Fourfold Action of Surfactants with Superacid Head Groups: Polyoxometalate-Silicone Nanocomposites as Promising Candidates for Proton-Conducting Materials.

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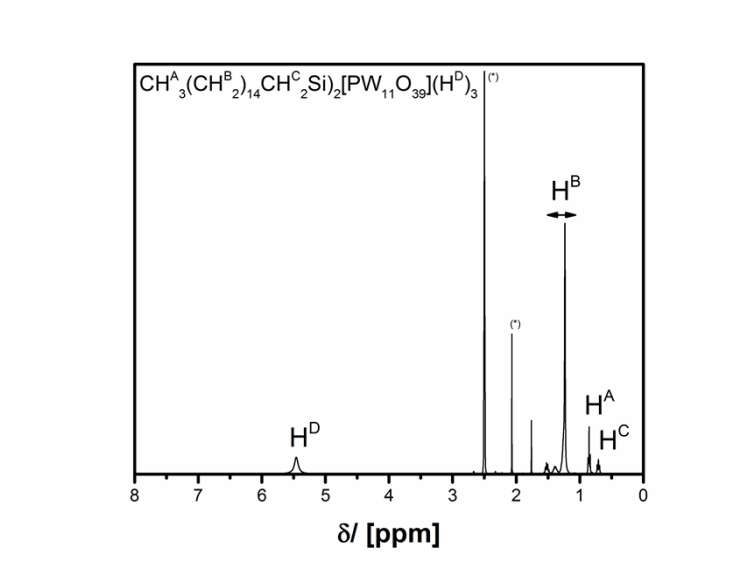
Electronic Supplementary Information.

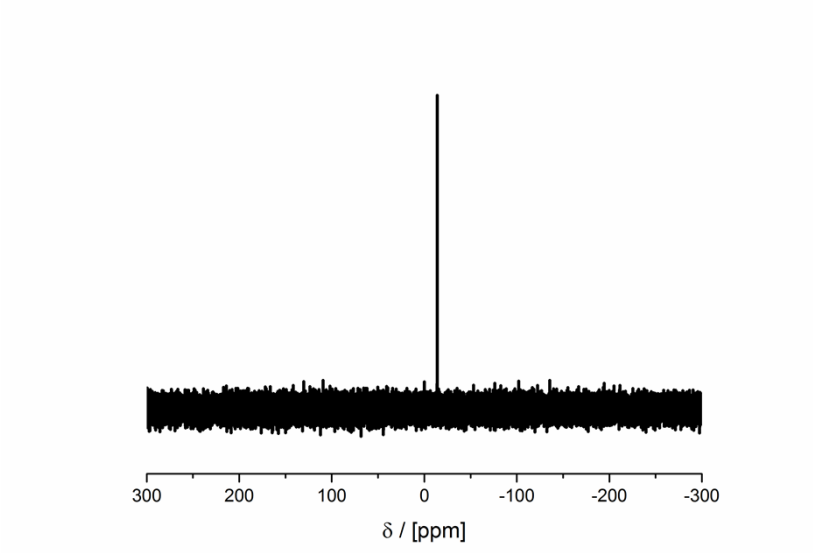
ESI-1. Additional information for the surfactant with heteropolyacid head $[(C_{16}H_{33}Si)_2PW_{11}O_{39}](H)_3$ (**1**).

(a) ^{1}H NMR data.

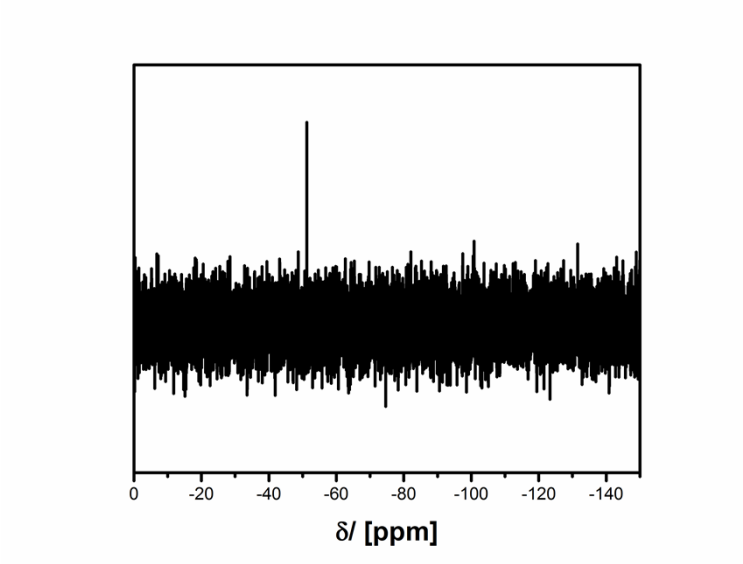


(*) solvent signals.

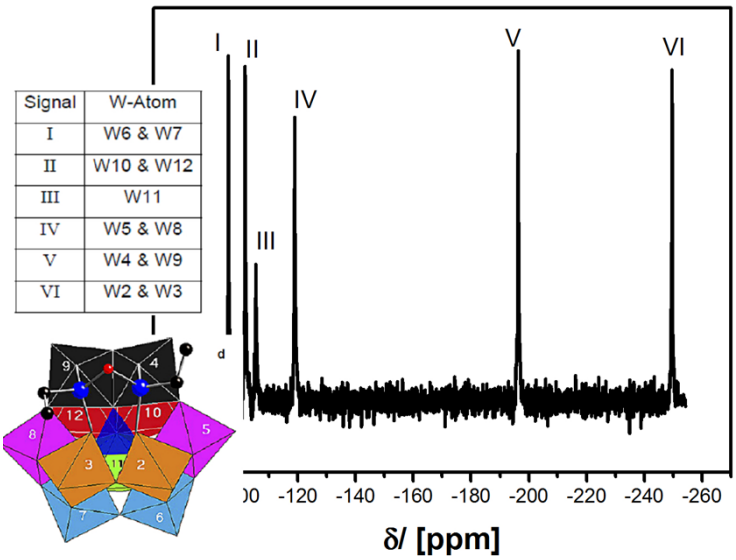
(b) ^{31}P NMR data.



(c) ^{29}Si-NMR data

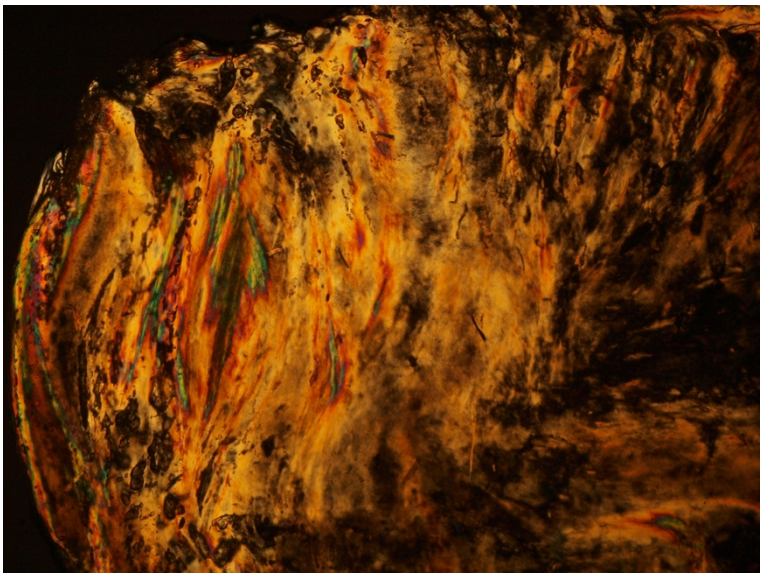


(d) ^{183}W NMR data

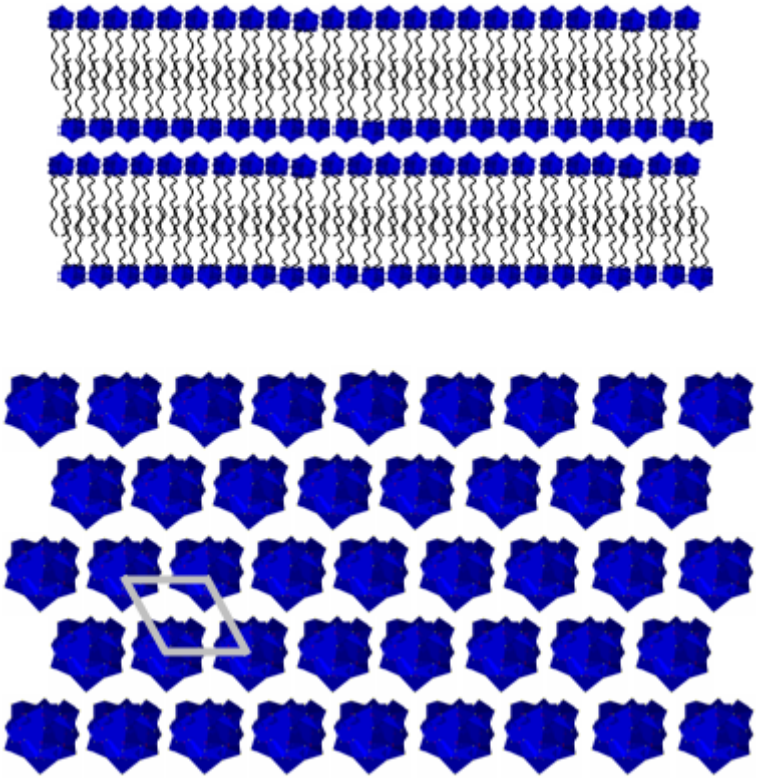


Signal	W-Atom
I	W6 & W7
II	W10 & W12
III	W11
IV	W5 & W8
V	W4 & W9
VI	W2 & W3

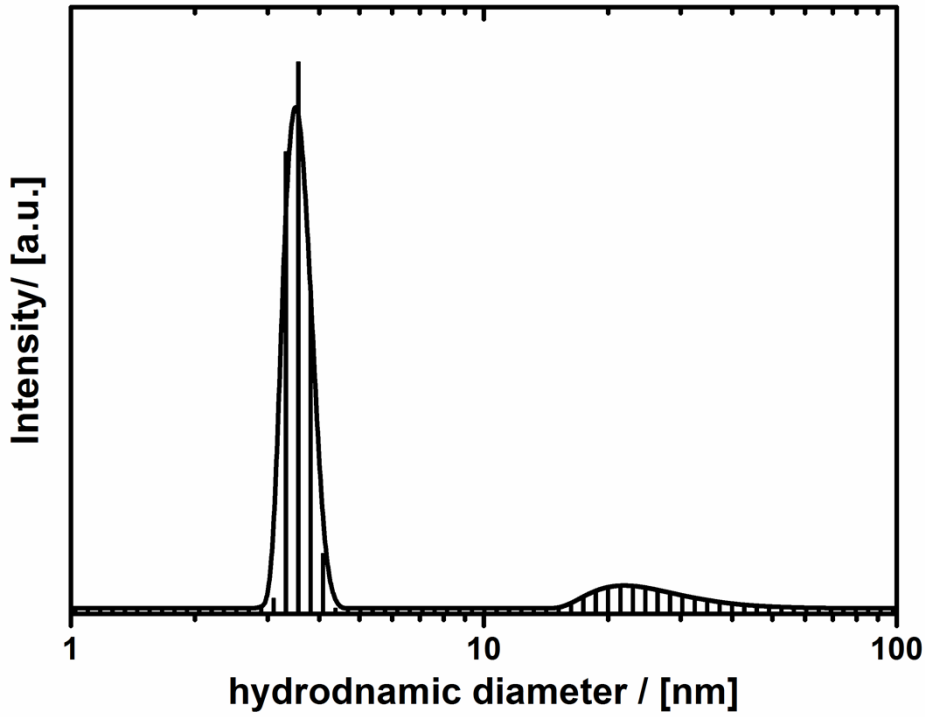
(e) Polarization microscopy of a LCC formed with (**1**) in water.



(f) Schematic image of the POM-surfactant packing in the lamellar LCC phase.



(g) Particle size distribution curve of a micellar solution of (**1**) obtained by DLS.



ESI-2.

Additional information for the emulsion formed with TSIL, water and (1) as an emulsifier.

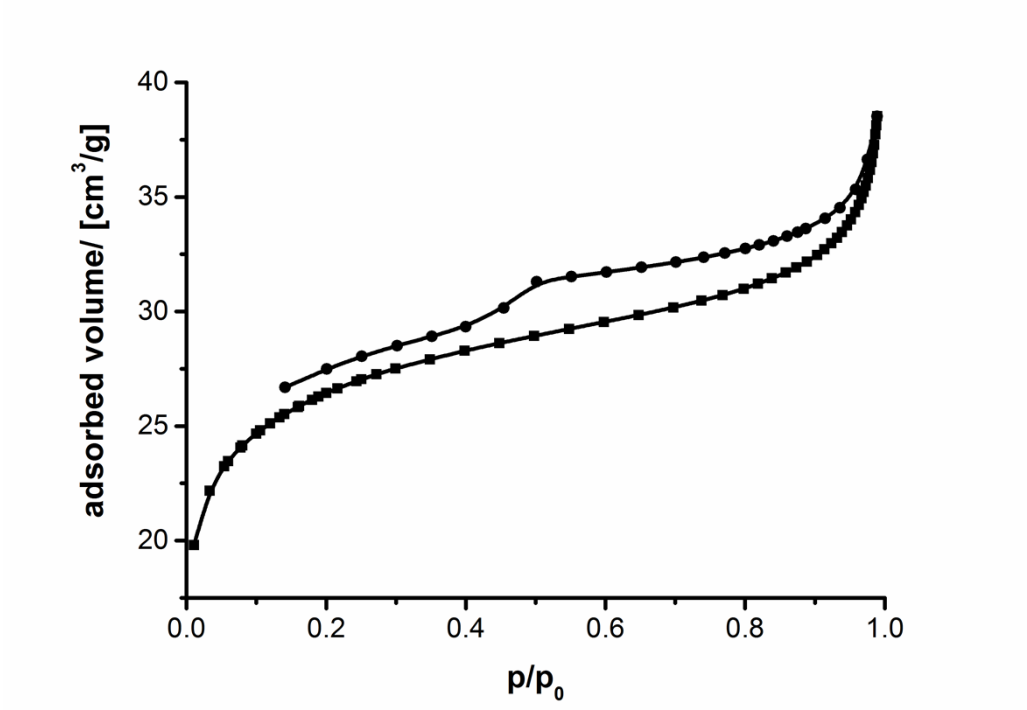
(a) Photographic image of the emulsion after 5 weeks.

ESI-3.

Additional data for the solid PDMS-POM-surfactant nanohybrid.

(a) Photographic image of the PDMS-POM-surfactant nanohybrid after freeze drying.

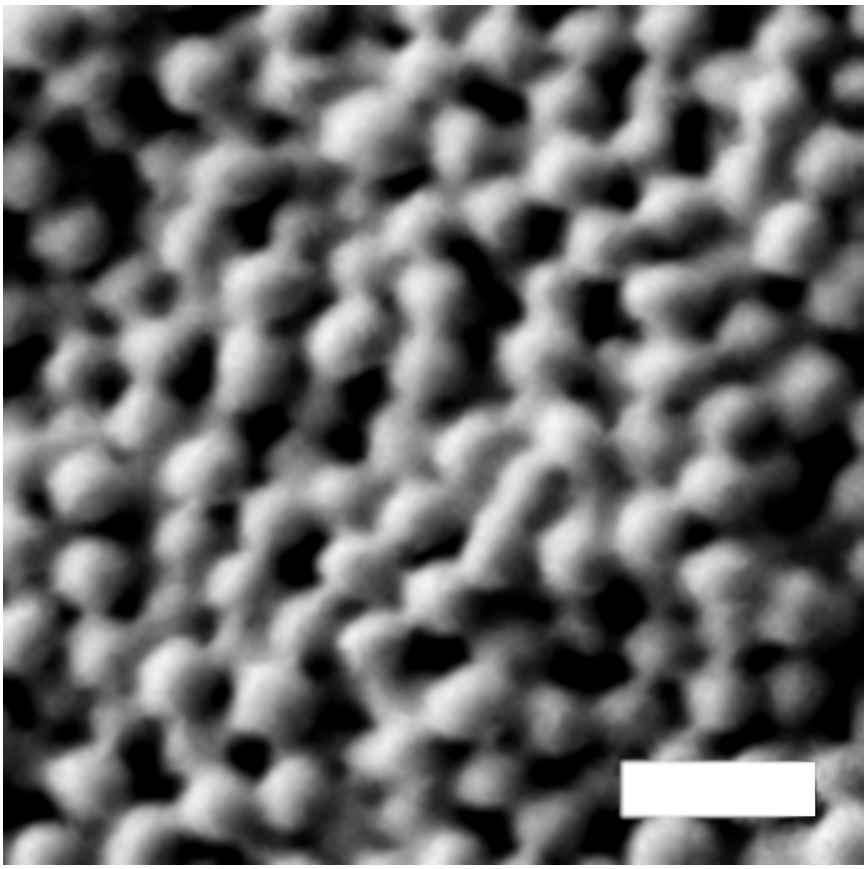
(b) N_2 physisorption isotherm of the of the PDMS-POM-surfactant nanohybrid after freeze drying.



squares ≅ adsorption branch

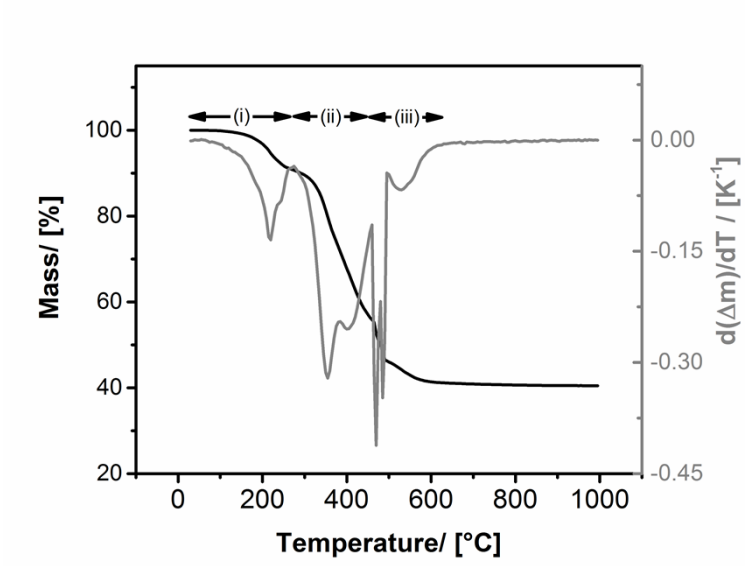
circles ≅ desorption branch

(c) Enlarged SEM picture showing the partial fusion of PDMS/POM-surfactant hybrid particles inside the porous network.



scalebar = 500 nm.

(d) TGA data (black graph) in air and first derivative of TGA data (grey graph).

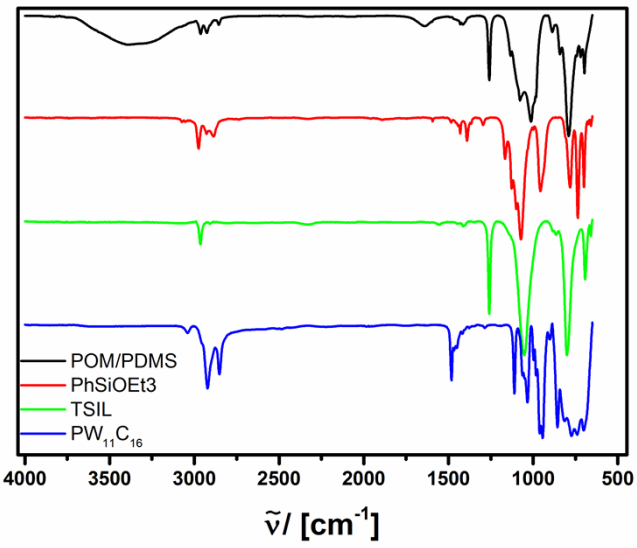


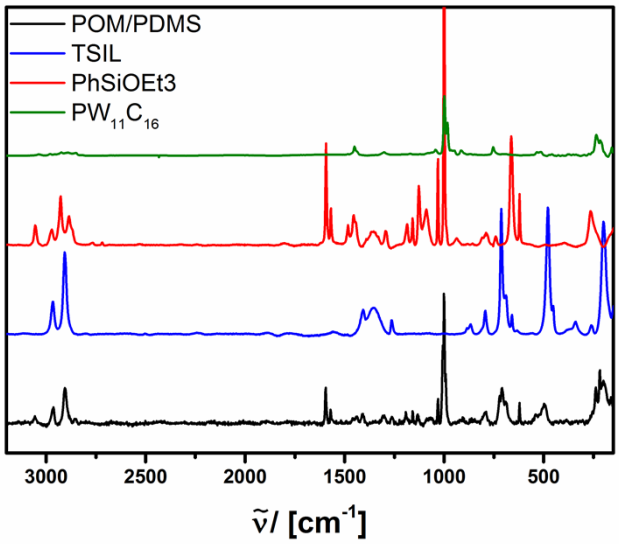
Step (i): Removal of residual solvent.

Step (ii): Conversion of organosilsesquioxane species to SiO_2

Step (iii): Conversion of POM-surfactant to WO_3; sublimation of resulting P_2O_5

(e) IR and RAMAN data of the produced PDMS/POM material and the starting materials





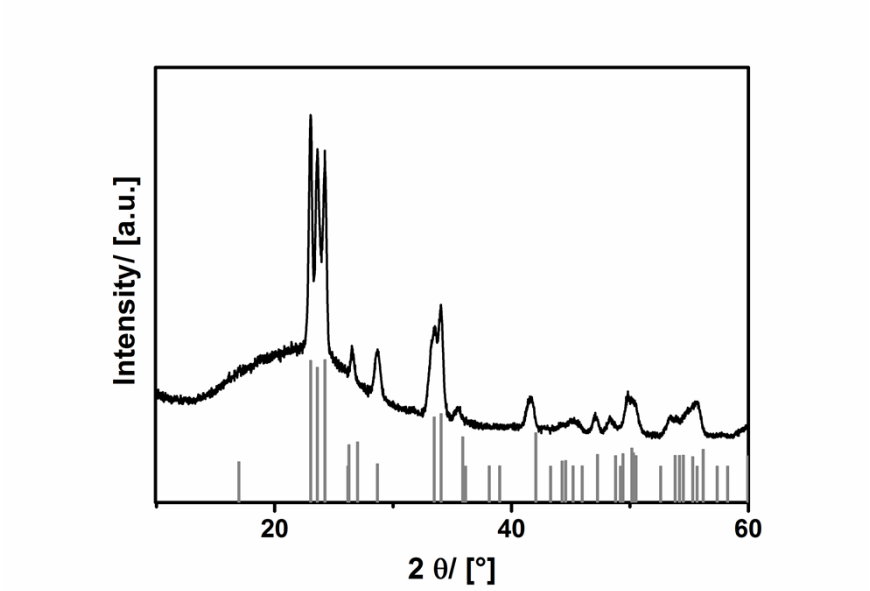
We would like to highlight the unique signals, proving the presence of all of the three starting materials. Those are:

- the peak at 1009 cm^{-1} (IR) indicating the P-O vibration of the $PW_{11}O_{39}$-Cluster
- the very prominent symmetrical C-H-deformation of the TSIL Si-CH_3 groups at 1259 cm^{-1} (IR)
- typical phenyl-vibrations at 1595 and 1569 cm^{-1} in the Raman spectrum indicating the presence of $PhSiOEt_3$.

ESI-4.

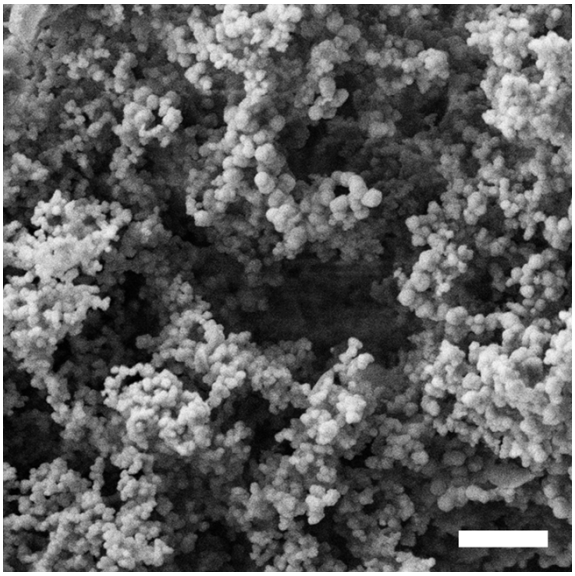
Additional data for material obtained after calcination of the PDMS-POM-surfactant nanohybrid.

(a) PXRD analysis



The reference pattern of tetragonal WO_3 is shown as grey bars. In addition, one sees a very broad signal at 22°, which is typical for substantial amounts of amorphous SiO_2 present in the sample.

(b) SEM image showing the structure of the WO_3-SiO_2 material after calcination of the PDMS-POM-surfactant nanohybrid.



ESI-5.

Synthesis of PDMS/POM materials:

The synthesis of $H_3[PW_{11}O_{40}(SiC_{16}H_{33})_2]$ (H-PW11C16) was performed according to known literature.[20]

To 100 mg (0.031 mmol) of H-PW11C16 in 16 ml of destilled water was added octamethylcyclotetrasiloxane (TSIL) (1.7 mmol) and $PhSi(OEt)_3$ (1.5 mmol) as crosslinker. The emulsion was generated by sonification with a Bandelin-Sonoplus TT13/F2 (65%, 5 mins). After stirring the emulsion for 20 h at 80° C the material was obtained by freeze-drying the reaction mixture.

For the synthesis of the H^+:Si 1:20 material 0.37 mmol of TSIL and 0.31 mmol of crosslinker were used.