Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Highly degradable imine-doped mesoporous silica particles

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1. Instruments

Nuclear magnetic resonance (NMR): ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer. The ^{1}H NMR chemical shifts δ are reported in parts per million (ppm) with residual protons of the deuterated solvent as the reference standard. Signal splittings are described as singlet (s), quartet (q), triplett (t), multiplet (m).

Scanning (SEM) and Scanning Transmission (STEM) Electron Microscopy: SEM and STEM images were recorded with a FEI Quanta FEG 250 instrument (FEI corporate, Hillsboro, Oregon, USA) with an acceleration voltage of 20 kV. The SEM samples were prepared by drop-casting a dispersion of particles in EtOH onto a glass cover slip, subsequently sputter coated with Au (Emitech K575X Peltier cooled) for 30s at 60 mA prior to fixation on an Al support. The STEM samples were prepared by drop casting dispersions of particles in EtOH (0.1 mg/mL) onto Formvar-coated Cu grids (400 mesh) and allowed to dry overnight prior visualization.

Transmission Electron Microscopy (TEM): TEM samples were analyzed on a FEI/PHILIPS CM120 system operating at 100 kV. Samples were prepared by drop casting dispersions of particles in EtOH (0.1 mg/mL) onto Formvar-coated Cu grids (400 mesh) and allowed to dry overnight prior visualization.

Porosimetry: Nitrogen physisorption isotherms were obtained with a Micromeritics ASAP-2020 physisorption instrument. The **MSPs** sample was degassed at 350 °C for 4h, while the **Im-MSPs** ones at 80 °C for 6h. The N_2 adsorption/desorption measurements were performed at -196 °C. The surface areas were calculated by Brunauer-Emmett-Teller (BET) method in the relative pressure range p/p^0 0.06-0.3.[1] The pore size distributions and pore volumes were calculated by density functional theory (DFT) method on the adsorption branch using a cylindrical model. The total pore volume was estimated at $p/p^0 = 0.99$.

Small Angle X-ray Scattering (SAXS): SAXS set-up comprised the SAXSess mc2 instrument from Anton Paar GmbH, containing a slit collimation system, and the PW3830 laboratory X-ray generator (40 kV, 50 mA) with a long-fine focus sealed X-ray tube (CuKα wavelength of $\lambda = 0.1542$ nm) from PANalytical. Detection was performed with the 2D imaging-plate reader Cyclone® by Perkin Elmer. Measurements were performed on powder samples for 5 min and the data collected up to a scattering vector q value of 7 nm^{-1}, where $q = (4\pi\sin\theta)/\lambda$ and 2θ the scattering angle. The 2D data were converted to 1D data and background-corrected by using the SAXSQuant software (Anton Paar GmbH, Austria)

X-ray Photoelectron Spectroscopy (XPS): XPS analysis was performed using a K-Alpha™+ X-ray Photoelectron Spectrometer (XPS) System (Thermo Scientific). Monochromatic Al K alpha X-rays were used (15 keV, 72 W, 200 mm spot diameter). Spectra were measured using pass energy of 200 eV for survey spectra and 50 eV for core level spectra. The analysis was conducted on powders. The Advantage software was used for background subtraction (Smart-type), and deconvolution of peaks.

Thermogravimetric analysis (TGA) was conducted on a Netzsch model STA 449 fi Jupiter instrument. The samples (1.0-3.0 mg) were kept at 100 °C for 30 minutes for stabilization, and then heated from 25 to 800 °C at a speed of 10 °C/min, before being held at this temperature for further 30 minutes, and finally cooled. The analyses were performed under a 20 mL/min air flow.

Dynamic light scattering (DLS)*:* the measurements were conducted on a Delsa Nano C Particle Analyzer (Beckman Coulter, operative wavelength 655 nm). The DLS measurements were performed on dispersions of the particles in EtOH (ca 0.1 mg/mL).

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) the spectra were measured with a Shimadzu IRAffinity-1 spectrometer. The powders were deposited onto the ATR crystal surface and the transmittance spectra were collected using a spectral resolution of $\Delta = 4$ cm^{-1}, accumulating 64 scans and performing the ATR correction (penetration depth mode).

UV-vis absorption spectroscopy absorption spectra were measured on a Shimadzu UV-3600 double-beam UV–VIS–NIR spectrophotometer and baseline corrected. Quartz cuvettes with 10 mm path length were used.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analyses were performed with a Thermo Scientific instrument, ICAP 6500. All buffer solutions were freshly prepared from UV sterilised deionised (about 18 MΩ) water. Standard Si solutions (0.01 ppm, 0.1 ppm, 1 ppm) were used for calibration.

2. Supporting images

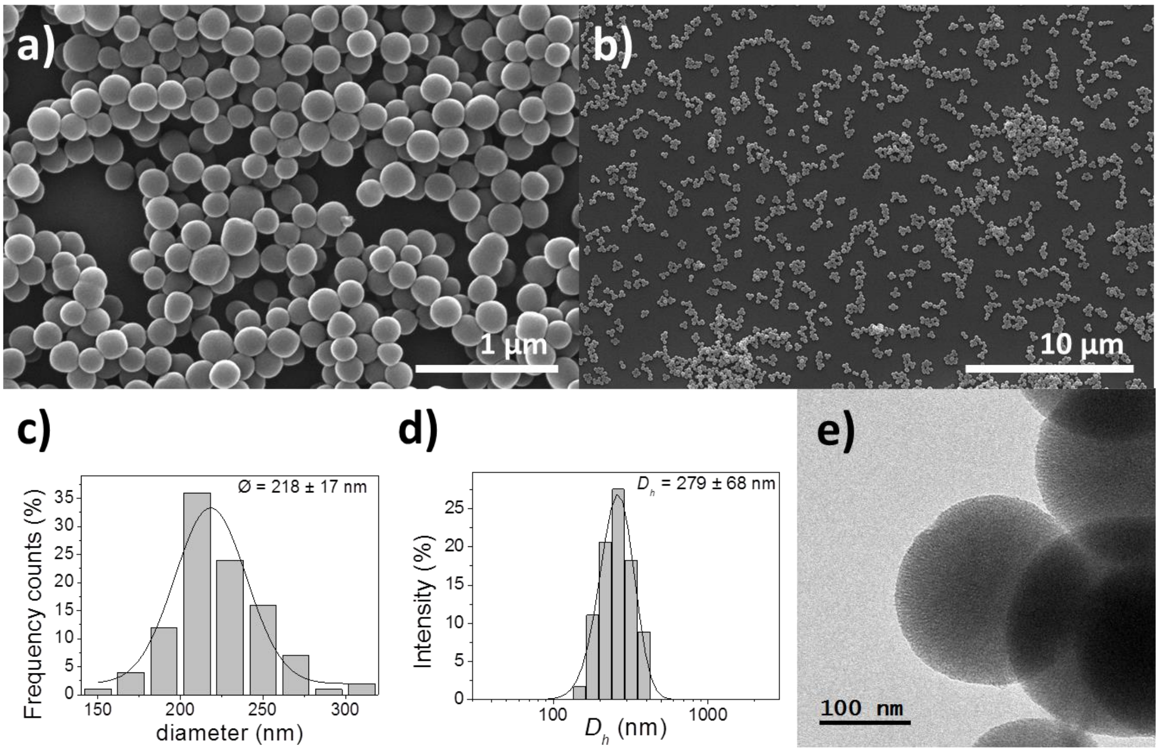

Figure S1 a) and b) Additional SEM pictures of **MSPs**, c) size distribution from SEM micrographs, counts on 100 particles, the mean diameter was extrapolated from the Gaussian distribution, d) DLS intensity distribution of **MSPs** dispersed in EtOH, e) additional TEM image of **MSPs**.

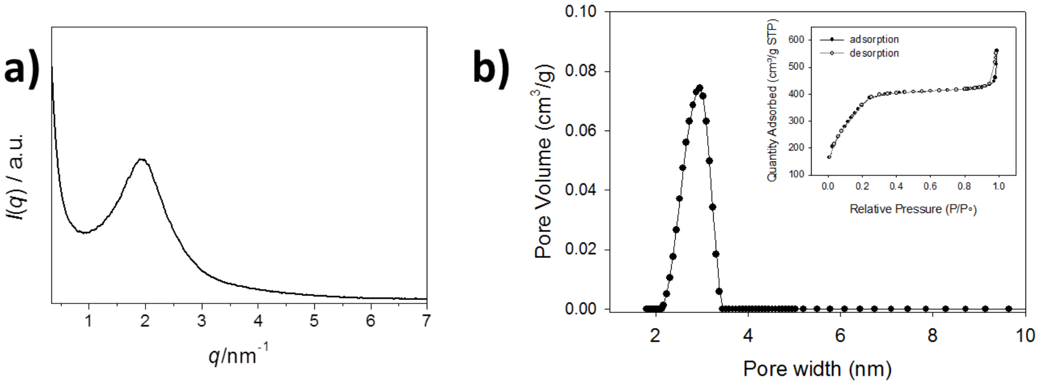

Figure S2 a) SAXS patterns recorded on **MSPs;** b) Adsorption/desorption isotherm obtained on **MSPs**, in the inset the pore width distribution.

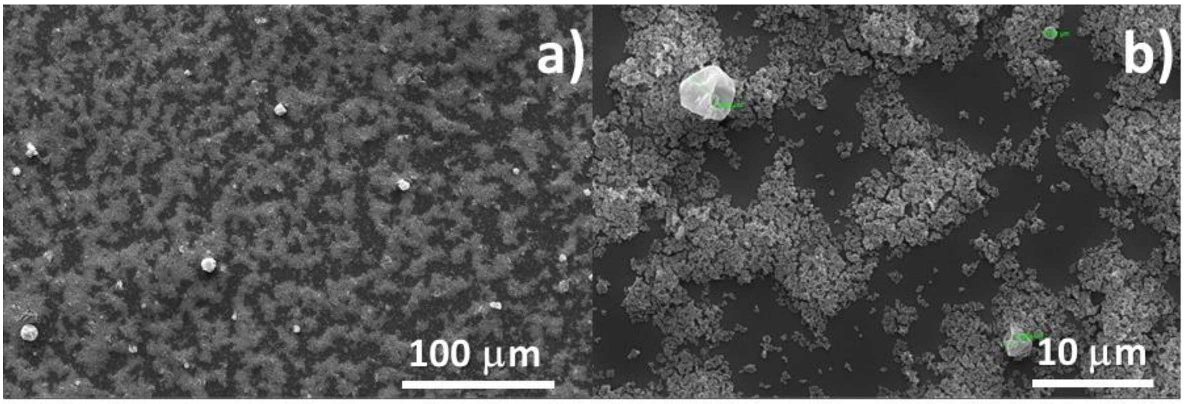

Figure S3. SEM images recorded on the reaction mixture after recovering and washing the collected material for a) **Im-MSPs-10%** and b) **Im-MSPs-25%** reactions.

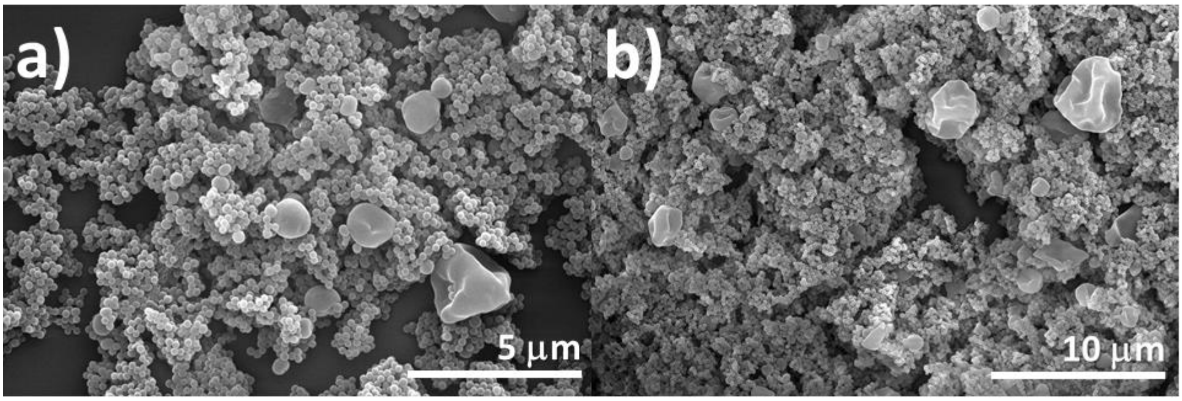

Figure S4. SEM images recorded on the precipitate left after the purification by means of centrifugation cycles on a) **Im-MSPs-10%** and b) **Im-MSPs-25%**.

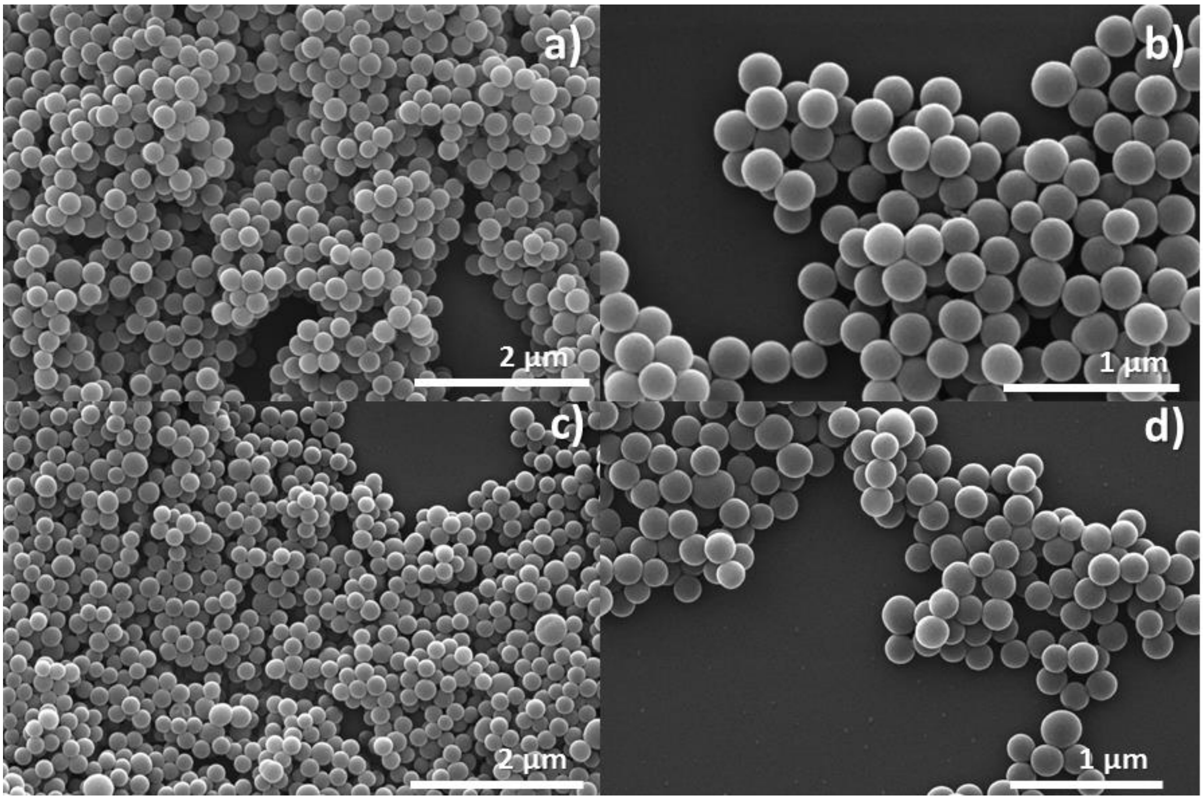

Figure S5. Additional SEM images of the purified a) and b) **Im-MSPs-10%**; c) and d) **Im-MSPs-25%**.

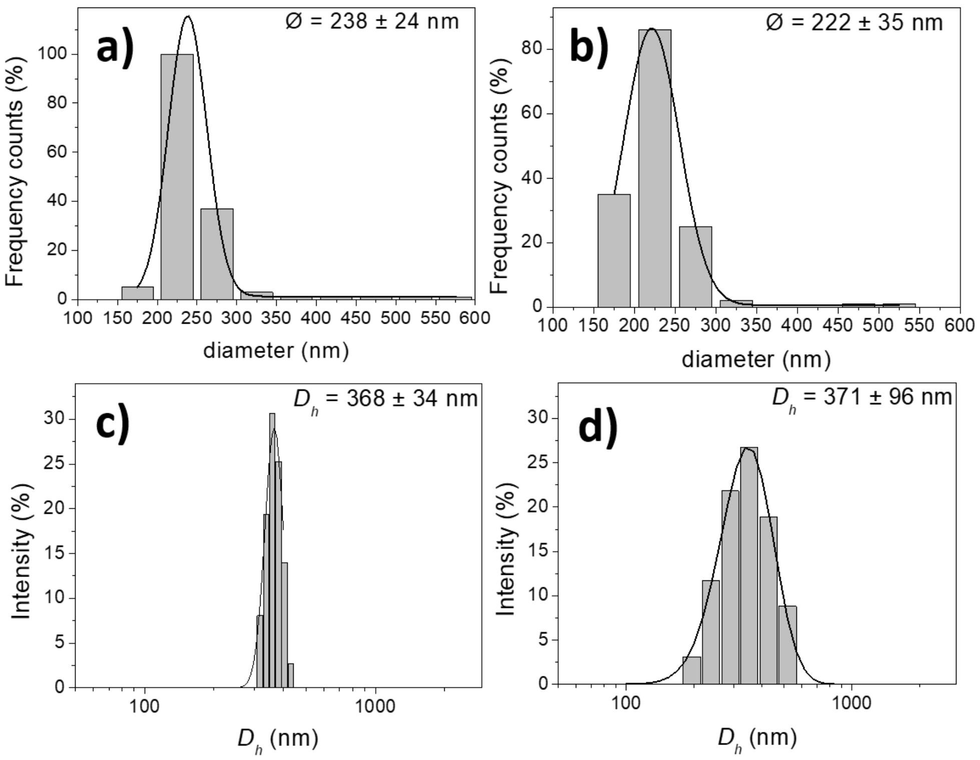

Figure S6 Size distribution from SEM micrographs of a) **Im-MSPs-10%** and b) **Im-MSPs-25%** after purification. The distribution was calculated on 150 particles. The mean diameter values were extrapolated from the Gaussian distribution. DLS intensity distribution of c) **Im-MSPs-10%** and d) **Im-MSPs-25%**. The slight larger values determine from DLS can be attributed to the presence of aggregates, given the hydrophobic nature of the organic functionalization.

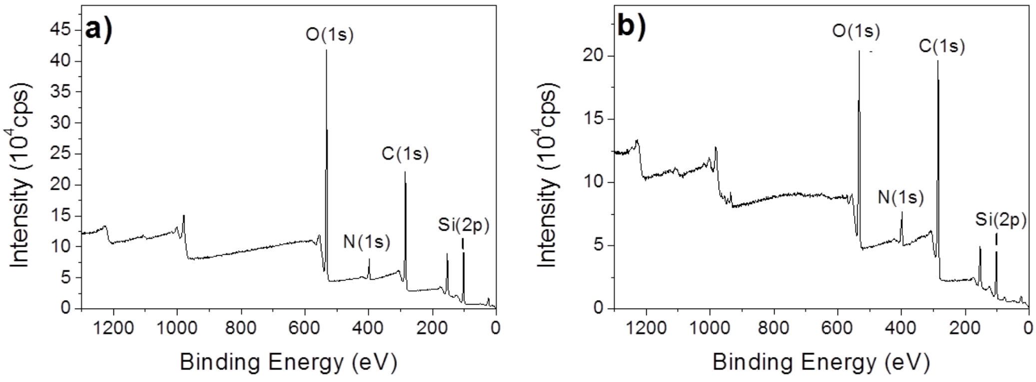

Figure S7. XPS survey spectra of a) **Im-MSPs-10%** and b) **Im-MSPs-25%**.

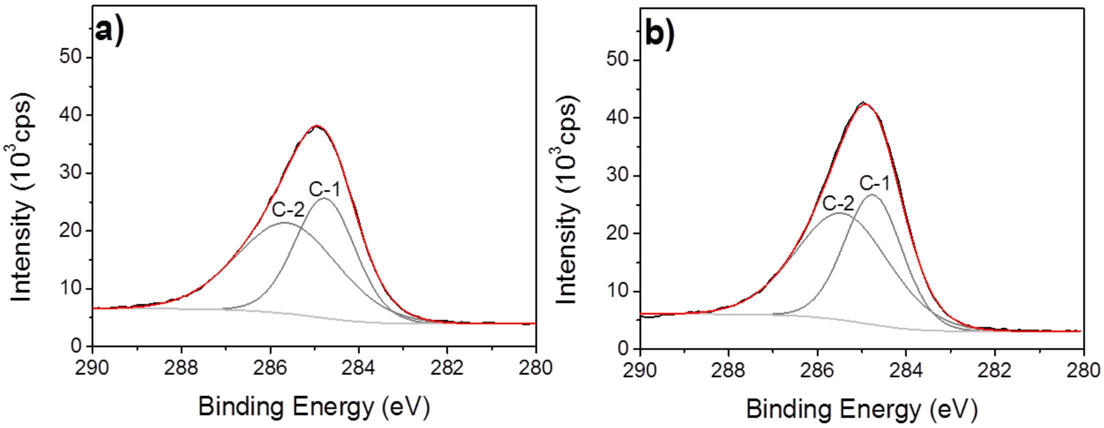

Figure S8. XPS high resolution scans of C(1s) level recorded on a) **Im-MSPs-10%** and b) **Im-MSPs-25%** (black lines) and calculated peak (red line). The deconvolution of the peak reveals the presence of two components (C-1 and C-2). The C-1 component (284.8 eV) can be attributed to *C*-C, *C*-H and *C*-Si while the second component C-2 (285.5 eV) to C=N and aromatic *C*. The ratio between the two components is 44:56 for both **Im-MSPs-10% and** C- **Im-MSPs-25%**.

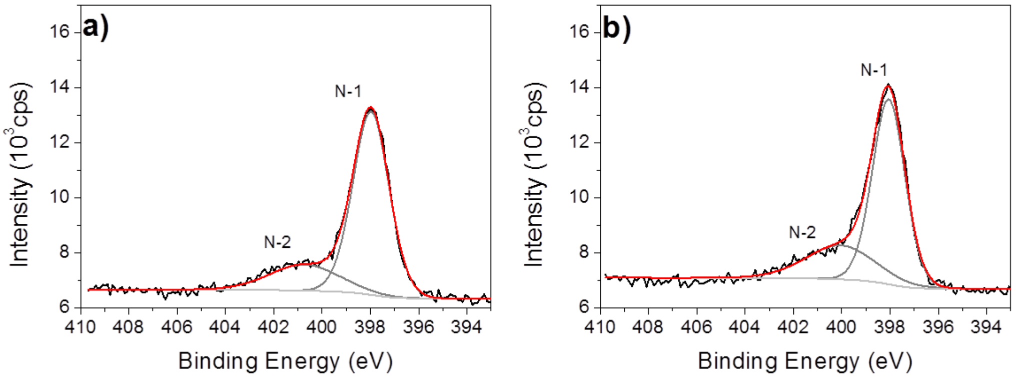

Figure S9. XPS high resolution scans of N(1s) level recorded (black lines) on a) **Im-MSPs-10%** and b) **Im-MSPs-25%** and calculated peak (red line). The deconvolution of the peak reveals the presence of two components (N-1 and N-2). For the **Im-MSPs-10%** the N-1 component is centered at 398.8 eV, the N-2 one at 401.7 eV. For the 398.8 and 401.7 eV for **Im-MSPs-25%**, the N-1 component is centered at 398.8 and the N-2 one at 400.8 for **Im-MSPs-25%.** The N-1 component can be attributed to imine nitrogen (C=*N*-), while the second component to amine and/or protonated imine (-*N*H$_2$, C=NH$^+$-) that probably have been formed on the surface upon imine hydrolysis during the synthesis or the washings. The ratio between the two components is 77:23 for **Im-MSPs-10%**, while 72:28 for **Im-MSPs-25%**.

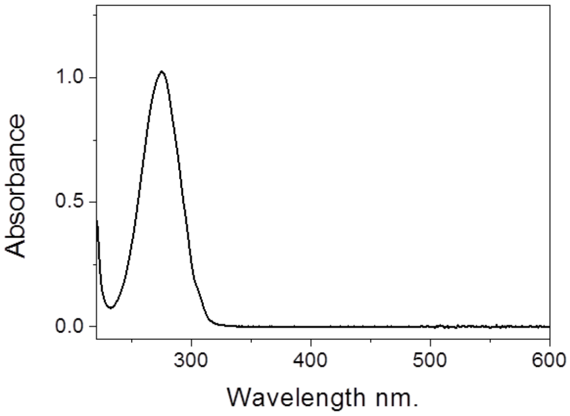

Figure S10 UV-vis absorption spectrum of the organosilane **1** in EtOH (c = 15.2 μM), λ_{max} = 275 nm.

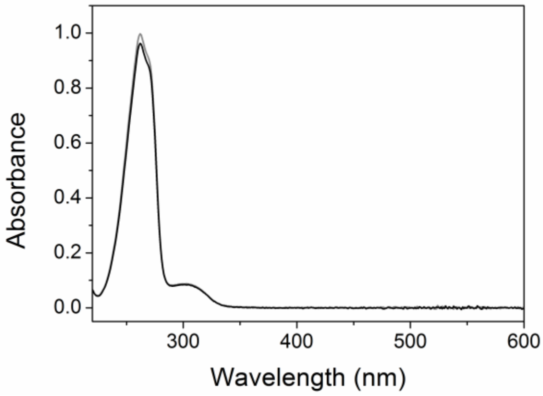

Figure S11 UV-vis absorption spectra of solutions of terephthalaldehyde in PBS pH = 7.4 (c = 47.5 μM, black line) and in AcOH/AcONa buffer solution pH = 5.2 (c = 49.0 μM, grey line).

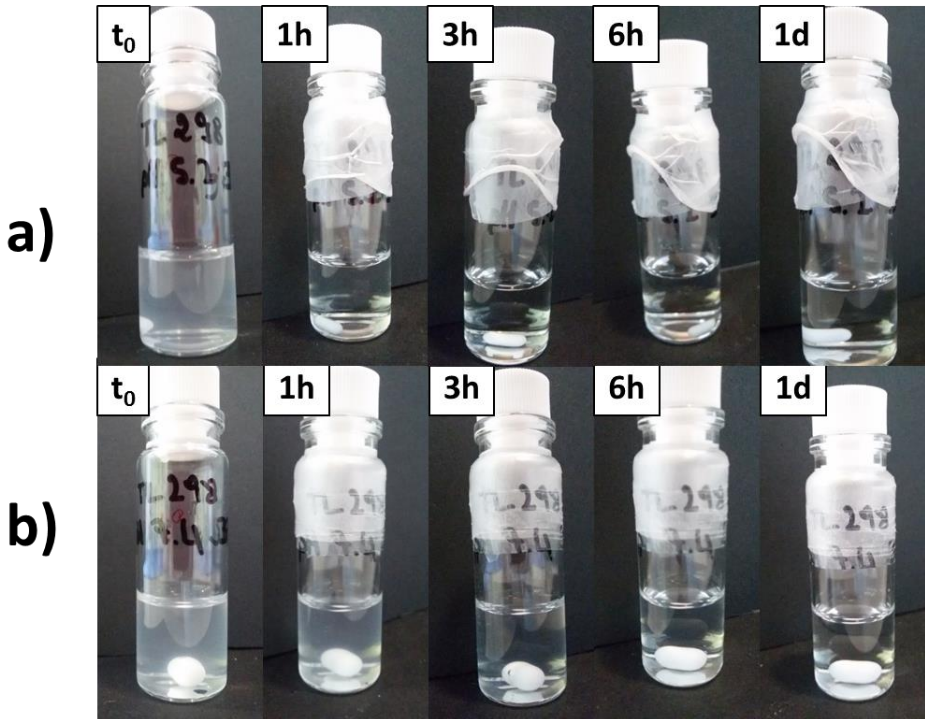

Figure S12 Pictures of **Im-MSPs-25%** 0.1 mg/mL dispersions over time within 24 hours in a) AcOH/AcONa buffer solution at pH 5.2 and b) in PBS at pH 7.4.

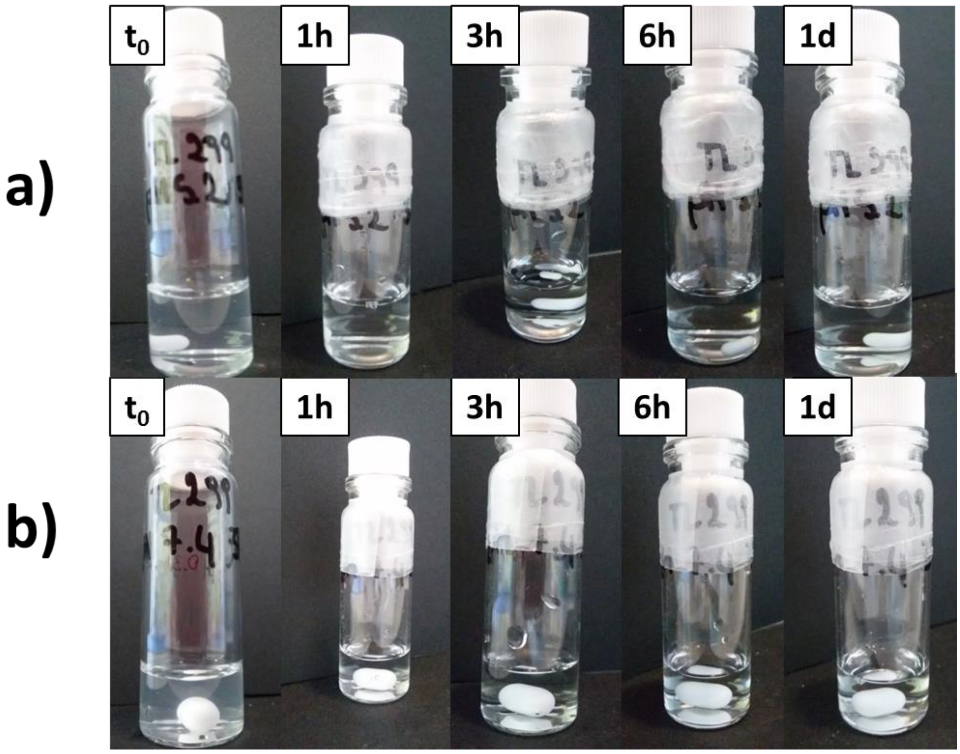

Figure S13 Pictures of **Im-MSPs-10%** 0.1 mg/mL dispersions over time within 24 hours in a) AcOH/AcONa buffer solution at pH 5.2 and b) in PBS at pH 7.4.

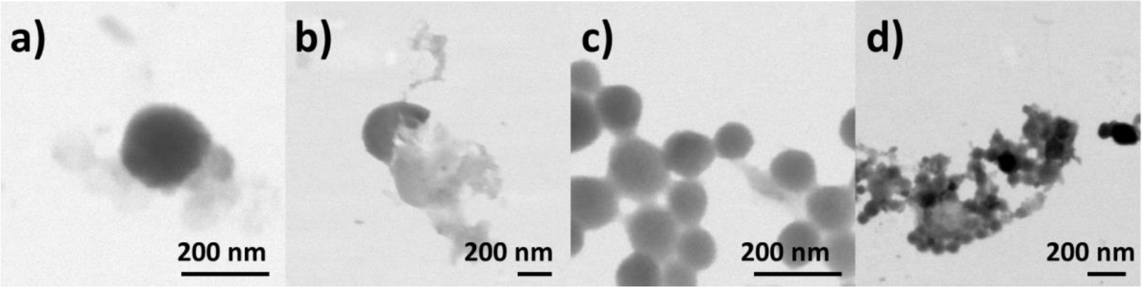

Figure S14 Details of STEM images of **Im-MSPs-10%** 0.1 mg/mL in AcOH/AcONa buffer solution at pH 5.2 at a) and b) 3h; c) 1d; d) 5d (zoom of Figure 6a, 5d).

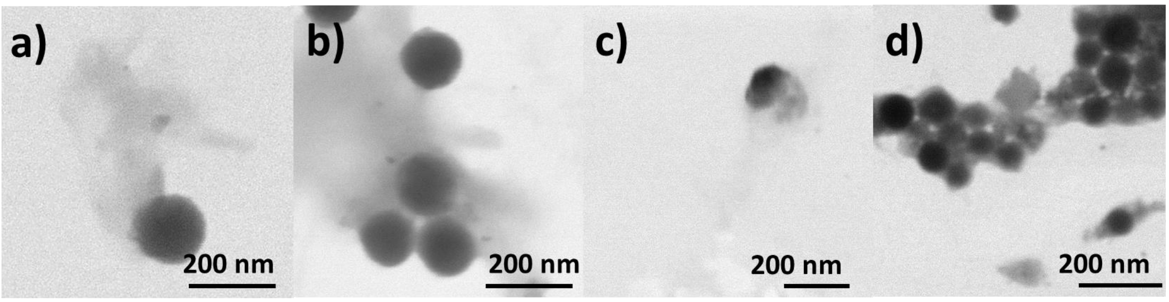

Figure S15 Details of STEM images of **Im-MSPs-25%** 0.1 mg/mL in AcOH/AcONa buffer solution at pH 5.2 at a) and b) 3h; c) 1d; d) 5d.

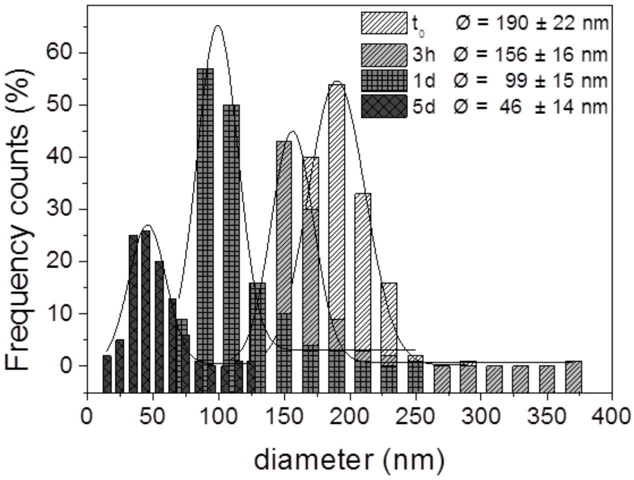

Figure S16 Size distributions calculated from STEM micrographs of **Im-MSPs-10%** in AcOH/AcONa buffer solution (pH 5.2) over time. Counts performed on 100 particles. The distributions at 3h, 1d and 5d have been calculated on the particles that could be visualized, and they are not representative of the entire sample.

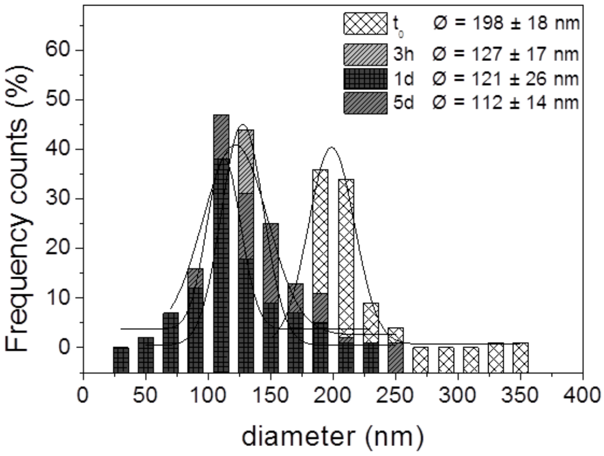

Figure S17 Size distributions calculated from STEM micrographs of **Im-MSPs-25%** in AcOH/AcONa buffer solution (pH 5.2) over time. Counts performed on 100 particles. The distributions at 3h, 1d and 5d have been calculated only on the particles that could be imaged, and they are not representative of the entire sample.

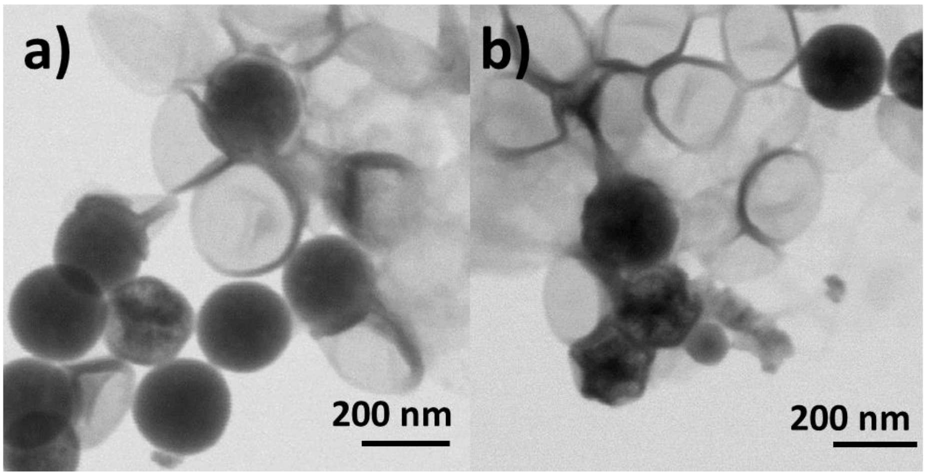

Figure S18 Details of STEM images of a) **Im-MSP-10%** and b) **Im-MSPs-25%** at 0.1 mg/mL in AcOH/AcONa buffer solution at pH 5.2 at a) and b) 3h; c) 1d; d) 5d.

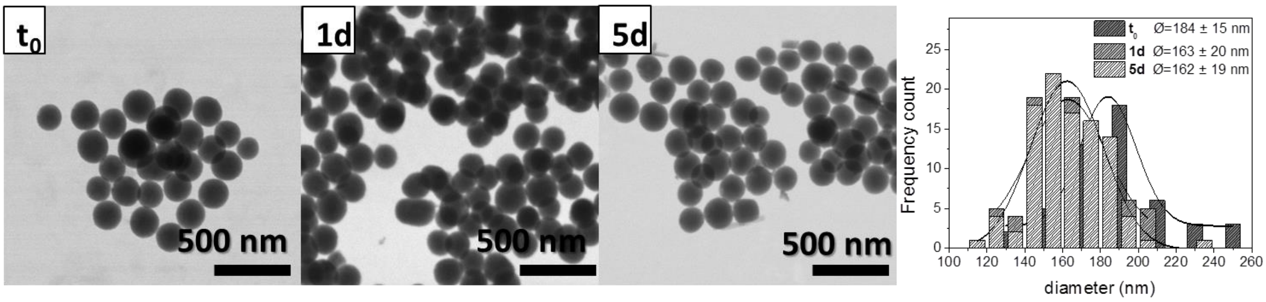

Figure S19 STEM images of **MSPs** in acetate buffer (pH 5.2) at r.t. at t_0 and after 1 and 5d. On the right the size distributions of the imaged particles are reported.

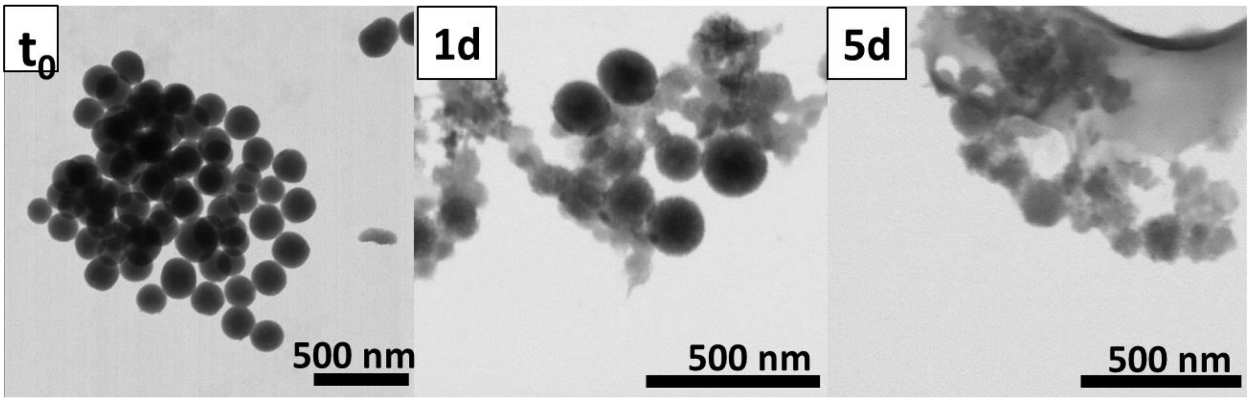

Figure S20 STEM images on **MSPs** in PBS (pH 7.4) at r.t. at t_0 and after 1 and 5d.

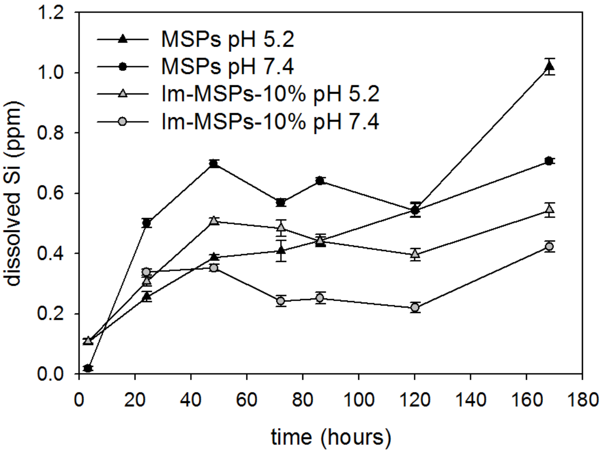

Figure S21 Dissolved Si (ppm) found over time for **Im-MSPs-10%** and **MSPs** at pH 5.2 and 7.4. The data here reported are raw data.

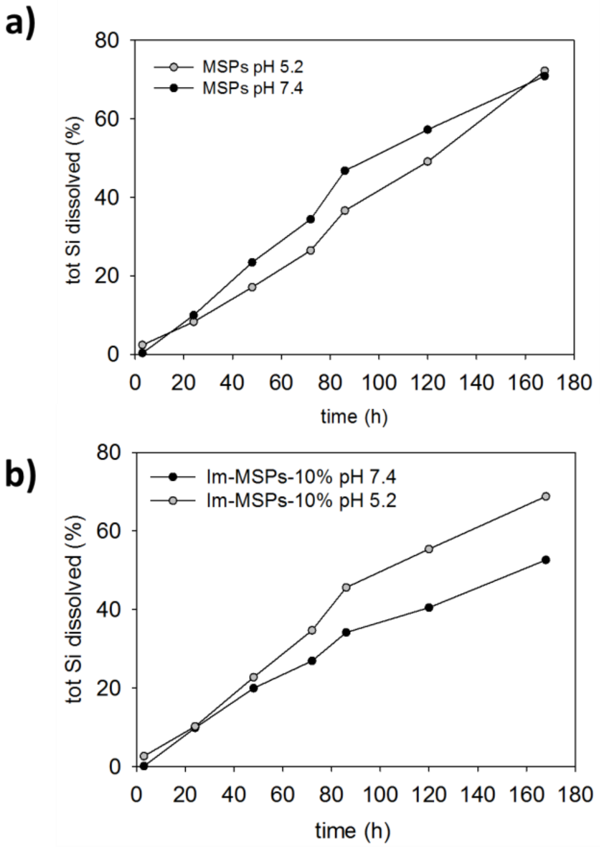

Figure S22 Total percentage Si dissolved calculated from ICP-AES data for a) **MSPs-1** and b**) Im-MSPs-10%** at 25 °C in buffer solutions at pH 5.2 and 7.4

3. NMR spectra of compound 1

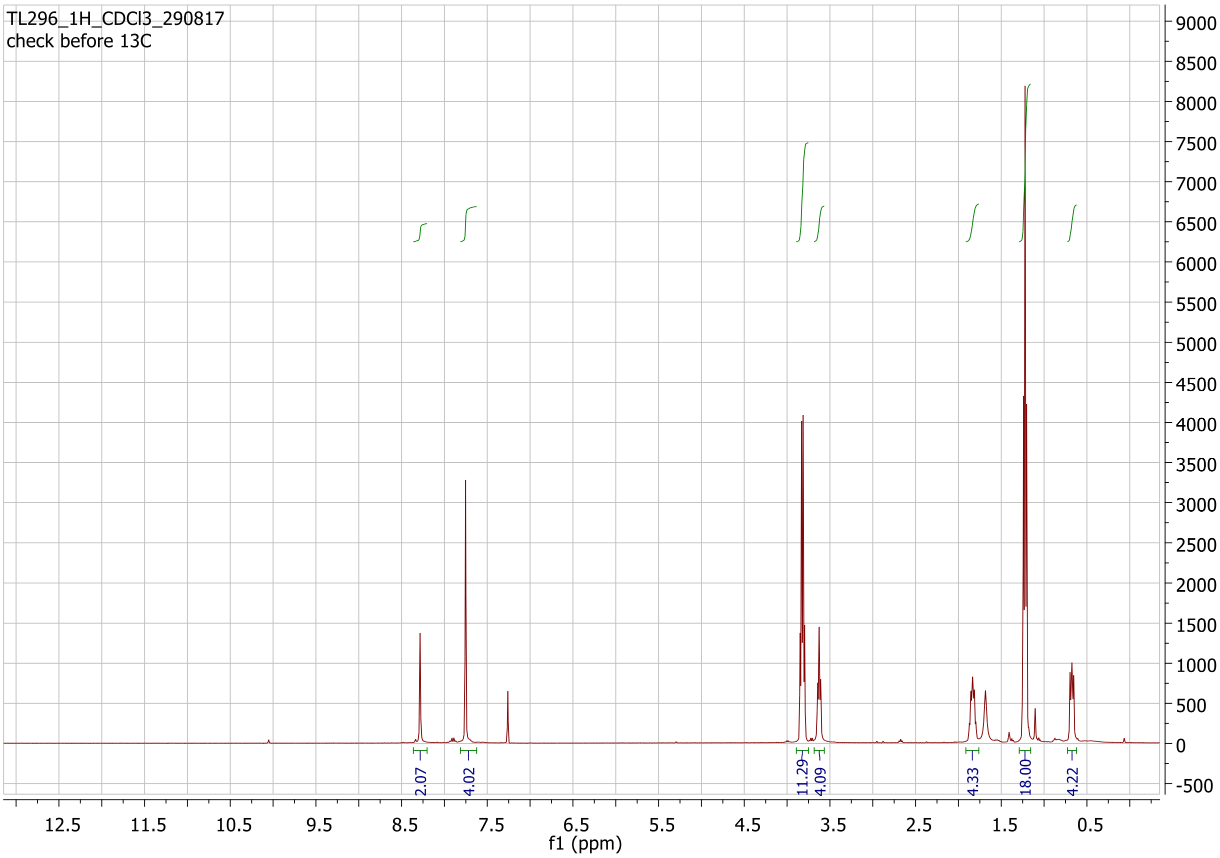

Figure S23: ^{1}H NMR spectrum of the di-imine silane linker **1**

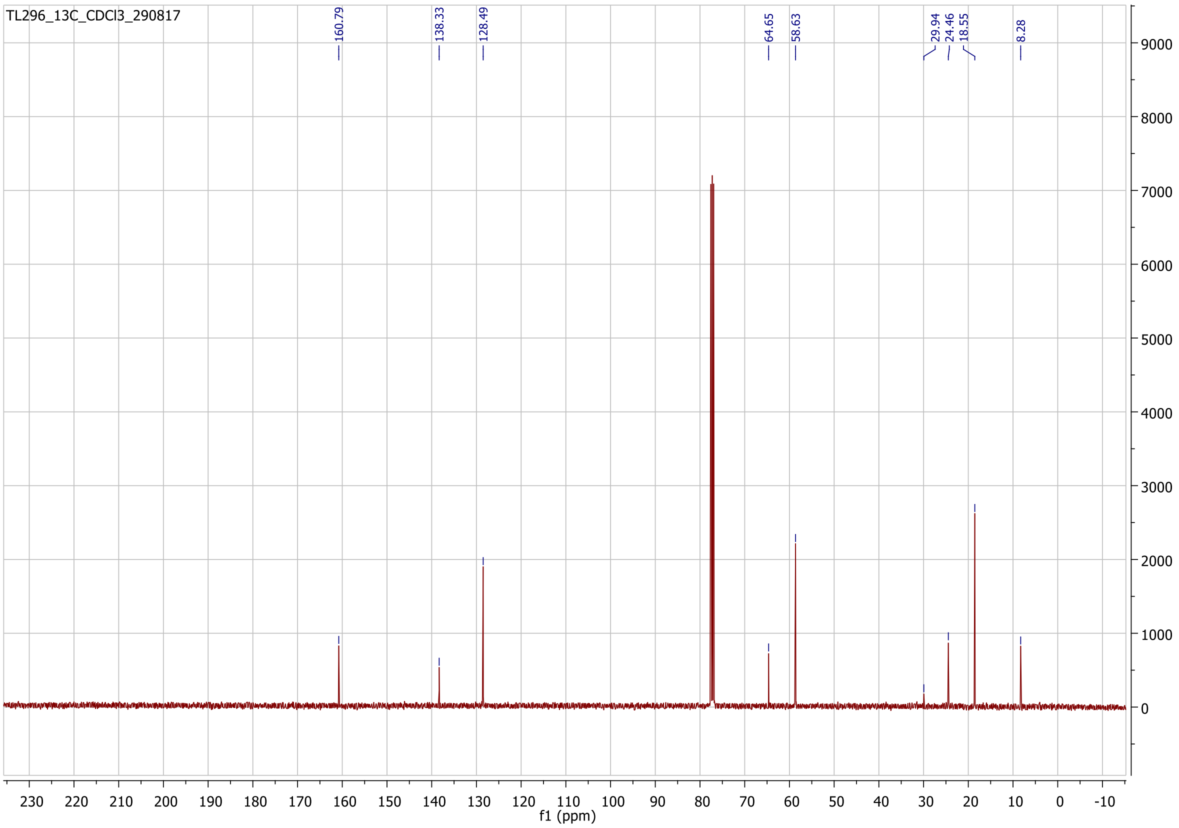

Figure S24: ^{13}C NMR spectrum of the di-imine silane linker **1**

4. References

[1] S. Brunauer, P. H. Emmett and E. Teller, *Journal of the American Chemical Society* **1938**, *60*, 309-319.