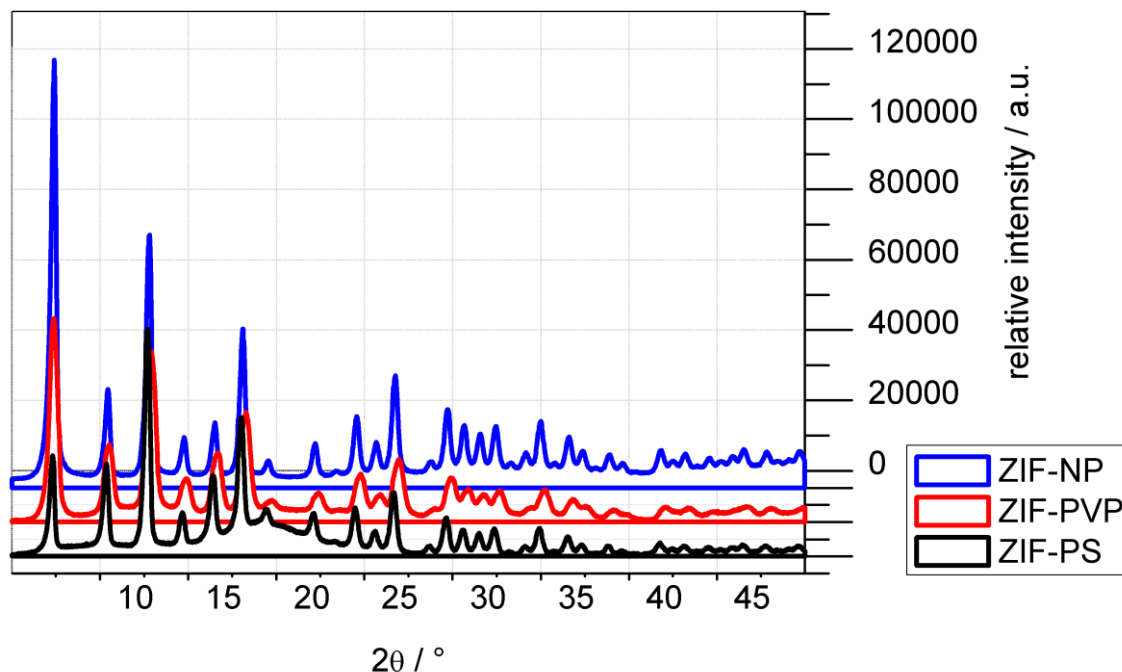


## Supporting Information

XRD measurements showed that the crystalline ZIF-8 nanoparticles were preserved in the nanofibers.



**SI Fig. 1:** XRD patterns of pure ZIF-8 nanoparticles and ZIF-8 inside PVP or PS

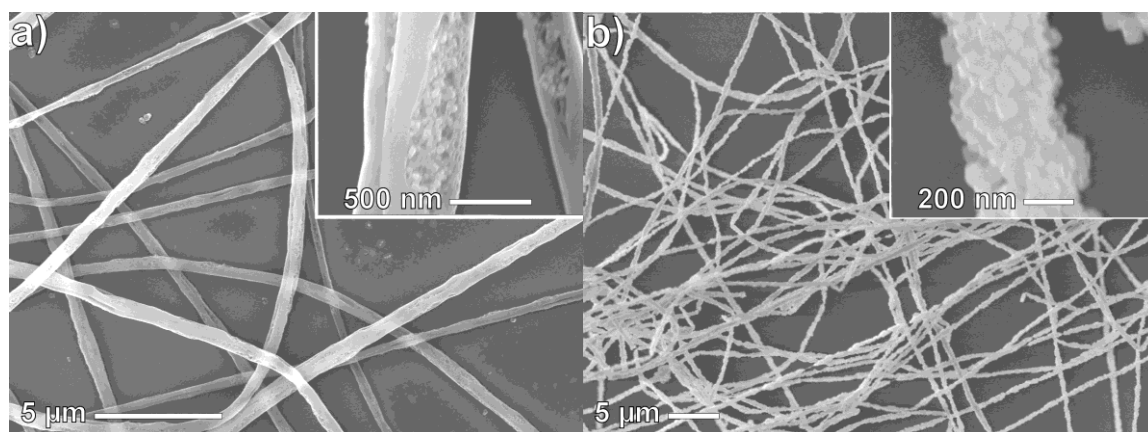
The nanofibers were obtained in the form of non-woven mats and were stable up to 60% relative humidity in the case of PVP. The PS-based fibers were stable in water and alcohol. All fiber mats had a paper-like appearance and were mechanically robust.

Similarly to PVP, it was possible to electrospin the ZIF-8 nanoparticles from PEO (MW = 300,000) in H<sub>2</sub>O with a concentration of 3 wt% ZIF-8 and 2.5 wt% PEO. The relative humidity needed to be below 20% and the flow rate was 0.45 ml/h at a voltage of 6 kV.

However, the obtained nanofibers did not show any significant N<sub>2</sub> adsorption, although the nanofibers seem well-defined. Probably the PEO molecules completely block the ZIF-8 nanoparticles or even enter inside. A blend of 1:1 PVP and PEO allowed electrospinning nanofibers with accessible ZIF-8 nanoparticles and surface areas of 500 m<sup>2</sup>/g. The characterization of polymer blends for ZIF-8 nanofibers will be discussed in another publication.

To stabilize the fibers in polar solvents like water and alcohol, a suitable approach was found by exchanging the solvent of the ZIF-8 dispersion from pure methanol to a mixture of THF (tetrahydrofuran), toluene and methanol with a weight ratio of 4:1:1. PS (MW = 240,000) could be dissolved in this solution at sufficient concentrations (approx. 8 wt%) for electrospinning. To increase the conductivity of the solution 0.2 wt% tetrabutylammoniumperchlorate were added, before electrospinning with a flow rate of 0.65 ml/h at a voltage of 5 kV.

The resulting PS-ZIF-8 nanofibers were stable in alcohols and water and the surface area was fully accessible, even if the ZIF-8 loading up to 25 wt% were slightly lower. Higher loadings should be possible by tuning the synthesis parameter and functionalizing the surface of the ZIF-8 nanoparticles with less polar molecules.



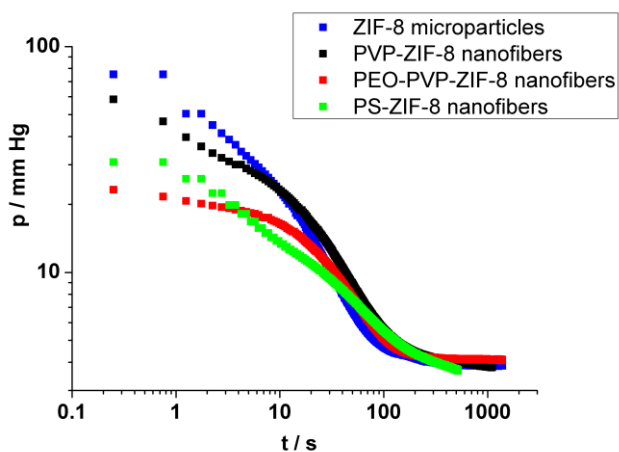
**SI Fig. 2:** SEM of a) PS-ZIF-8 and b) PEO-ZIF-8 nanofibers

We developed a method for measuring adsorption kinetics on a Quantachrome Autosorb-1 instrument operated in manual mode. This instrument possesses a manifold with calibrated volume separated from the measurement cell by a magnetic valve. Both manifold and measurement cell are equipped with pressure gauges. Sorption kinetics were determined by setting a defined nitrogen pressure in the manifold with subsequent expansion into the evacuated sample cell cooled to 77K by opening the magnetic valve. The sample cell pressure during the adsorption process was recorded every 250 ms until equilibrium was reached. Since both manifold and sample cell volume as well as the absolute amount of ZIF were kept rather constant for all samples, the slope of the pressure drop and the time to reach equilibrium pressure should correspond to the kinetics of nitrogen uptake.

We are aware that especially in the beginning of this experiment, the adsorption is superimposed by transport effects into the cell and therefore we focused on the evolution of pressure near the equilibrium and the time to attain equilibrium. We adjusted the initial manifold pressure to obtain the same final pressure (4 torr) corresponding to the same characteristic point in the adsorption isotherm for all sample irrespective of ZIF-8 content.

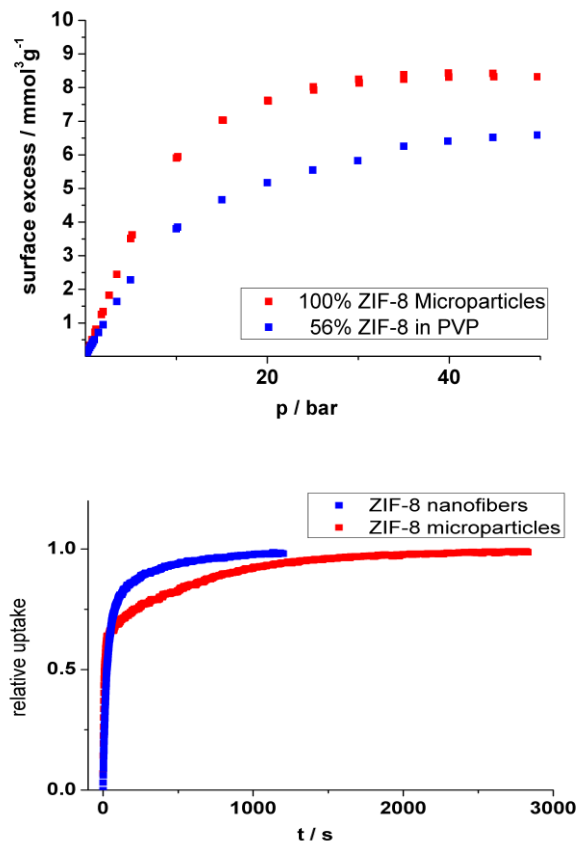
The evolution of pressure is reproducibly recorded in this manner and shows significant differences among the various polymers which are used to identify PVP to be the best carrier polymers for the desired application. Nevertheless, the exact interpretation on a molecular scale is obviously more difficult, as no model exists and the contributions from the superimposed processes are hard to separate.

The adsorption kinetics of the PS-ZIF-8 nanofibers was rather slow, taking over twice the time of PVP-based fibers to reach equilibrium, which might result from the generally thicker polymer layer on the particles (can be seen from SEM, the fibers were mostly smooth, apart from some cracks).



**SI Fig. 3:** Adsorption kinetics studied as cell pressure over time

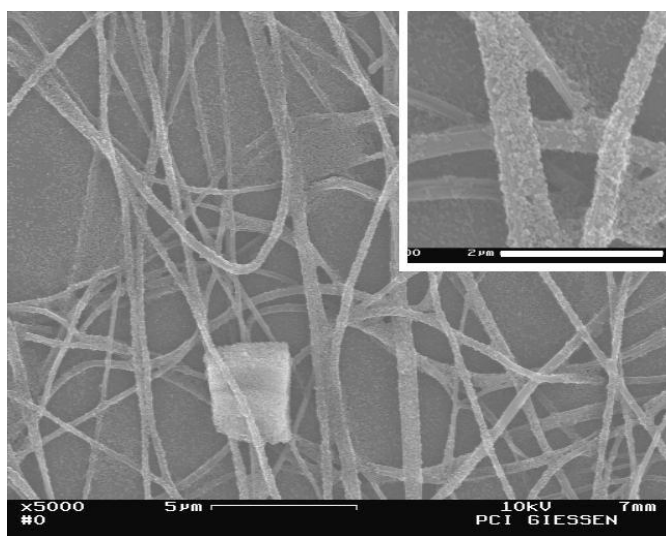
To further corroborate our findings, CO<sub>2</sub> was also used as adsorbate to determine the isotherms and the kinetics of adsorption at higher pressures. As for N<sub>2</sub>, the ZIF-8 nanoparticles are accessible within the fibers (the amount of CO<sub>2</sub> adsorbed scales with ZIF-8 content of the fibers) and the kinetics of the nanofibers are slightly faster than for the microparticles.



**SI Fig. 4:** CO<sub>2</sub> Isotherm and adsorption kinetics of ZIF-8 microparticles and nanofibers

Another approach to stabilize the nanofibers in polar solvents using layer-by-layer adsorption of the ZIF-8 nanoparticles on polyelectrolyte nanofibers only resulted in lower ZIF-8 loadings. (see Müller, K.; Quinn, J. F.; Johnston, A. P. R.; Becker, M.; Greiner, A.; Caruso, F. *Chemistry of Materials* **2006**, *18*, 2397-2403.)

To produce non-soluble nanofibers PS (polystyrene) fibers were electrospun and treated with conc.  $\text{H}_2\text{SO}_4$  to functionalize the surface with sulfonate groups, thereby creating an anionic polyelectrolyte as described in the literature<sup>1</sup>. Using their positive surface charge, the ZIF-8 nanoparticles could then be adsorbed. However, the loading of ZIF-8 and the stability were quite low, even after a layer-by-layer adsorption by alternated immersion of the fibers in ZIF-8 dispersion and a solution of the anionic polyelectrolyte PSS (polystyrenesulfonate). Therefore, this approach was not developed further.



**SI Fig. 5:** SEM of ZIF-8 nanoparticles deposited by LBL adsorption on PS