Supplementary information

Influence of the hydrophilic-hydrophobic contrast of porous surfaces on the enzymatic performance

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1. Characterization of MCF

1.1 Sorption results

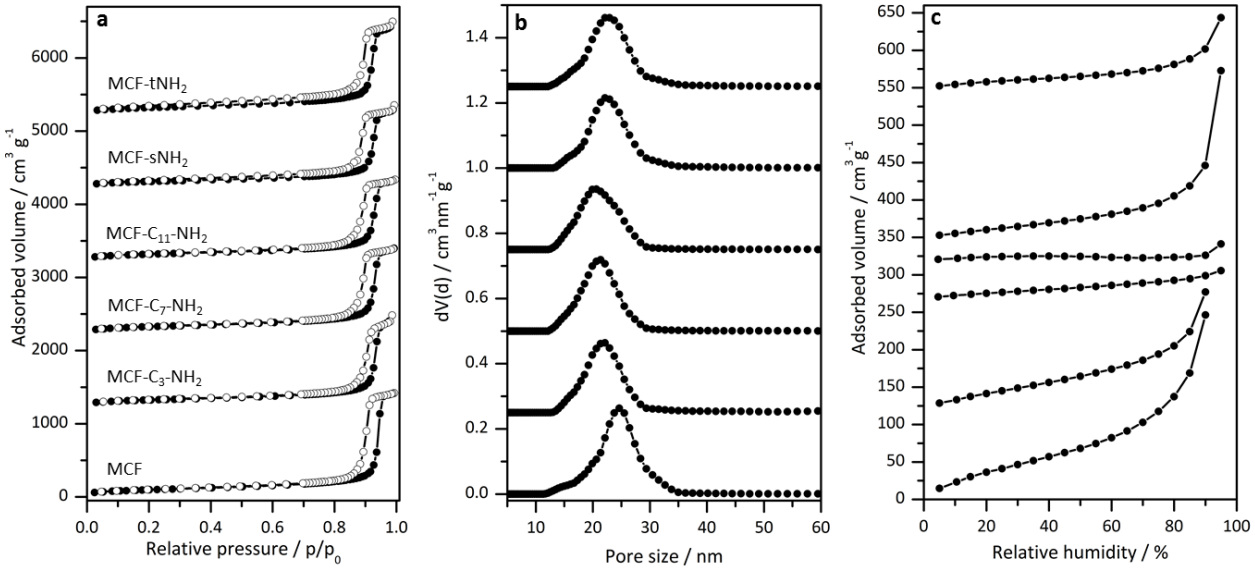


Figure S1 Nitrogen physisorption isotherms (77 K, **a**, shift: 11250, 2250, 3250, 4250, 5250 $cm^3\ g^{-1}$) with their corresponding NLDFT (kernel: cylindrical pores, adsorption) pore size distributions (**b**, shift: 0.25, 0.5, 0.75, 1.0, 1.25 $cm^3\ (nm\ g)^{-1}$). Water vapour adsorption isotherms (**c**) at 298 K are shown on the right side and are shifted by 120, 270, 320, 350 and 550 $cm^3\ g^{-1}$ for the respective MCF samples.

1.2 IR spectra

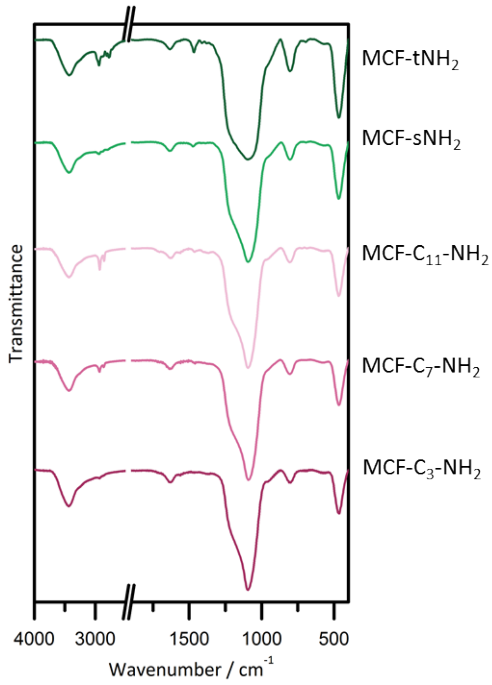


Figure S2 Normalized IR spectra of amine-modified MCFs. Most of the vibrations can be assigned to the silica network whereas some weaker bands indicate the presence of the organic moieties attached to the walls of the MCF.

Sample	Wavenumber / cm^{-1}	Vibration
MCF-C_3/C_7/C_{11}-NH_2	2930	ν_{as} (CH_2)
	2865	ν_s (CH_2)
MCF-s/tNH_2	2941	ν_{as} (CH_2), ν_{as} (CH_3) overlapped
	2870	ν_s (CH_2), ν_s (CH_3) overlapped
	2815	ν_s (CH_2)
	1467	δ_{as} (CH_3)
	1411[a]	δ_s (CH_3)
	1377[a]	δ_s (CH_3)

ν_{as}: asymmetric stretching, ν_s: symmetric stretching, δ: deformation, a: only observed for MCF-tNH_2

1.3 Argon physisorption (87 K)

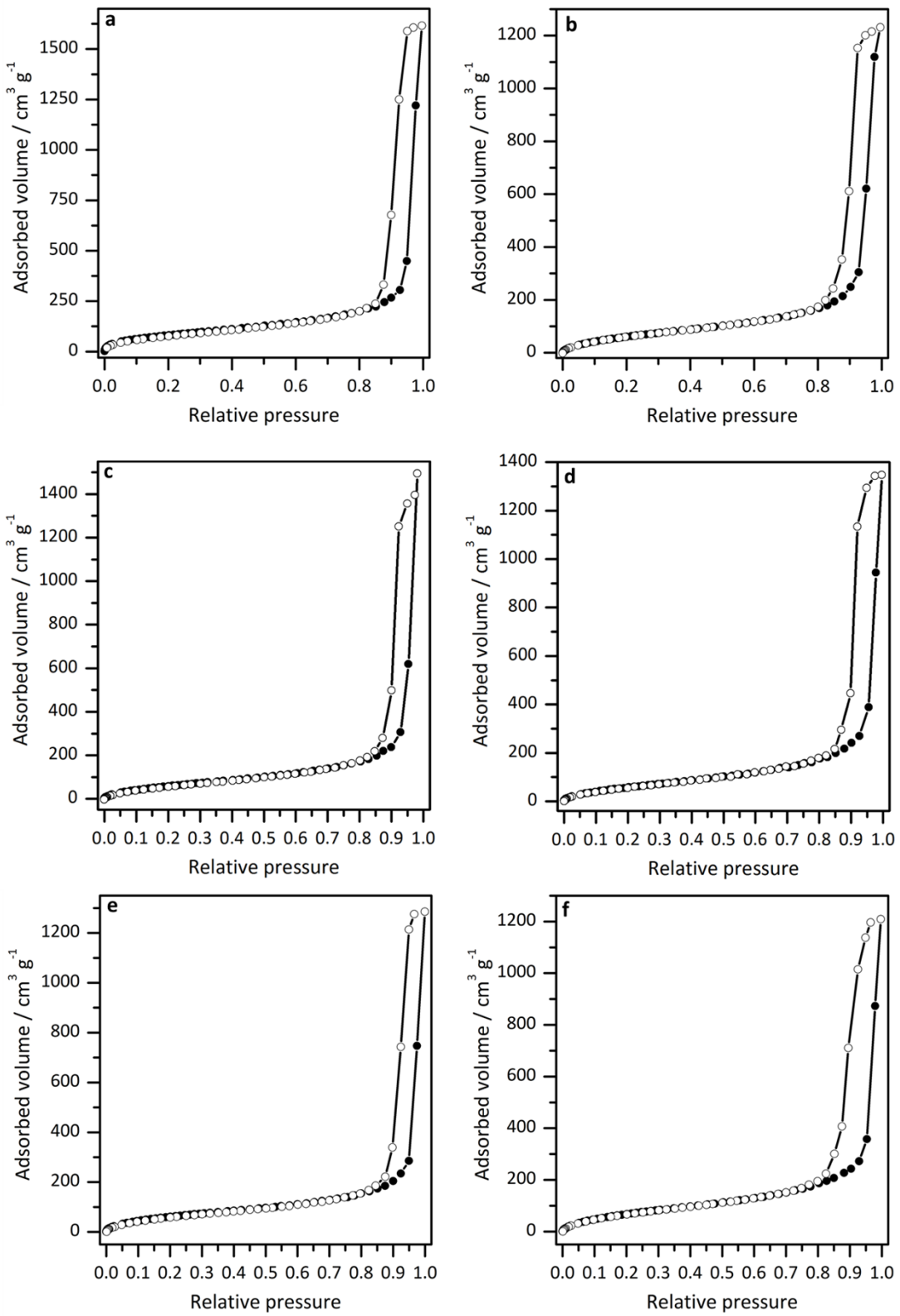


Figure S3 Argon physisorption isotherms at 87 K of pure MCF (a), MCF-C_{11}-NH_2 (b), MCF-sNH_2 (c), MCF-tNH_2(d), MCF-C_3-NH_2 (e) and MCF-C_7-NH_2 (f).

1.4 Quantification of the hydrophobicity

$$n_m = \frac{S_{BET} M}{N_A a_m}$$

n_m : monolayer capacity

S_{BET}: specific surface area

- S_{BET} (Ar): determination of the maximum theoretical n_m
- S_{BET} (H_2O): experimental n_m

M: molecular weight of water (18.015 g mol^{-1})

N_A: Avogadro's number

a_m: cross-sectional area of water (10.5 $Å^2$)

Hydrophilicity index χ:

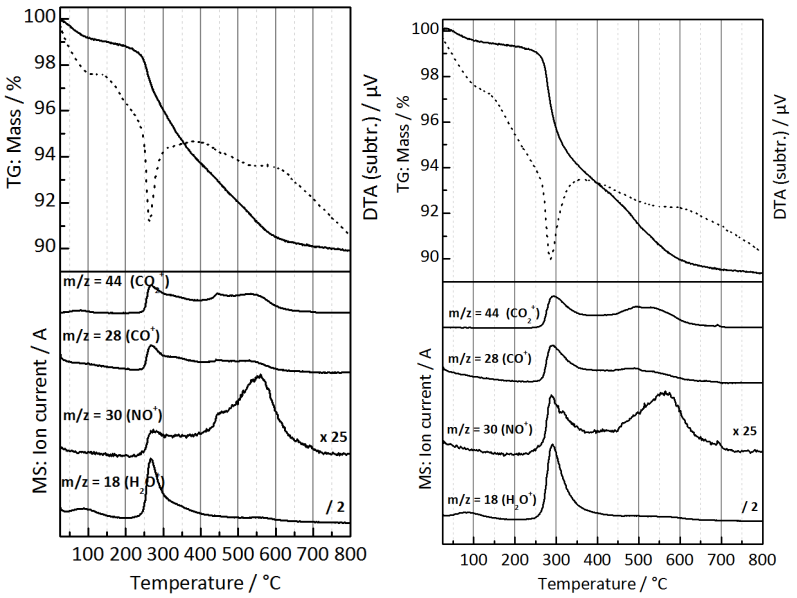
$$\chi = \frac{n_m(H_2O)}{n_m(Ar)}$$

Values determined from Argon and water sorption to calculate χ_1 and χ_2:

Sample	S_{BET} (Ar) / $m^2\ g^{-1}$	S_{BET} (H_2O) / $m^2\ g^{-1}$	V (Ar) / $cm^3\ g^{-1}$	V (H_2O) / $cm^3\ g^{-1}$
MCF	278	114	0.789[a]	0.179[a]
MCF-C_3-NH_2	224	76	0.261[a]	0.126[a]
MCF-C_7-NH_2	255	30	0.455	0.029
MCF-C_{11}-NH_2	234	14	0.791	0.017
MCF-sNH_2	225	48	0.789	0.179
MCF-tNH_2	223	32	0.494	0.075

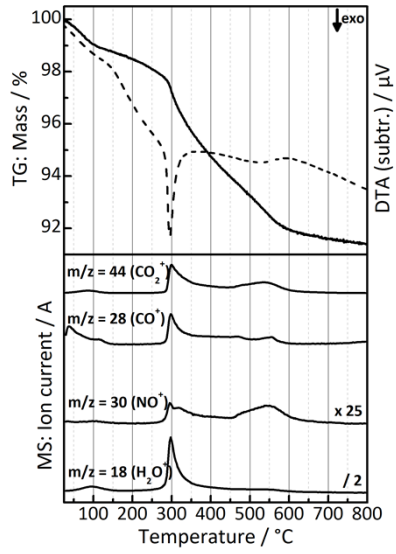
a: Values determined at p/p_0 = 0.90. All other volumes were determined at p/p_0 = 0.95.

1.5 TG/DTA/MS



Sample	Mass loss / % <250 °<750 °C		ρ_F / mmol g^{-1}
MCF-C_3-NH_2	2.2	6.2	1.2
MCF-C_7-NH_2	1.3	10.6	1.1
MCF-C_{11}-NH_2	0.7	14.4	1.0
MCF-sNH_2	1.2	8.8	1.3
MCF-tNH_2	0.7	9.8	1.3

Figure S4 TG/MS/DTA of MCF-sNH_2 (left) and MCF-tNH_2 (right) under synthetic air. The diagram at the top shows the TG (solid line) and DTA (dotted line) curves whereas the ion currents detected by a mass spectrometer are depicted at the bottom of each diagram.



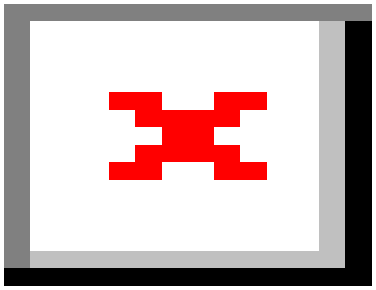


Figure S5 TG/MS/DTA of MCF-C3-NH_2 (left), MCF-C7-NH_2 (middle) and MCF-C11-NH_2 (right) under synthetic air. The diagram at the top shows the TG (solid line) and DTA (dotted line) curves whereas the ion currents detected by a mass spectrometer are depicted at the bottom of each diagram.

Calculation of the functionalization density:

$$\frac{m(\text{functionalization per g material})}{M(\text{organic residue})} = \delta_F \qquad \delta_F \cdot (100 - \textit{mass loss}(\%)) = \delta_F \text{/g Silica}$$

2. Biochemical characterization

2.1 G6PDH uptake

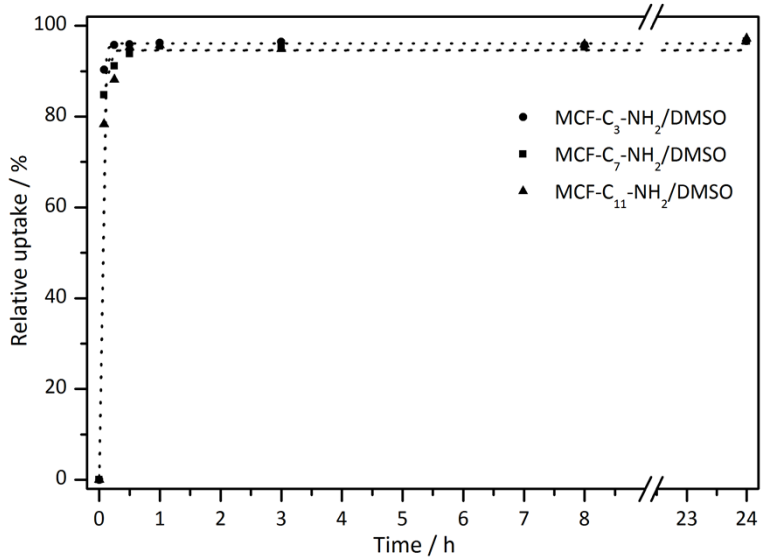


Figure S6 Uptake curves (addition of DMSO) for the immobilization of G6PDH onto amine-modified supports with varied spacer chain length.

2.2 $NADP^+$ uptake – Calibration curve

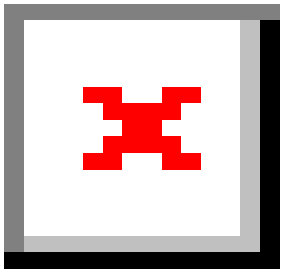


Figure S7 Calibration curve for various $NADP^+$ concentrations. Therefore $NADP^+$ was converted by G6PDH with addition of G6P to measure the adsorption of NADPH.

2.3 Storage stability of immobilized G6PDH at 4 °C

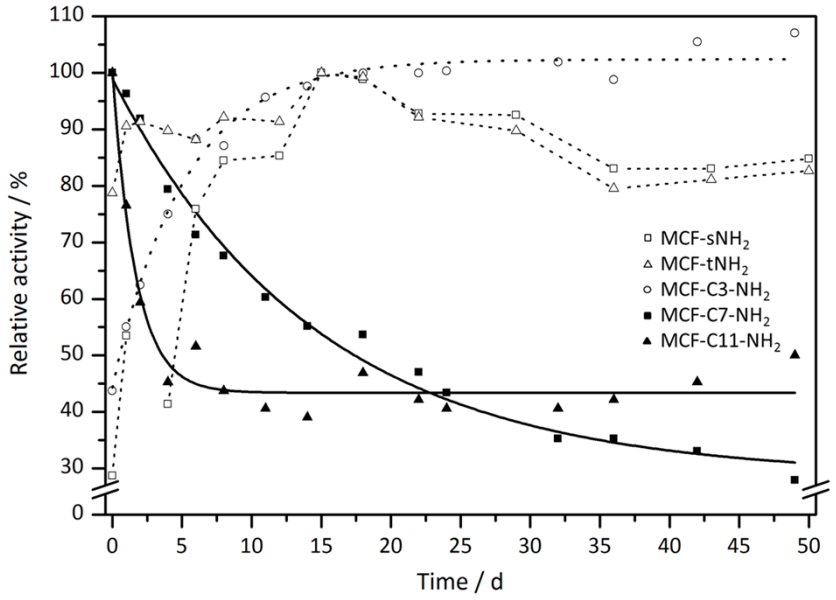


Figure S8 Storage stability of immobilized G6PDH samples at 4 °C.