Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Integration of accessible secondary metal sites into MOFs for H_2S removal

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1. General information

All chemicals were obtained commercially and used without further purification. For the calculation of the metal ion concentration in the liquid phase via UV/vis measurements we used a copper standard containing 1000 mg copper ($CuCl_2$ in H_2O) from MERCK (Titrisol®).

Powder X-ray diffraction patterns (PXRD) were collected in transmission geometry with a STOE STADI P diffractometer operated at 40 kV and 30 mA with monochromatic Cu-Kα_1 ($\lambda = 0.15405$ nm) radiation and with a scan speed of 30 s/step and a step size of 0.1°.

Nitrogen physisorption isotherms were measured on a Belsorp max apparatus at 77 K using high purity nitrogen (N_2 99.999%). BET surface areas were determined using multipoint analysis in the pressure range from $p/p_0 = 0.01$ to $p/p_0 = 0.1$.

The UV/vis measurements of the liquid phase were carried out using a UV-1650 PC spectrometer (Shimadzu). The absorbance of liquid samples was measured using 10 mm cuvettes. For kinetic measurements absorption of the supernatant solution was measured every minute at the wavelength of 815 nm. The loading of the MOF was calculated via the decrease of the copper(II) concentration in the liquid phase. The copper(II) chloride solution contained two equivalents copper(II) chloride per linker at the beginning of the measurement. The copper(II) chloride solution was obtained by required dilution of the copper standard. A calibration was performed prior to all measurements. Solid state UV/Vis measurements were carried out using a Varian Cary 4000 UV/vis Spectrophotometer.

Determination of the metal content of the loaded samples was performed by energy dispersive X-ray (EDX) measurements using a ZEISS DSM-982 Gemini. An acceleration voltage of 20 kV was used. Before measurement sputtering with gold was performed. The metal content was obtained by averaging three different measurements.

For breakthrough experiments, the sample is placed in an adsorption column of 0.5 cm in diameter. A gas flow of 118 ml min^{-1} (20 °C, 1013 mbar) containing 1000 ppm hydrogen sulfide in humid air (70 % rel. humidity) is applied. The hydrogen sulfide concentration is measured using an AlphaSense H_2S-AE electrochemical sensor. Calculation of the hydrogen sulfide adsorption capacity is done by integration of the measured breakthrough curve using the hydrogen sulfide mass flow which is calculated by the volumetric flow of the test gas (ideal gas law).

2. Synthesis of UiO-67(bipy)

50 mg (0.2 mmol) 2,2´-Bipyridine-5,5´-dicarboxylic acid, 50 mg (0.2 mmol) $ZrCl_4$ and 20 ml *N,N*-Dimethylformamide (DMF) were put in a 100 mL teflon-capped flask. Afterwards, 0.93 ml (30 eq.) acetic acid or 2.349 g (30 eq.) benzoic acid, respectively, were added as modulator. The mixture was subject to a five minute ultrasonification treatment before it was heated to 120 °C for three days. After cooling down the mother liquid was exchanged against DMF for three times and afterwards DMF was exchanged against ethanol for five times. Final evacuation under dynamic vacuum at 150 °C gives a white microcrystalline powder. Yield: 72 %.

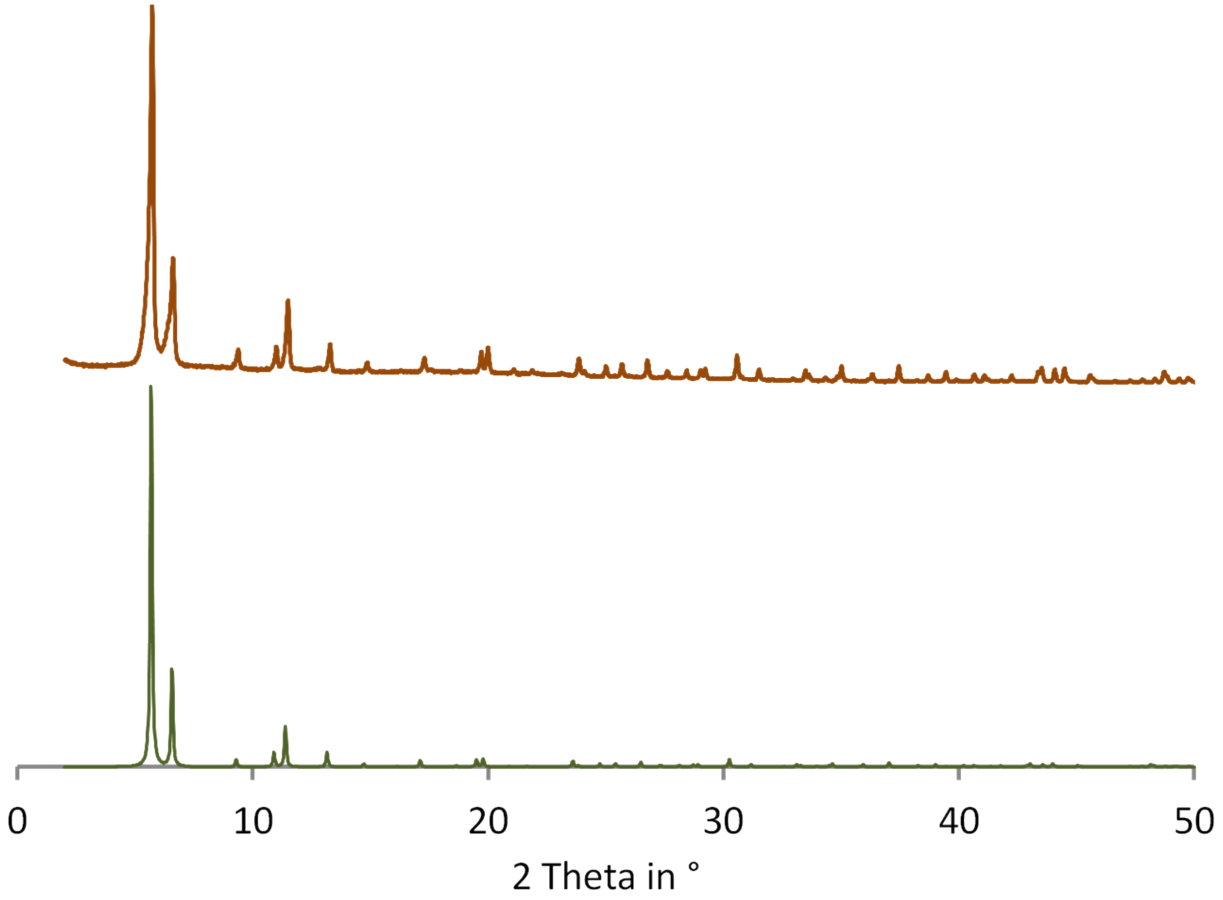

Figure S1: Calculated PXRD pattern of UiO-67 derived from single crystal structure (green) and measured PXRD pattern of UiO-67(bipy) (brown).

3. Synthesis of $M^{2+}X$@UiO-67(bipy) (M = Cu, Co, Ni)

To 100 mg UiO-67(bipy) (containing 0.281 mmol linker) 100 ml aqueous or ethanolic solution, containing 0.562 mmol (2 equivalents per linker) metal salt are added. The mixture is left statically for 24 h. After this the solid is washed several times with the corresponding solvent. Samples loaded from ethanolic solutions are dried in vacuum at room temperature and samples loaded from aqueous solutions are dried in an argon stream in order to remove the water on the outer sphere of the particles but not the water from the pores.

4. Water stability of UiO-67(bipy)

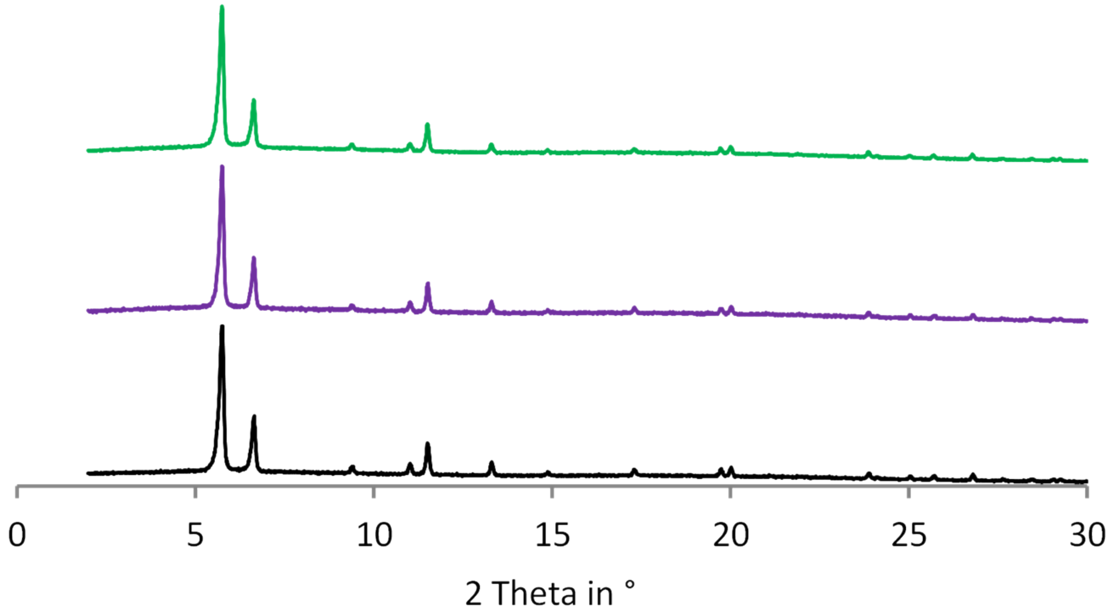

Figure S2: PXRD pattern of as made UiO-67(bipy) (black), UiO-67(bipy) after being in liquid water for 1 h (purple) and UiO-67(bipy) after being in liquid water for 24 h.

5. Stability towards hydrogen sulfide and ammonia

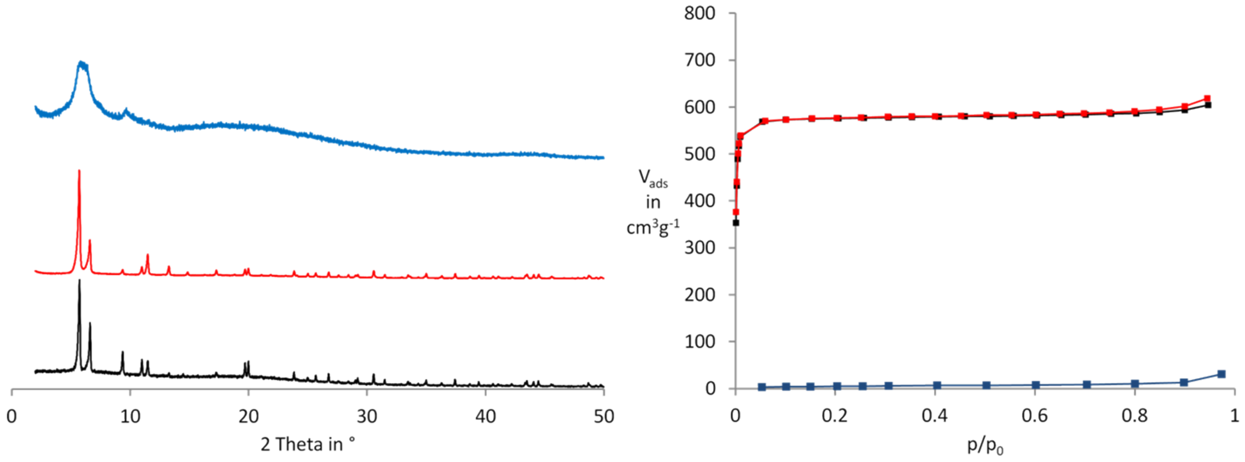

Figure S3: Left: PXRD patterns of UiO-67(bipy) (black) treated with hydrogen sulfide (red) and ammonia (blue); right: nitrogen adsorption isothermes of UiO-67(bipy) (black) treated with hydrogen sulfide (red) and ammonia (blue).

6. Solid state UV/vis spectroscopy

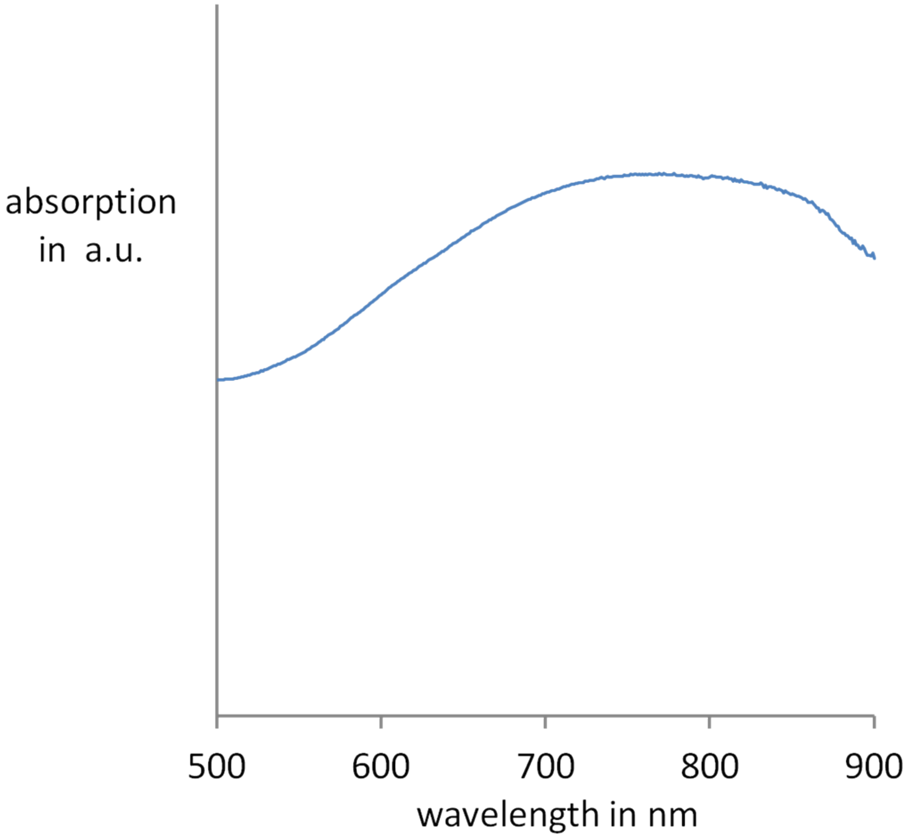

Figure S4: UV/vis spectrum of UiO-67(bipy) loaded with an aqueous solution of copper(II) chloride.

7. Nitrogen physisorption and XRD data of $M^{2+}X$@UiO-67(bipy)

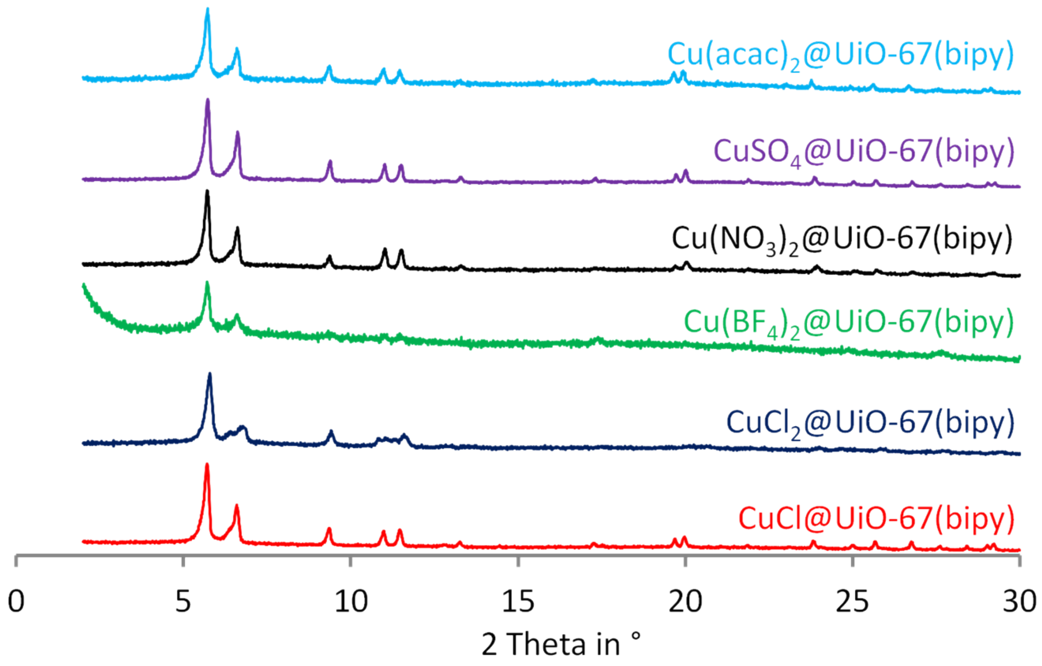

Figure S5: PXRD pattern after UiO-67(bipy) being loaded with the corresponding copper salt from ethanolic solution.

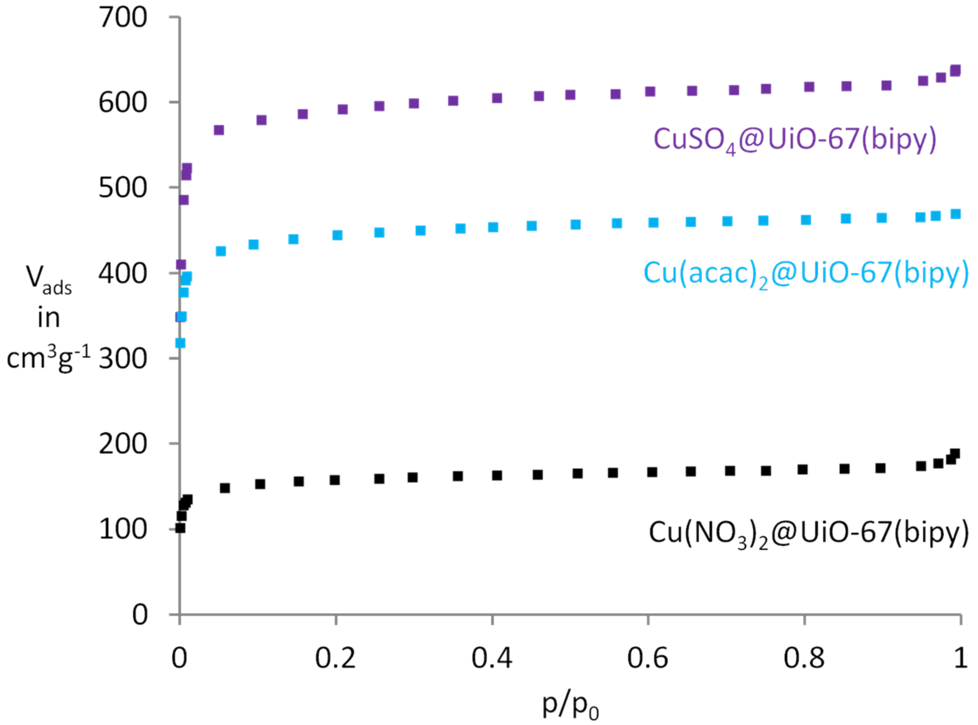

Figure S6: Nitrogen adsorption isothermes at 77 K of UiO-67(bipy) loaded with the corresponding copper salt from ethanolic solution and activated under dynamic vacuum at room temperature.

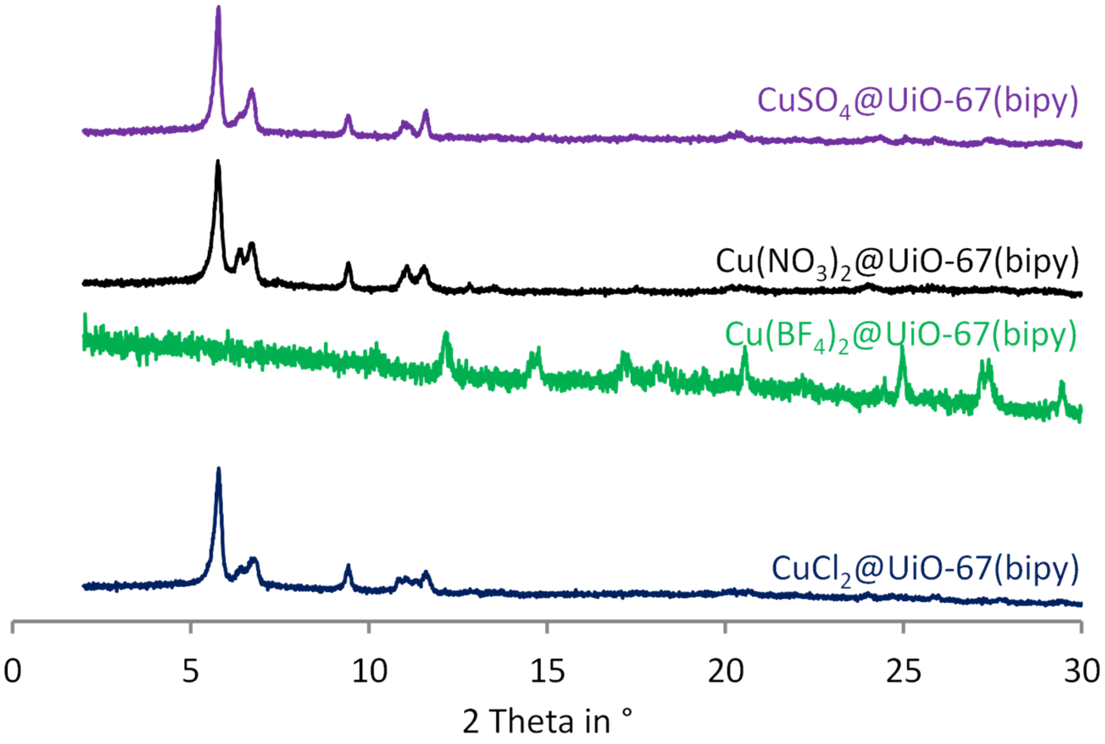

Figure S7: PXRD pattern after UiO-67(bipy) loaded with the corresponding copper salt from aqueous solution.

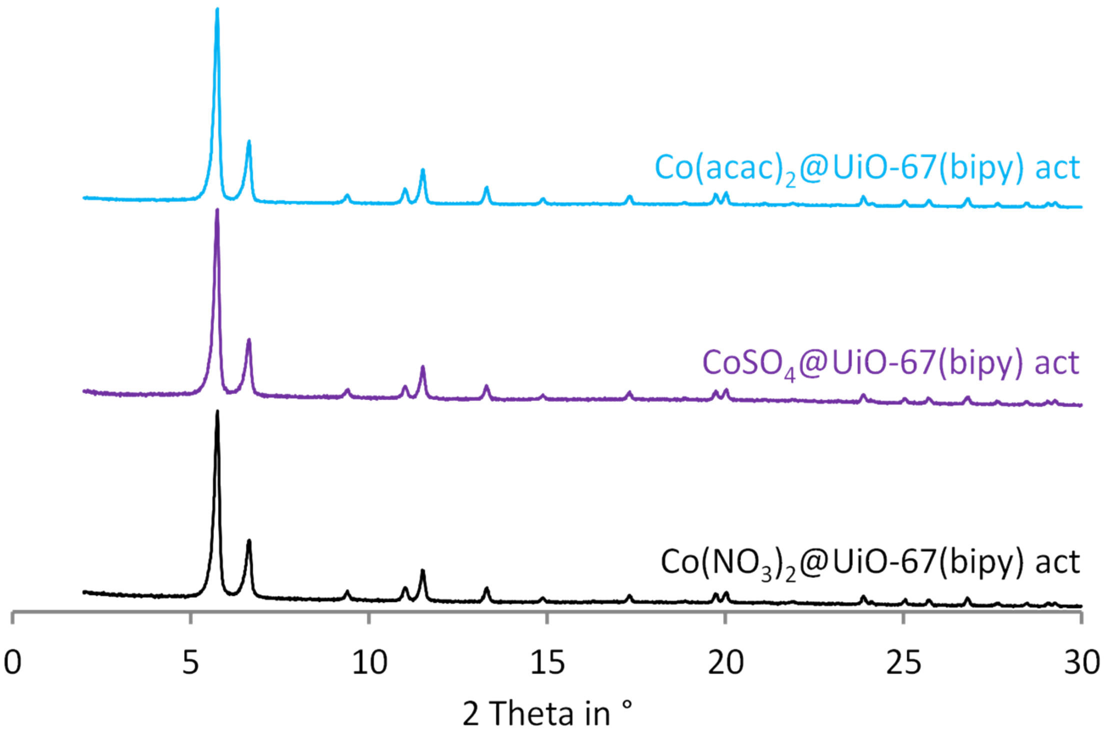

Figure S8: PXRD pattern after UiO-67(bipy) loaded with the corresponding cobalt salt from ethanolic solution and activated under dynamic vacuum at room temperature.

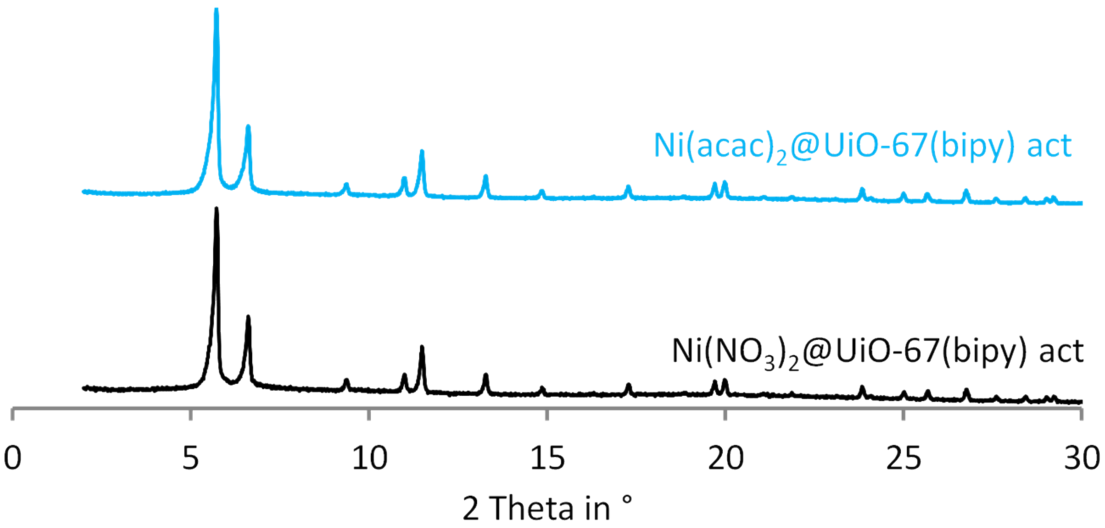

Figure S9: PXRD pattern after UiO-67(bipy) loaded with the corresponding nickel salt from ethanolic solution and activated under dynamic vacuum at room temperature.

8. Breakthrough measurements

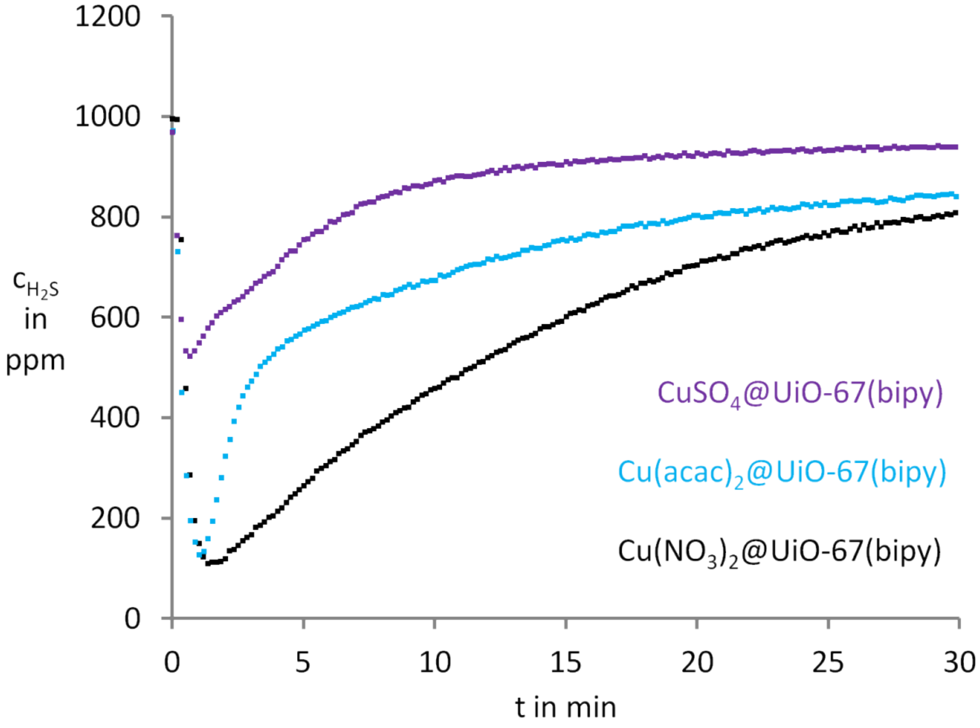

Figure S10: Breakthrough curves of UiO-67(bipy) loaded with the corresponding copper salt from ethanolic solution.

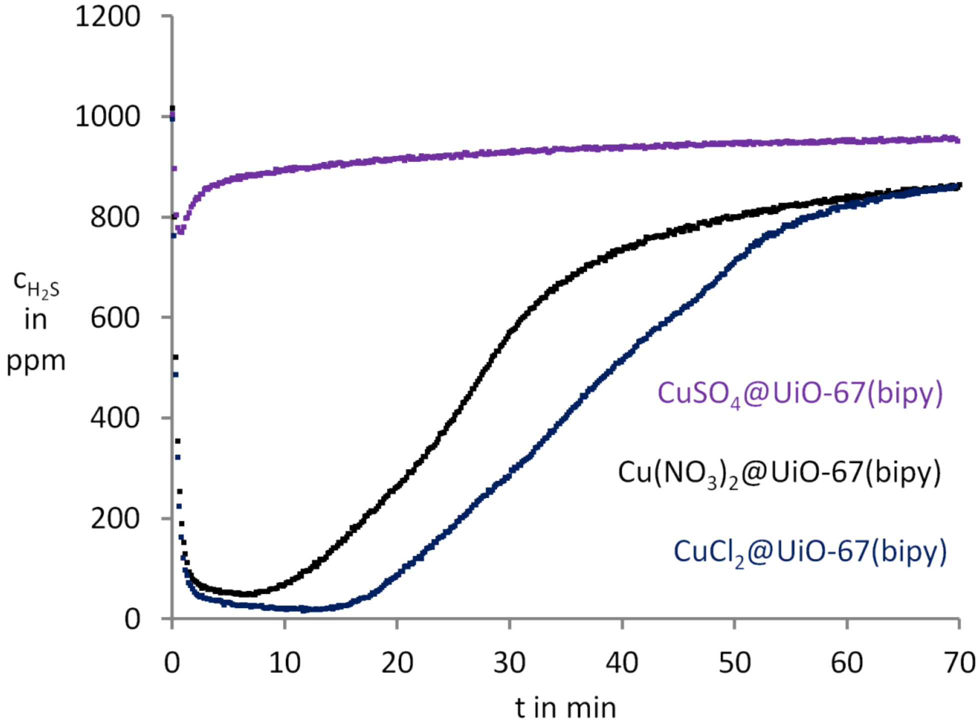

Figure S11: Breakthrough curves of UiO-67(bipy) loaded with the corresponding copper salt from aqueous solution.

9. Synthesis and crystal structure of UiO-67

34.9 mg (0.15 mmol) of $ZrCl_4$ were dissolved in DMF (2.4 ml, p.a. grade) by sonication for 10 minutes in an ultrasonic bath. 24.9 mg (0.1 mmol) of H_2bpdc was added to the solution and dissolved by sonicating for 10 minutes. 1 ml of acetic acid was added to the solution that was transferred into a pyrex tube. The tube was put into the oven with constant temperature regime of 120 °C for 8 days. After the synthesis, the mother liquid was exchanged with fresh DMF. The octahedral single crystals, suitable for X-ray diffraction experiment were grown on the reactors wall.

The octahedral shaped single crystal of UiO-67 was placed into a glass capillary with some amount of solvent. After that the capillary was sealed with melted wax. The dataset was collected on STOE IPDS-II image plate diffraction system.[1] The image frames were integrated and scaled using X-Area software. The structures were solved by direct methods and refined by full-matrix least square on F^2 using SHELXS and SHELXL programs respectively.[2] All non hydrogen atoms were refined in anisotropic approximation. The hydrogen atoms were positioned geometrically and refined using a riding model. The lattice solvent molecules could not be located from difference Fourier map due to disorder in the highly symmetrical space group. Thus, the SQUEEZE procedure in PLATON[3] was performed to correct the intensities, corresponding to disordered part of the structure. CCDC-960486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for UiO-67 (after SQUEEZE) $C_{84}H_{48}O_{32}Zr_6$, M_r = 2116.54, cubic *Fm-3m*, a = 26.896(3) Å, V = 19458(4) Å^3, Z = 4, D_c = 0.723 g cm^{-3}, 977 independent reflections observed, $R1$ = 0.0768 ($I > 2\sigma(I)$), $wR2$ = 0.1887 (all data), and *GOF* = 0.893.

1. Stoe & Cie (2002). X-Area v.1.55. Stoe & Cie, Darmstadt, Germany

2. Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

3. Spek, A. L. (2009). Acta Cryst. D65, 148-155.