Electronic Supplementary Information, ESI:

Programming MOFs for water sorption: Amino-functionalized MIL-125 and UiO-66 for heat transformation and heat storage applications

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Contents

Synthesis procedures:

Synthesis was performed by a procedure adapted from the literature.[1]

UiO-66 $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C{-}C_6H_4{-}CO_2)_{12}]$ In a 100 mL round bottom flask, $ZrCl_4$ (0.084 g, 0.343 mmol), CH_3COOH (0.618 g, 10.29 mmol) and HCl (0.36 g, 10 mmol) were dissolved in DMF (20 mL). To the clear solution was added H_2BDC (benzene-1,4-dicarboxylic acid, 0.057 g, 0.343 mmol). The mixture was transferred to a 100 mL Teflon-lined stainless-steel auto-clave. The system was heated for a day (24 h) at 120 ^oC. After 24 h, the solution was cooled to room temperature and the precipitate was isolated by centrifugation. The solid was suspended in DMF (10 mL). After standing at room temperature for 2-6 h, the solid was recovered by centrifugation. The obtained particles were washed with ethanol (10 mL) in the same way as described for washing with DMF. Finally, the solids were dried under reduced pressure.

H_2N-UiO-66 $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C{-}C_6H_3(NH_2){-}CO_2)_{12}]$.

Synthesis was performed as adapted from literature. In 100 mL glass flask $ZrCl_4$ (0.084 g, 0.343 mmol), C_6H_5COOH (1.256 g, 10.29 mmol) and HCl (0.36 g, 10 mmol) were dissolved in DMF (20 mL). To the clear mixture solution BDC-NH$_2$ (HO$_2$C-C$_6$H$_3$(NH$_2$)-CO$_2$H, 0.062 g, 0.343 mmol) was added. The mixture was transferred to a 100 mL PTFE-lined stainless-steel autoclave. The assembly was heated for a day (24 h) at 120^{o}C. After 24 h, the solution was cooled to room temperature and the precipitate was isolated by centrifugation. The solid was suspended in DMF (10 mL). After standing at room temperature for 2-6 h, the suspension was centrifuged and the solvent was decanted off. The obtained particles were washed with ethanol (10 mL) in the same way as described for washing with DMF. Finally, the solids were dried under reduced pressure.

UiO-67 [$Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2C{-}C_6H_4{-}C_6H_4\text{-}CO_2)_{12}$]. In a 100 mL round-bottom flask, ZrCl$_4$ (0.120 g, 0,514 mmol), C$_6$H$_5$COOH (1.256 g, 10.29 mmol) and HCl (0.36 g, 10 mmol) were dissolved in DMF (20 mL). To the clear solution was added H$_2$BPDC (Biphenyl-4,4´-dicarboxylic acid, 0.125 g, 0.514 mmol). The mixture was transferred to a 100 mL PTFE-lined stainless-steel autoclave. The assembly was heated for a day (24 h) at 120^{o}C. After 24 h, the solution was cooled to room temperature and the precipitate was isolated by centrifugation. The solid was suspended in DMF (10 mL). After standing at room temperature for 2-6 h, the solid was recovered by centrifugation. The obtained particles were washed with ethanol (10 mL) in the same way as described for washing with DMF. Finally, the solids were dried under reduced pressure.

H$_2$N-MIL-125 [$Ti_8O_8(OH)_4{-}(O_2C{-}C_6H_3(NH_2){-}CO_2)_6$]

H$_2$N-MIL-125 [Ti$_8$O$_8$(OH)$_4$-(O$_2$C-C$_6$H$_3$(NH$_2$)-CO$_2$)$_6$] was prepared according to literature[2] from a mixture of titanium isopropoxide Ti(O^{i}Pr)$_4$ (Acros Organics, 98%), 2-amino-terephthalic acid HO$_2$C-C$_6$H$_3$(NH$_2$)-CO$_2$H (Aldrich, 99%), methanol (Aldrich, 99.9%) and DMF (Acros Organics, extra-dry) in a 1.5 mmol: 3 mmol : 12.5 mL : 12.5 mL ratio. The slurry was then introduced in a 100 mL PTFE-lined stainless-steel autoclave. The system was heated overnight (16 h) at 150 °C. The resulting light yellow product was filtered off, washed with DMF (10 mL) to remove the excess of unreacted organic ligand, then washed again with methanol (10 mL) for 6 h to exchange DMF with methanol, which is easily removable by moderate heating.

Instrumentation

Powder X-ray diffractograms were acquired at ambient temperature on a Bruker D2 Phaser using a flat sample holder and Cu-Kα radiation (λ = 1.54182 Å) at 30 kV covering 2theta angles 5-80° over a time of 2 h, that is. 0.01°/sec. Diffractograms were obtained on flat layer sample holders where at low angle the beam spot is strongly broadened so that only a fraction of the reflected radiation reaches the detector which leads to the low relative intensities measured at $2\theta < 10°$.

Nitrogen adsorption isotherms were acquired on a *Quantachrome* Nova®, w/ 24h degassing at a temperature of 120°C *in vacuo* prior to each measurement.

Water adsorption isotherms were acquired on a *Quantachrome* Hydrosorb® volumetric water sorption analyzer, w/ 24h degassing at a temperature of 120°C *in vacuo* prior to each measurement.

Cycling experiments were performed in a *Setaram® TGA-DSC 111*. A humidified argon gas flow (5.6 kPa H_2O vapour pressure) was generated by a *Setaram* WetSys® humidity controller and was continously passed through the sample chamber.

Powder X-ray diffractograms

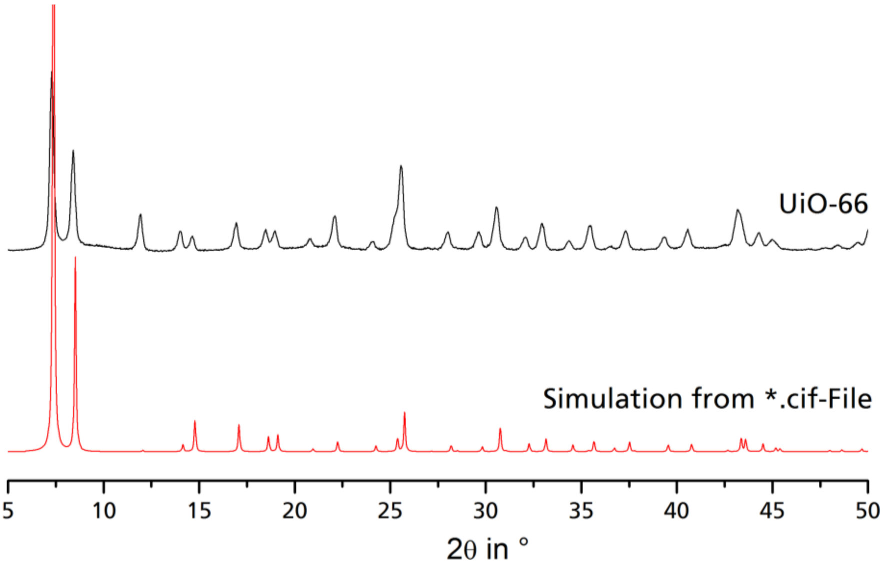

Figure S1 Powder X-ray diffractogram of UiO-66. *) Simulated pattern from cif-File for CCDC 837796 for comparison.[3] Note that at low angle the beam spot is strongly broadened on the flat layer sample holder so that only a fraction of the reflected radiation reaches the detector which leads to the lower than simulated relative intensities measured at $2\theta < \sim 10°$.

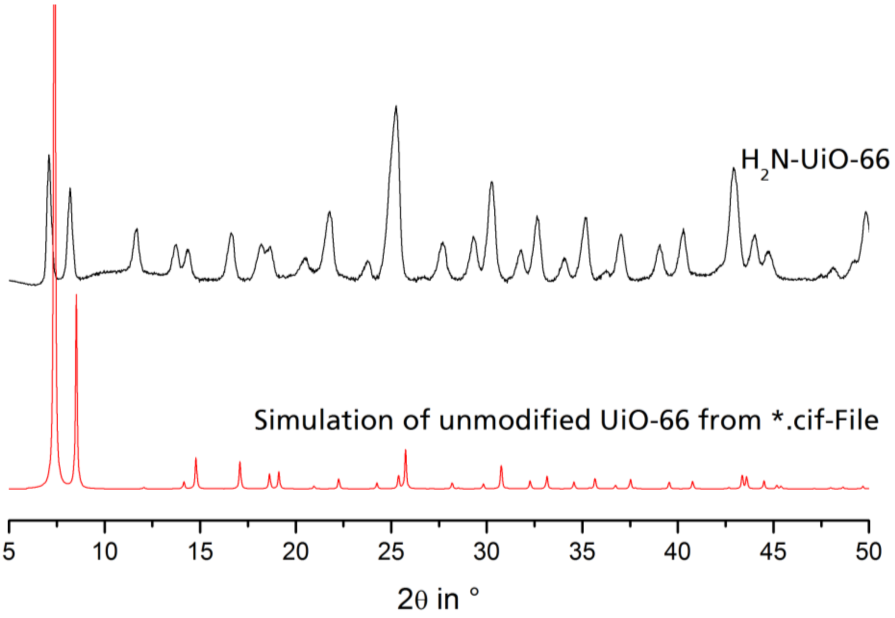

Figure S2 Powder X-ray diffractogram of H_2N-UiO-66. *) Simulated pattern from cif-File CCDC 837796 due to not-existing X-ray structure for the H_2N-modified material, therefore, the two patterns differ. Note that at low angle the beam spot is strongly broadened on the flat layer sample holder so that only a fraction of the reflected radiation reaches the detector which leads to the lower than simulated relative intensities measured at $2\theta < \sim 10°$.

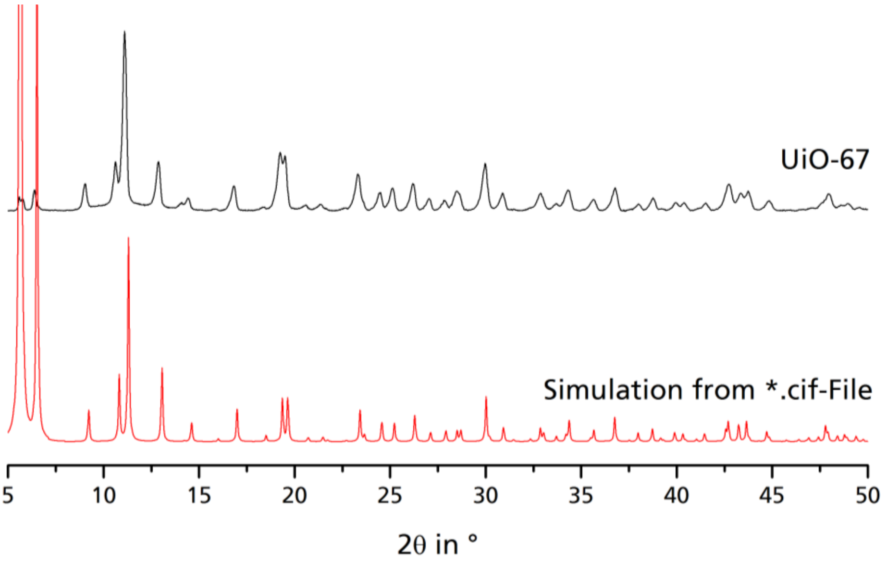

Figure S3 Powder X-ray diffractogram of UiO-67. *) Simulated pattern from cif-File for comparison.[4] Note that at low angle the beam spot is strongly broadened on the flat layer sample holder so that only a fraction of the reflected radiation reaches the detector which leads to the lower than simulated relative intensities measured at $2\theta < \sim 10°$.

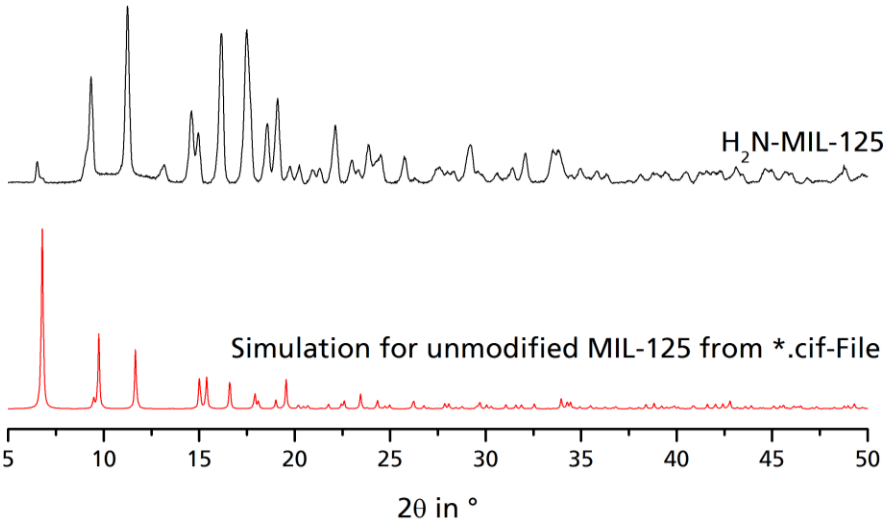

Figure S4 Powder X-ray diffractogram of H_2N-MIL-125. *) Simulation for unmodified MIL-125 from cif-file CCDC 751157 for comparison (M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, *J. Am. Chem. Soc.*, 2009, **131**, 10857-10859.) due to not-existing X-ray structure for the H_2N-modified material, therefore, the two patterns differ. Note that at low angle the beam spot is strongly broadened on the flat layer sample holder so that only a fraction of the reflected radiation reaches the detector which leads to the lower than simulated relative intensities measured at $2\theta < \sim 10°$.

N_2 sorption isotherms

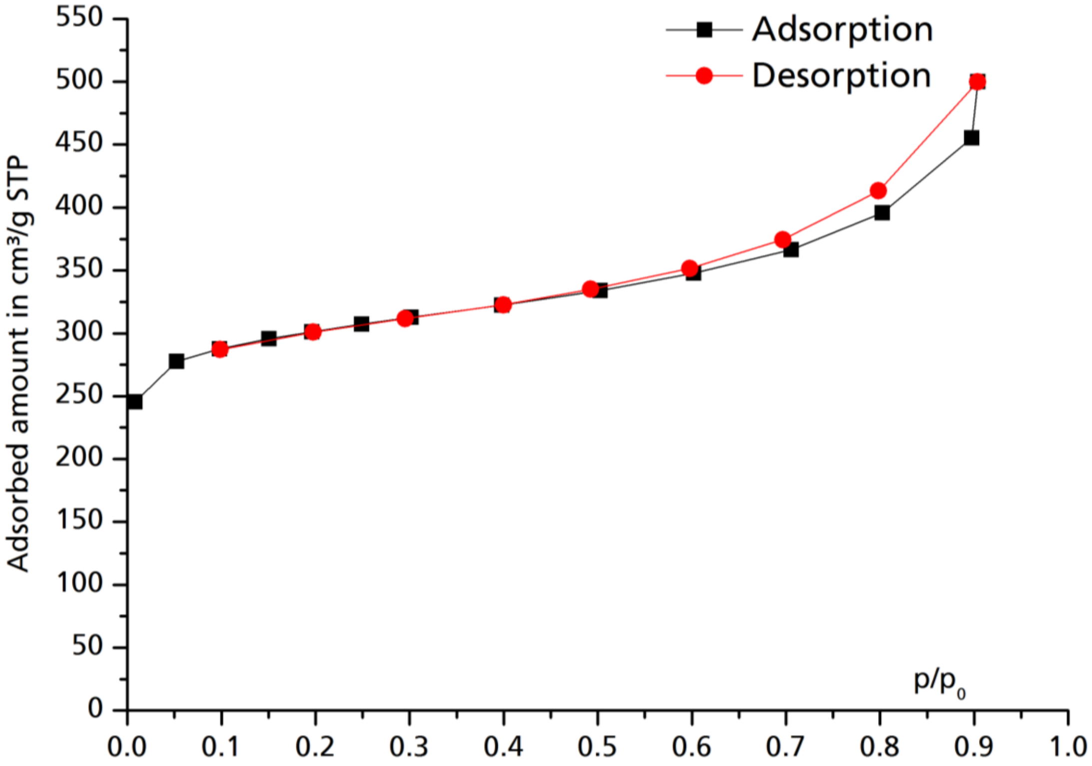

Figure S5 N_2 ad-/desorption isotherm of UiO-66, acquired at 77 K. The rise of the isotherm in the $p/p_0 > 0.6$ region, combined with the occurrence of desorption hysteresis, points to the presence of additional, mesoporous cavities (probably interparticle volume).

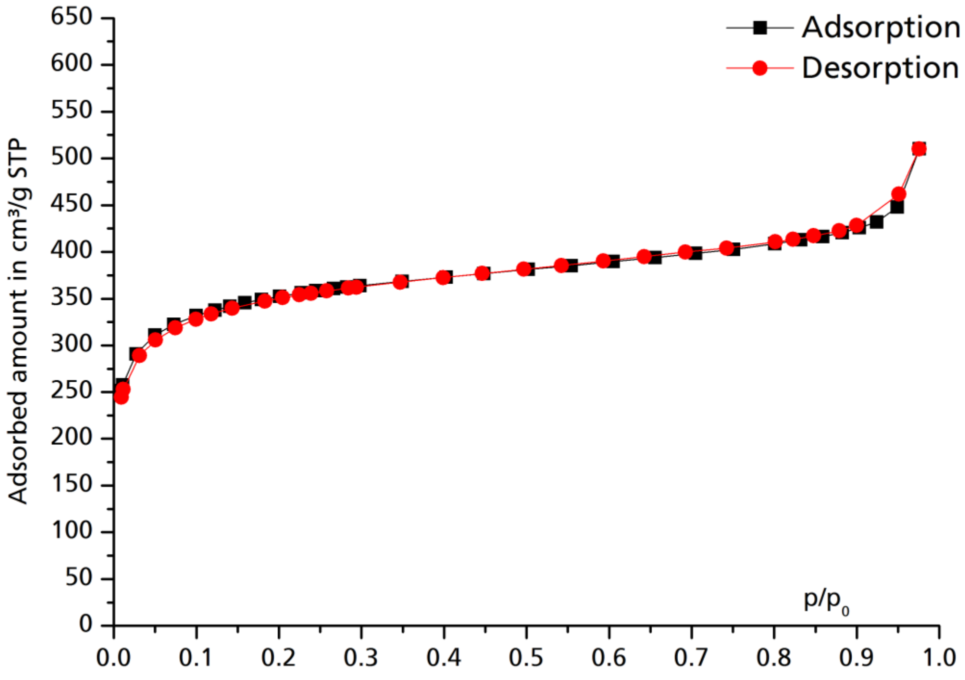

Figure S6 N_2 ad-/desorption isotherm of H_2N-UiO-66, acquired at 77 K.

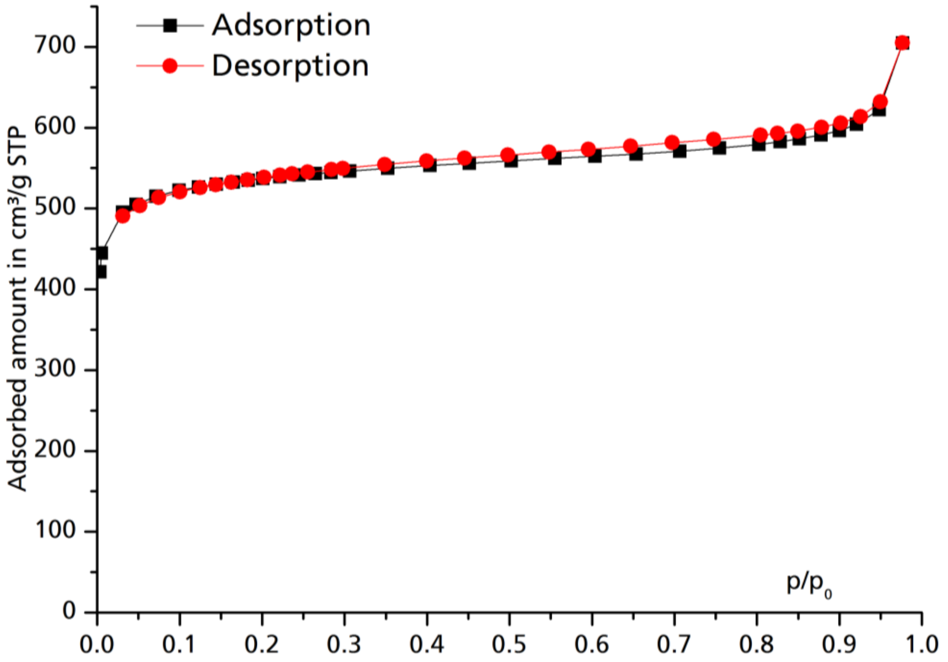

Figure S7 N_2 ad-/desorption isotherm of UiO-67, acquired at 77 K.

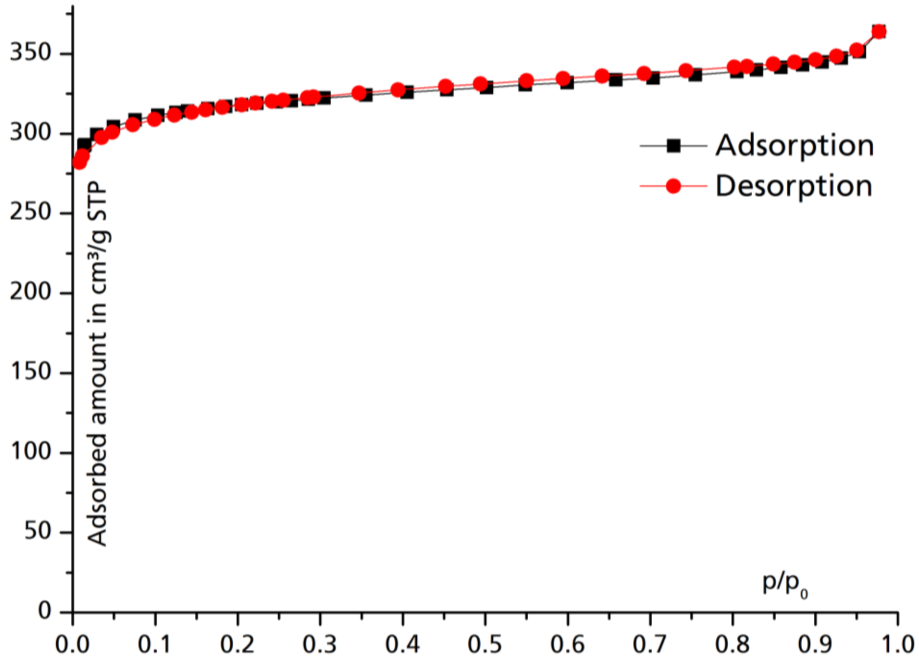

Figure S8 N_2 ad-/desorption isotherm of H_2N-MIL-125, acquired at 77 K.

H_2O sorption isotherms at 40 °C

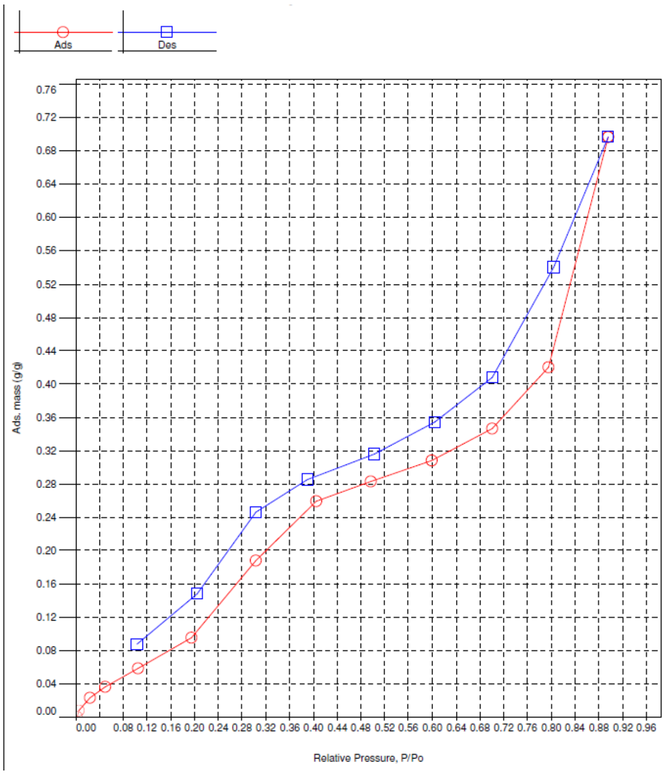

Figure S9 H_2O adsorption/desorption isotherm of UiO-66 at 40 °C.

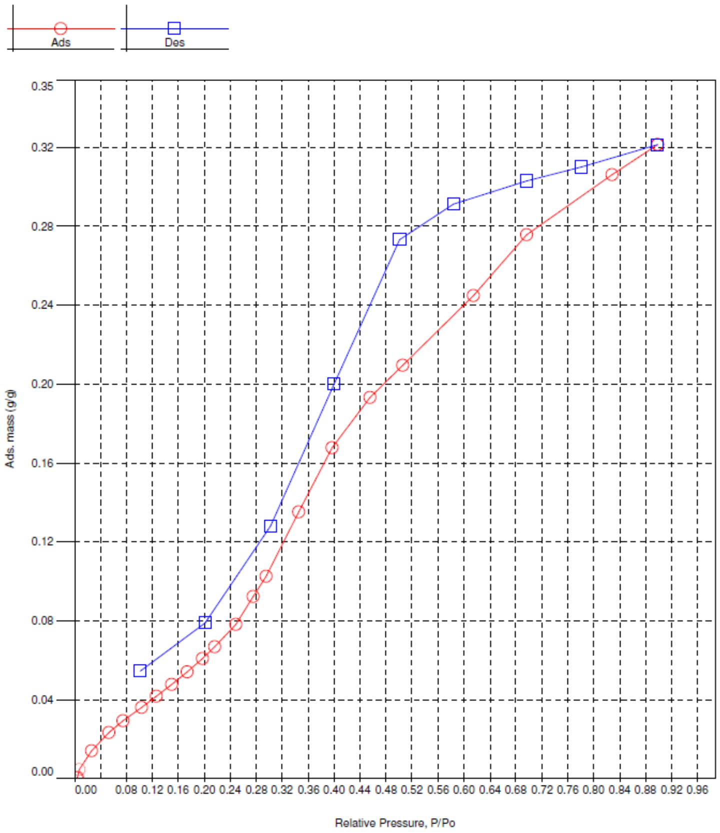

Figure S10 H_2O adsorption/desorption isotherm of H_2N-UiO-66 at 40 °C.

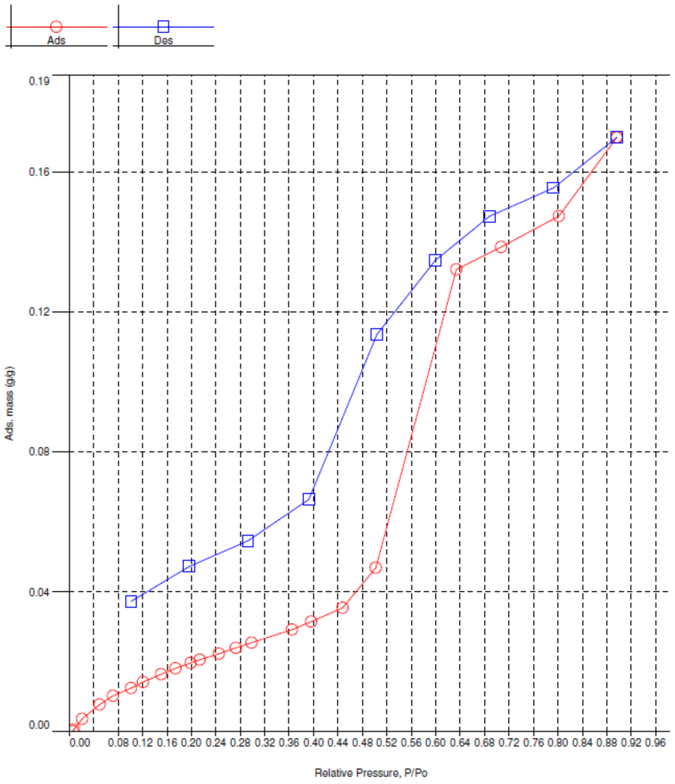

Figure S11 H_2O adsorption/desorption isotherm of UiO-67 at 40 °C.

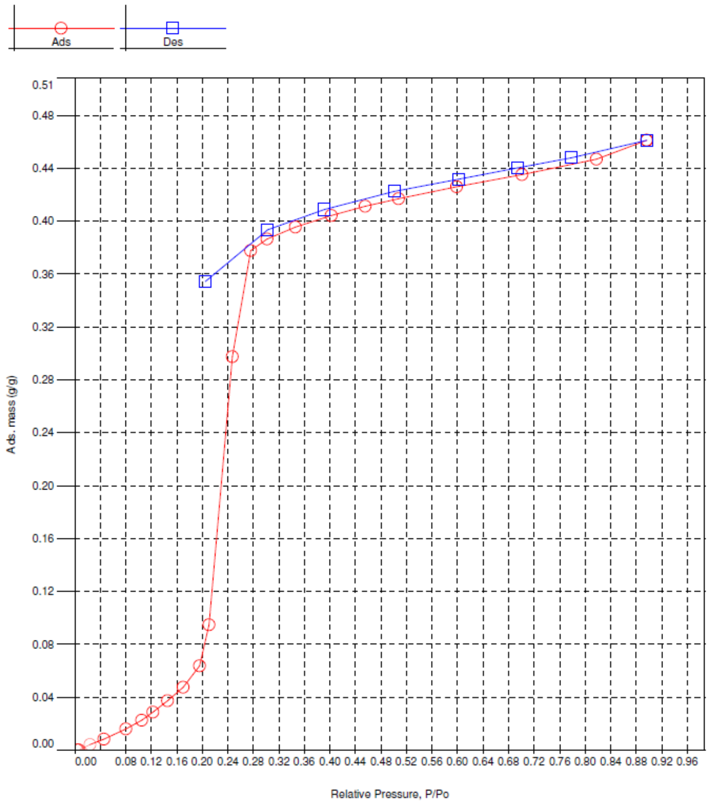

Figure S12 H_2O adsorption/desorption isotherm of H_2N-MIL-125 at 40 °C.

Literature

1. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chemistry*, 2011, **17**, 6643-6651.
2. C. Volkringer, T. Loiseau, M. Haouas, F. Taulelle, D. Popov, M. Burghammer, C. Riekel, C. Zlotea, F. Cuevas, M. Latroche, D. Phanon, C. Knöfelv, P. L. Llewellyn and G. r. Férey, *Chem. Mater.*, 2009, **21**, 5783-5791.
3. L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700-1718.
4. Q. Yang, V. Guillerm, F. Ragon, A. D. Wiersum, P. L. Llewellyn, C. Zhong, T. Devic, C. Serre and G. Maurin, *Chem. Commun.*, 2012, **48**, 9831-9833.