

Electronic Supporting Information

Diaryliodonium Salts as Hydrosilylation Initiators for the Surface Functionalization of Silicon Nanomaterials and their United Capability as Ring Opening Polymerization Initiators

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General Information

All experiments were performed under Schlenk conditions. Reactants and reagents were purchased from *Sigma-Aldrich* and used without further purification if not stated otherwise. 1-dodecene, methyl 10-undecenoate, 1-octyne, trimethylvinylsilane, acetone, chloroform and ethyl acetate were dried over molecular sieves and stored under argon prior to use. THF was dried with an *MBraun* solvent purification system, *MB SPS-800*, whereby argon 5.0 (99.999%, *Westfalen AG*) was used as inert gas. For polymerization reactions and storage of exfoliated SiNSs, a *LABmaster 130 (MBraun)* glove box was used with nitrogen 4.8 (99.998%, *Westfalen AG*).

Fourier transform infrared spectroscopy (**FTIR**) samples were prepared as a thin film by drop-casting the sample on a silicon wafer from a suitable solvent and the FTIR spectra were obtained using a *Nicolet 8700 FTIR* in combination with a *Nicolet Continuum* FTIR microscope. Nuclear magnetic resonance (**NMR**) spectra were recorded on an *ARX-300* from *Bruker* at 300 K. Chemical shifts (δ) are calibrated to the residual proton signal of the deuterated solvent and given in ppm. For functionalized SiNC samples, a concentrated solution (5 mg/mL) in benzene- d_6 was used to obtain the spectrum. **PL** spectra were measured in toluene on an *AVA-Spec 2048* from *Avantes* using a *Prizmatix* (LED current controller) as a light source. Thermogravimetric analysis (**TGA**) was performed on a *Mettler Toledo STARe* TGA/DSC system by heating the freeze-dried SiNC sample to 600 °C at a heating rate of 10 K/min. Dynamic light scattering (**DLS**) data was collected on a *Dyna Pro NanoStar* from *Wyatt* with toluene as the solvent. Gel permeation chromatography (**GPC**) measurements were conducted on a *Varian PL-GPC 50 Plus* at 30 °C with a constant flow rate of 1 mL/min THF, stabilized with 220 mg/L BHT. Transmission electron microscopy (**TEM**) was performed on a JEOL-2012 electron microscope equipped with LaB₆ filament and operated at an accelerating voltage of 200 kV. For contact mode atomic force microscopy (**AFM**) measurements, a Veeco Dimension V instrument equipped with a Veeco Nanoscope V controller in tapping mode with Si cantilever probes (Veeco OTESPA) was used. Thin films of SiNS-C₁₂H₂₅ (15 mg of exfoliated sheets in 2 mL of toluene) were dip coated on Si/SiO₂ substrates and dried with a nitrogen gas flow. Energy dispersive x-ray (**EDX**) spectra were taken on a HITACHI TM-1000 table microscope with SwiftED-TM detector.

Syntheses and Procedures

Synthesis of oxide embedded silicon nanocrystals was achieved through a known method.¹ 7.00 g polymeric hydrogen silsesquioxane (HSQ) synthesized according to a published method² was placed in a quartz reaction boat, transferred in a furnace and heated under a slightly reducing atmosphere (H₂/N₂ = 5/95). As such the HSQ was heated to 1100 °C over 1 h and then kept at that temperature for 1 hour. Upon cooling to room temperature, the resulting solid was ground to a fine powder.³

Liberation of silicon nanocrystals: In a polytetrafluoroethylene (PTFE) beaker, 200 mg of ground SiNC/SiO₂ composite are suspended in 2 mL ethanol and 2 mL water. 2 mL HF (48%) is added and the mixture stirred for 45 minutes. The liberated SiNCs are extracted with toluene (3 × 10 mL) and isolated *via* centrifugation (3000 rpm for 5 min). After subsequent washing with dry toluene and centrifugation, the hydride-terminated SiNCs are dispersed in 2 mL dry chloroform for use in further reactions.

Iodonium induced functionalization of silicon nanocrystals with alkenes and alkynes: The hydride-terminated SiNCs obtained from the previously described procedure are dispersed in 2 ml dry chloroform and transferred to a heat-dried Schlenk tube. 2.50 mmol of alkene/alkyne are added and the reaction mixture is degassed via three freeze-pump-thaw cycles. After addition of 22.2 μmol of bis(4-*tert*-butylphenyl)iodonium hexafluorophosphate (BIP), the reaction mixture was stirred for 16 hours. The clear orange dispersion is precipitated into a 3:1 ethanol/methanol mixture (for methyl 10-undecenoate and trimethylvinylsilane only methanol is used) and centrifuged (9000 rpm/5 min). Washing is performed three times by redispersing the residue in a minimal amount of toluene, adding the anti-solvent methanol and centrifuging the suspension (9000 rpm/5 min). The thus obtained functionalized SiNCs can be dispersed in organic solvents (e.g., toluene) or freeze-dried from benzene.

Synthesis of CaSi₂ was performed as previously published.^{4,5} Stoichiometric amounts of calcium (Alfa Aesar, 99.5 %) and silicon (Wacker, 99.99 %) are mixed and pressed to a pellet. The resulting pellet is then melted in an arc-furnace set up in an argon-filled glovebox. Homogenization is achieved by twice-repeated grinding in an agate-mortar of the obtained metallic regulus and melting from both sides. Final grinding yields CaSi₂ that can be used in the synthesis of SiNSs.

Synthesis of layered polysilanes via chemical exfoliation was performed as published earlier.^{4,5} Under inert-gas conditions, 1.00 g of CaSi_2 is exfoliated in 100 mL HCl (conc.) at $-25\text{ }^\circ\text{C}$ for seven days. The resulting SiNSs are then filtered off, washed with acetone (dry and degassed) and dried under vacuum before storage under argon in a glove box.

Etching of silicon nanosheets: Under argon, a given amount of exfoliated SiNSs are dispersed in 2 mL ethanol and sonicated for 5 minutes. The dispersion is transferred to a PTFE container and 2 mL water and 0.25 mL HF (48%) are added. The etched SiNSs are immediately extracted into PTFE centrifuge tubes with dichloromethane ($3 \times 5\text{ mL}$) and 40 mL of toluene is added. The dispersion is centrifuged (9000 rpm for 4 min), the supernatant discarded and the obtained SiNSs are washed with dry acetone and centrifuged to remove any residual water. Per 15 mg of etched SiNSs, 2 mL of dry ethyl acetate (EtOAc) is used to disperse the hydride-terminated SiNSs.

Iodonium induced functionalization of silicon nanosheets with alkenes and alkynes: 2 mL of the hydride-terminated SiNS-dispersion are transferred to a heat-dried Schlenk-tube and 2.50 mmol of substrate is added. The mixture is degassed via three freeze-pump-thaw cycles and stirred for 16 hours after addition of 9 μmol BIP. The reaction mixture is precipitated in a solution of ethanol and methanol (2:1) and subsequently centrifuged. The supernatant is discarded, the residue redispersed in toluene and centrifuged with methanol. The cycle is repeated twice to obtain the functionalized SiNSs, which can be dispersed in toluene or freeze-dried from benzene.

SiNS/Iodonium initiated ring opening polymerization: After etching, extraction, washing with dry toluene and centrifugation, the hydride-terminated SiNSs are freeze-dried from benzene and transferred to a glove box. There, they are dispersed in 1 mL of dried and degassed THF. 15 mg of BIP are added and the mixture is stirred until polymerization was completed. Work-up of the nanocomposite SiNS@pTHF is conducted by dissolving it in 2 mL THF and precipitating in 20 mL methanol. The composite is then dried under vacuum or freeze-dried from benzene.

Iodonium Salts as Functionalization Initiators for Silicon Nanocrystals (SiNCs)

Time Dependence of SiNC Functionalization with Iodonium Salts

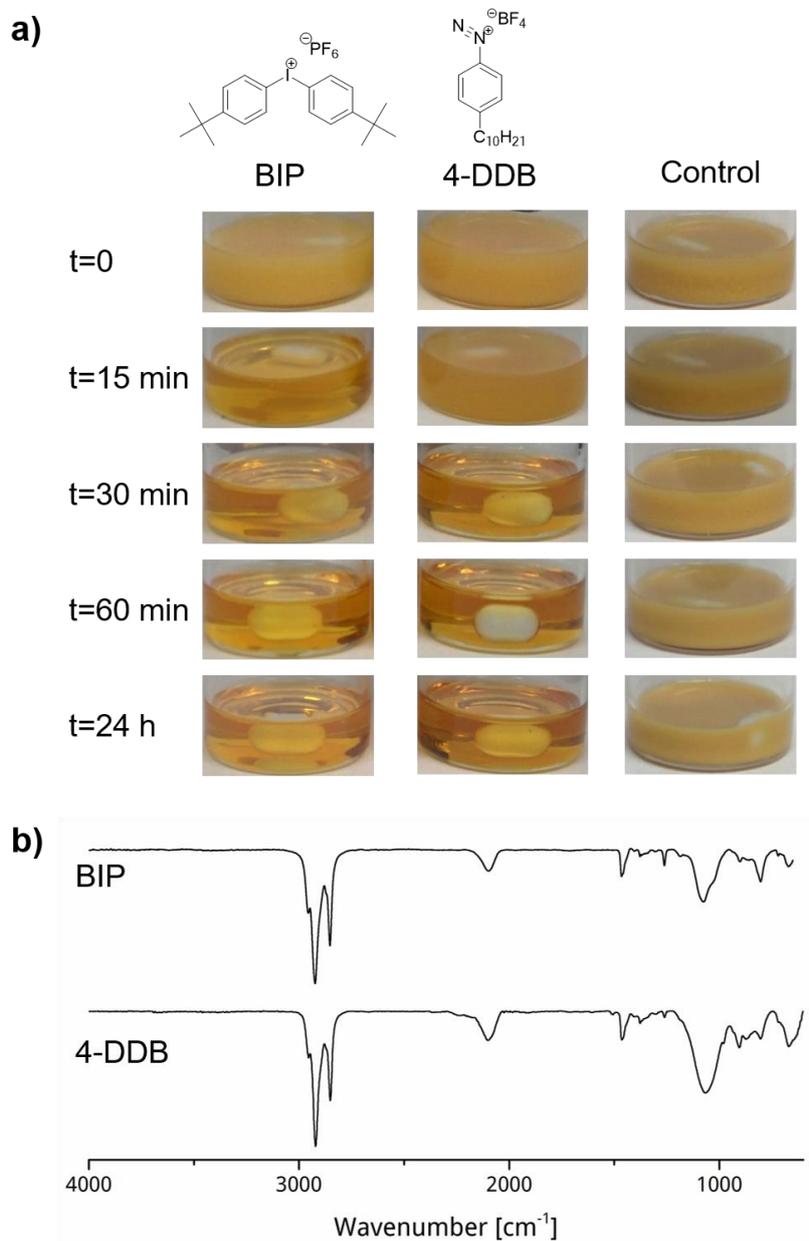


Fig. S1 a) Time and initiator dependent functionalization of SiNCs with 1-dodecene. Left: BIP initiated hydrosilylation in chloroform. Middle: DDB initiated reaction in toluene. Right: Control reaction in chloroform without any initiator. b) IR spectra of SiNCs-C₁₀H₂₅ initiated with BIP and DDB respectively show smaller Si-H bands as well as Si-O bands.

NMR of SiNC-C₁₂H₂₅

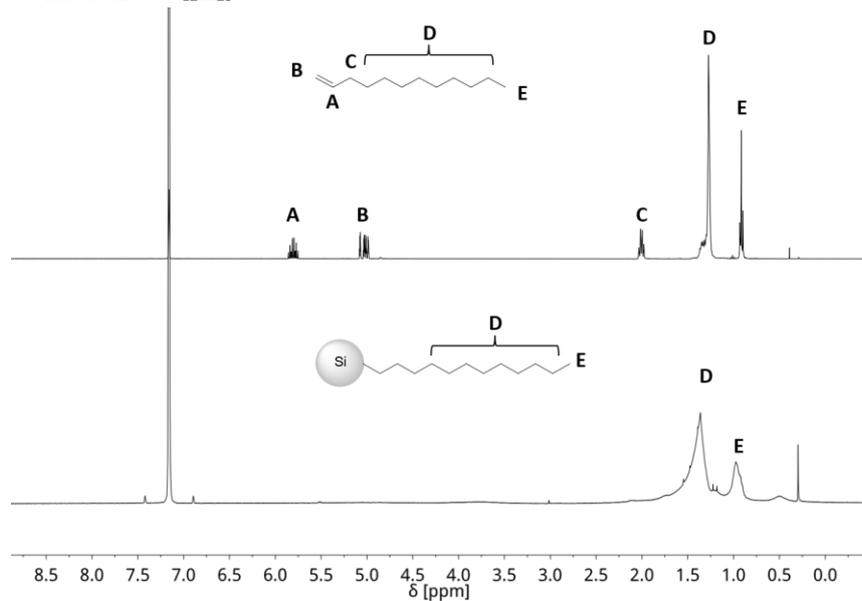


Fig. S2 NMR spectrum (CDCl₃, 300 K) of 1-dodecene (top) and SiNC-C₁₂H₂₅ (bottom).

Dynamic Light Scattering Data of functionalized SiNCs

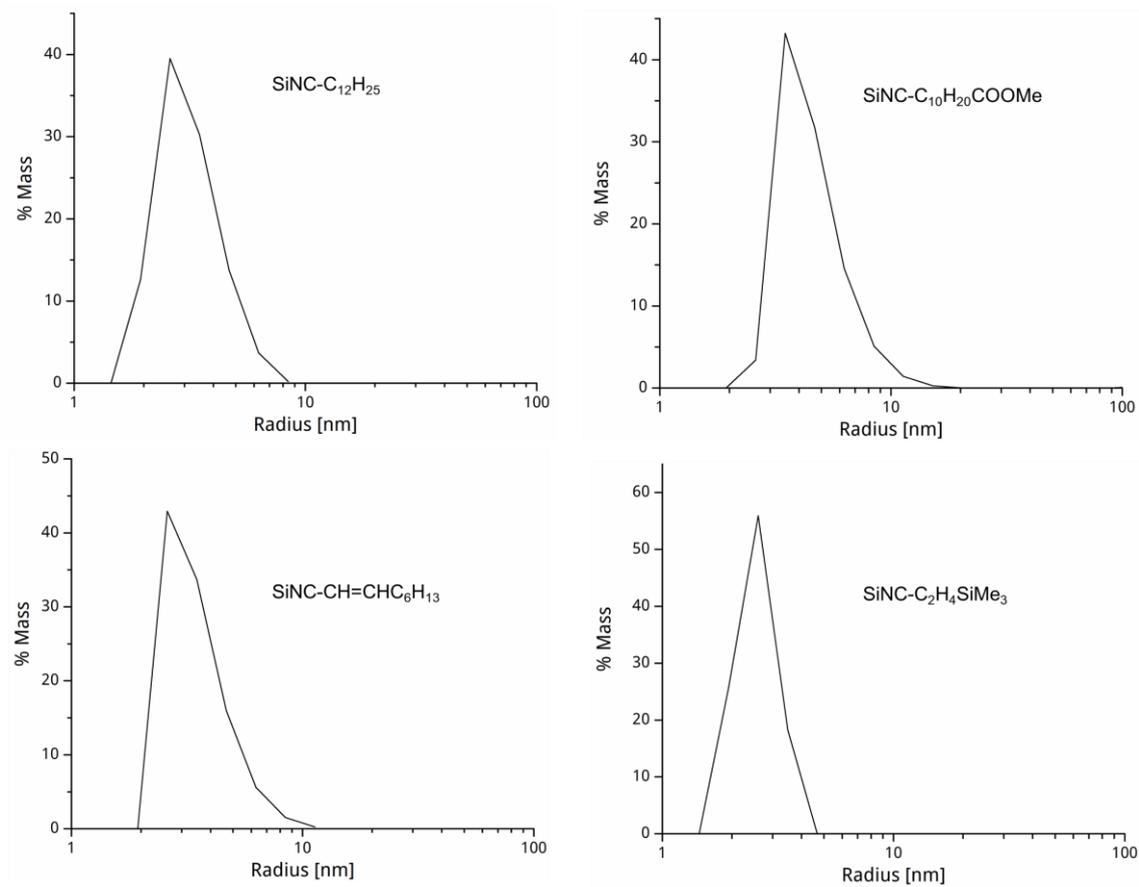


Fig. S3 DLS data of functionalized 3 nm SiNCs.

Table S1 Hydrodynamic radii with polydispersities of the different functionalized SiNCs (d = 3 nm) by diaryliodonium induced hydrosilylation determined with DLS measurement.

Substrate	Hydrodynamic radius [nm]	Polydispersity [%]
dodecene	3.1	32.1
methyl 10-undecenoate	4.3	35.6
octyne	3.9	28.4
trimethylvinylsilane	2.3	32.9

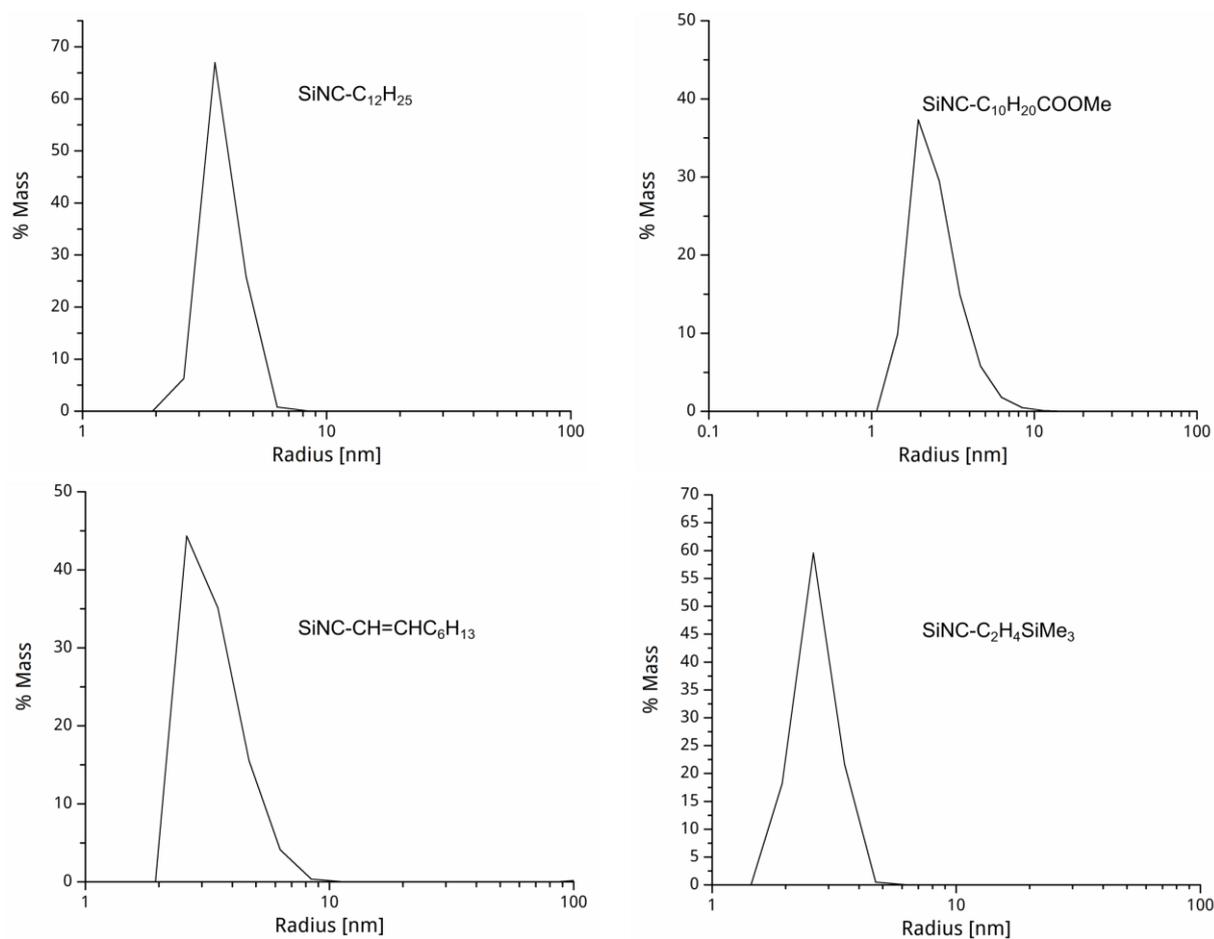


Fig. S4 DLS data of functionalized 5 nm SiNCs.

Table S2 Hydrodynamic radii with polydispersities of the different functionalized SiNCs (d = 5 nm) by diaryliodonium induced hydrosilylation determined with DLS measurement.

Substrate	Hydrodynamic radius [nm]	Polydispersity [%]
dodecene	3.5	22.3
methyl 10-undecenoate	2.3	51.5
octyne	3.5	22.3
trimethylvinylsilane	2.5	26.7

IR Spectra of Functionalized 5 nm SiNCs

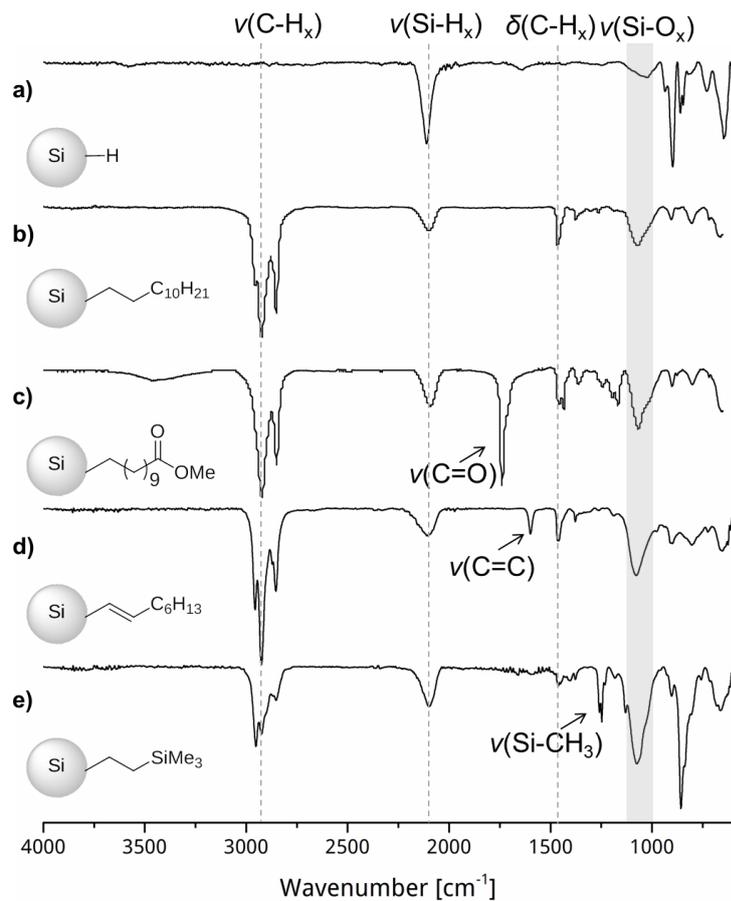


Fig. S5 IR spectra of SiNCs (5nm): a) hydride terminated, b) SiNC-C₁₂H₂₅, c) SiNC-C₁₀H₂₀COOMe, d) SiNC-CHCH-C₆H₁₃, e) SiNC-C₂H₄SiMe₃.

Iodonium Salts as Functionalization Initiators for Silicon Nanosheets (SiNSs)

FTIR Measurements of functionalized SiNSs

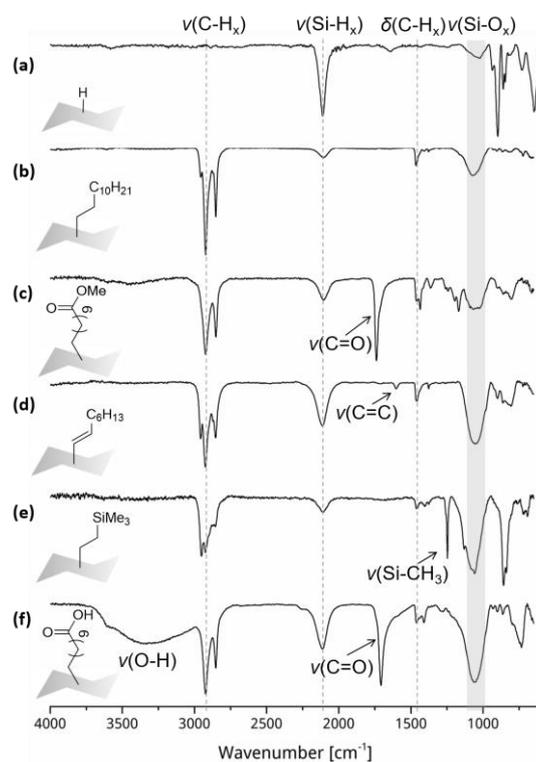


Fig. S6 FTIR spectra of freshly etched SiNSs (a) freshly etched, (b) dodecene functionalized SiNS-C₁₂H₂₅, (c) methyl 10-undecenoate functionalized SiNS-C₁₀H₂₀COOMe, (d) octyne functionalized SiNS-CH=CHC₆H₁₃, (e) vinyltrimethylsilane functionalized SiNSs-C₂H₂SiMe₃ and (f) undecenoic acid functionalized SiNSs-C₁₀H₂₀-COOH.

Visualization of SiNSs Dilution

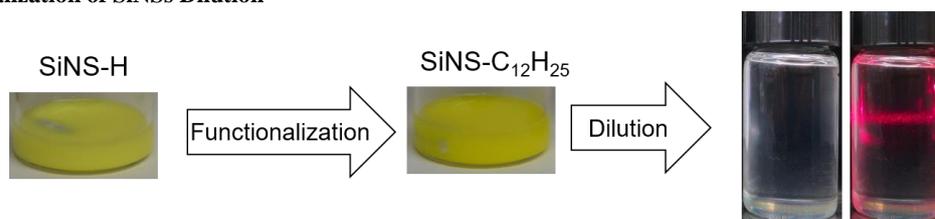


Fig. S7 Functionalization of SiNSs with 1-dodecene in concentrated dispersions only leads to clear dispersions when the reaction mixture is further diluted. When irradiated with a laser (here: red laser pointer), a Tyndall effect is visible due to the presence of the SiNSs.

Material Dependent Comparison of Reactivity

TGA Measurements of Functionalized SiNMs

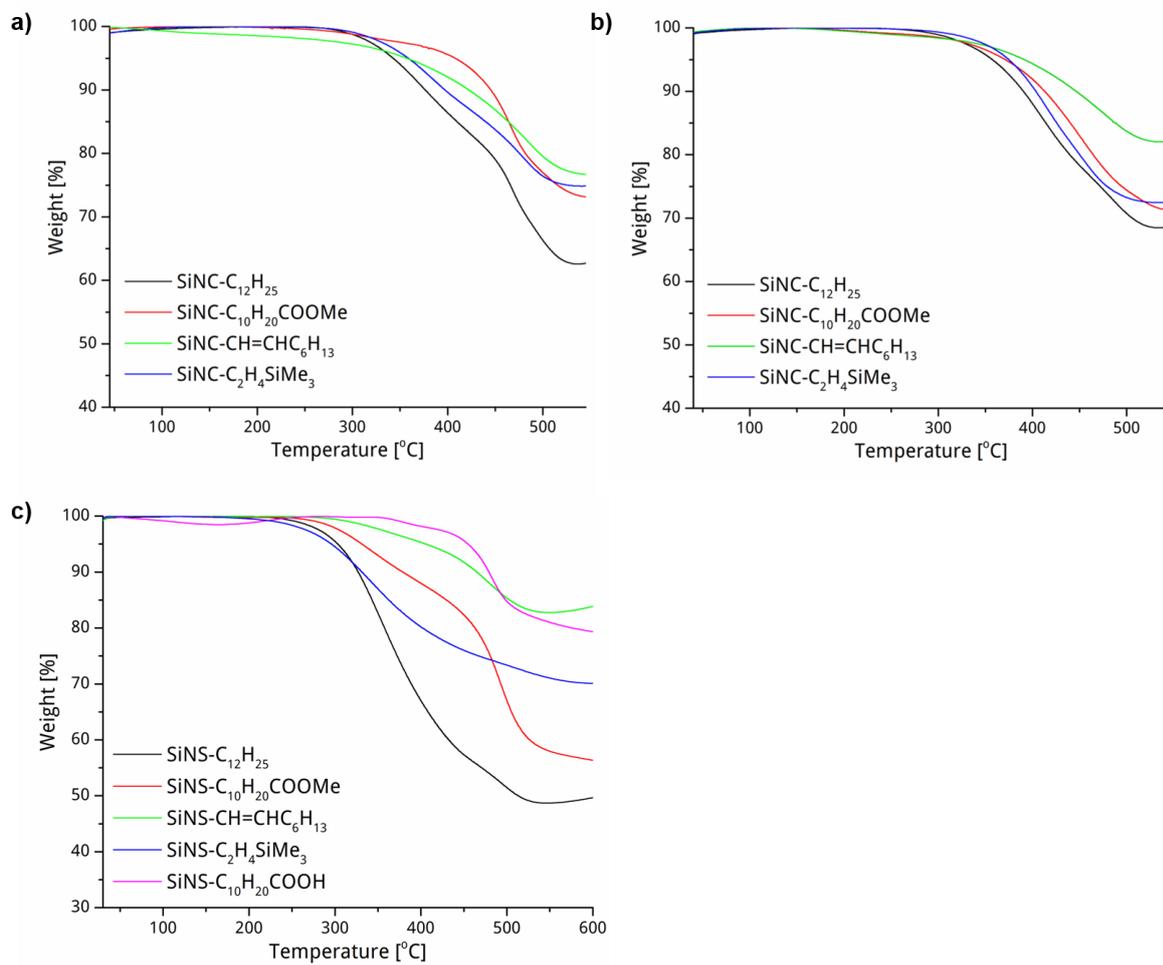


Fig. S8 TGA data of functionalized SiNCs with diameters of a) 3 nm and b) 5 nm and c) SiNSs.

Table S3 TGA data from functionalized SiNCs and SiNSs.

SiNM	Substrate	Molecular Weight	Weight loss [%]	Weightloss/ molecular weight
SiNC 3 nm	Dodecene	168.3	36.3	0.22
SiNC 3 nm	Methyl 10-undecenoate	198.3	26.4	0.13
SiNC 3 nm	Octyne	110.2	23.3	0.21
SiNC 3 nm	Trimethylvinylsilane	100.2	25.1	0.25
SiNC 5 nm	Dodecene	168.3	30.6	0.18
SiNC 5 nm	Methyl 10-undecenoate	198.3	28.6	0.14
SiNC 5 nm	Octyne	110.2	17.9	0.16
SiNC 5 nm	Trimethylvinylsilane	100.2	26.3	0.26
SiNS	Dodecene	168.3	51	0.30
SiNS	Methyl 10-undecenoate	198.3	45.1	0.23
SiNS	Octyne	110.2	17.2	0.16
SiNS	Trimethylvinylsilane	100.2	29.9	0.30
SiNS	Undecenoic acid	184.3	22.7	0.12

To get comparable values of how many molecules are on the surface, Table S1 shows the ratio of weight loss/molecular weight of the attached organic substrates. The substrates seem to have the same reactivity towards SiNCs of different sizes as can be seen by the same trend in weight loss (trimethylvinylsilane < dodecene < octyne methyl < 10-undecenoate).

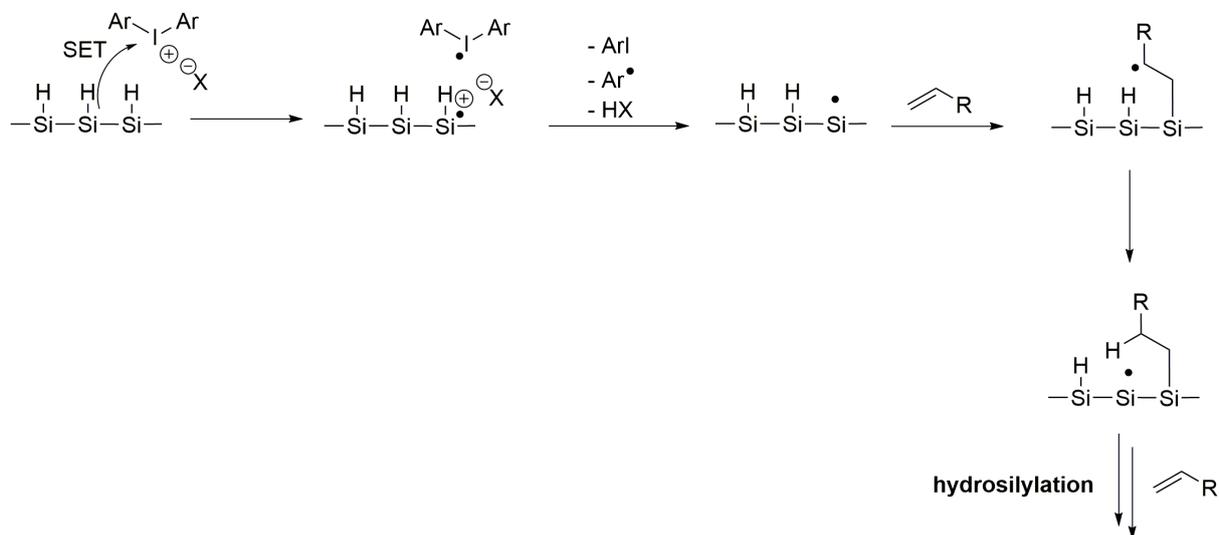
Mechanistic Considerations

As a potential mechanism for the diaryliodonium salt initiated hydrosilylation, we suggest a reaction scheme similar to the decomposition of diazonium salts induced by a single-electron transfer (SET). This concept is based on the accepted mechanisms of the molecular iodonium initiated polymerization^{6,7} and the decomposition of diazonium salts in the presence of SiNMs^{3,4,8}:

Diazonium salts can be electrochemically grafted on flat bulk silicon. The power source provides electrons that reduce the diazonium compound and lead to surface grafting.⁹ For silicon nanomaterials, no further bias is necessary to activate the diazonium salt. A spontaneous SET from the nanomaterial to the diazonium compound leads to the cleavage of nitrogen and the generation of an aryl radical.^{3,4,8} The SET additionally leaves the silicon surface activated (*i.e.*, hole). In the presence of unsaturated substrates these activated species then react *via* radical induced hydrosilylation, leading to the surface functionalization of the SiNMs.

Diaryliodonium salt initiated (molecular) polymerization reactions are generally induced by UV light and the subsequent decomposition of the iodonium salt to free aryl radicals and cation-radicals. The cation-radicals further decompose to generate an acidic proton, which initiates the cationic polymerization.^{6,7} Additionally, Crivello *et al.* could show that a reducing agent, such as ascorbic acid or triethylsilane, in combination with a catalyst, Cu(II) or Pt, reduces the diaryliodonium salt in redox initiated cationic polymerizations with diaryliodonium compounds, resulting in the formation of a strong acid, HMTX_n, which subsequently initiates cationic polymerizations.^{10,11}

For **diaryliodonium salt induced surface functionalizations** of silicon nanomaterials a combination of these two mechanisms might explain the proceeding reaction. An electron is transferred from the nanomaterial to the iodonium salt *via* SET. Subsequently the diaryliodonium radical decomposes to iodobenzene and a phenyl radical. Both compounds can be detected in NMR measurements, underlining the proposed mechanism. The cationic surface proton is abstracted by the counter ion X⁻ of the iodonium salt. In the next step, the thus formed surface silyl radical undergoes hydrosilylation with unsaturated substrates as generally accepted for radical induced surface functionalizations of silicon (nano)materials.^{3,4,8}



Scheme S1 Schematic of the potential mechanism for the diaryliodonium salt initiated hydrosilylation: An electron is transferred from the nanomaterial to the iodonium salt *via* a single-electron transfer (SET). Subsequently the diaryliodonium radical decomposes to iodobenzene and a phenyl radical (as known for UV induced iodonium salt decompositions), while the cationic surface proton is abstracted from the counter ion X⁻ of the iodonium salt. In the next step, the silyl radical undergoes hydrosilylation with unsaturated substrates as generally accepted for radical induced surface functionalizations of silicon (nano)materials.

Cationic Ring Opening Polymerizations Induced by Si Nanomaterial/Diaryliodonium Salt Initiators

PL Spectrum of SiNS@pTHF Composite

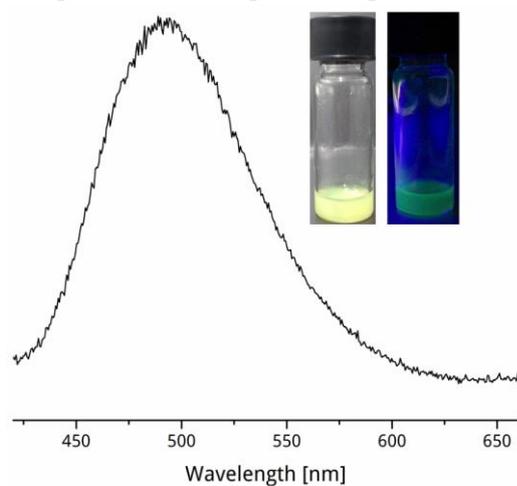


Fig. S9 PL spectrum of SiNS@pTHF and pictures taken under visible (left) and UV light (right).

IR Spectra of SiNS@pTHF Composite

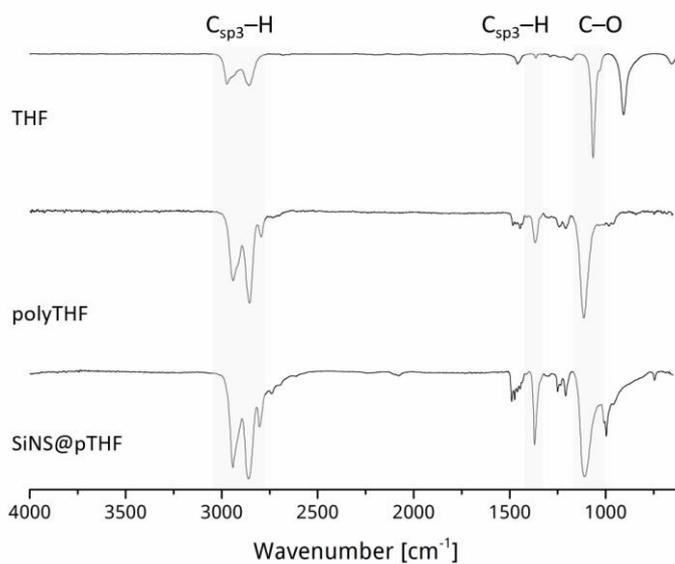


Fig. S10 FTIR spectra of (a) the monomer THF, (b) pTHF, (c) SiNS@pTHF.

NMR Spectra of SiNS@pTHF Composite

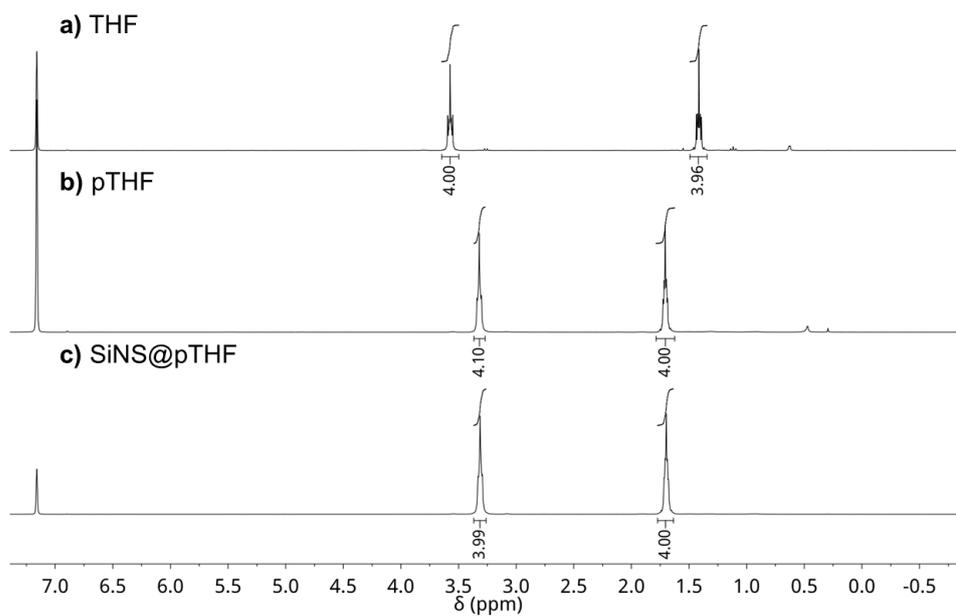


Fig. S11 NMR spectra of (a) the monomer THF, (b) pTHF, (c) SiNS@pTHF in CDCl_3 .

EDX Spectrum of SiNS@pTHF Composite

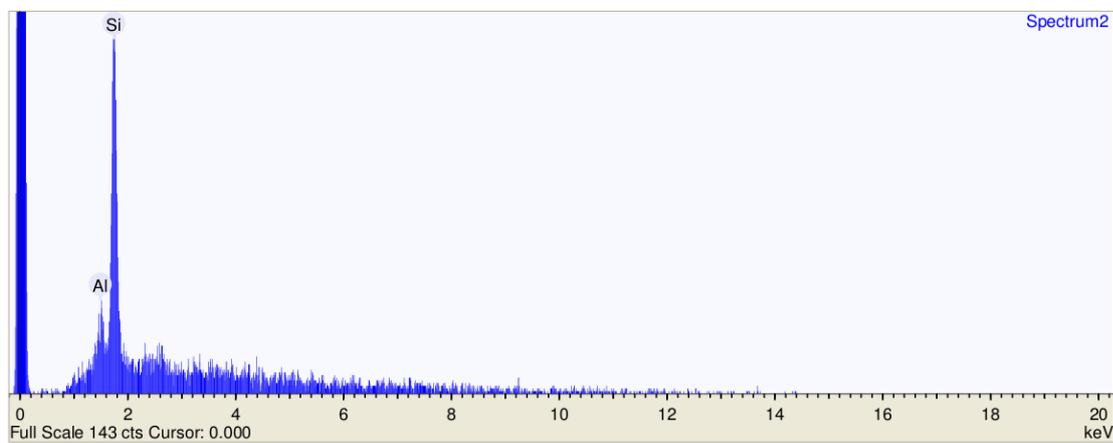


Fig. S12 EDX spectrum of SiNS@pTHF. *elements starting with Na can be detected with the instrument. Aluminum is present from the sample holder.

GPC Measurements of SiNS@pTHF Composite

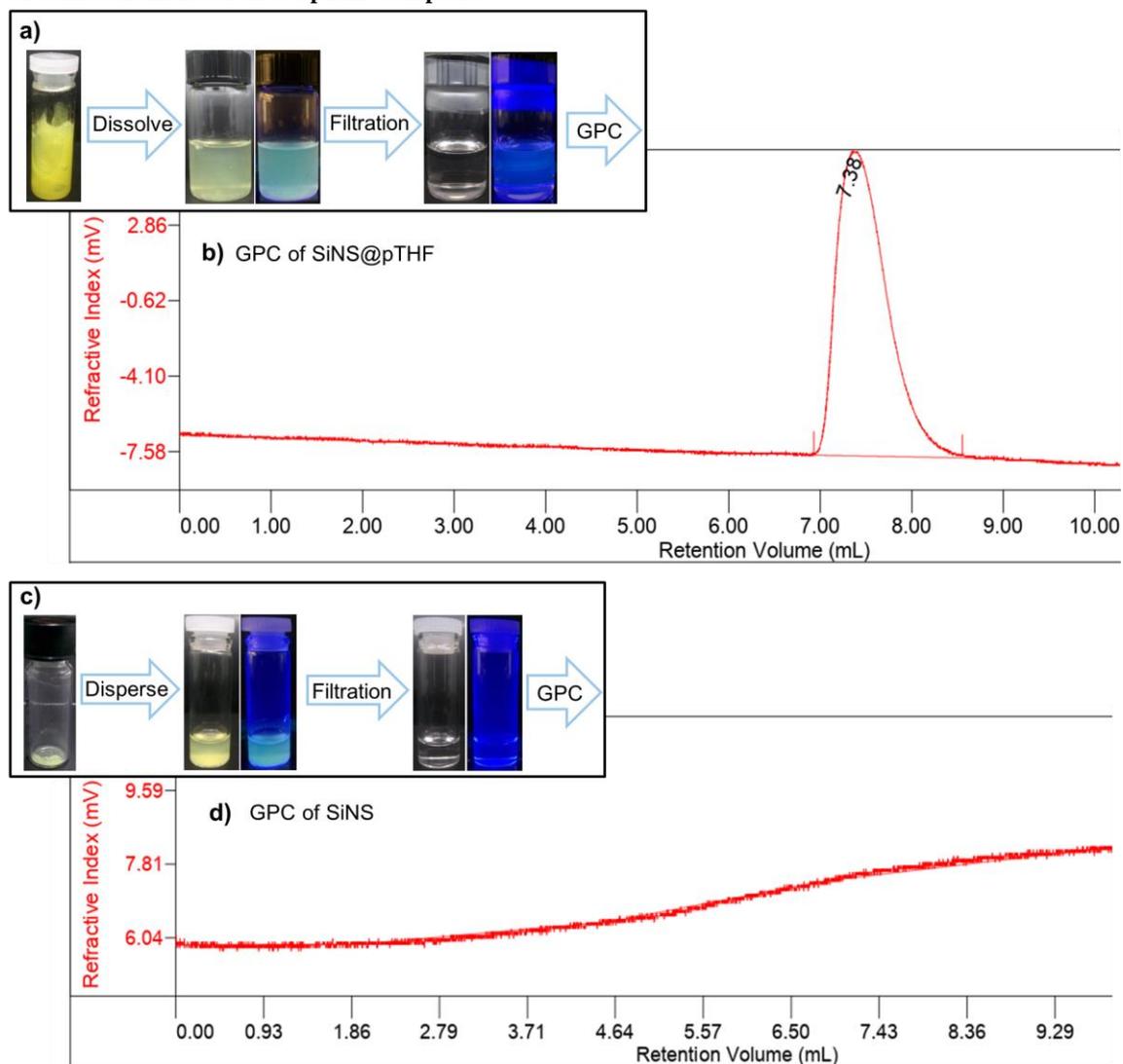


Fig. S13 GPC was performed to confirm successful separation of the polymer matrix and SiNSs. a) The solid SiNS@pTHF is dissolved in THF to render slightly yellow dispersions (left) which show PL under UV light (right). Before GPC measurements, the SiNSs (agglomerates) are removed by filtration with a 450 nm PTFE syringe filter, confirmed by loss of the characteristic yellow color (left) and absence of PL (right). b) GPC data of the filtered nanocomposite shows the signal of the polymer matrix surrounding the inorganic SiNSs. c) After removal of the pTHF matrix by centrifugation in THF, the residual SiNSs are dispersed in THF rendering yellow dispersions (left) which still exhibit PL under UV light (right). After filtration of the SiNSs (agglomerates), the clear solvent shows no characteristic yellow color anymore (left) and without the SiNSs, no PL can be detected under UV light (right). d) GPC data of the filtered nanosheet dispersion in THF shows the successful separation of the polymer matrix by the workup procedure as no signal is detected.

Analytics of Residual SiNSs after Removal of pTHF Matrix

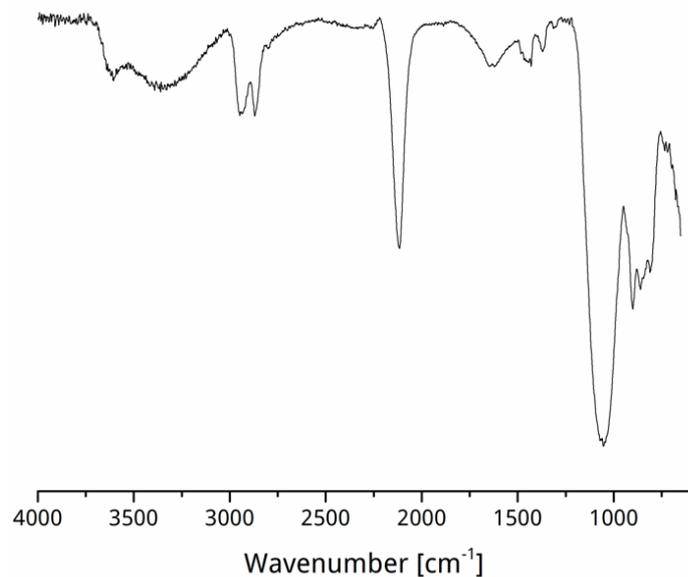


Fig. S14 FTIR spectrum of the residual SiNSs from the nanocomposite SiNS@pTHF after removal of pTHF by centrifugation show no functionalization.

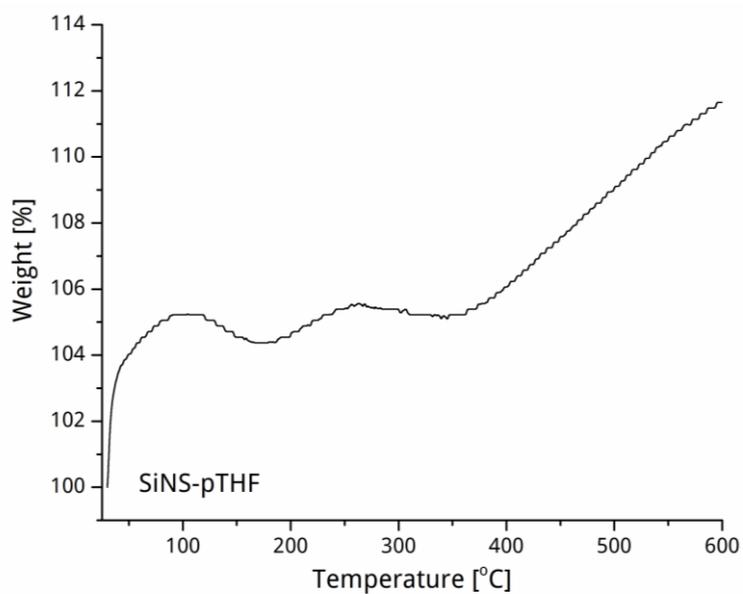


Fig. S15 TGA of the residual SiNSs after removal of pTHF by centrifugation show no weight loss corresponding to no functionalization. Most likely the gain in weight arises from minor oxidations by oxygen impurities in the carrier gas.

SiNC@pTHF Nanocomposites

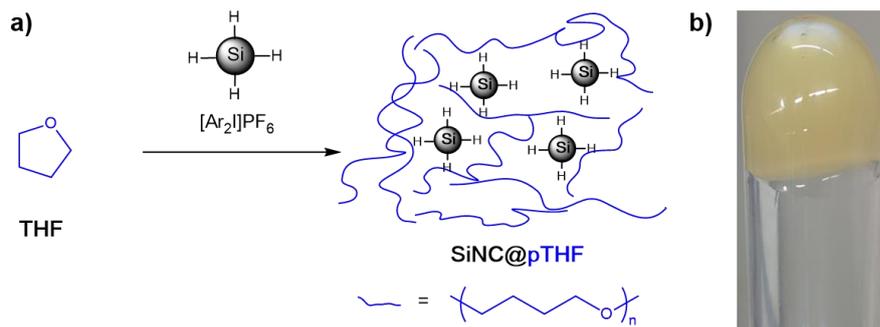


Fig. S16 a) Schematic of the SiNC/BIP initiated cationic ring opening polymerization of THF leading to the SiNC@pTHF nanocomposite. b) Picture of the turbid SiNC@pTHF nanocomposite after the reaction. Functionalized SiNCs render clear dispersions, especially when covered with long polymer chains. The consistency therefore suggests that the SiNCs are not functionalized, but merely initiate the polymerization.

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