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Supporting Information for

A Thermolytic Route to a Polysilyne

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General experimental details

Synthesis and reagents. Unless otherwise noted, all reactions and manipulations were performed under nitrogen in a glovebox or using conventional Schlenk techniques. A “bomb” flask is a thick-walled flask with a 4 mm teflon needle valve and side-arm with a ground glass joint for connection to a Schlenk line. Benzene was distilled from sodium/benzophenone under nitrogen; toluene and hexanes were degassed by sparging with nitrogen and dried over activated alumina in a solvent purification system. THF was distilled from sodium/benzophenone and degassed by three freeze-pump-thaw cycles before use. Isopropanol was refluxed with Mg turnings for 3h, distilled, deoxygenated by sparging with nitrogen for 12h, and stored over Linde type 5 Å molecular sieves. Deuterated C_6D_6 was freeze-pump-thaw degassed and vacuum transferred from sodium/benzophenone. Degassed HPLC grade tetrahydrofuran (THF) was used for Gel Permeation Chromatography (GPC) analysis. Spectroscopic grade dichloromethane was dried and stored over activated molecular sieves and degassed by three freeze-pump-thaw cycles before use.

Spectroscopic characterization. Solution ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE 300 spectrometer. ^{1}H NMR spectra were referenced to the residual proton peak in C_6D_6 (δ 7.16 ppm) relative to tetramethylsilane (TMS) at 0 ppm. ^{13}C NMR spectra were referenced to solvent peaks relative to tetramethylsilane (TMS) at 0 ppm. CP-MAS ^{29}Si NMR spectra were acquired on a Bruker AVANCE 400 spectrometer (9.39T) operating at 79.49 MHz for ^{29}Si. (See below for details of solid-state NMR experiments and analysis.) Chemical shifts are reported in ppm at ambient temperature. Infrared spectra were obtained for KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Routine UV-Vis spectra were acquired for samples in spectroscopic grade dichloromethane, at RT on a Varian Cary-1 or Cary-100 spectrophotometer. (See below for description of photolysis experiments.)

Other polymer characterization. Molecular weights (MWs) were determined from triple detection gel permeation chromatography with multi-angle light-scattering (MALS-GPC), using an Agilent 1200 series isocratic pump, Agilent 1200 series standard autosampler, three Phenomenex Phenogel 5 µm narrow bore columns (4.6 x 300 mm) [10^4 Å (5,000-500,000 Da), 10^3 Å (1000-75,000 Da), and 500 Å (1,000-15,000 Da)], Wyatt Optilab rEX differential refractometer (λ = 658 nm, 40 ºC), Wyatt miniDAWN TREOS (laser light scattering detector at λ = 659.4 nm), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL/min was used and samples were dissolved in THF (ca. 1mg/mL). For absolute MW determinations dn/dc values were calculated using 100% mass recovery methods using the ASTRA software version 6.1. For conventional calibration MW determinations polystyrene standards were used. For each sample, results are representative of data obtained from multiple repeat runs (≥3). Thermogravimetric analysis (TGA) was carried out on a TA Instruments SDT Q600 in a nitrogen atmosphere with temperature increased from 20 to 1000 °C at a rate of 10 °C/min.

Polymer syntheses

*Poly(phenylsilane) (**1**).* The parent polysilane was prepared via Zr-catalyzed dehydrocoupling of phenylsilane as described previously.[1] This polymer exists primarily as straight polysilane chains up to 20-30 silicons long, mixed with small amounts of cyclic oligomers that are primarily Si_6.[2] Molecular weights (MW) are typically in the range of M_W 1500-3500 Da, with PDIs of 1.3-1.7.[3] For the present sample, Mw = 2690 Da, Đ = 1.59, Mark-Houwink coefficients: K = 0.294 mL/g, α = 0.294.

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[1] P. T. K. Lee, M. K. Skjel and L. Rosenberg, *Organometallics*, 2013, **32**, 1575.
[2] T. D. Tilley, *Acc. Chem. Res.*, 1993, **26**, 22.
[3] P. T. K. Lee and L. Rosenberg, *Dalton Trans.*, 2017, **46**, 8818.

*General method for thermolysis of poly(phenylsilane) (**1**) to give poly(phenylsilyne) (**2**).*

Important safety consideration! Monosilane products form during this synthesis, from scrambling of Si-Si, Si-Ph, and Si-H bonds. We did ***not*** observe formation of SiH_4, a pyrophoric gas, during these experiments, but appropriate precautions should be taken when removing the monosilane by-products under vacuum and during purification of the crude reaction mixture.

Solvent was removed under vacuum from a solution of **1** in benzene in a pre-weighed bomb flask. The polymer was then heated to constant mass at 125 °C under vacuum to remove residual monomer, $PhSiH_3$, and solvent. The flask was sealed under static vacuum and heated to 500 °C (as determined by a thermocouple inserted between the flask and heating mantle), in 25-50 °C increments over 2-3 h. The temperature was held at 500 °C for up to 30 min, then the flask was allowed to cool to RT and the head space was evacuated (≤ 3 freeze-pump-thaw cycles), giving a viscous oil (~90% of original mass) that varied in color from dark red-brown to bright orange. ^1H NMR of this residue showed signals due to $PhSiH_3$, Ph_2SiH_2, and Ph_3SiH, as determined by comparison with authentic samples.[4] The residue was dissolved in benzene to give a yellow solution.[5] Solvent was removed under vacuum to give a yellow, oily residue, from which a yellow solid was precipitated by the addition of pentane or hexanes, leaving a clear and colorless supernatant. The yellow powder was filtered, washed with hexanes to remove as much residual Ph_3SiH as possible, and dried under vacuum at 50 °C. The reaction has been carried out for samples of **1** ranging from 0.94 g to 8.2 g, with isolated yields of **2** of 35-58% (mass recovery). ^1H data for all samples are comparable to those shown in Figure 1b,c.

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[4] In preliminary trials the reaction flask was connected via a glass T-piece to a second flask that was cooled in $N_2(l)$, with the entire apparatus under static vacuum. Similar results were obtained, but the monosilane products were mostly separated from the thermolysis residue, which often solidified.

[5] In some trials a small amount of precipitate was removed by filtration at this stage (2% mass recovered).

Precipitation of poly(phenylsilyne) ***2****.* Under argon, a THF solution of **2** (300 mg in 2 mL) was added to rapidly stirred ^{i}PrOH (30 mL), which caused a yellow precipitate to form. The procedure was repeated three times to afford a light yellow solid. Yield: 261 mg (87% recovered mass). The ^{1}H NMR is shown in Figure 1d.

Air sensitivity of the crude and purified polymer **2**:

Exposure of bright yellow, solid samples of **2** to air causes a colour change to white (~hours for a small sample) and corresponding loss of solubility. We attribute this to autoxidation leading to the incorporation of Si-O units within the polymer structure, which is known to occur also for the Wurtz-coupled polysilynes.[6] Despite efforts to exclude oxygen (*vide infra)*, this extreme sensitivity affected our ability to obtain TGA and IR analyses of **2** as shown below.

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[6] M. W. Pitcher, S. J. Joray and P. A. Bianconi, *Adv. Mat.*, 2004, **16**, 706.

Polymer characterization

*^{13}C NMR spectra of **2** before and after fractionation*

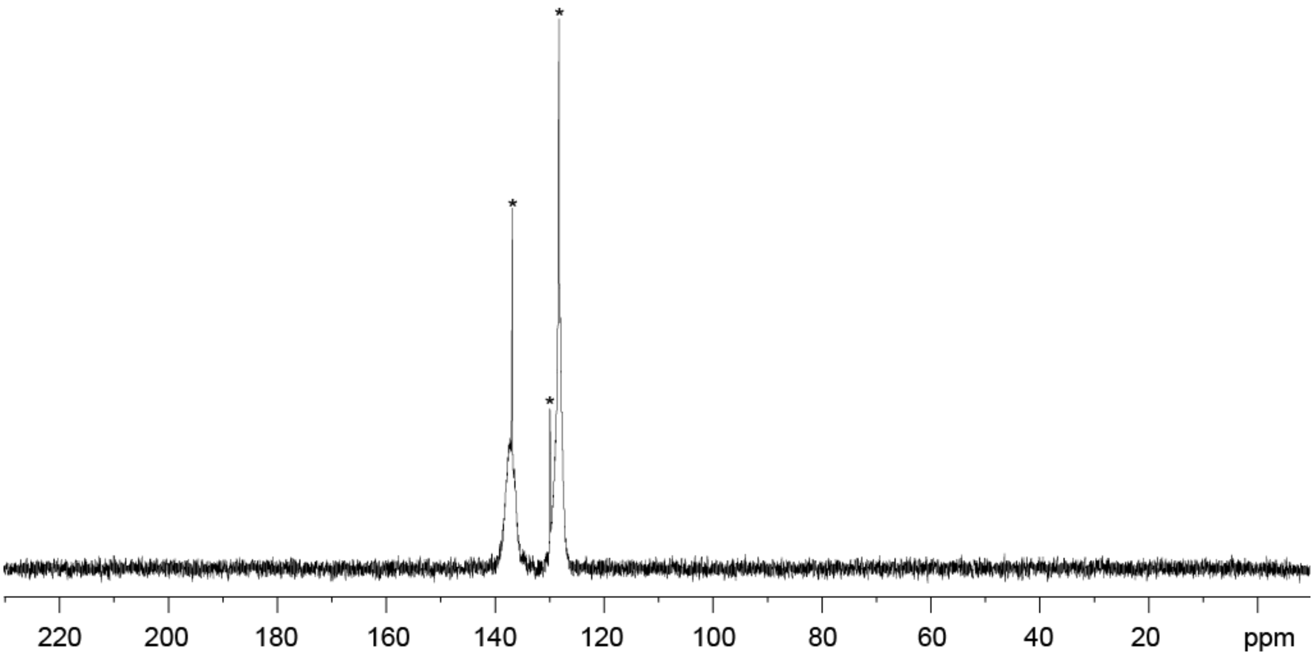

Figure S1. 75.51 MHz ^{13}C DEPT135 NMR spectrum of hexanes-precipitated **2** in C_6D_6. The * marks signals due to residual Ph_3SiH.

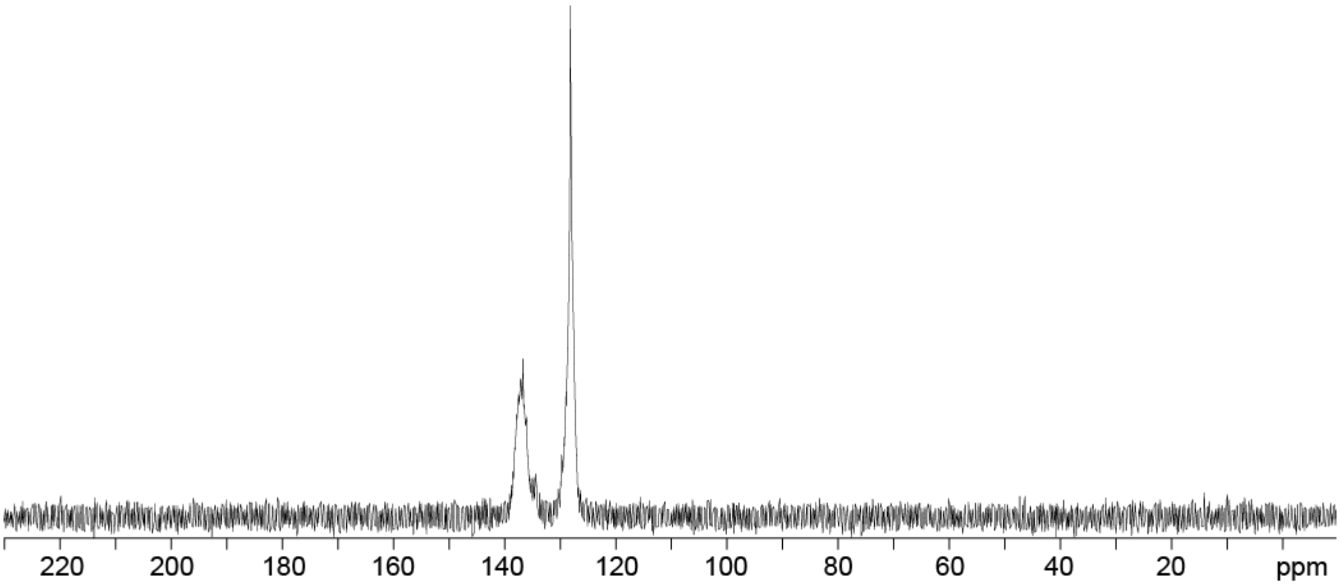

Figure S2. 75.51 MHz ^{13}C DEPT135 NMR spectrum of fractionated **2** in C_6D_6.

Infrared spectra

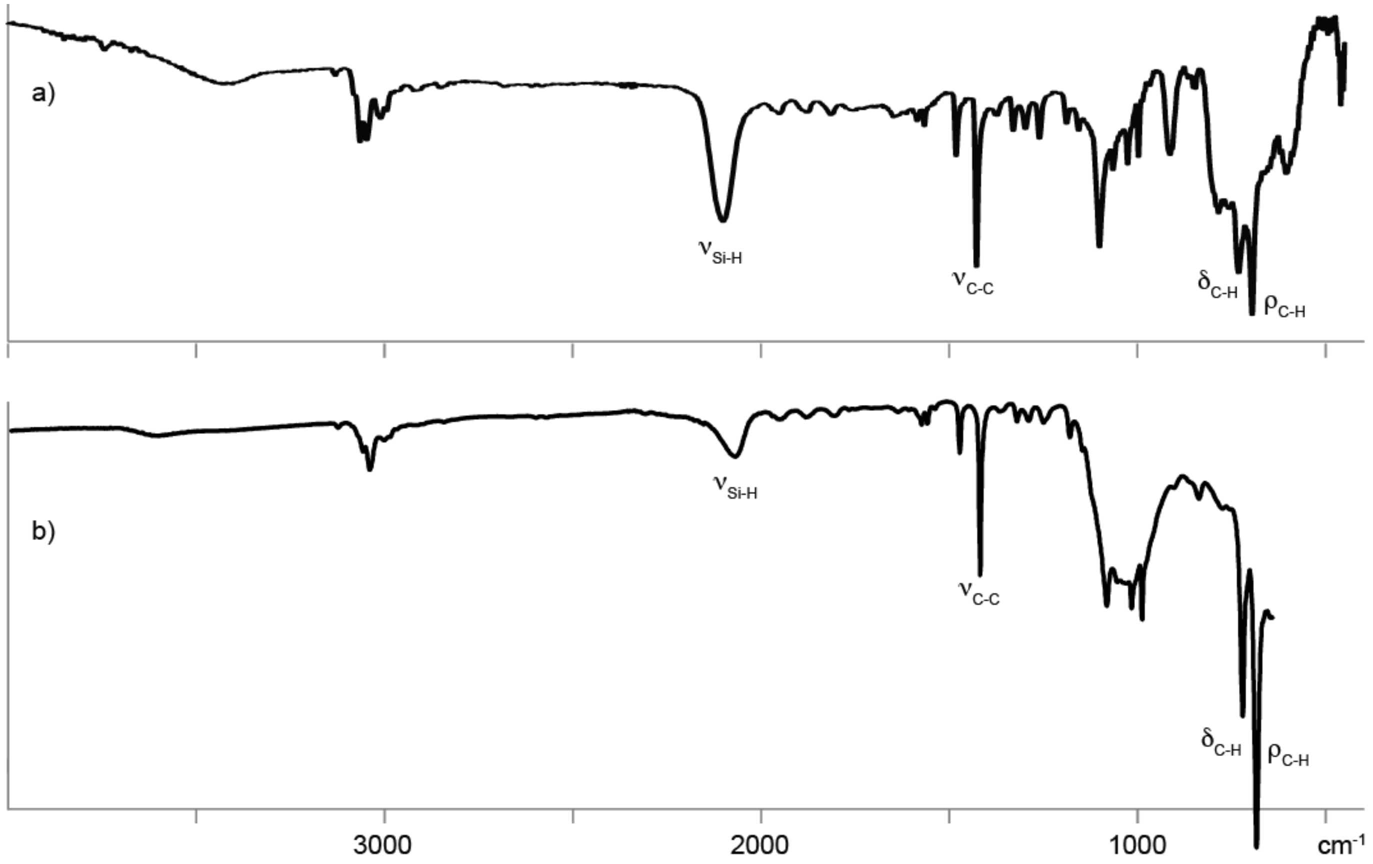

Figure S3. Infrared spectra (KBr pellets) for a) the parent poly(phenylsilane) **1** (data from reference 3) and b) purified polysilyne **2**, with labels indicating the key diagnostic peaks due to Si-Ph and Si-H groups in the two polymers. We assume the peaks near 3000 cm^{-1} arise from residual solvent (pentane or hexanes). Broad, weak bands (~3300-3600 cm^{-1}) may result from trace water in the KBr pellet. Spectrum b) is comparable to that reported for poly(phenylsilyne) prepared by Wurtz coupling,[7] except that ν_{SiH} is more intense for polymer **2**, ,as expected, and we observe a slightly broader band at ~1100 cm^{-1}. Clearly this is a complex fingerprint region (~800-1200 cm^{-1}) for these Si-Si-containing polymers: it is present for polymers **1** and **2** *and* Wurtz coupled polysilyne $[PhSi]_n$. Nevertheless, we cannot rule out the possibility that broadening of this band in spectrum b) could arise from partial autoxidation of the highly air-sensitive polymer **2** during analysis (*vide supra*).

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[7] D. A. Smith, S. J. Joray and P. A. Bianconi, *J. Polym. Res.*, 2005, **12**, 393.

GPC analysis of purified ***2***

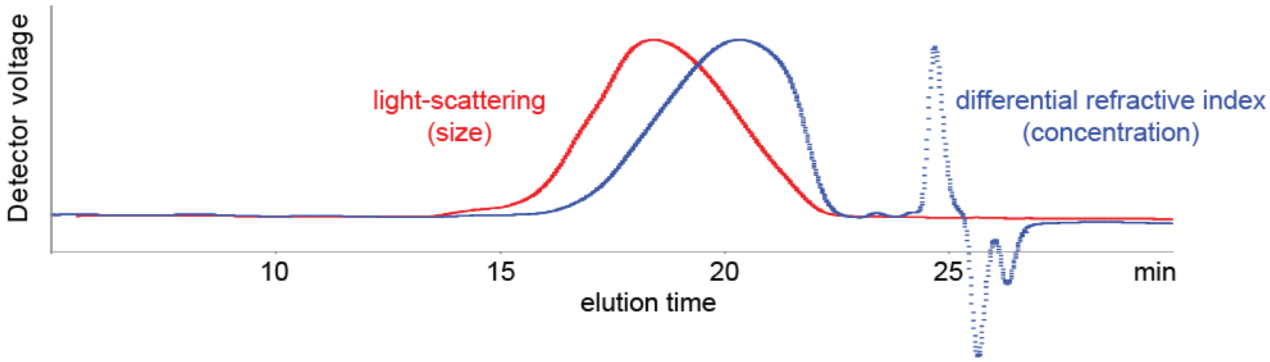

Figure S4. Representative MALS-GPC trace for fractionated **2** in THF.

Table S1. MW data for **2** in THF.

method	dn/dc (mL/g)	M_W (kDa)	M_n (kDa)	Đ
calibrated (vs polystyrene)	n/a	5.65	3.39	1.67
absolute (MALS)[a]	0.3263	20.8	12.1	1.72

[a] Mark-Houwink α = 0.153, K = 0.507 mL/g.

*Thermogravimetric analysis of **1** and **2***

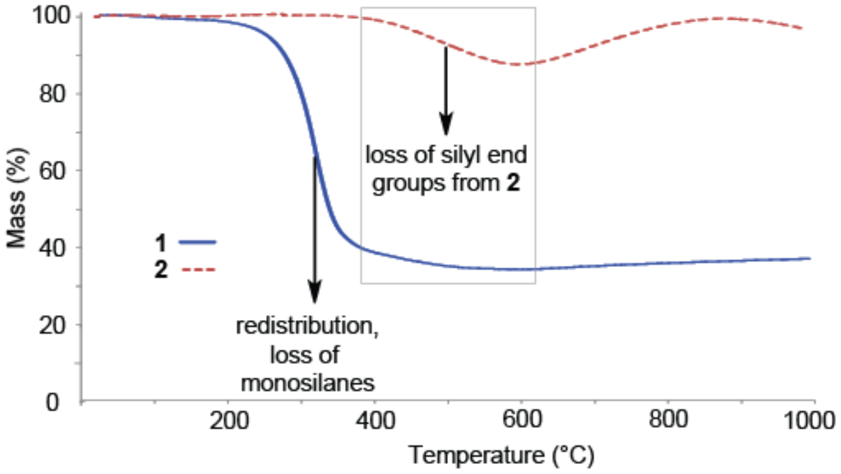

Figure S5. TGA traces for polymers **1** and **2**.[8] Samples were heated at 10 °C/min from room temperature (approximately 20 °C) to 1000 °C, while the oven was flushed with N_2(g). The grey rectangle highlights a mass loss event that is apparently common to both polymers, suggesting that the major inflection point for **1** at 320°C represents the thermal redistribution that produces **2**. In the trace for **2**, the mass increase beginning at ~600°C may be attributed to oxidation resulting from either trace O_2 or the alumina pan.

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[8] Similar TGA data to the trace we observe for **2** was reported for Wurtz-coupled polysilynes in: a) A. Watanabe and M. Matsuda, *Chem. Lett.*, 1991, 1101; b) R. Shankar and U. Sahoo, *J. Polym. Sci. Pol. Chem.*, 2012, **50**, 1158; c) R. Shankar, U. Sahoo and V. Shahi, *Macromolecules*, 2011, **44**, 3240.

Solid-state ^{29}Si NMR of ***2***

^{1}H-^{29}Si cross-polarization was established using a 5 ms contact time, samples were spun at a MAS speed of 6 kHz, and the total number of scans was ~40k with a recycle delay of 10 s. Spectra were referenced to sodium 3-(trimethylsilyl)-propane-1-sulfonate, $(CH_3)_3Si(CH_2)_3SO_3Na$, at 1.534 ppm relative to tetramethylsilane (TMS) at 0 ppm. The NMR data were apodized with a 100 Hz Lorentzian broadening function and zero filled once prior to Fourier transform. Deconvolution of the spectra was carried out using the Line Fitting tool as implemented in the MestRe Nova 11.0.4 software package.[9]

Table S2. Details of the deconvoluted CP-MAS ^{29}Si NMR spectrum for **2**.

δ (ppm)	5.4	–4.1	–17.6	–33.6	–47.9	–92.6
intensity (%)	2	6	47	31	12	2
fwhm (Hz)	769	1000	864	1000	1000	988
assignment	*Si*R$_2$ (edge)	*Si*R$_2$ (edge)	*Si*Ph$_3$	*Si*Ph$_2$, *Si*Ph$_2$H	Ph*Si*(Si)$_3$	SiH$_3$

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[9] M. R. Willcott, *J. Am. Chem. Soc.*, 2009, **131**, 13180.

Photolysis experiments

Photolysis was carried out using 0.02 mg/mL solutions of poly(phenylsilane) **1** and purified poly(phenylsilyne) **2** in dichloromethane. All stock solutions and samples were wrapped in aluminum foil prior to use, to avoid exposure to light. Absorption spectra shown in Figure 4 were recorded at room temperature with a Cary 1 or Cary 100 spectrophotometer before and after the continuous irradiation/UV-Vis monitoring experiments, which were carried out using custom built instrumentation.[10] Both the irradiation and monitoring lamps were 75 W PTI xenon arc lamps. Samples were irradiated continuously over a 20 nm bandwidth centered at 300 nm and sample absorbances were measured at 320 and 325 nm. Absorbance data was collected over 500 time points at intervals of 15 s, for a total of 2h 5 min of monitoring.

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[10] C. S. Santos, A. C. Miller, T. C. S. Pace, K. Morimitsu and C. Bohne, *Langmuir*, 2014, **30**, 11319.