# A New Series of Isoreticular Copper-Based Metal-Organic Frameworks Containing Non-Linear Linkers with Different Group 14 Central Atoms

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# Supporting Information

**(1)** EDX-analyses of **UHM-3-4**.

**(2)** Magnified view of the P-XRD patterns of **UHM-2** and **UHM-4** in the region 20 – 35 ° 2θ.

**(3)** PXRD pattern of activated **UHM-2**, **UHM-4**, and **UHM-3-4**.

**(4)** Thermal analyses of **UHM-2**, **UHM-4,** and **UHM-3-4**.

**(5)** Isotherm series for determination of the isosteric heats of adsorption.

(**6**) Illustration of the mode of interactions of the hydrogen molecule with the model linker systems.

**(1) EDX-analyses of UHM-3-4**.

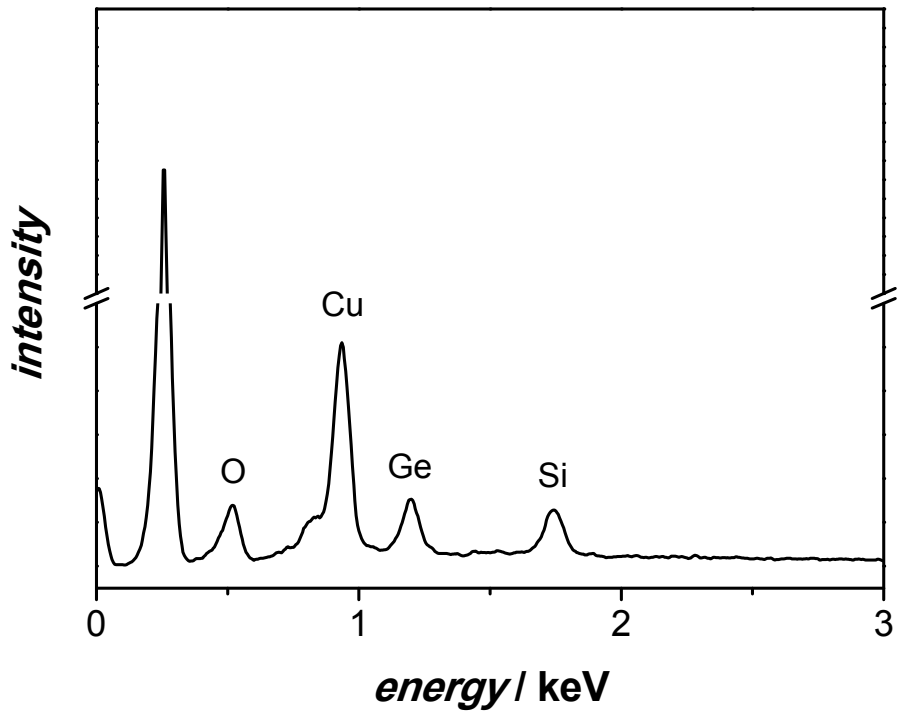


**Figure S-1:** EDX-Analyses of **UHM-3(50)-4(50).**

**(2) Magnified view of the P-XRD patterns of UHM-2 and UHM-4 in the region 20 – 35 ° 2θ.**

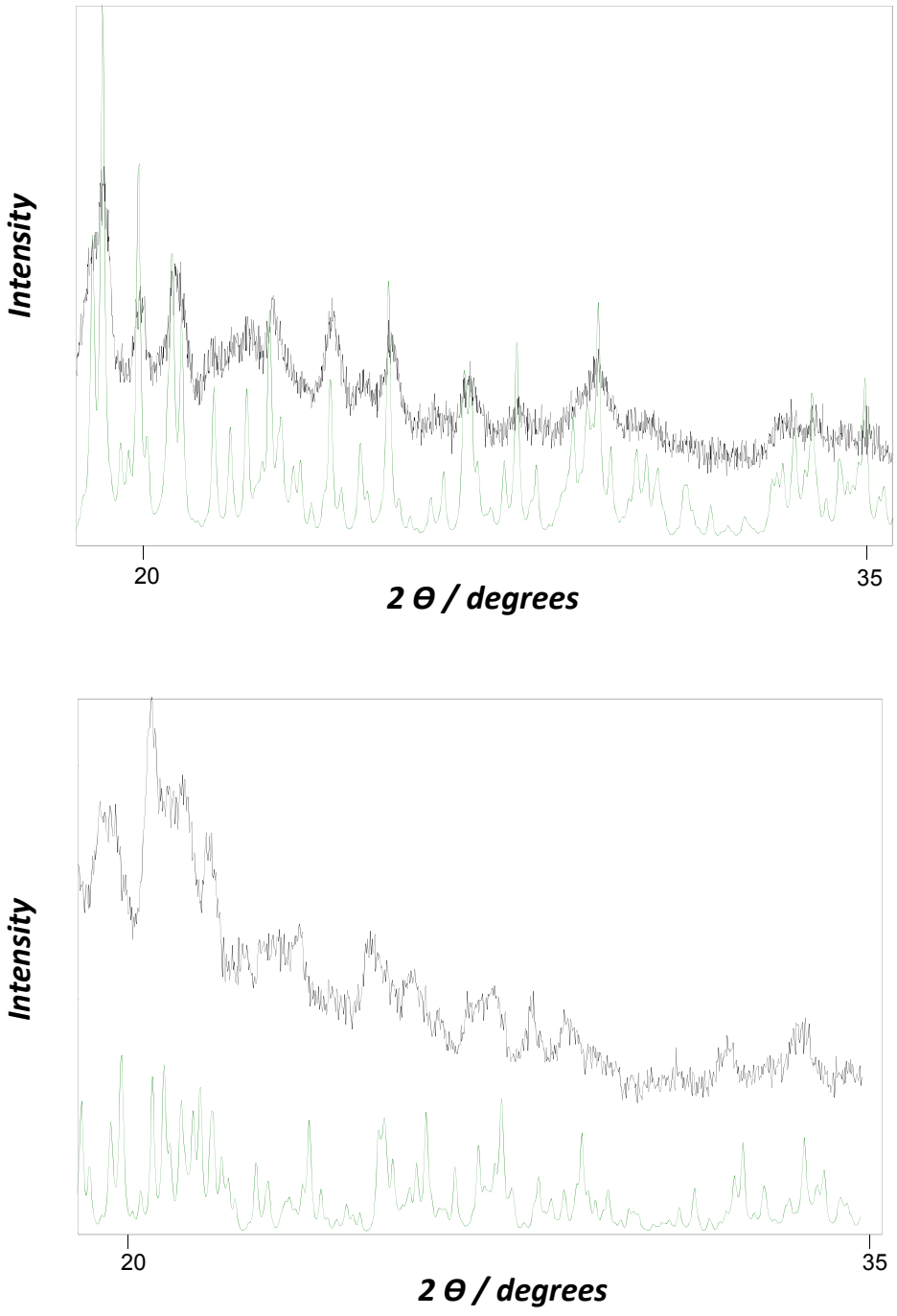


**Figure S-2:** Comparison of the experimental (black) and simulated (green) P-XRD patterns of **UHM-2** (top) and **UHM-4** (bottom).

**(3) PXRD pattern of activated UHM-2, UHM-4, and UHM-3-4.**

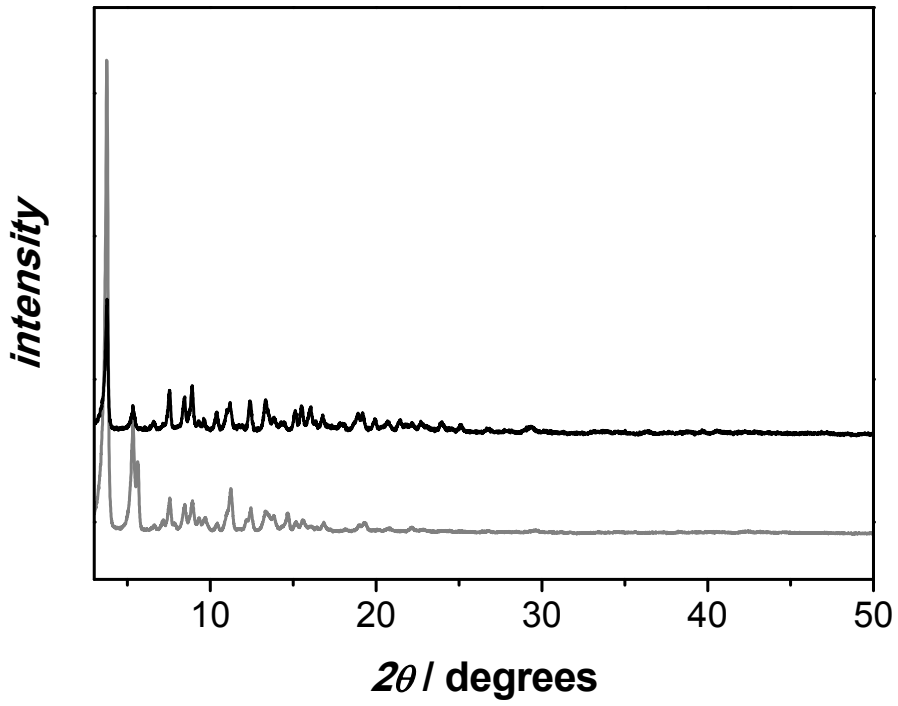


**Figure S-3a:** Powder X-Ray diffraction patterns of as synthesized **UHM-2** (black) and activated **UHM-2** (gray, 24 h, 170 °C).

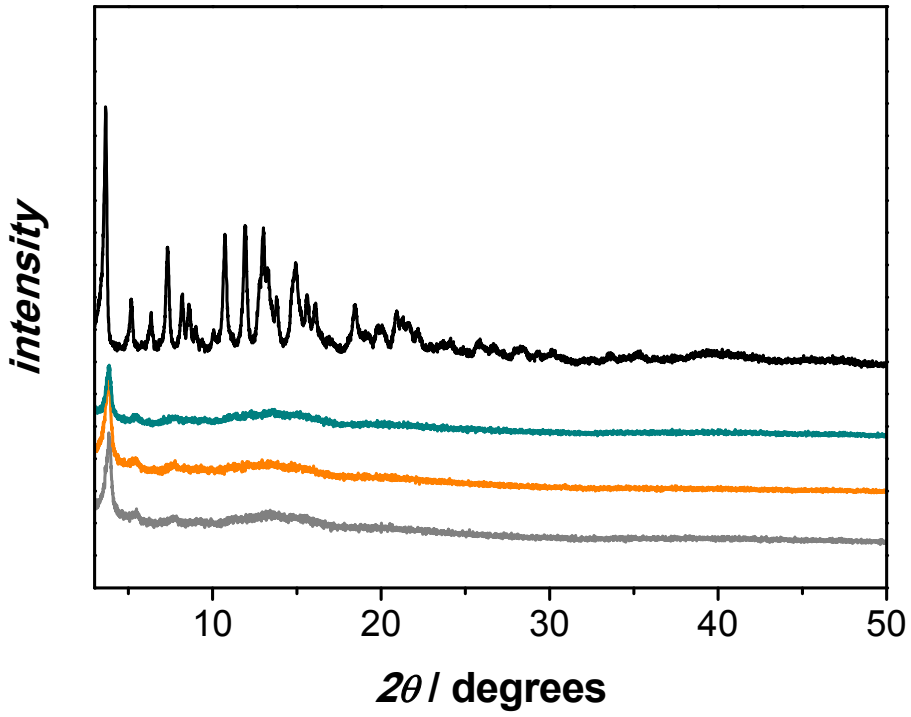


**Figure S-3b:** Powder X-Ray diffraction patterns of as synthesized **UHM-4** (black) and activated **UHM-4** (green, 24 h, 100 °C; orange, 24 h, 120 °C and gray, 24 h, 150 °C).

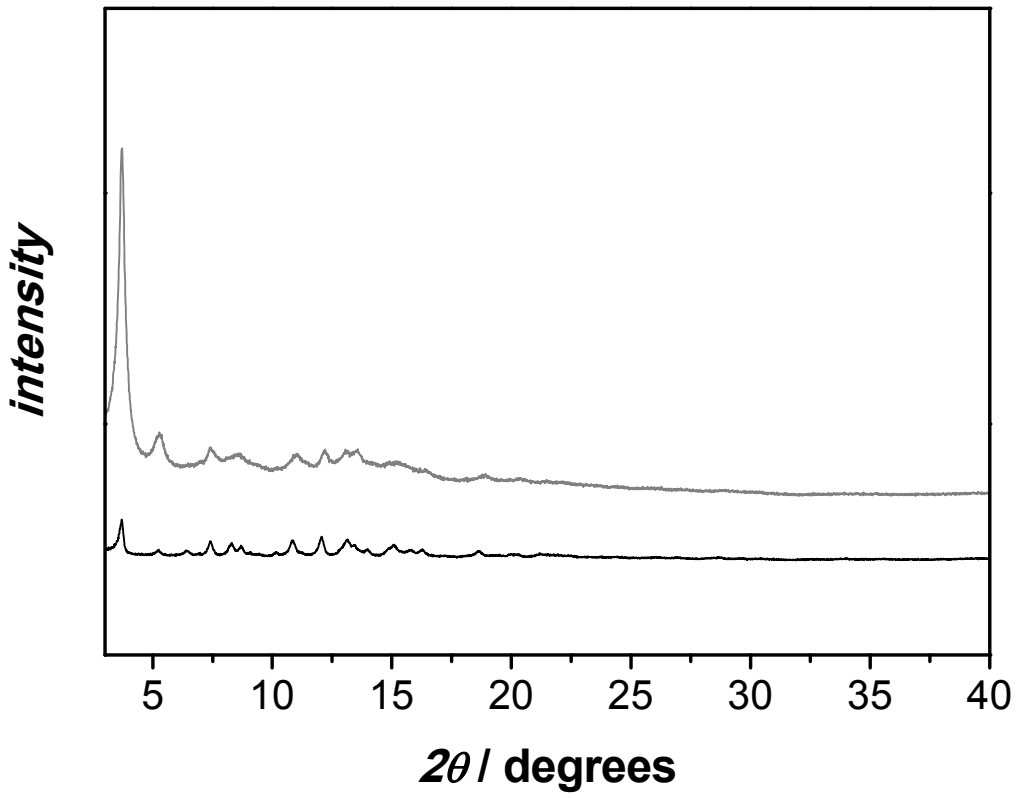


**Figure S-3c:** Powder X-Ray diffraction patterns of as synthesized (black) and activated **UHM-3(50)-4(50)** (gray, 24 h, 150 °C).

**(4) Thermal analyses of UHM-2, UHM-4, and UHM-3-4.**

**Thermal Analyses.**

To study the thermal stability of as synthesized **UHM-2** and **UHM-4** TG-MS and DTA were carried out (figure S-4a and S-4b).

The overall mass decrease of **UHM-2** can be roughly divided into two parts. In a first step between 25 °C and 226 °C, the material shows a mass loss of 22 % due to the loss of DMSO corresponding to the detected mass *m/z* =63, which is characteristic for the fragment ion $CH_3SO^+$. At 226 °C the thermal decomposition of the network starts generating water and carbon dioxide ($H_2O^+$, *m/z* = 18; $CO_2^+$, *m/z* = 44). In this step up to 678 °C a weight loss of 49 % is observed. However, DMSO is still detected up to 337 °C indicating a delayed desolvation, which slightly overlaps with the thermal decomposition of the material.

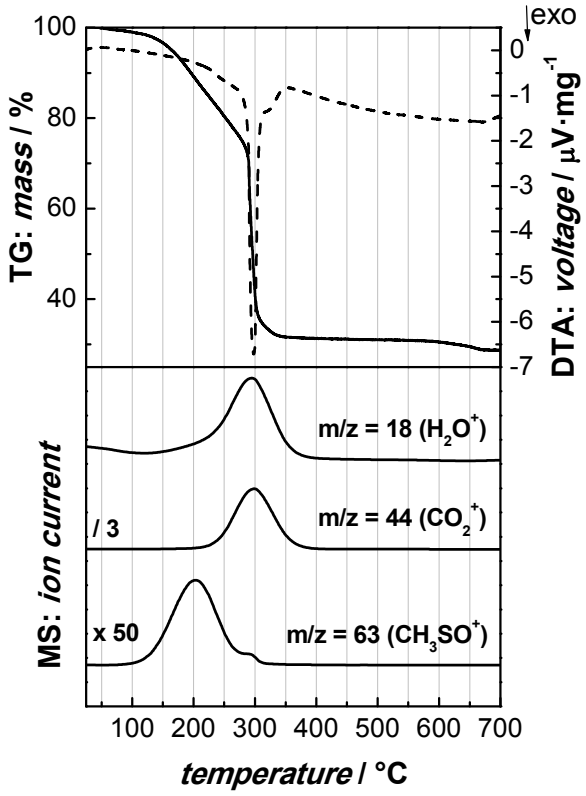


**Figure S-4a:** TG-MS and DTA of as synthesized UHM-2.

The mass loss of **UHM-4** can be roughly divided into three steps. The first weight decrease of 26 % up to 93 °C is caused by dehydration and accompanied by the detection of water ($H_2O^+$, *m/z* = 18). In the second step between 93 °C and 223 °C with a weight loss of 22% predominantly DMA ($C_4H_9NO^+$, *m/z* = 87) is detected. The thermal decomposition of **UHM-4** starts at 223 °C ($H_2O^+$, *m/z* = 18; $CO_2^+$, *m/z* = 44) indicating that the material is less stable than **UHM-2** caused by the weak Ge-C-bond. Up to 608 °C a weight loss of 45 % is observed in this step. Analogue to **UHM-2** solvent loss overlaps slightly with thermal composition.

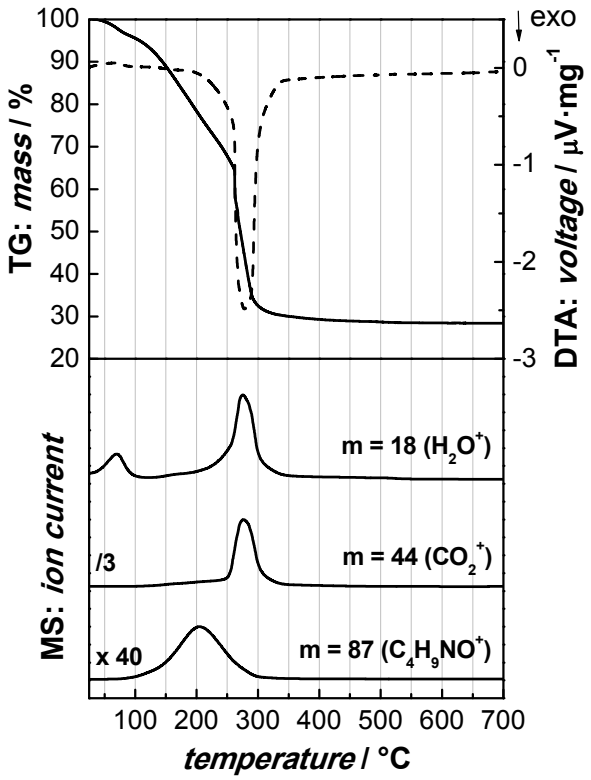


**Figure S-4b:** TG-MS and DTA of as synthesized **UHM-4**.

For **UHM-3(50)-4(50)** overall mass decrease occurs in three steps (Figure S-4c). First, up to 96 °C dehydration takes place, The corresponding weight loss of 1.2 % is accompanied by the detection of water ($H_2O^+$, *m/z* = 18). Up to 224 °C a mass loss of 14.5 % is observed, which is predominantly caused by the loss of DMA ($C_4H_9NO^+$, *m/z* = 87). Thermal decomposition starts at 224 °C (similar to UHM-4) generating thereby water and carbon dioxide ($H_2O^+$, *m/z* = 18; $CO_2^+$, *m/z* = 44). At 523 °C the weight

loss of additional 46.7 % ends. During thermal decomposition of the mixed MOF DMA was also detected, which again proves a delayed desolvation.

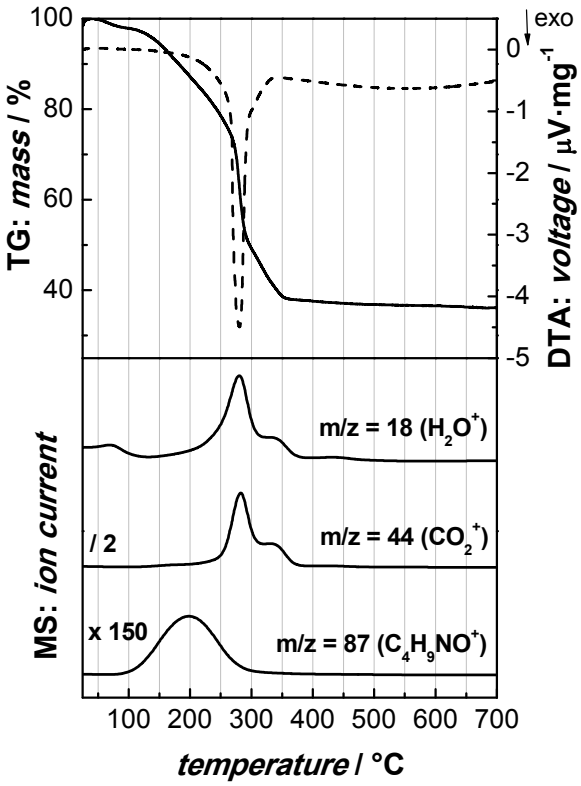


**Figure S-4c:** TG-MS and DTA of as synthesized **UHM-3(50)-4(50)**.

**(5) Isotherms for determination of the isosteric heats of adsorption.**

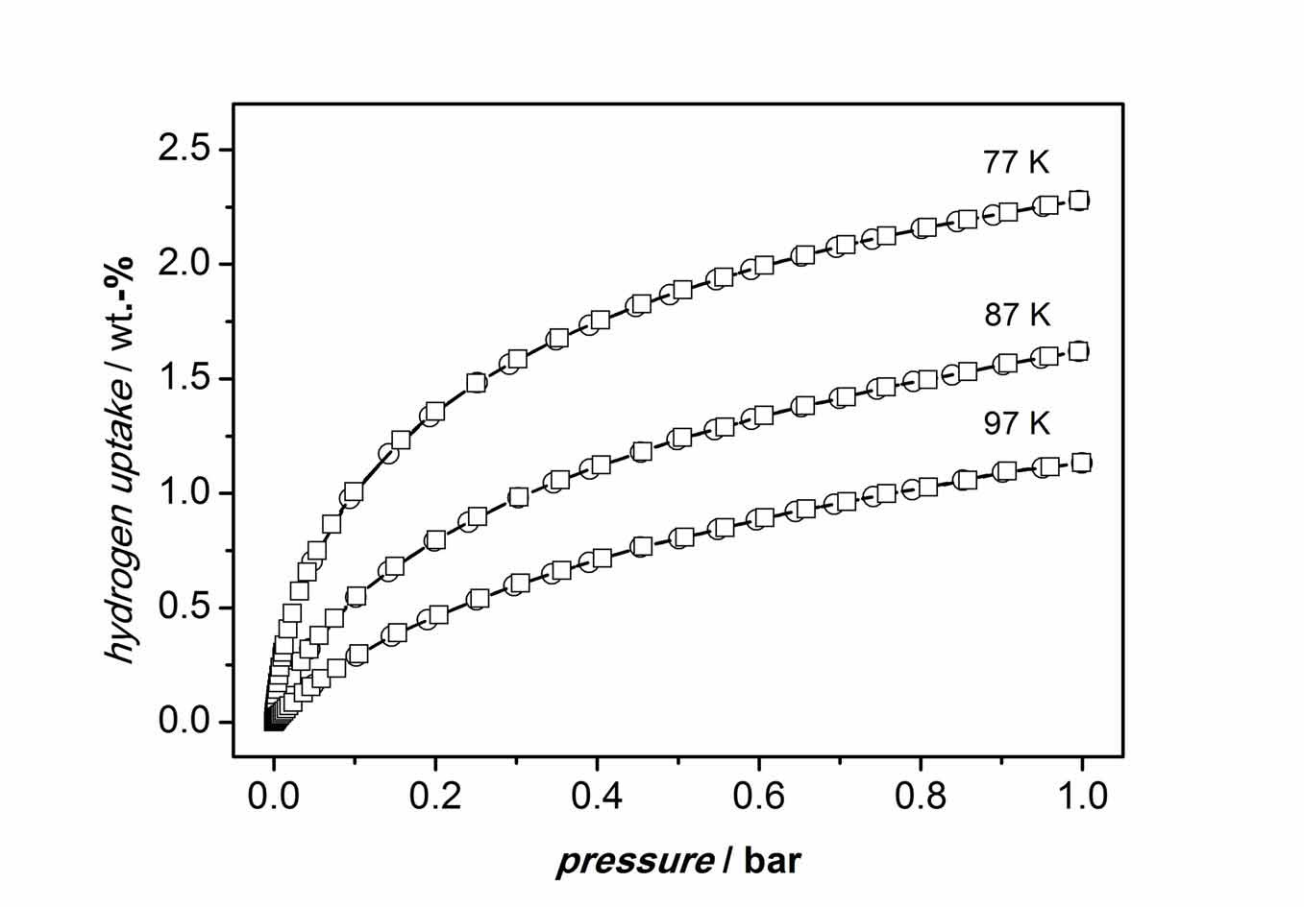


**Figure S-5a:** Hydrogen physisorption isotherms (□, adsorption; ○, desorption) of activated **UHM-2** at 77 K, 87 K and 97 K.

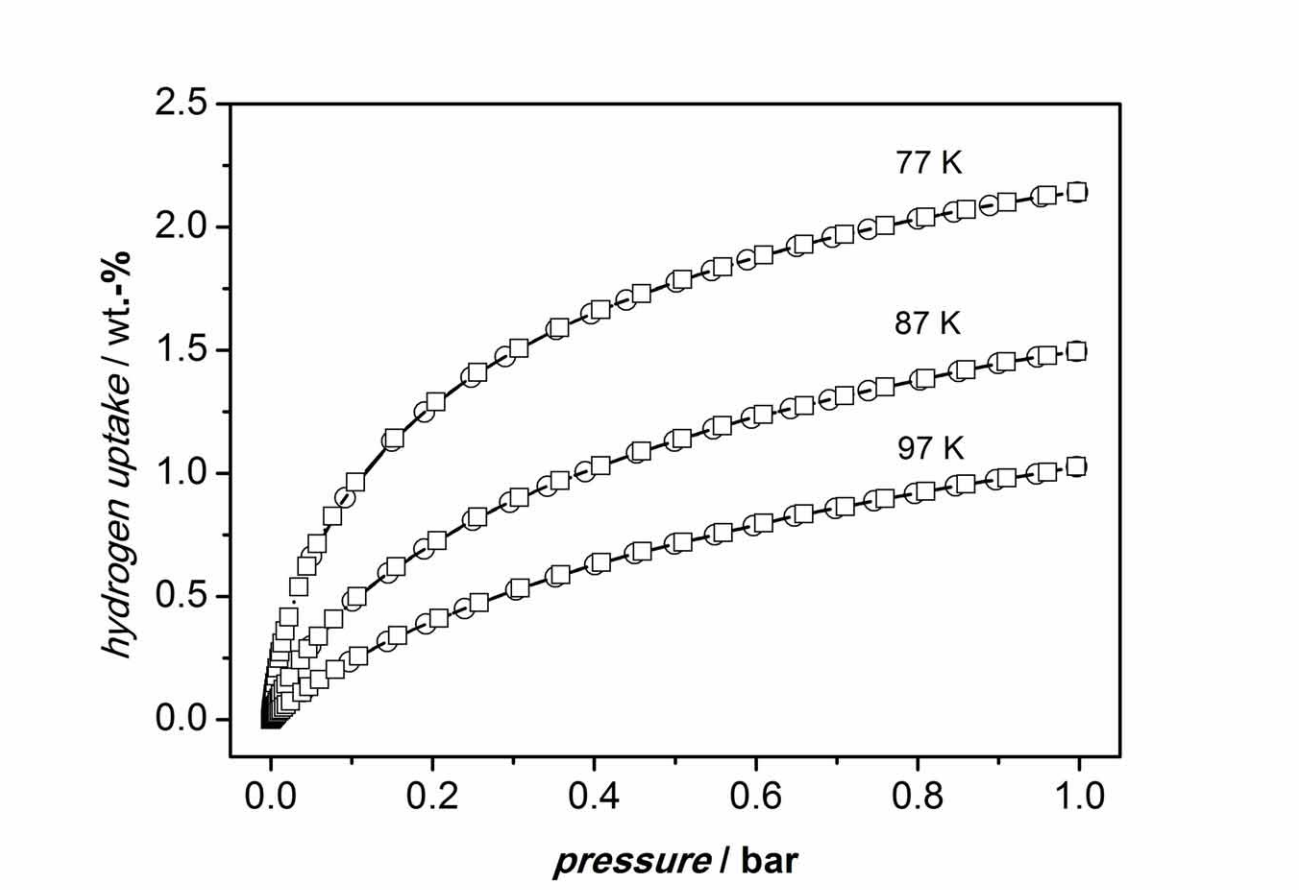


**Figure S-5b:** Hydrogen physisorption isotherms (□, adsorption; ○, desorption) of activated **UHM-3** at 77 K, 87 K and 97 K.

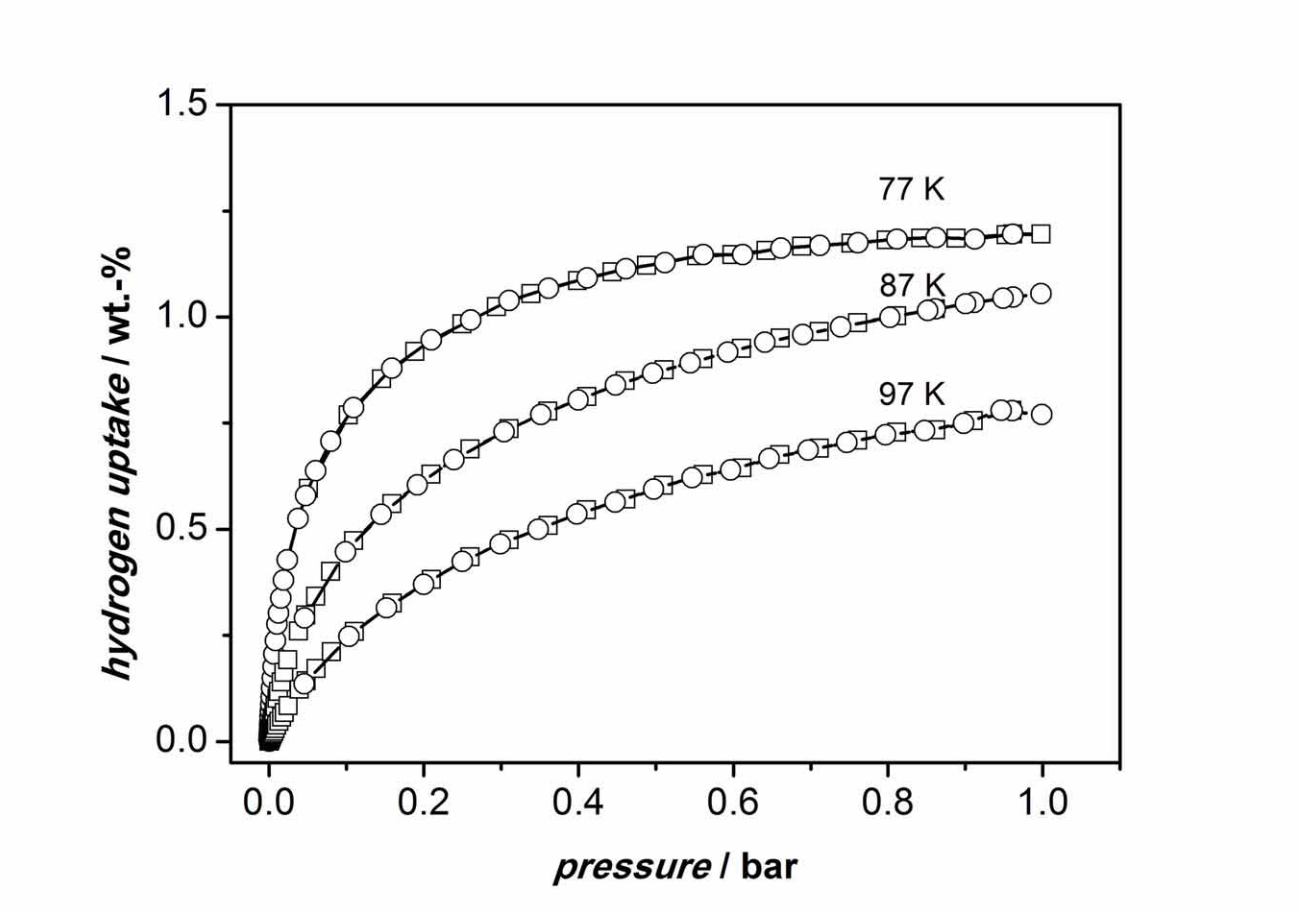


**Figure S-5c:** Hydrogen physisorption isotherms (□, adsorption; ○, desorption) of activated **UHM-4** at 77 K, 87 K and 97 K.

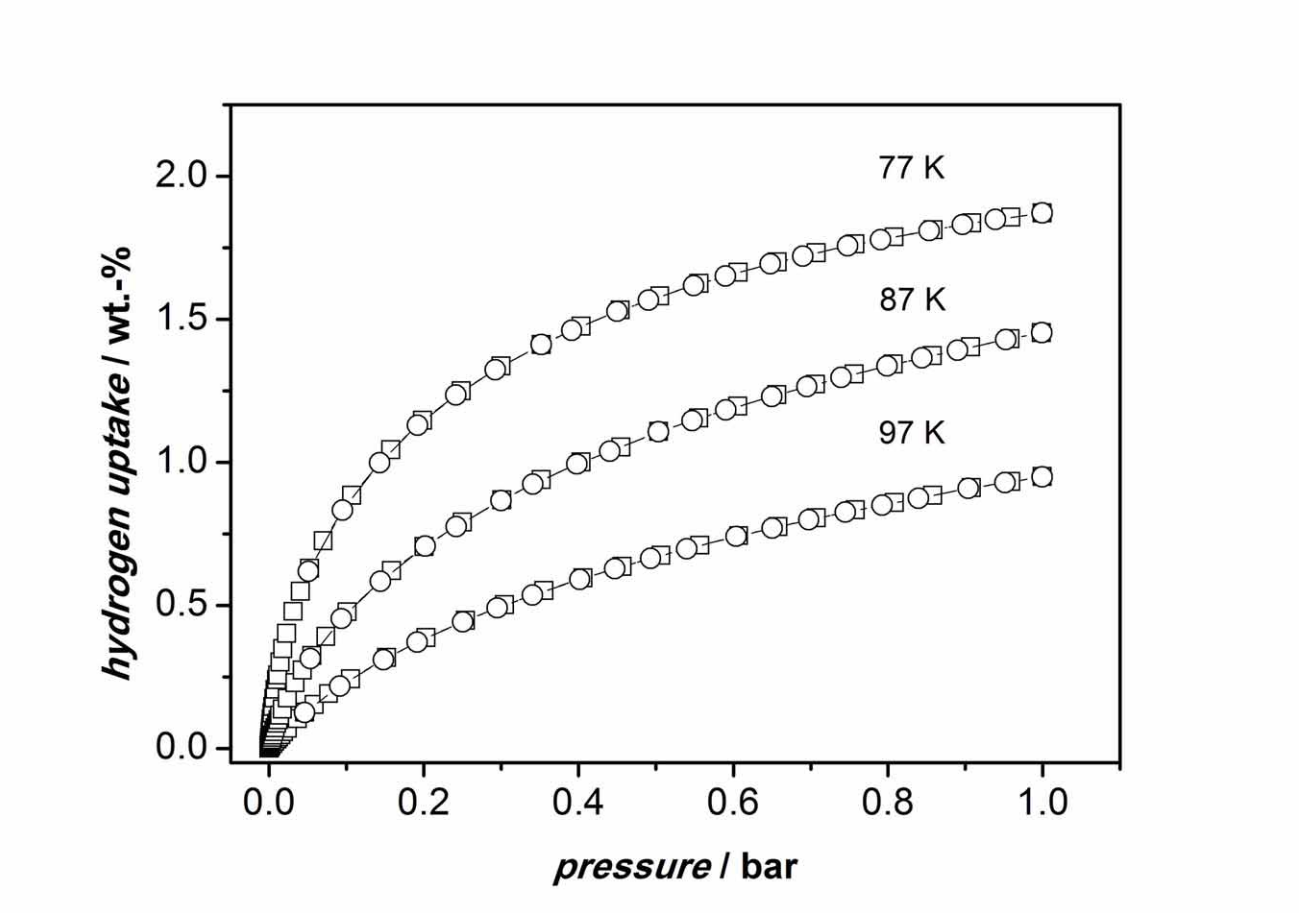


**Figure S-5d:** Hydrogen physisorption isotherms (□, adsorption; ○, desorption) of activated **UHM-3(50)-4(50)** at 77 K, 87 K and 97 K.

**(6) Illustration of the mode of interactions of the hydrogen molecule with the model linker systems.**

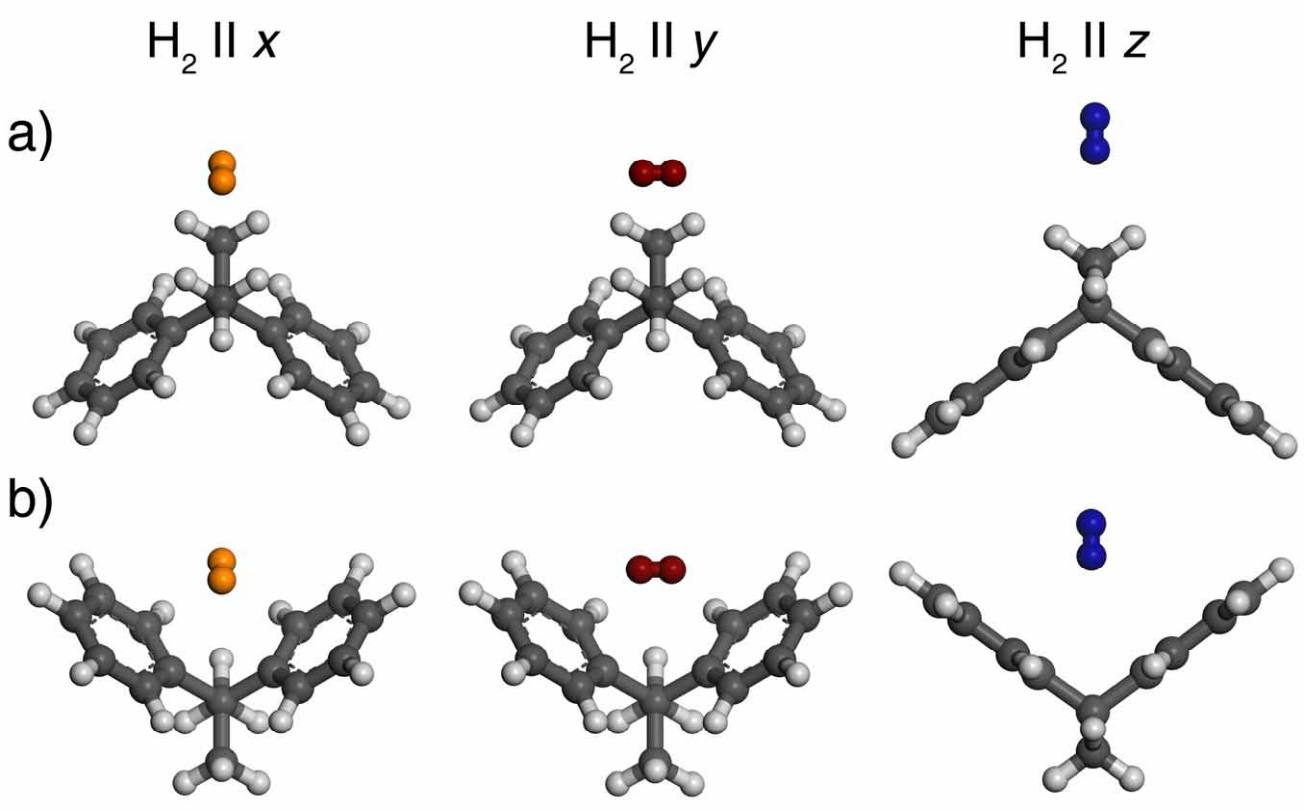


**Figure S-6:** Illustration of the approach of the hydrogen molecule towards the central unit of the model linker systems, along the *z*-axis from the side of the methyl groups (a, b) and along the *z*-axis from the side of the phenyl groups (c).