Metal-assisted Salphen Organic Frameworks (MaSOFs) with High Surface Areas and Narrow Pore-Size Distribution

-Supporting Information-

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General Remarks: Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded as KBr-pellets on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. Thermal gravimetric analyses were measured on a Mettler Toledo, TGA/SDTA 851 with a heating rate of 10 °C/min and a nitrogen (or oxygen) flow of 50 mL/min. NMR spectra were recorded on a Bruker DRX 400 at 278 K at 400 MHz (^{1}H) and 100 MHz (^{13}C) or on a Bruker DRX 500 at 500 MHz (^{1}H) or 125 MHz (^{13}C). ^{13}C MAS NMR spectra were measured on a Bruker DS400WB calibrated on adamantane as external standard (38.48 ppm) with the pulse program CP4C.98 (parameters are as follows: rotational frequence: 10 KHz and 12KHz, 7000 scans, D1: 3s, Aq: 50ms, contact puls: 4ms, broadband decoupling: TPPM, BF1: 100.564993 MHz, O1p 100ppm, SW 267.3 ppm, BF2 399.94, O2p: 8ppm, p3: 3us).[S1] MALDI-TOF MS experiments were carried out on a Bruker Daltonik Reflex III with DCTB (98.5%, Aldrich) as matrix. Elemental analyses were determined with an Elementar Vario *EL*. PXRD-measurements were taken on a PANalytical X'Pert MPD Pro using copper radiation ($K_{\alpha 1}$ =1.5405980 Å).The surface areas and porosities of cage compounds were characterized by nitrogen adsorption and desorption analysis at 77.35 K with an autosorb computer controlled surface analyzer (AUTOSORB-1, Quantachrome). Each sample was degassed at 200 °C for 24 h before analysed. The Brunauer-Emmett-Teller (BET) surface area was calculated assuming a value of 0.162 nm^2 for the cross-sectional area of the nitrogen molecules in the pressure range P/P_0 = 0.01-0.1. The Non linear–differential function theory (NL-DFT model) and isotherm data were used to calculate the pore size distribution. Salicylaldehydes **1** and **4** were synthesized by procedures published before.[S2]

Synthesis of nickel salphen 3a: In a screw-capped vessel salicylaldehyde **1** (116 mg, 0.32 mmol), *o*-phenylenediamine **2** (20 mg, 0.18 mmol) and nickel acetate tetrahydrate (48 mg, 0.17 mmol) were suspended in ethanol (8 mL) and heated to 100 °C for 17 h. After cooling to room temperature, the red colored precipitate was collected by filtration, washed with ethanol (2 x 2 mL) and dried in vacuum ($9.7 \cdot 10^{-2}$ mbar) to give 112 mg (82%) of nickel salphen **3a** as wine red solid. Mp. > 410 °C. ^{1}H NMR (500 MHz, DMSO-d6, 375 K) δ (ppm) = 8.61 (s, 2H), 8.06 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.45 (d, *J* = 2.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 12H), 7.27-7.17 (m, 20H), 7.02 (dd, *J* = 9.1, 2.6 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.5, 154.4, 146.6, 142.8, 139.9, 134.3, 133.4, 131.1, 127.6, 127.2, 126.1, 121.3, 118.7, 114.9, 64.0. FT-IR (KBr) ṽ (cm^{-1}) = 3054 (w), 3026 (w), 1616 (vs), 1600 (s), 1574 (s), 1520 (s), 1490 (s), 1459 (s), 1445(m), 1419 (w), 1389 (w), 1360 (w), 1335 (w), 1255 (w), 1189 (m), 1164 (w), 1111 (w), 1083 (w), 1035 (w), 1001 (w), 969 (w), 943 (w), 834 (m), 744 (m), 706 (s), 647 (w), 632 (m), 563 (m), 541 (m), 506 (w). MALDI-TOF MS (DCTB) m/z = 856 (M$^+$), Elemental analysis calcd. for $C_{58}H_{42}N_2NiO_2$: C 81.22 H 4.94 N 3.27, found 80.95 H 4.93 N 3.23

Synthesis of zinc salphen 3b: In a screw-capped vessel salicylaldehyde **1** (110 mg, 0.30 mmol), *o*-phenylenediamine **2** (19 mg, 0.18 mmol) and zinc acetate dihydrate (33 mg, 0.15 mmol) were suspended in ethanol (6 mL) and heated to 80 °C for 3d. After cooling to room temperature, the bright yellow precipitate was collected by filtration, washed with ethanol (3 x 1 mL) and dried in vacuum ($9.7 \cdot 10^{-2}$ mbar) to give 90 mg (69%) of zinc salphen **3b** as bright yellow solid. Mp. 350 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d6, 375 K): δ = 8.70 (s, 1H), 8.00-7.58 (m, 1H), 7.50-7.12 (m, 18H), 7.04-6.91 (m, 1H), 6.65 (d, *J* = 9.0 Hz, 1H), 1.85 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ = 170.5, 162.0, 146.5, 139.0, 136.9, 136.1, 130.1, 130.0, 127.0, 126.5, 125.2, 121.9, 117.6, 115.9, 63.3. FT-IR (KBr) ṽ (cm^{-1}) = 3055 (w), 3026 (w), 1615 (vs), 1581 (m), 1519 (m), 1474 (m), 1445(m), 1419 (m), 1383 (m), 1286 (w), 1174 (m), 1035 (w), 834 (m), 747 (m), 703 (s), 646 (w), 624 (m), 546 (m). MALDI-TOF

MS (DCTB) m/z = 863 $(M)^+$, 886 $(M+Na)^+$, 1726 $(2M)^+$, 1749 $(2M+Na)^+$.Elemental analysis calcd. for $C_{58}H_{42}N_2ZnO_2\cdot H_2O$: C 78.95 H 5.05 N 3.17, found 78.82 H 4.94 N 3.15

Synthesis of MaSOF-1: In a screw-capped vessel tetrakis salicylaldehyde **4** (25 mg, 0.05 mmol), o-phenylenediamine **2** (11 mg) and nickel acetate tetrahydrate (29 mg) were suspended in DMF (4 mL) and heated without stirring at 100 °C for 3d. The mixture was cooled to room temperature and the dark red solid collected on a Büchner funnel. The solid was extensively washed with several portions of ethanol until the extraction solution shows no further coloration. Drying in air gives 56 mg of **MaSOF-1as**. The brown-red solid was further dried at 200 °C in high vacuum, resulting in 38 mg (98%) of **MaSOF-1** as reddish brown solid. ^{13}C MAS NMR: δ (ppm) = 166, 159-153, 147-110, 62. FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 3429 (br, s), 1612 (vs), 1576 (s), 1523 (s), 1489 (s), 1464 (s), 1416 (w), 1377 (w), 1321 (w), 1255 (w), 1195 (m), 814 (m), 751 (m), 642 (w), 550 (m). Elemental analysis calcd. for $C_{41}H_{24}N_4Ni_2O_4\cdot 2/3DMF\cdot 7H_2O$ (**MaSOF-1as**): C 55.60 H 4.63 N 7.04, found 55.53 H 3.86 N 7.03.

Synthesis of MaSOF-2: In a screw-capped vessel tetrakis salicylaldehyde **4** (26 mg, 0.05 mmol), o-phenylenediamine **2** (11 mg) and zinc acetate dihydrate (24 mg) were suspended in DMF (4 mL) and heated without stirring at 100 °C for 3d. The mixture was cooled to room temperature and the bright yellow solid collected on a Büchner funnel. The solid was extensively washed with several portions of ethanol until the extraction solution shows no further coloration. yellow solid was further dried at 200 °C in high vacuum, resulting in 35 mg (91%) of **MaSOF-2** as yellow powder. ^{13}C MAS NMR: δ (ppm) = 166, 159-153, 146-109, 61. FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 3434 (br, s), 2924 (w), 1615 (vs), 1582 (m), 1523 (m), 1473 (m), 1381 (m), 1308 (w), 1177 (m), 747 (m), 634 (m), Elemental analysis calcd. for $C_{41}H_{24}N_4Zn_2O_4\cdot 1/3DMF\cdot 3H_2O$ (**MaSOF-1as**): C 59.64 H 3.85 N 7.18, found 59.63 H 3.90 N 7.58.

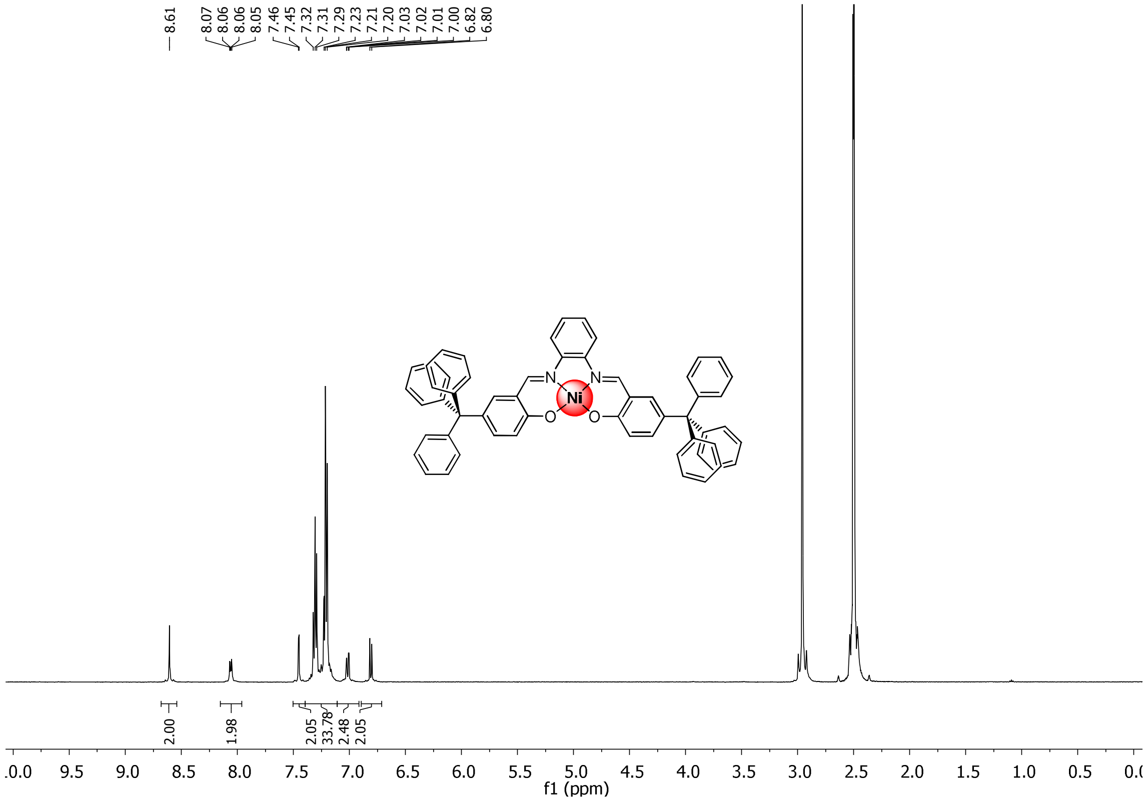


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO-d6) of **3a**.

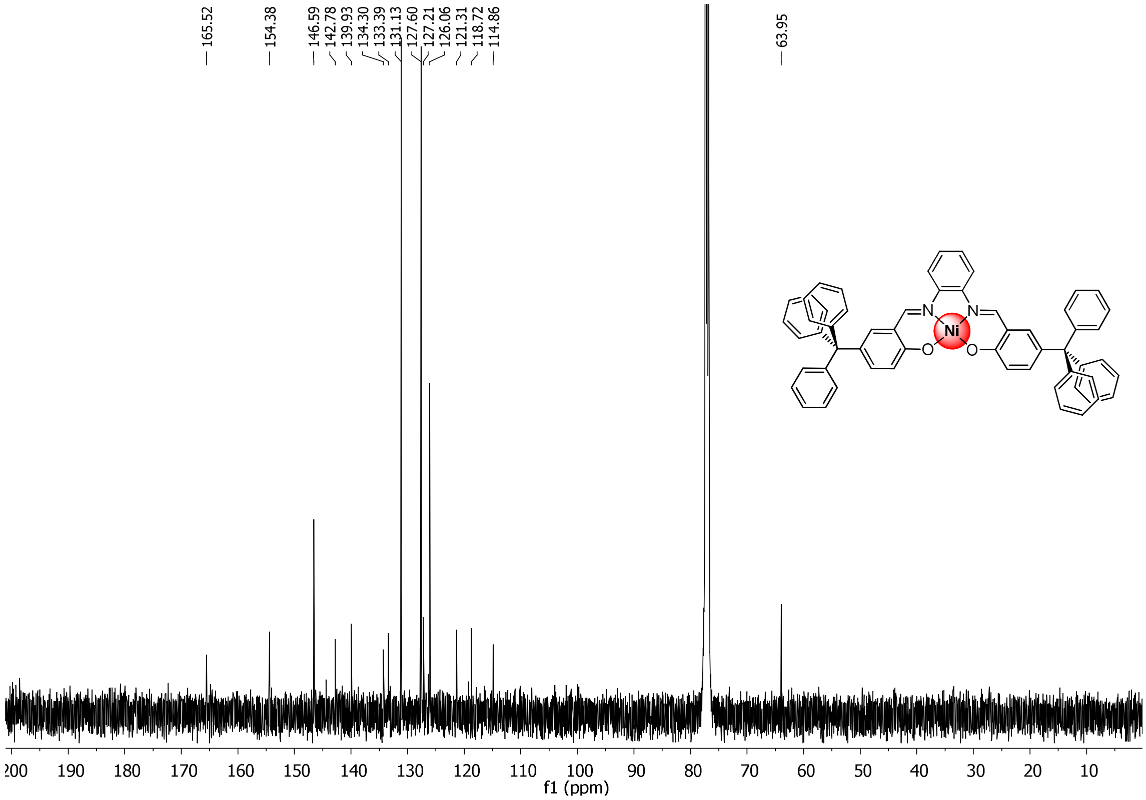


Figure S2. ^{13}C NMR spectrum (125 MHz, DMSO-d6)of **3a**.

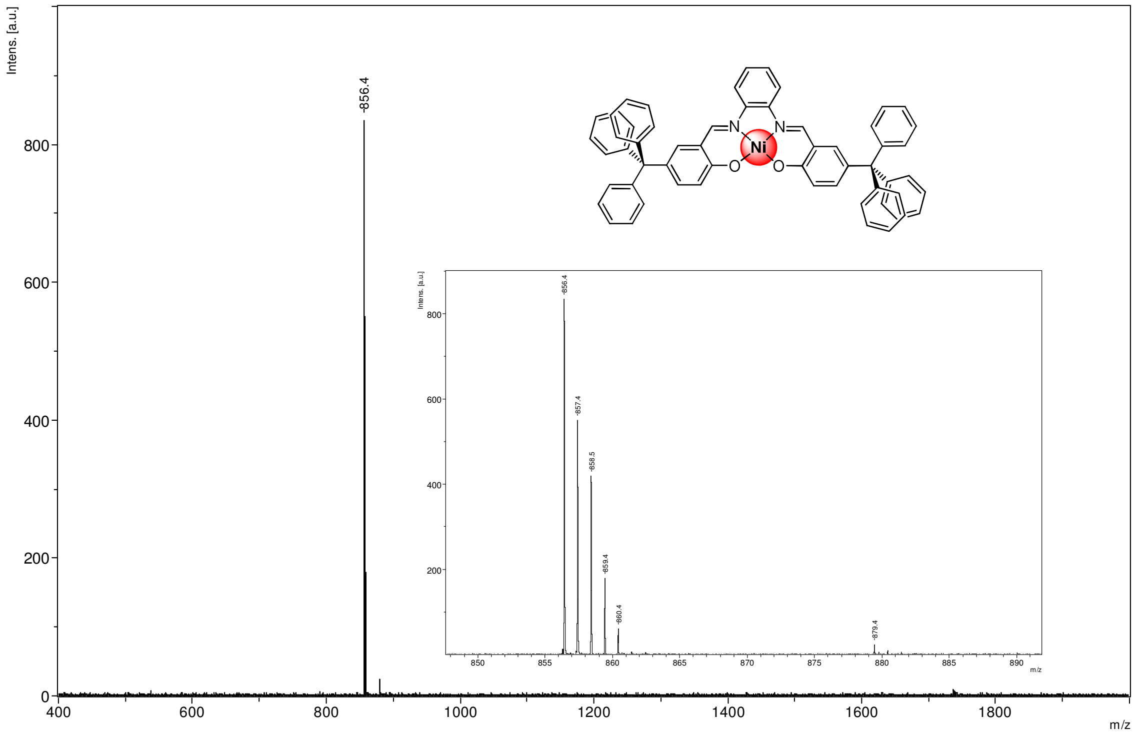


Figure S3. MALDI TOF mass spectrum of **3a**.

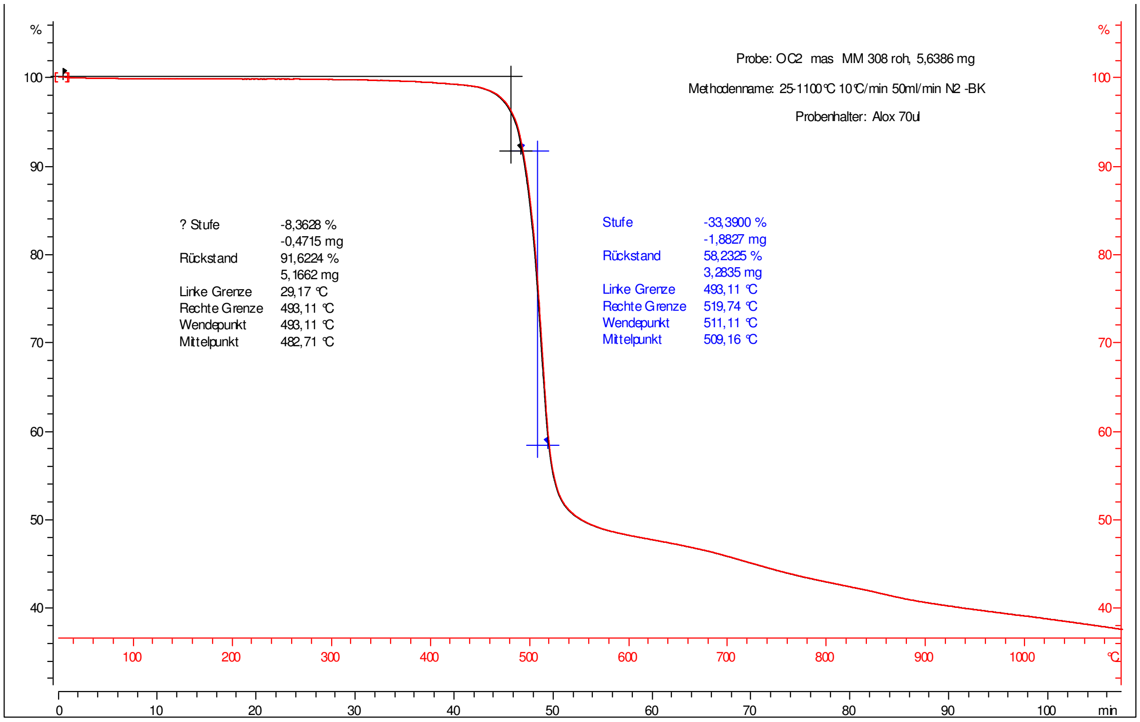


Figure S4. TGA of **3a** in nitrogen atmosphere.

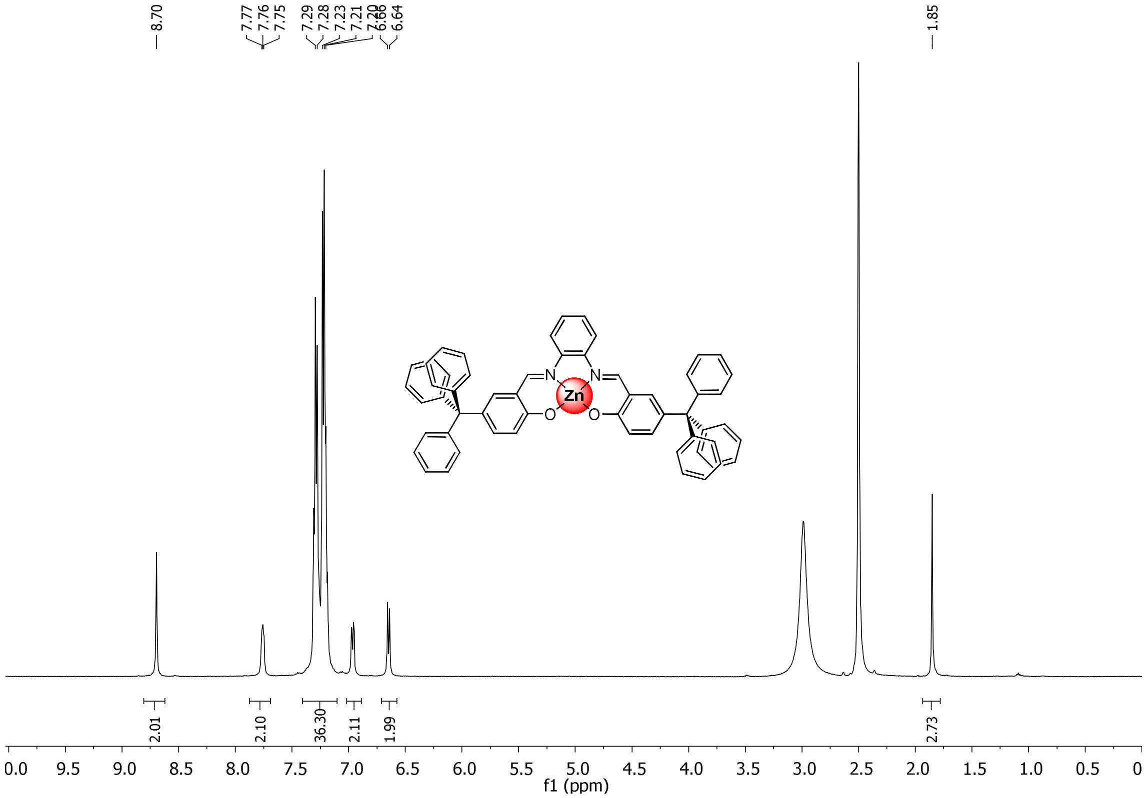


Figure S5. ^{1}H NMR spectrum (400 MHz, DMSO-d6)of **3b**.

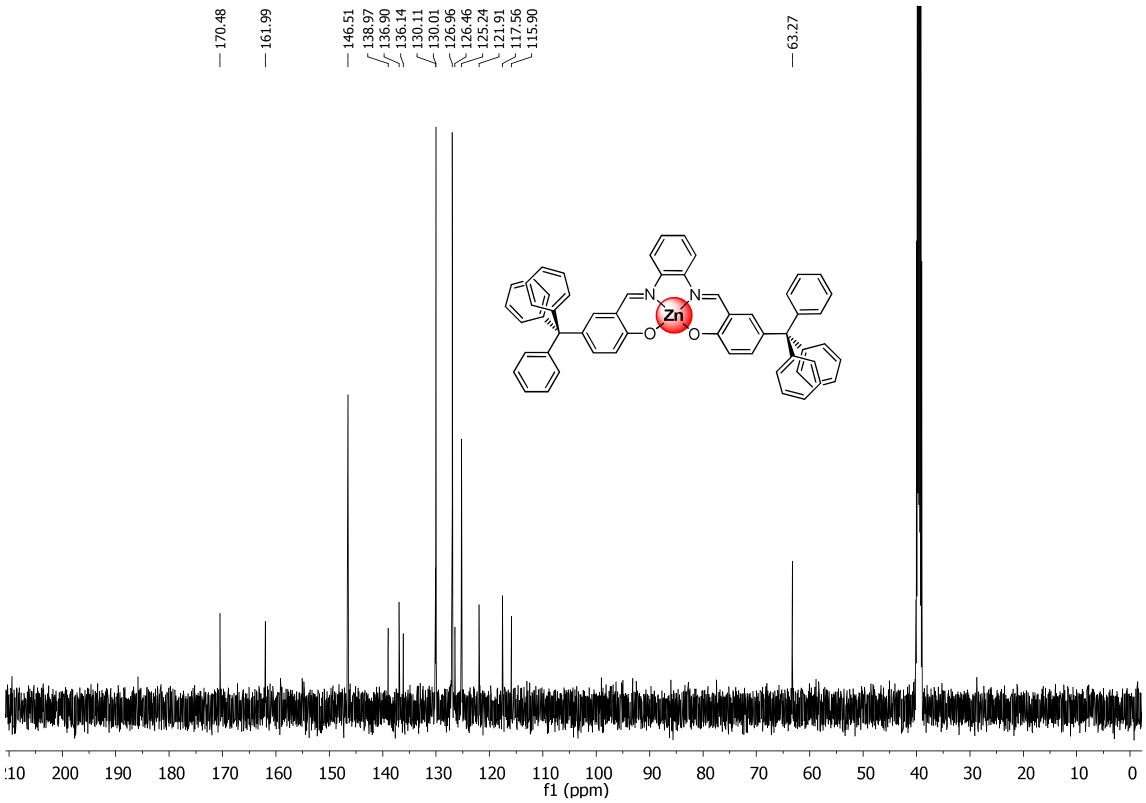


Figure S6. ^{13}C NMR spectrum (125 MHz, DMSO-d6)of **3b**.

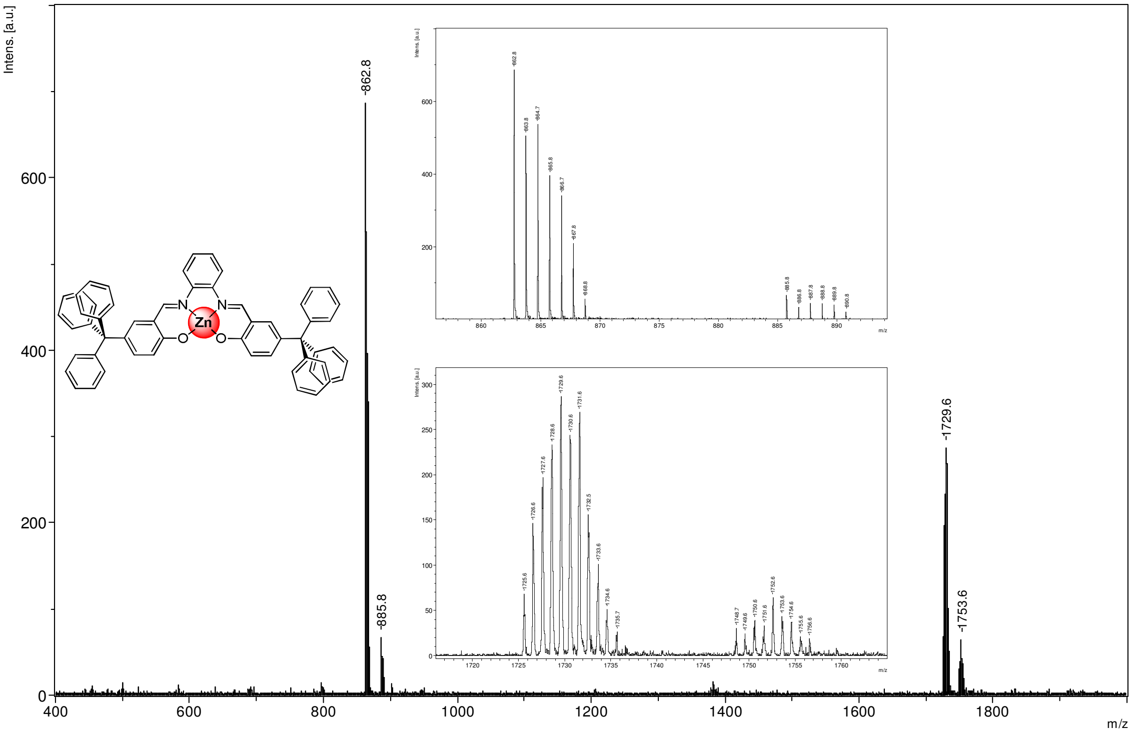


Figure S7. MALDI TOF mass spectrum of **3b**.

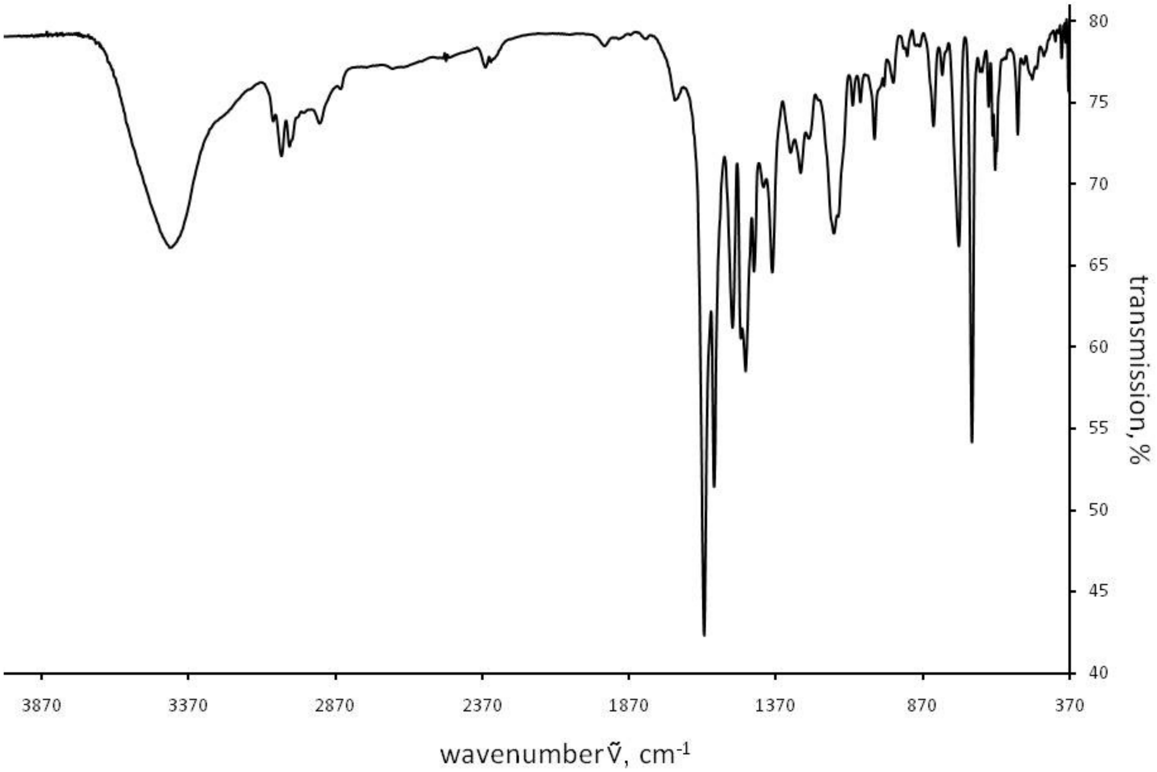


Figure S8. FT-IR spectrum of **3b**.

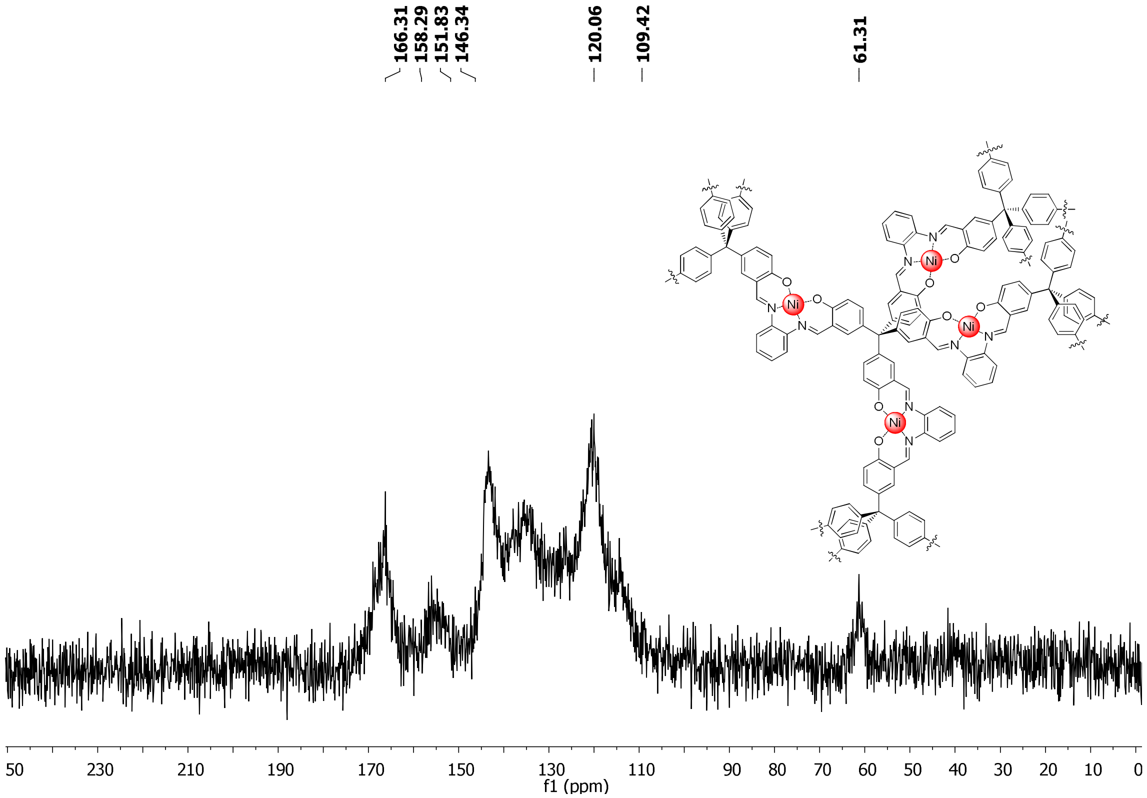


Figure S9. ^{13}C MAS NMR spectrum of **MaSOF-1**.

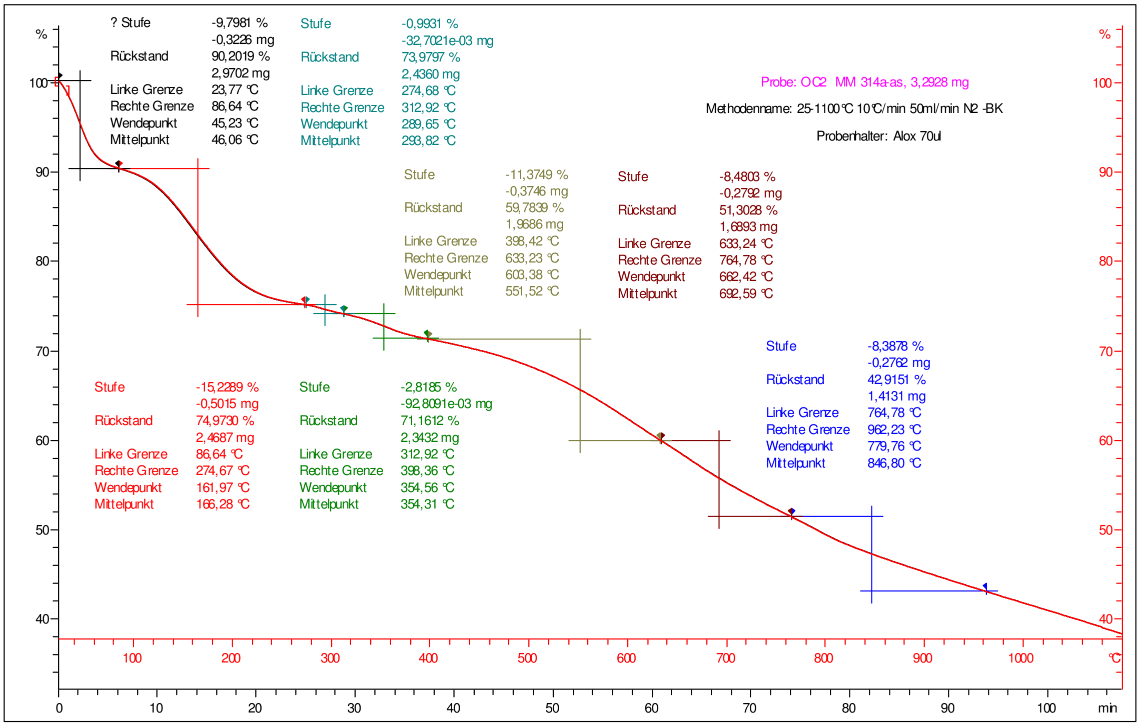
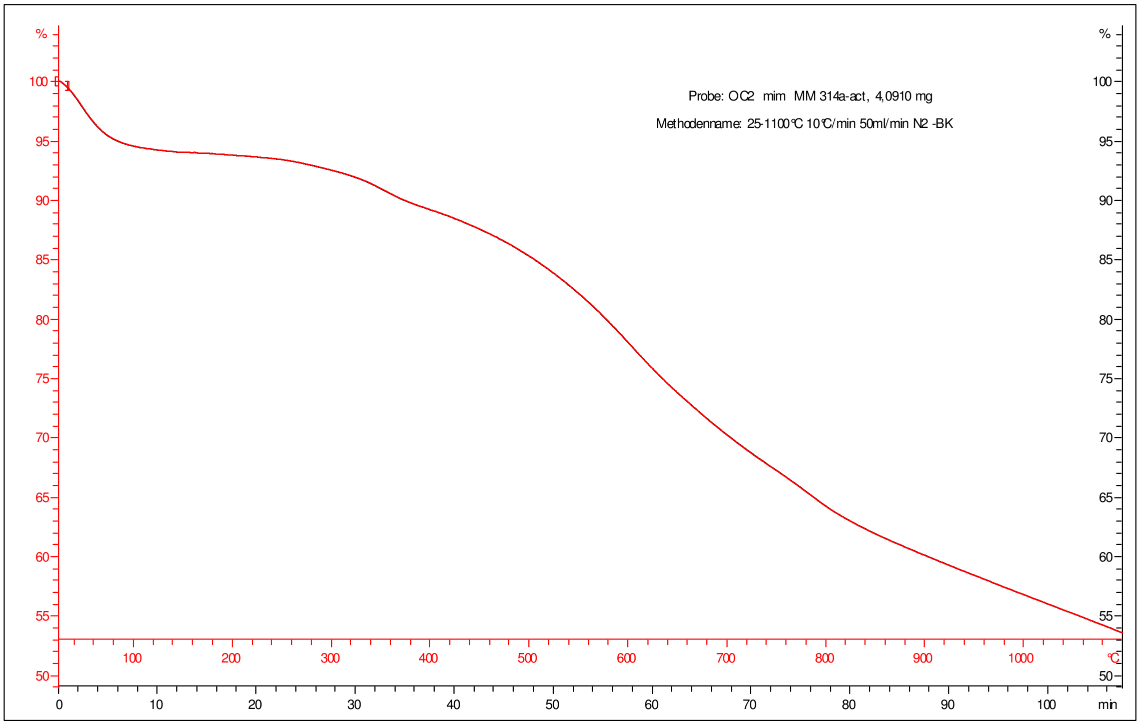


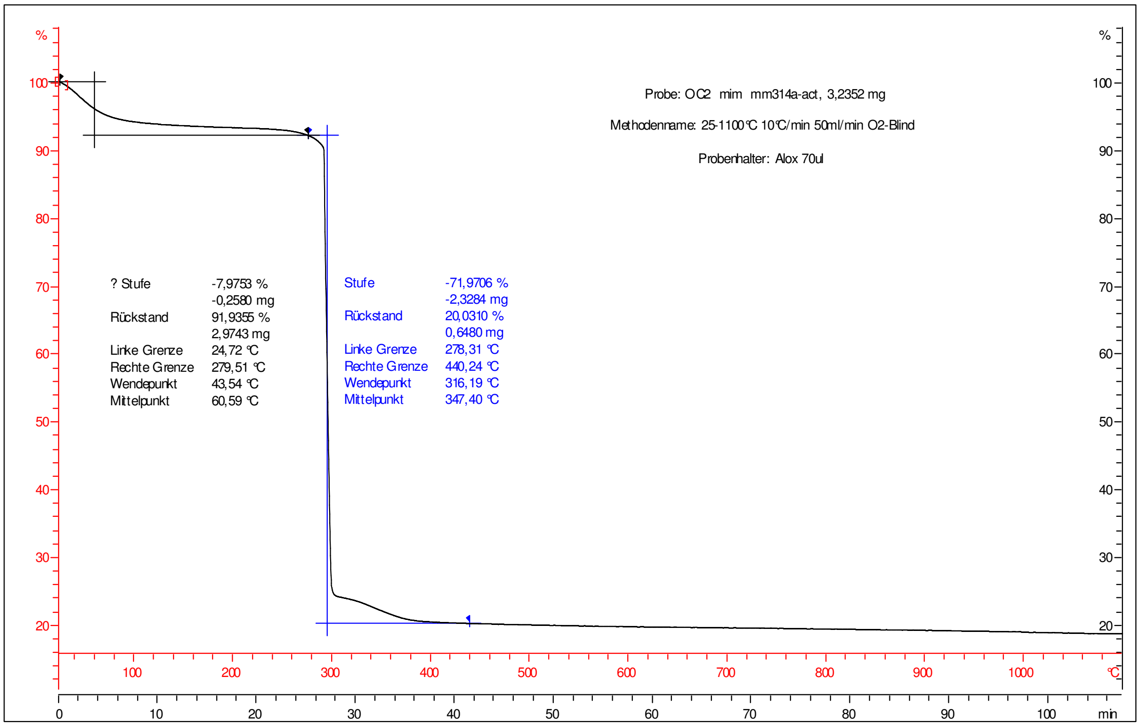
Figure S10. TGA of as synthesized **MaSOF-1** measured in N$_2$-atmosphere.



Probe: OC2 mim MM 314a-act, 4,0910 mg

Methodenname: 25-1100°C 10°C/min 50ml/min N2 -BK

Figure S11. TGA of ” activated” **MaSOF-1** measured in N_2-atmosphere.



Probe: OC2 mim mm314a-act, 3,2352 mg

Methodenname: 25-1100°C 10°C/min 50ml/min O2-Blind

Probenhalter: Alox 70ul

? Stufe	-7,9753 % -0,2580 mg
Rückstand	91,9355 % 2,9743 mg
Linke Grenze	24,72 °C
Rechte Grenze	279,51 °C
Wendepunkt	43,54 °C
Mittelpunkt	60,59 °C

Stufe	-71,9706 % -2,3284 mg
Rückstand	20,0310 % 0,6480 mg
Linke Grenze	278,31 °C
Rechte Grenze	440,24 °C
Wendepunkt	316,19 °C
Mittelpunkt	347,40 °C

Figure S12. TGA of **MaSOF-1** measured in O_2-atmosphere.

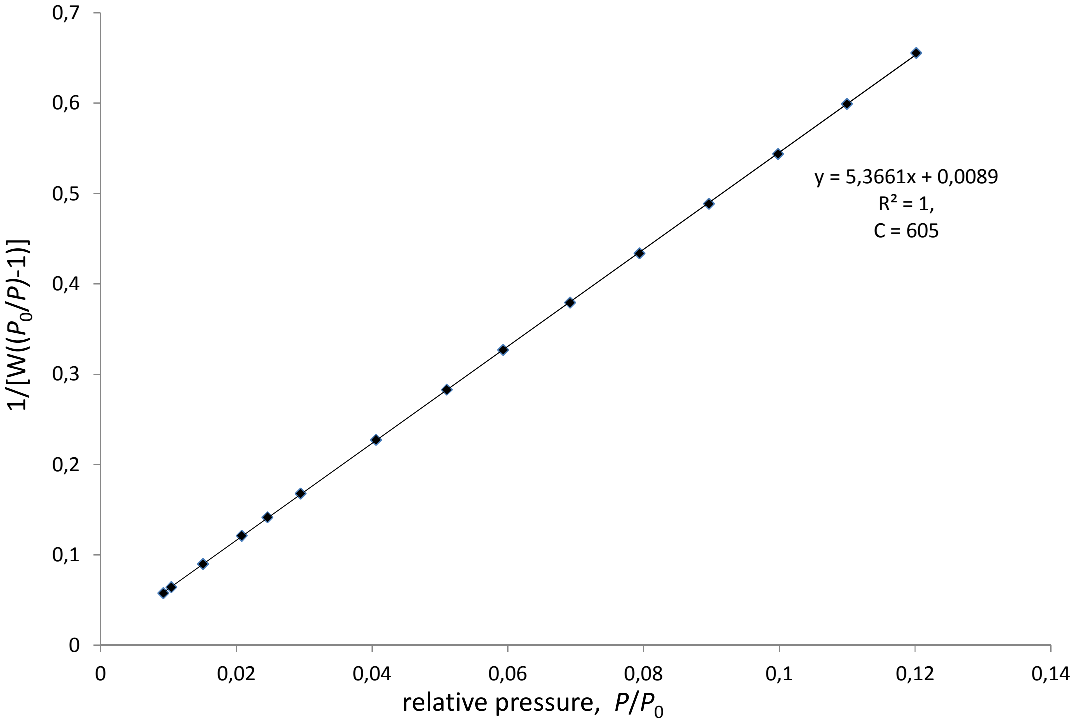


Figure S13. BET plot of nitrogen sorption of **MaSOF-1** at 77K.

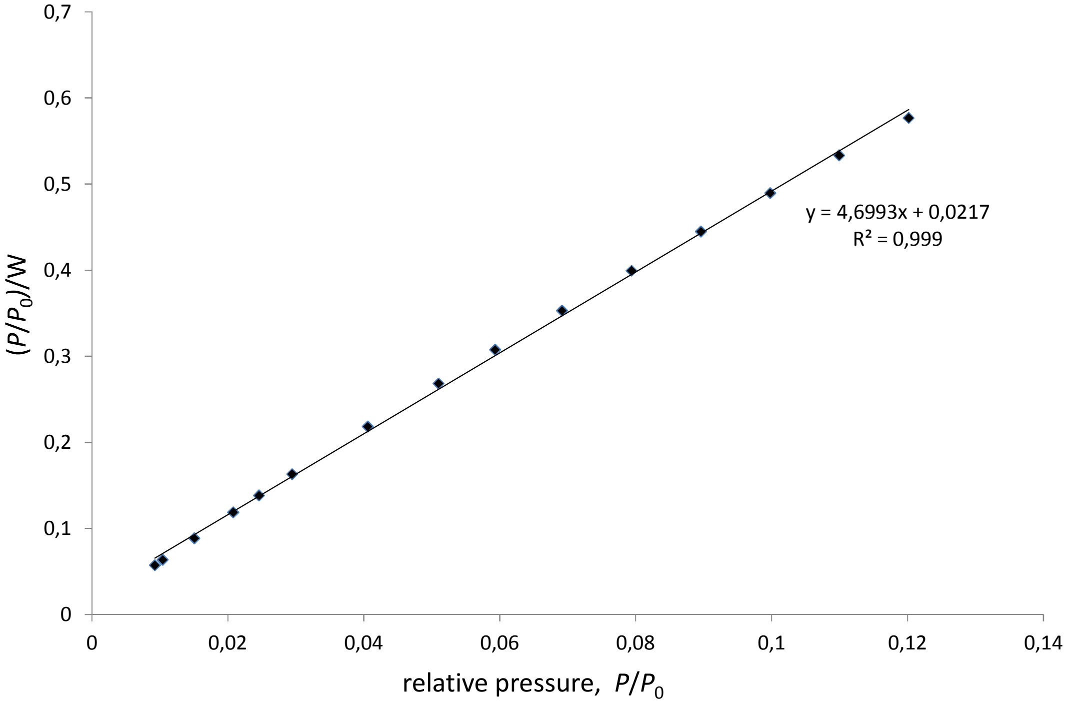


Figure S14. Langmuir plot of nitrogen sorption of **MaSOF-1** at 77K.

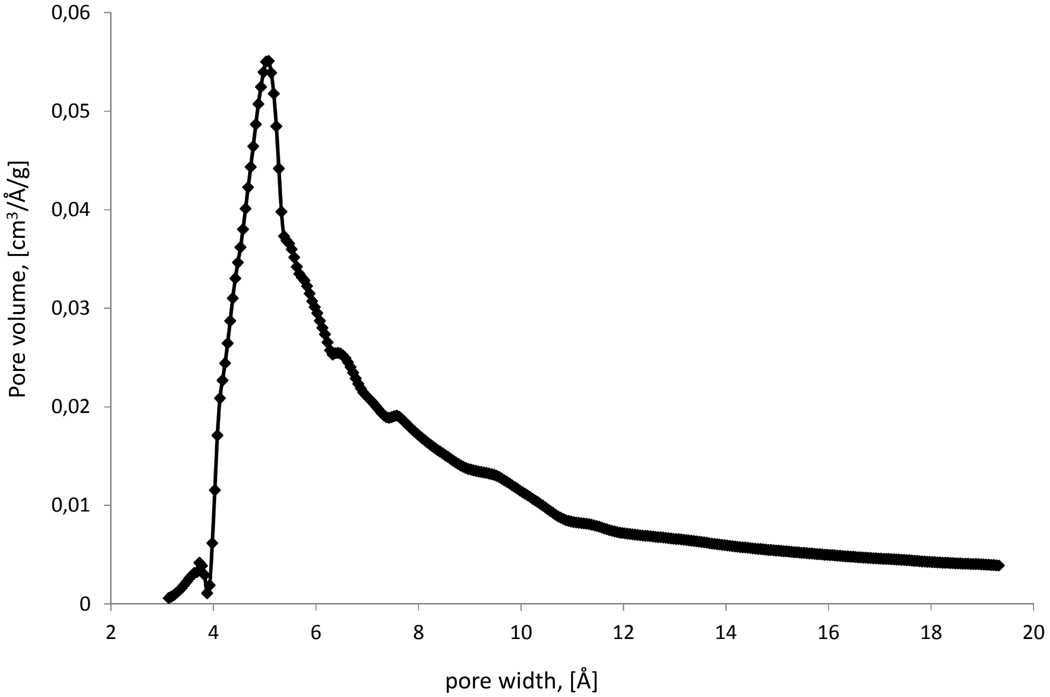


Figure S15. Horvath-Kawazoe model derived pore size distribution of **MaSOF-1**.

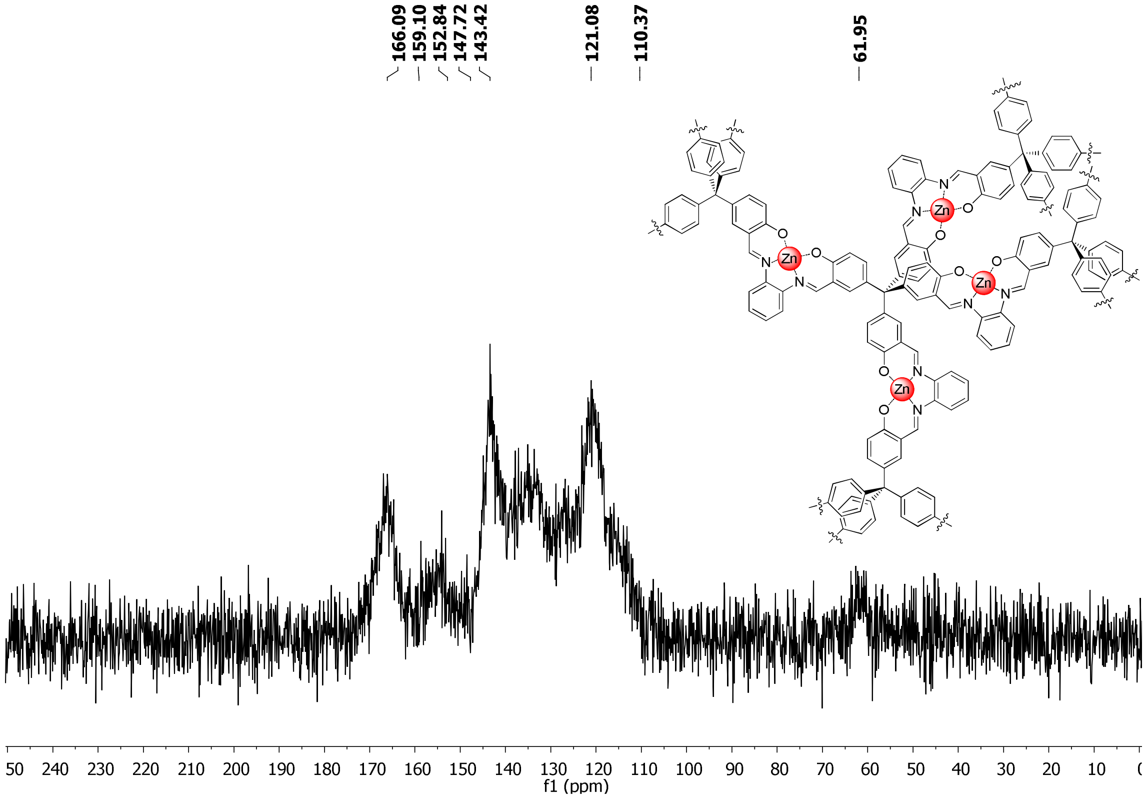


Figure S16. ^{13}C MAS NMR spectrum of **MaSOF-2**.

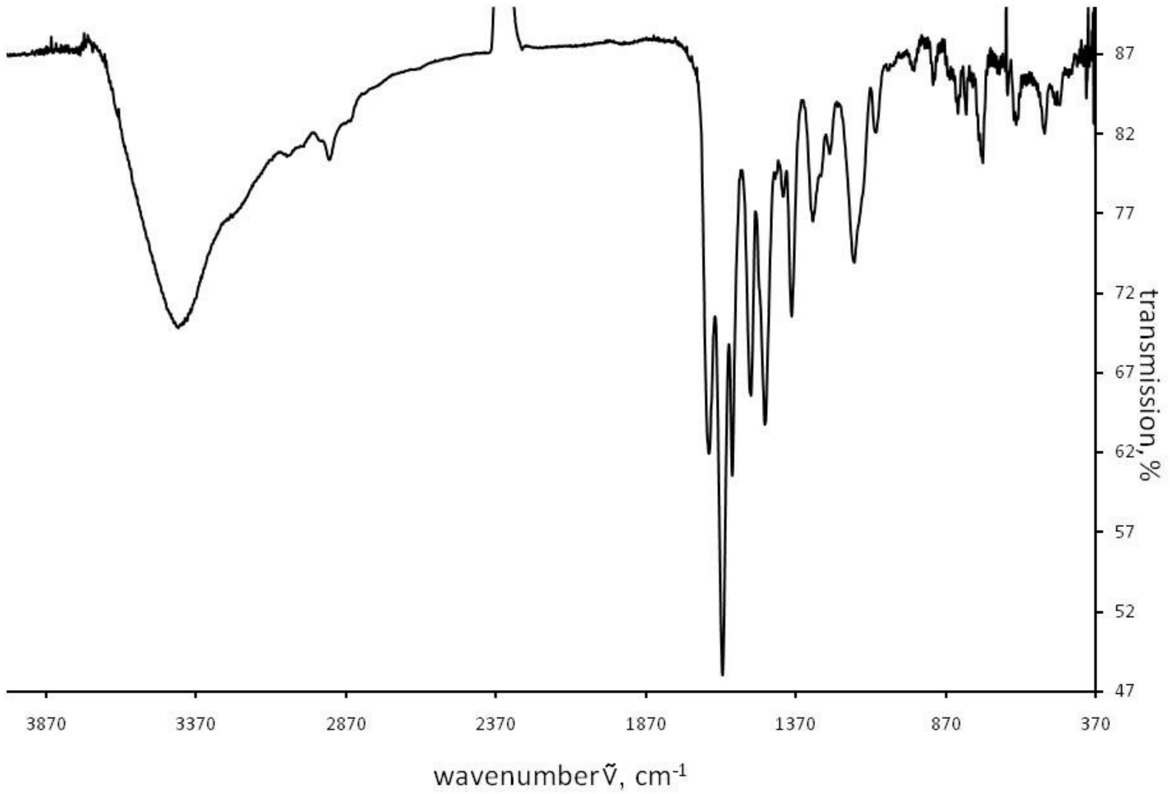


Figure S17. FT-IR spectrum of as-synthesized **MaSOF-2**.

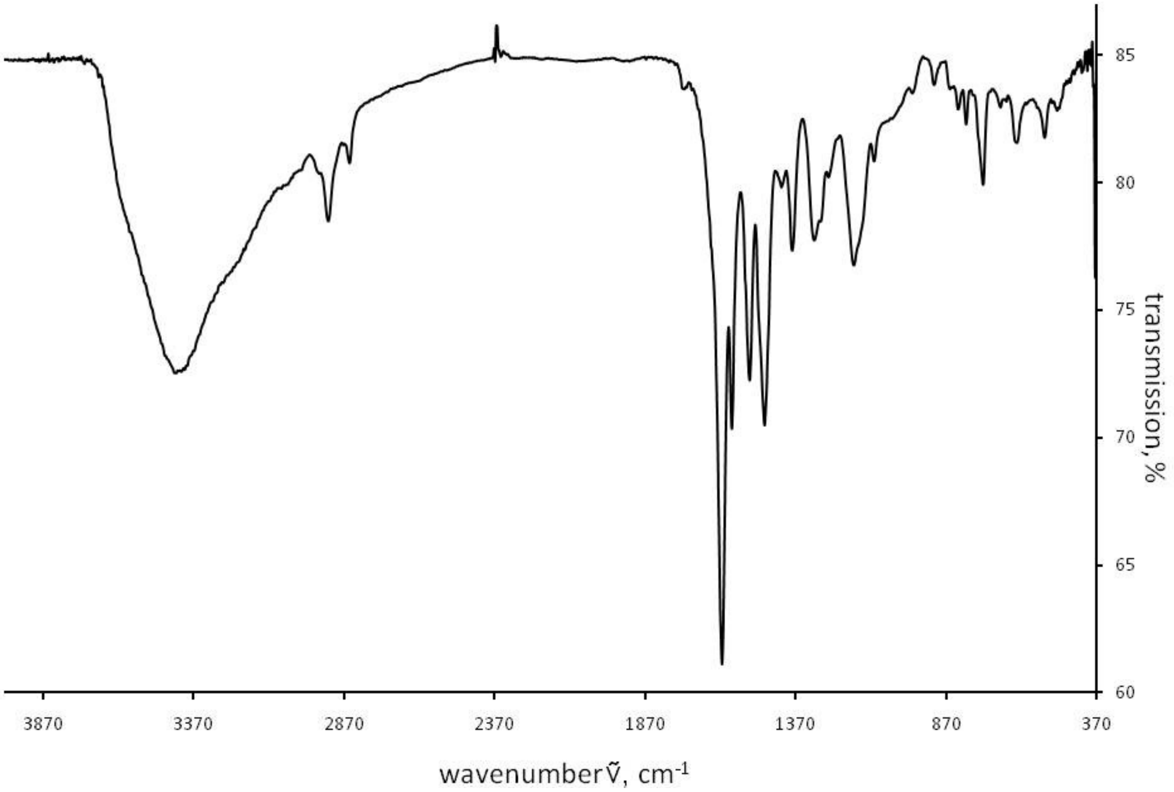


Figure S18. FT-IR spectrum of “activated” **MaSOF-2**.

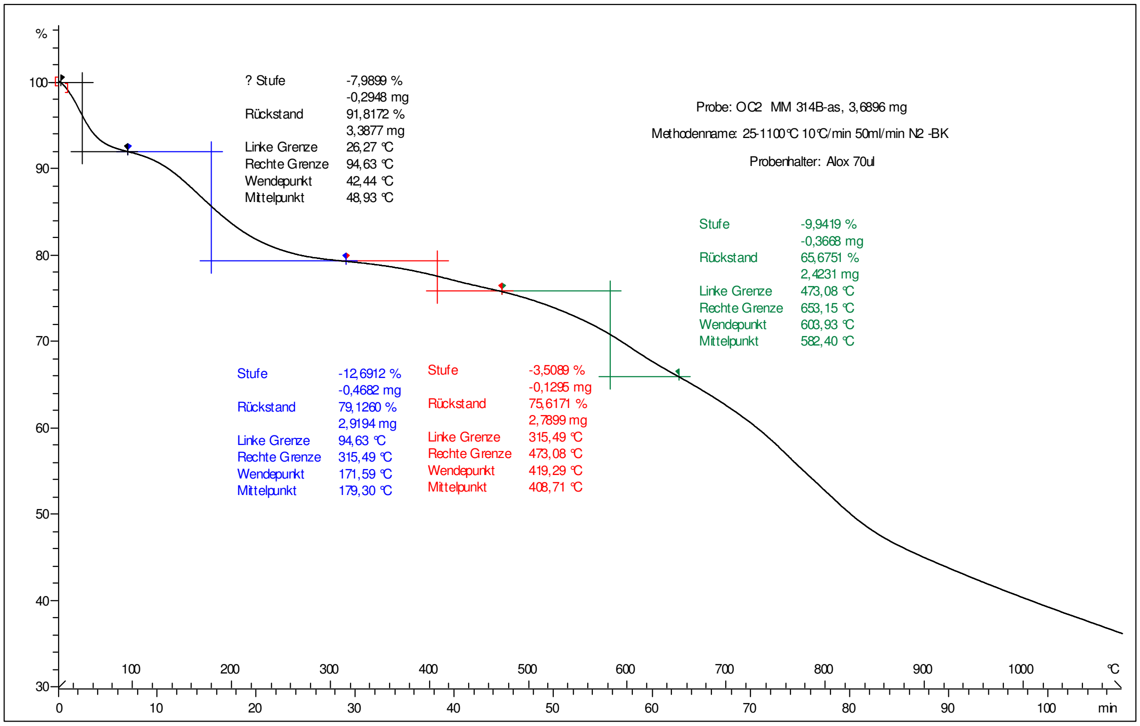


Figure S19. TGA of as synthesized **MaSOF-2** measured N_2-atmosphere.

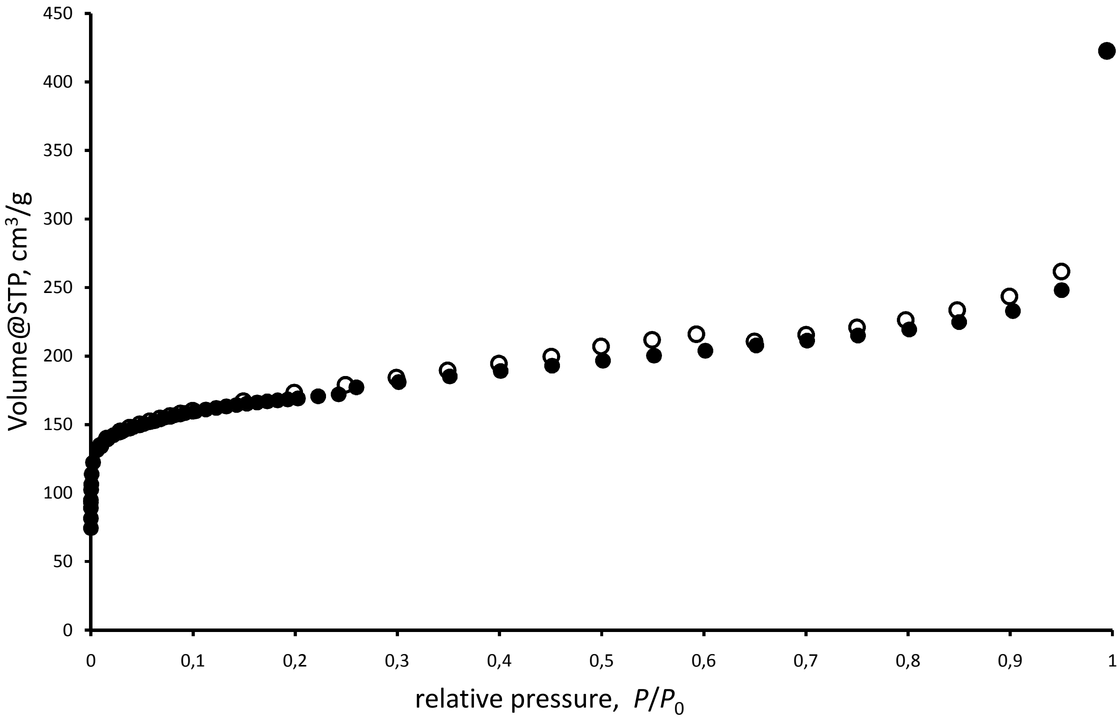


Figure S20. Nitrogen sorption of **MaSOF-2** at 77K.

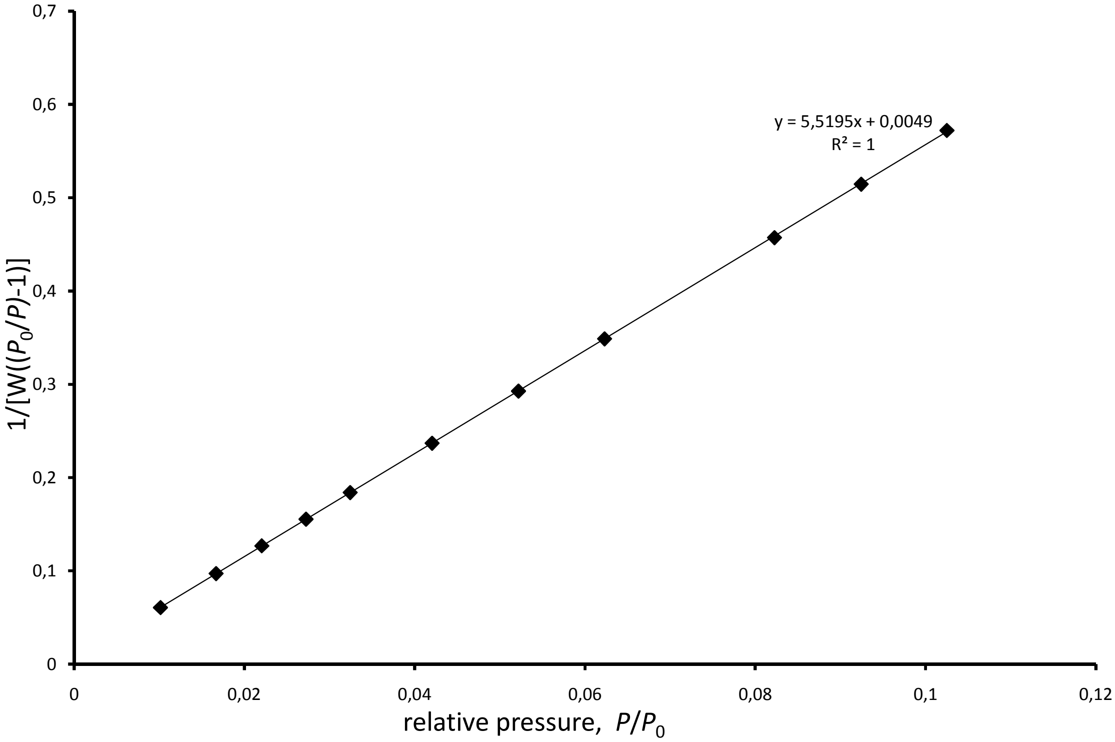


Figure S21. BET plot of nitrogen sorption of **MaSOF-2** at 77K.

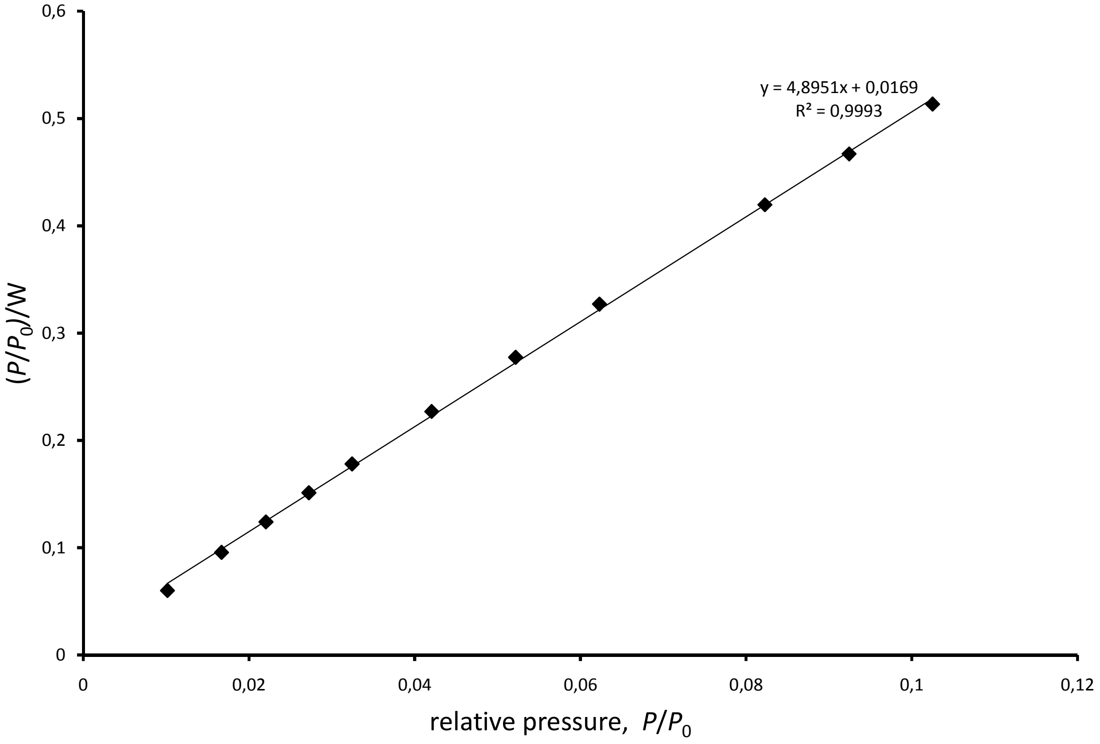


Figure S22. Langmuir plot of nitrogen sorption of **MaSOF-2** at 77K.

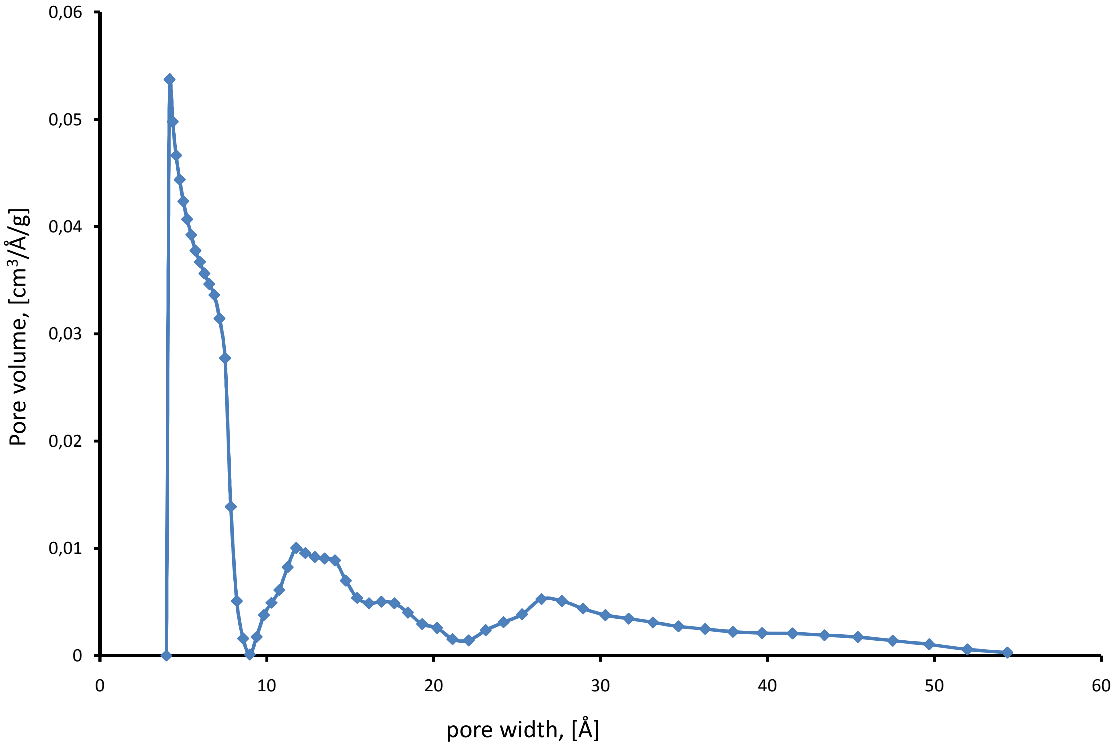


Figure S23. NL-DFT derived pore size distribution of **MaSOF-2**.

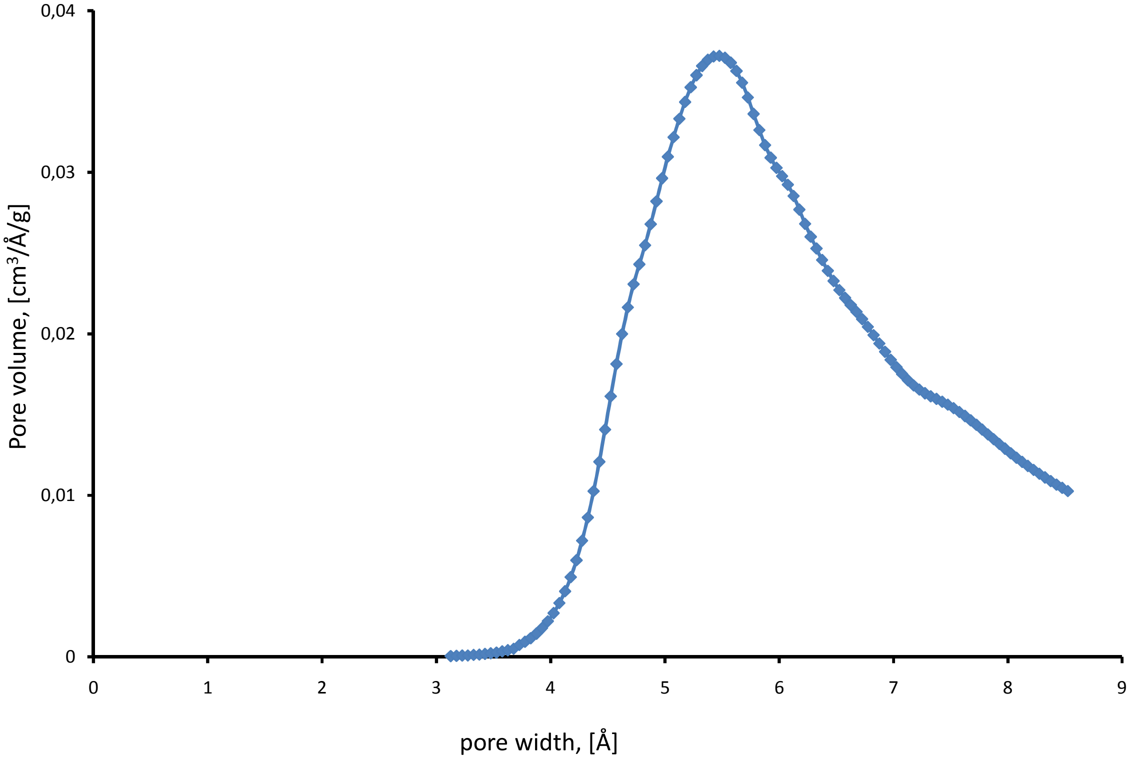


Figure S24. HK derived pore size distribution of **MaSOF-2**.

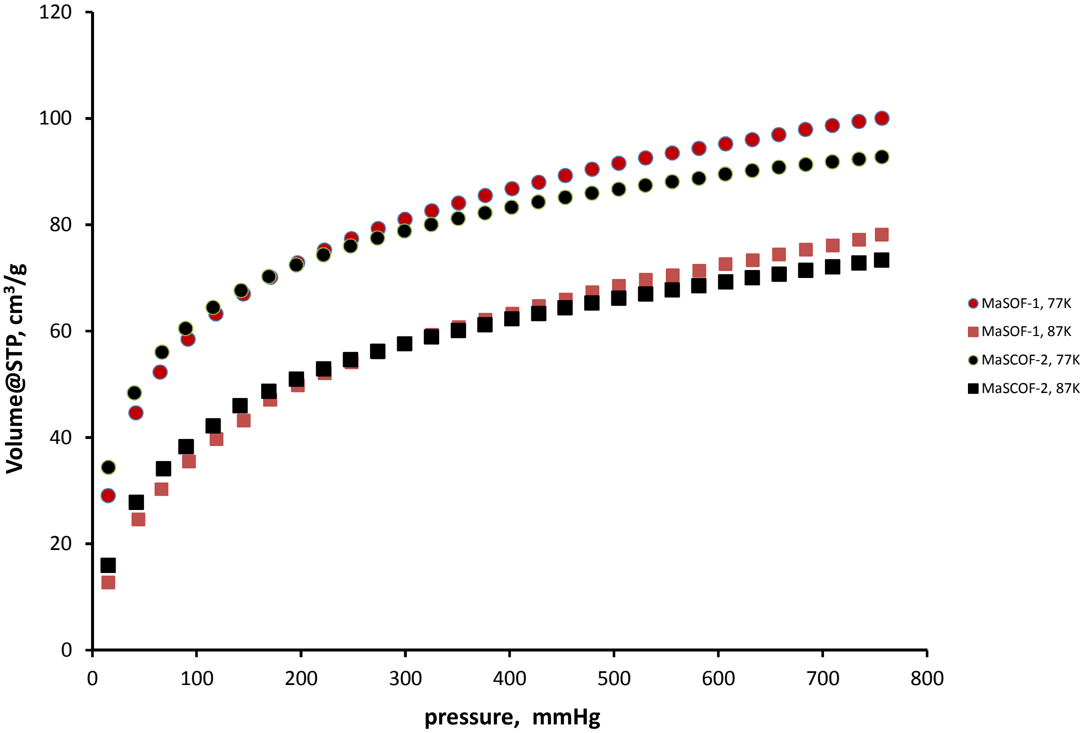


Figure S25. Comparison of hydrogen adsorption of **MaSOF-1** and **MaSOF-2** at 77 K and 87 K.

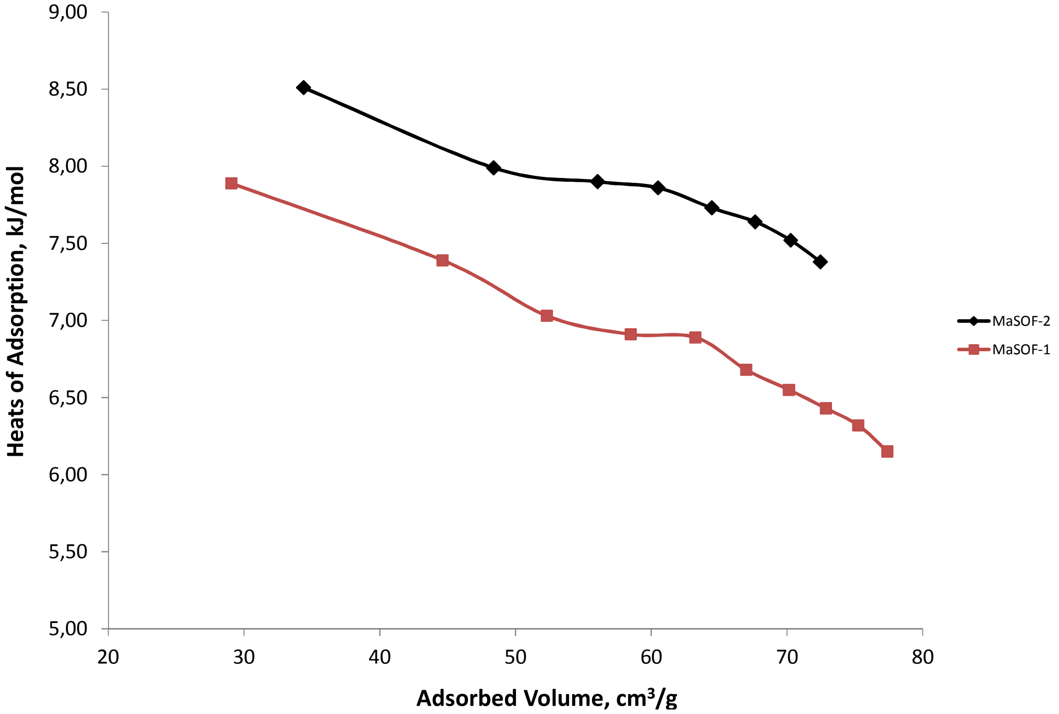


Figure S26. Heat of hydrogen adsorption of **MaSOF-1** and **MaSOF-2** at 77 K and 87 K.

References:

[S1] E. O. Stejskal, J. D. Memory, High-Resolution NMR in the solid state, Fundamentals of CP MAS NMR. Oxford University Press, **1994**.

[S2] M. Mastalerz, I. M. Oppel, *Eur. J. Org. Chem.,* **2011**, DOI5971-5980.