The design and synthesis of an innovative octacarboxy-silsesquioxane building block

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Supporting Information

Experimental Section

Materials. All commercially available chemicals were of reagent-grade quality and were used without further purification. The synthesis of octa(*para*-iodophenyl)-silsesquioxane **2** was carried out under nitrogen gas flow, whereas the synthesis of octa(*para*-carboxyphenyl)-silsesquioxane **5** was performed under nitrogen gas atmosphere in a Schlenk line. The empty syringes were purged with nitrogen gas before being used for the injection of the solvents and reagents.

Characterisation methods. ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were measured on Bruker AM-400S spectrometer using tetramethylsilane (TMS) as internal standard and deuterated tetrahydrofuran (THF-D8) as solvent. Matrix-assisted laser desorption/ionisation-time of flight mass spectra (MALDI-TOF-MS) were recorded on a Bruker Ultraflex II spectrometer using α-cyano-4-hydroxycinnamic acid as matrix. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker IFS 66v/s infrared spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a TGA Q500 thermogravimetric analyser over the temperature range 20-800 ºC, at a heating rate of 5 ºC/min, under N_2 or O_2. Analysis by means of scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) spectroscopy was performed on a Philips XL30 FEG equipped with EDX detector and Genesis EDAX software. The accelerating voltage was 10 kV. The powder samples were deposited on a carbon tape supported on an aluminum stub. The samples were then covered with an Au-Pd alloy (60% Au) using a Balzers sputtering device (sputtering conditions: 1 min, pressure of 0.15 torr, Ar atmosphere, 20 mA). HPLC analyses were performed on a Shimadzu HPLC system equipped with an apolar column (Prevail, C18, l = 250 mm, d = 4.6 mm), a UV detector (Shimadzu SP-10A) set at 254 nm and 280 nm, a pump (Shimadzu LC-10AT) and a low-pressure gradient (Shimadzu FCV-10AL). The analyses were performed in reverse phase HPLC with a gradient of CH_3OH-H_2O as eleuent (25% CH_3OH for 5 min; ramp to 90% CH_3OH in 10 min; 90% CH_3OH for 20 min; ramp to 25% CH_3OH in 5 min). Before the analysis, compound **5** was dissolved in methanol (1% wt) and then diluted 1:50 vol. with the eluent solution.

Synthesis of octa(*para*-iodophenyl)-silsesquioxane 2. This compound was prepared with a method based on a previously reported procedure.[1] 110 mL of a 1.0 M solution of iodine monochloride (ICl) in dichloromethane was added with a syringe to a double-neck 250 mL glass flask under N_2 flow. The iodine monochloride solution was cooled to −40 °C in a dry ice/ethanol/ethylene glycol bath, and 10 g (9.7 mmol) of octaphenyl-silsesquioxane **1** (Sigma-Aldrich) were added through a funnel inserted in the rubber septum closing the flask, under high N_2 flow, at an approximate rate of 2 g/min while stirring. HCl gas started to evolve upon addition of the octaphenyl-silsesquioxane **1** and was flushed from the flask by N_2 flow. The reaction mixture was stirred for 36 h at −40 °C, always under N_2 flow, and then allowed to warm up to room temperature while stirring over another 24 h without N_2 flow to prevent evaporation of dichloromethane. The remaining unreacted iodine monochloride was quenched by addition of 100 mL of a 2M aqueous solution of sodium metabisulfite ($Na_2S_2O_5$). The organic layer was separated, washed three times with water, and dried over anhydrous sodium sulfate (which was pre-dried overnight at 100 °C) for 3 h. The dichloromethane was removed by rotary evaporation to yield an off-white solid. This solid was redissolved in 100 mL of THF and then precipitated out by adding 1 L of cold methanol. The mixture was heated in ethyl acetate to remove the insoluble nonaiodinated octaphenyl-silsesquioxane (I_9), yielding an ethyl acetate solution of octa(iodophenyl)-silsesquioxane (I_8), with high regioselectivity for iodination in *para*-position on the aromatic ring.[1] Octa(*para*-iodophenyl)-silsesquioxane **2** was precipitated out as a first fraction in 30-40% yield by slow evaporation of the ethyl acetate solution over 2 days. ^1H NMR (300 MHz, THF-D8, TMS, ppm): δ = 7.5 (d, 2H; Ar-H), 7.8 (d, 2H; Ar-H). ^{13}C NMR (75.5 MHz, THF-D8, TMS, ppm): δ = 135.4 and 133.5 (Ar-carbons). ^{29}Si NMR (79.30 MHz, THF-D8, TMS, ppm): $\delta = -78.3$.

Synthesis of octa(*para*-carboxyphenyl)-silsesquioxane 5. 500 mg of octa(*para*-iodophenyl)-silsesquioxane **2** were weighed and placed into an oven-dried three-neck flask. The flask was connected to a Schlenk line with a nitrogen inlet tube, a carbon dioxide inlet tube and with the third neck being closed with a septum. The flask was evacuated and re-filled with N_2 (at least three evacuation/refilling cycles). THF (40 mL) was injected with a syringe into the flask through the septum, under flow of N_2. The solution was cooled to −78 °C using a liquid nitrogen and acetone bath, and 2.5 mL of BuLi (2.5 M in hexane) were added drop-wise with a syringe under flow of N_2. The reaction mixture was stirred for 4 h until a pale yellow precipitate appeared because of the formation of octa(*para*-lithiophenyl)-silsesquioxane **3**. Then,

CO_2 was flowed through the flask at a rate of 40 cm^3/min for another 20 h, at room temperature. The reaction was terminated by adding 5 mL of methanol, 10 mL of water and finally 3.5 mL of 2M aqueous HCl. The clear solution was evaporated in a rotary evaporator until the volume was ~5 mL, followed by filtration from the remaining acidic water solution to yield a pale yellow gel. The gel was washed four times with dichloromethane and then four times with water. Then, it was dissolved in THF and precipitated out by drop-wise addition of water. The colourless solid was collected by filtration and dried in vacuum to give octa(*para*-carboxyphenyl)-silsesquioxane **5** with 61 % yield. ^{1}H NMR (300 MHz, THF-D8, TMS, ppm): δ= 7.8 (d, 2H; Ar-H), 8.1 (d, 2H; Ar-H). ^{13}C NMR (75.5 MHz, THF-D8, TMS, ppm): δ= 164.2 (-COOH), 132.1 and 127.0 (Ar-carbons). ^{29}Si NMR (79.30 MHz, THF-D8, TMS, ppm): δ= −78.5. MS (MALDI-TOF): $[M-OH]^+$, m/z = 1367, 69%; $[M-OH-CO_2]^+$, m/z = 1323, 100%; $[M-OH-2CO_2]^+$, m/z = 1279, 41%; and $[M-OH-3CO_2]^+$, m/z = 1235, 9%. IR (in cm^{-1}, KBr pellet): $\bar{\upsilon}$ = 2600-3600(br), 1702(s), 1608(w), 1560(w), 1504(w), 1393(m), 1284(w), 1109(m), 1022(s), 918(w), 762(w), 699(m), 523(m). TGA (in O_2): temperature range: 90-600 °C, mass loss: 66%. TGA (in N_2): temperature range: 90-800 °C, mass loss: 42%.

Solvent	Solubility of compound **5** [g/L]
DMF	120
DMSO	120
Methanol	100
Ethanol	100
THF	70
1,4-Dioxane	70

Table S1. Solubility of octa(*para*-carboxyphenyl)-silsesquioxane **5** in selected solvents.

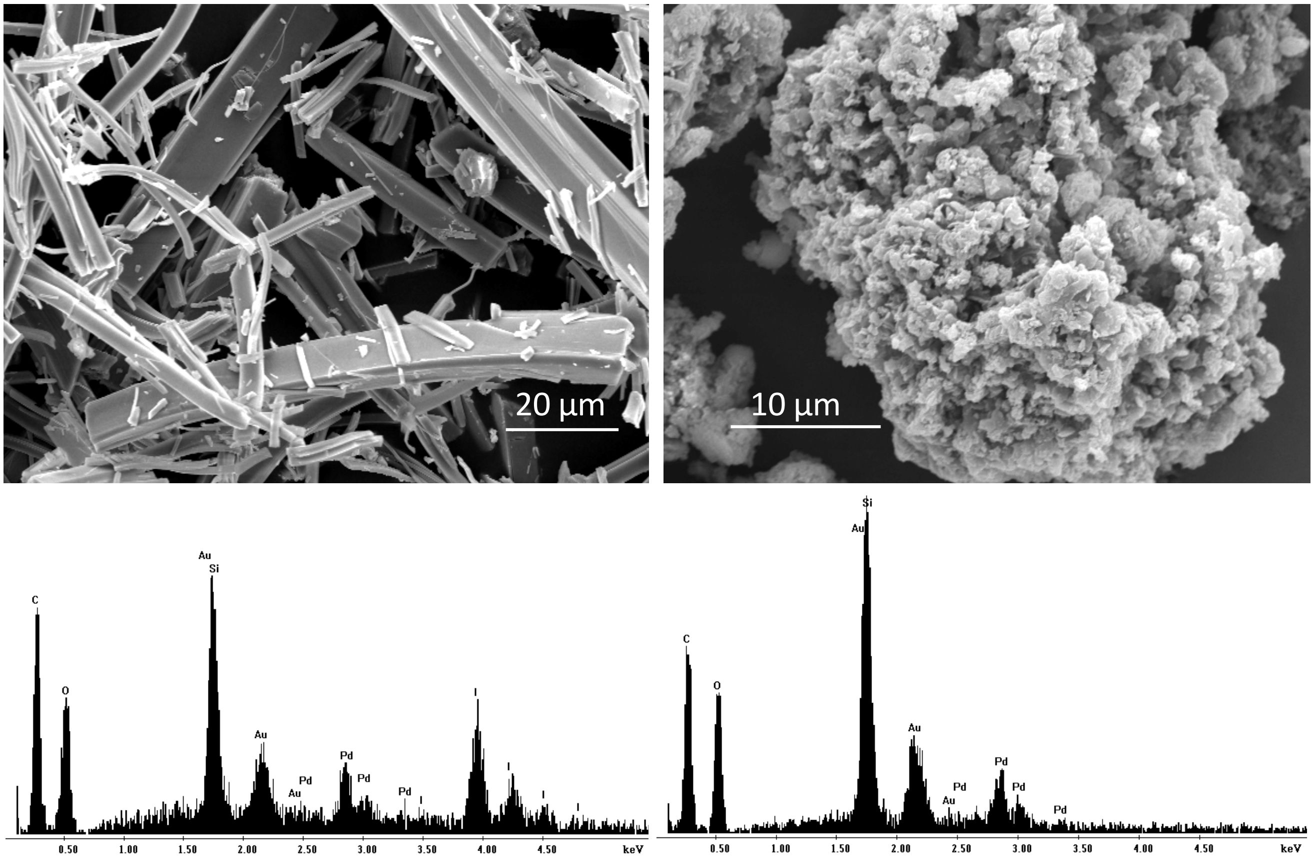

Figure S1. Representative SEM images and EDX analyses of compound **2** (left) and **5** (right). EDX analysis of compound **2** gives an average I/Si = 1.04 (theoretical value I/Si = 1). No iodine was detected by EDX in compound **5**. The peaks of Au and Pd originate from the alloy used to coat the samples. [It is worth reporting that elemental analysis by XPS is not applicable to these silsesquioxane compounds, which tend to deteriorate during analysis with this technique].

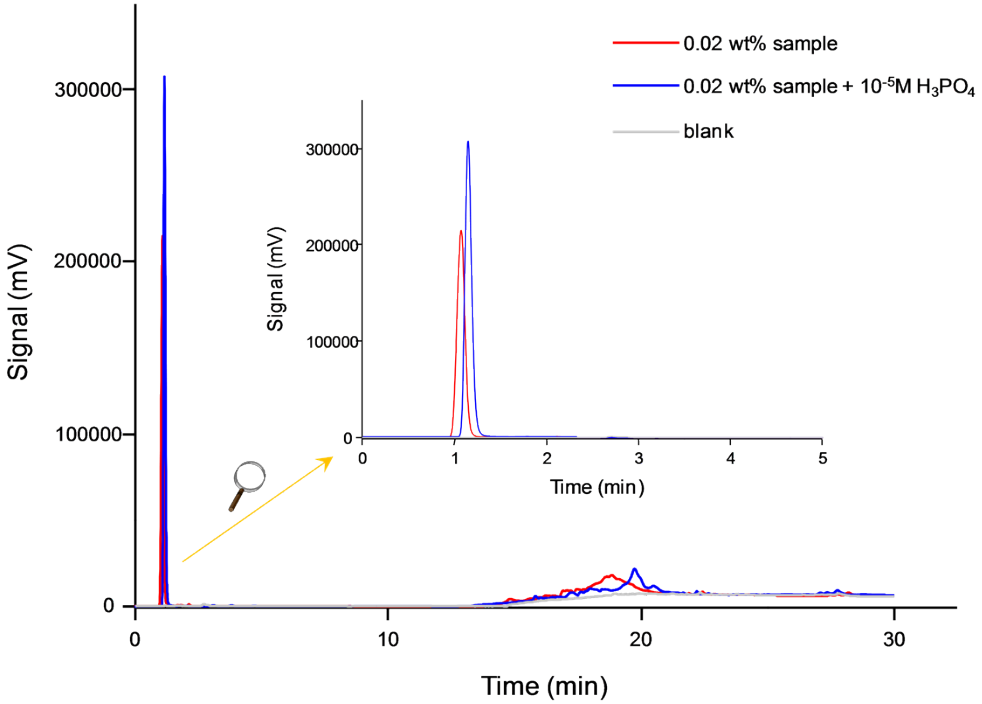

Figure S2. HPLC analysis of silsesquioxane **5**. The intense peak at low retention time is assigned to the deprotonated octacarboxy-silsesquioxane on the basis of the position of the peak (an anionic compound is expected to have low interaction with the column) and considering that this signal disappears if the acid dissociation is prevented by performing the analysis with higher concentration of phosphoric acid in the eluent (10^{-3} M). The analysis of the carboxy-silsesquioxane is made complex by its different possible degrees of acid dissociation, to which we ascribe the presence of the small, broad peaks at higher retention time whose position and shape change with the pH of the eluent.

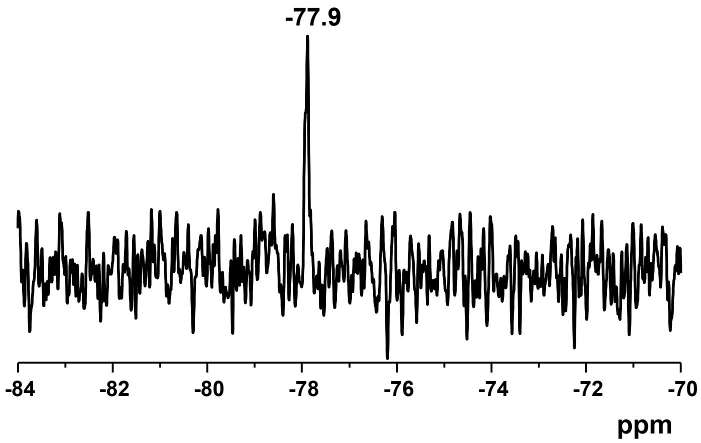

Figure S3. ^{29}SiNMR spectrum of the silsesquioxane salt obtained by reaction of compound **5** with triethylamine.

References

1 M. F. Roll, M. Z. Asuncion, J. Kampf, R. M. Laine, *ACS Nano* 2008, **2**, 320.