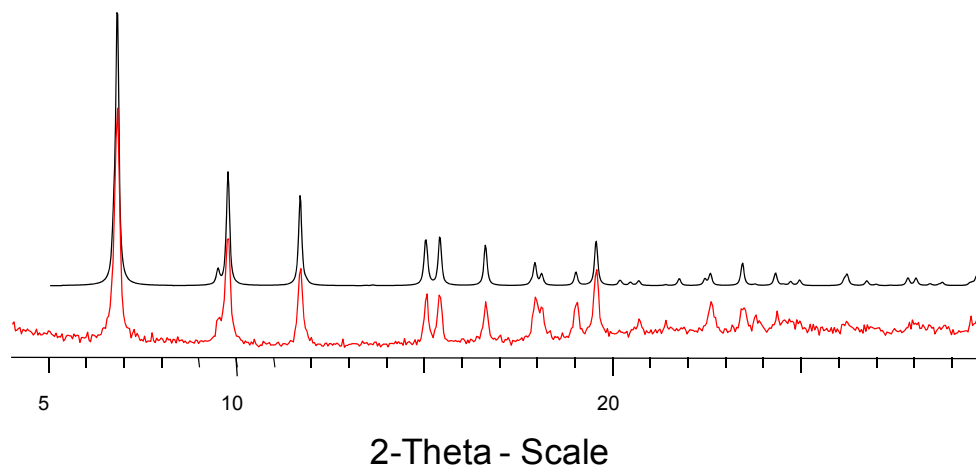


Figure S7. Comparison of the simulated XRD pattern of MIL-125(Ti) (black) with the experimental XRD pattern of MIL-125(Ti) (red).

MIL-125(Ti)-NH₂ was prepared for the first time from a large scale mixture of titanium isopropoxide TiOⁱPr (Acros Organics, 98%), 2-aminoterephthalic acid HO₂CC₆H₃NH₂-CO₂H (Aldrich, 99%), methanol (Aldrich, 99.9%) and DMF (Acros Organics, extra-dry) in the 1.5 mmol : 3 mmol : 12.5 mL : 12.5 mL ratio. The slurry was then introduced in a 125 mL Teflon liner and further introduced in a metallic PARR bomb. The system was heated overnight (16 h) at 150 °C. The resulting light yellow product was filtered off, washed with DMF to remove the excess of unreacted organic ligand, then washed again with methanol to exchange DMF with methanol, more volatile and easily removable by moderate heating. X-Ray powder diffractogram (Brüker D5000, λ_{Cu} ≈ 1.5406 Å) of the sample is in very good agreement with the one from the non-functionalised solid MIL-125(Ti) (see Figure S8). Nitrogen sorption measurements (BelSorp Mini apparatus) gave a BET surface area of 1130(3) m²/g.

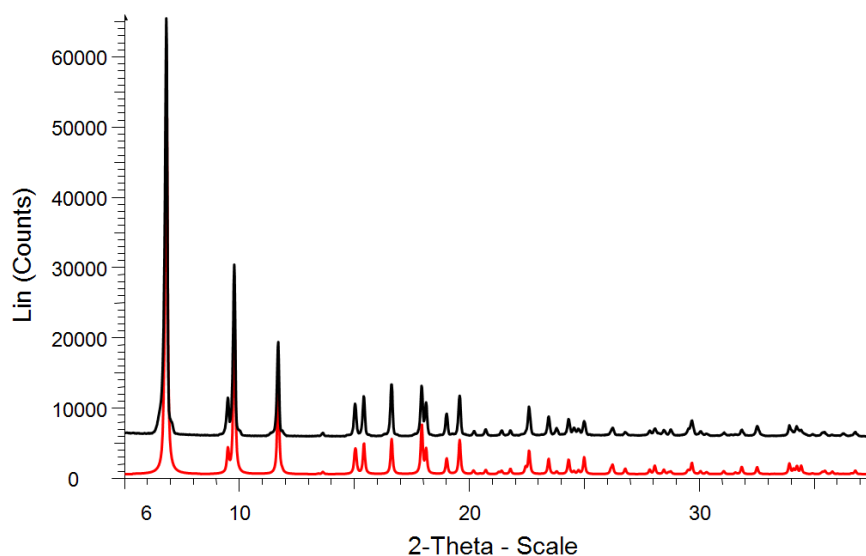


Figure S8. Comparison of the simulated XRD pattern of MIL-125(Ti) (red) with the experimental XRD pattern of MIL-125(Ti)-(NH₂) (black).

Figure S9 summarises the structures of different grafted and non-grafted MIL solids.

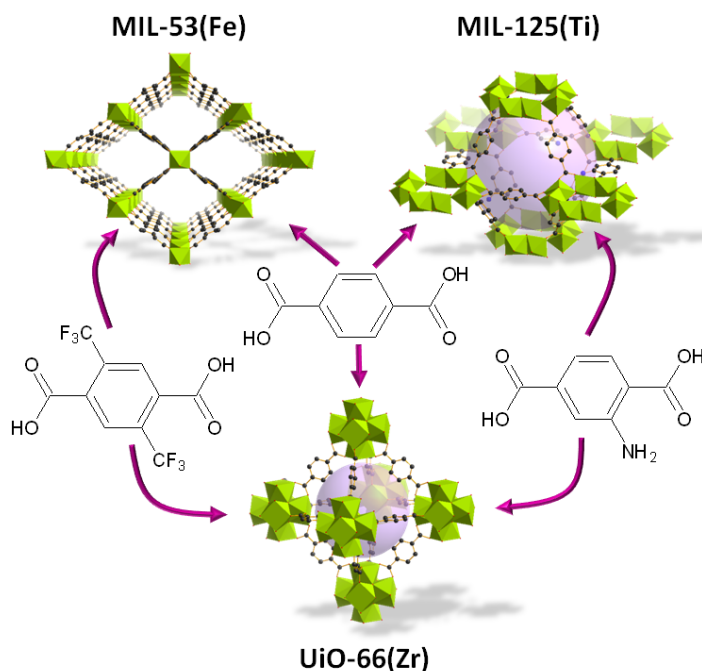


Figure S9. Structures of the different grafted and non-grafted MIL compounds.