**Supplementary Information** 

# *In-Situ* IR-Spectroscopy as Tool for Monitoring the Radical Hydrosilylation Process on Silicon Nanocrystal Surfaces

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# Content

1.	Experim	ental Procedures	3
	1.1.	Material Characterization and Instrumentation	3
	1.2.	Synthetic Procedures	4
	1.2.1.	SiNC Preparation and Functionalization	4
	1.2.1.1.	Synthesis of Polymeric Hydrogen Silsesquioxane (HSQ)	4
	1.2.1.2.	Preparation of the SiNC Composite Material	4
	1.2.1.3.	Liberation of SiNCs	4
	1.2.1.4.	Preparation of Functionalized SiNCs for Characterization	4
	1.2.1.5.	In-situ IR Monitoring of SiNC Functionalizations	5
	1.2.2.	Preparation of Vinylsilanes	5
	1.2.2.1.	Tris(trimethylsilyl)vinylsilane	5
	1.2.2.2.	1,1,1,3,3,-Pentamethyl-3-vinyldisiloxane	6
	1.2.2.3.	Triphenylvinylsilane	6
2.	Analysis	3	7
	2.1.	Characterization of SiNCs	7
	2.2.	Surface Coverage	8
	2.3.	Determination of the Radical Efficiency	8
3.	Figures.		9
4.	Tables		14
Ref	erences		19

## **1. Experimental Procedures**

#### 1.1. Material Characterization and Instrumentation

*X-ray photoelectron spectroscopy* (XPS) measurements were obtained using a Kratos Axis Ultra X-ray photoelectron spectrometer operated in energy spectrum mode at 210 W. XPS samples were prepared as a film drop-cast from SiNC toluene dispersion onto a copper foil substrate. Spectra were fit using CasaXPS (VAMAS) software and were calibrated to the lowest binding energy component of the C 1s emission at 284.8 eV.

*Transmission electron microscopy* (TEM) was performed on a JEOL-2010 (LaB6 filament) electron microscope with an accelerating voltage of 200 keV using samples of SiNCs drop-cast onto a holey carbon-coated copper grid (300 mesh, Electron Microscopy Science). High-resolution (HR) TEM images were obtained from Hitachi-9500 electron microscope with an accelerating voltage of 300 kV. The HRTEM images were processed using Gatan Digital Micrograph software (Version 2.02.800.0) and Image J.

*Photoluminescence* (PL) spectra were recorded using an AVANTES, AVA-Spec 2048 spectrometer with a Prizmatix Current Controller as 365 nm light source. The measurements were performed using a 90° cuvette holder and a 40 mm x 10 mm  $\times$  2 mm quartz glass cuvette using toluene as solvent. Intensity calibration of the spectrometer was performed by an AVANTES DH-Cal calibration light source using the halogen lamp.

*Dynamic light scattering* (DLS) was obtained on a DynaPro NanoStar using a Quartz cuvette. Samples were purified by centrifugation and filtrated via a syringe filter before the measurement. For measurements and analysis the software Dynamics V7 was used. One measurement consists of a statistic analysis of the results of five single measurements which were performed using 20 acquisitions à 5 seconds acquisition time. Cumulant analysis was implemented on the autocorrelation function for the analysis of the measurements. Temperature resolved measurements were obtained by heating from 20 to 80 °C at a heating rate of 2 °C with ongoing measurements using 5 acquisitions à 5 s, each.

*Elemental analysis* (EA) was performed in the microanalytic laboratory of the department for inorganic chemistry of the Technical University München using a vario EL cube analyzer from Elementar.

*Gas chromatography* (GC) was obtained on an Agilent 6890 using a HP-5 column and helium as carrier gas. Mass detection was conducted with a Agilent Network Mass Selective Detector (70 eV).

*Nano assisted laser desorption ionization* (NALDI) measurements were conducted on a Bruker Ultra Flex TOF/TOF. Samples were prepared by dip coating of the SiNC dispersions on the MALDI target. Measurements were performed in the linear positive or negative mode.

<sup>1</sup>*H*, <sup>13</sup>*C* and <sup>29</sup>*Si* Nuclear Magnetic Resonance (NMR) spectra were obtained on an Avance /// 300 MHz and a Avance /// 500 MHz spectrometer at 300 K. Signals are normalized to the solvents (CDCl<sub>3</sub>: <sup>1</sup>H:  $\delta = 7.26$  ppm, <sup>13</sup>C  $\delta = 77.2$  ppm; CD<sub>2</sub>Cl<sub>2</sub> <sup>1</sup>H:  $\delta = 5.32$  ppm, <sup>13</sup>C  $\delta = 54.0$  ppm; benzene-d<sub>6</sub> <sup>1</sup>H:  $\delta = 7.16$  ppm, <sup>13</sup>C  $\delta = 128.1$  ppm).

#### **1.2. Synthetic Procedures**

#### 1.2.1. SiNC Preparation and Functionalization

#### 1.2.1.1. Synthesis of Polymeric Hydrogen Silsesquioxane (HSQ).

The synthesis follows a literature-based procedure.<sup>1</sup> Toluene (45 mL) is added dropwise over 10 min to a mixture of sulfuric acid (22.7 g) and fuming sulfuric acid (13.9 g). After stirring for 20 min, trichlorosilane (21.5 g, 0.16 mol) dissolved in 110 mL toluene is added dropwise. Afterwards, the upper layer is separated and washed for three times with 50wt% sulfuric acid and stirred over night with MgSO<sub>4</sub> and CaSO<sub>4</sub>. After filtration and drying in vacuum, the product remains as colorless solid.

#### 1.2.1.2. Preparation of the SiNC Composite Material.

The preparation follows a literature-based procedure.<sup>2</sup> Previously prepared HSQ is placed in a quartz reaction boat and heated to 1100 °C over 1 h and afterwards kept at this temperature for 1 h under reducing atmosphere (4%  $H_2/96\%$  N<sub>2</sub>). After cooling to room temperature, the obtained composite material was ground and transferred to a wrist-action shaker with glass beads and EtOH for 20 h.

#### 1.2.1.3. Liberation of SiNCs.

Liberation of SiNCs follows a literature-based procedure.<sup>2</sup> Per 100 mg of the SiNC composite material 3 mL of a 1:1.1 mixture of ethanol, water and HF (48-51%) are added. The mixture is stirred for 30 min at room temperature using a stirrer speed of 200 min<sup>-1</sup>. Subsequently, the yellow dispersion of hydride terminated SiNCs is extracted for 3 times using toluene, transferred to centrifuge tubes and centrifuged for 2 min at 9000 min<sup>-1</sup>. After centrifugation, the pellet is redispersed in toluene, molecular sieves (3 Å) are added and the dispersion is transferred to a new centrifuge tube prior to centrifugation. The pellet is redispersed in 1 mL of dry toluene (related to 100 mg composite material) and can be used for reactions thereafter.

#### 1.2.1.4. Preparation of Functionalized SiNCs for Characterization.

SiNCs obtained from 400 mg composite material are redispersed in 4 mL of toluene and mixed with 9.56 mmol vinylsilane in a Schlenk tube. Afterwards, the concentration is adjusted to 1.26 mmol/mL and a maximum volume of 7.2 mL is obtained by the addition of toluene. The reaction mixture is then degassed *via* three freeze-pump-thaw cycles and after addition of 8 mg (48.8  $\mu$ mol) AIBN heated to 70°C for 16-36 h dependent on the monomer. The detailed reaction conditions are given in Table S1. Three times precipitation from methanol, centrifugation (9000 min<sup>-1</sup>, 10 min) and redispersion in toluene yields the final SiNC dispersion. To obtain a dry SiNC sample (e.g. for TGA measurements) the precipitate is redispersed in benzene and subsequently freeze dried.

*Trimethylvinylsilane-SiNCs* (*TMVS-SiNCs*). IR v [cm<sup>-1</sup>] 2955 (s), 2900 (m), 2083 (st, SiH), 1404 (w), 1248 (s), 1129 (s), 860 (s). EA (%) C 23.99, H 5.51, TGA [%] 25. DLS R<sup>h</sup> [nm]  $3.8 \pm 1.0$ . PL  $\lambda$  [nm] 716.

*Ethoxydimethylvinylsilane-SiNCs (EDMVS-SiNCs).* IR v [cm<sup>-1</sup>] 2922 (sst), 2853 (st), 2072 (w, SiH), 1742 (w), 1658 (w), 1633 (w), 1459 (m), 1377 (w), 1257 (m), 1107 (m), 1079 (m), 944 (w), 840 (m). EA (%)C 12.78, H 3.07.TGA [%] 22. DLS R<sup>h</sup> [nm]  $3.2 \pm 0.6$ . PL  $\lambda$  [nm] 729.

*Triethoxyvinylsilane-SiNCs (TEVS-SiNCs).* IR v [cm<sup>-1</sup>] 2972 (st), 2926 (st), 2890 (st), 2087 (m, SiH), 1448 (w), 1391 (m), 1245 (m), 1078 (s), 951 (s), 767 (s), 653 (m). EA (%) C 14.60, H 3.10.TGA [%] 27. DLS R<sup>h</sup> [nm]  $3.7 \pm 0.8$ . PL  $\lambda$  [nm] 704.

*Dimethylphenylvinylsilane-SiNCs (DMPVS-SiNCs).* IR v [cm<sup>-1</sup>] 3067 (w), 3049 (w), 2923 (s), 2853 (s), 2079 (m, SiH), 1463 (m), 1427 (m), 1377 (m), 1248 (m), 832 (s), 812 (s), 726 (m), 699 (m). EA (%) C 37.16, H 5.15.TGA [%] 32. DLS R<sup>h</sup> [nm]  $3.0 \pm 0.7$ . PL  $\lambda$  [nm] 727.

$$\label{eq:sinces} \begin{split} &\textit{Triphenylvinylsilane-SiNCs} (\textit{TPVS-SiNCs}). \ IR \ v \ [cm^{-1}] \ 3068 \ (m), 2923 \ (s), 2853 \ (s), 2087 \ (s, SiH), 1957 \\ (w), 1884 \ (w), 1819 \ (w), 1738 \ (w), 1662 \ (w), 1568 \ (w), 1460 \ (m), 1428 \ (s), 1261 \ (m), 1109 \ (s), 1056 \\ (s), 910 \ (m), 804 \ (m), 725 \ (s), 669 \ (s), 645 \ (s). \ EA \ (\%) \ C \ 44.15, H \ 4.26.TGA \ [\%] \ 28. \ DLS \ R^h \ [nm] \ 2.8 \ \pm 1.1. \ PL \ \lambda \ [nm] \ 711. \end{split}$$

1,1,1,3,3-Pentamethyl-3-vinyldisiloxane-SiNCs (PMVDS-SiNCs). IR v [cm<sup>-1</sup>] 2955 (s), 2923 (s), 2853 (s), 2082 (m, SiH), 1458 (m), 1409 (m), 1252 (s), 1129 (m), 1043 (s), 840 (s), 801 (s), 755 (s), 686 (m). EA (%) C 24.55, H 5.91. TGA [%]32. DLS R<sup>h</sup> [nm]  $3.8 \pm 0.9$ . PL  $\lambda$  [nm] 722.

$$\label{eq:sinces} \begin{split} &\textit{Tris(trimethylsiloxy)vinylsilane-SiNCs (TTMSVS-SiNCs). IR $v$ [cm^{-1}] 2955 (s), 2923 (s), 2853 (s), 2096 (m, SiH), 1741 (w), 1633 (w), 1463 (s), 1251 (s), 1096 (s), 1055 (s), 843 (s), 758 (s), 683 (m). EA (\%) C 20.53, H 5.10. TGA [\%] 23. DLS $R^h$ [nm] 3.1 $\pm$ 1.0. PL $\lambda$ [nm] 713. \end{split}$$

*Hexene-SiNCs.* IR v [cm<sup>-1</sup>] 2956 (s), 2923 (s), 2854 (s), 2074 (m, SiH), 1465 (m), 1260 (m), 1043 (m), 797 (m), 674 (m).EA (%) C 28.73, H 5.39. TGA [%] 29. DLS R<sup>h</sup> [nm]  $2.9 \pm 0.7$ . PL  $\lambda$  [nm] 735.

 $\begin{array}{l} \textit{Dodecene-SiNCs. IR v [cm^{-1}] 2956 (s), 2922 (s), 2852 (s), 2078 (w, SiH), 1466 (m), 1377 (w), 1026 (w), \\ \textit{801 (w), 674 (m). EA (\%) C 37.69, H 6.94. TGA [\%] 41. DLS R^h [nm] 3.3 \pm 0.9. PL \lambda [nm] 735. \end{array}$ 

#### 1.2.1.5. In-situ IR Monitoring of SiNC Functionalizations

*In situ* IR monitoring of SiNC functionalization is performed according to the procedure given in the main manuscript. The detailed reaction conditions for the experiments are given in table S2.

#### **1.2.2.** Preparation of Vinylsilanes

1.2.2.1. Tris(trimethylsilyl)vinylsilane

The synthesis follows a literature-based procedure.<sup>3</sup> 37.8 mL hexamethyldisiloxane (28.7 g, 177 mmol, 2.21 eq), 10.1 mL methanol (9.23 g, 288 mmol, 3.6 eq) and 10.9  $\mu$ L trifluoromethanesulfonic acid (18.6 mg, 124  $\mu$ mol) are stirred at 45 °C and 15.9 mL tri(acetoxy)vinylsilane (18.6 g, 90.0 mmol, 1 eq) are added dropwise over 30 min. After further stirring for 30 min, 9.42 g acetic anhydride (84.0 mmol, 1.05 eq) are added and the mixture is stirred for another 30 min at 45 °C. After cooling to room temperature, CaCO<sub>3</sub> is added and the reaction mixture filtered. Afterwards, volatile compounds are removed under reduced pressure (80.5 °C, 15 mbar) and the product is purified by column chromatography over silica using pentane as solvent (R<sup>f</sup>=0.46).18.8 g of the product (73 %) are obtained as colorless liquid.

<sup>1</sup>**H-NMR** (500 MHz,  $C_6D_6$ , 300 K):  $\delta$  (ppm) = 6.12 – 5.81 (m, 3H, CH=CH<sub>2</sub>), 0.20 (s, 27H, Si-CH<sub>3</sub>).

<sup>13</sup>C-NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  (ppm) = 134.0, 133.5, 1.5.

<sup>29</sup>Si-NMR (99 MHz,  $C_6D_6$ , 300 K):  $\delta$  (ppm) = 8.4, -78.2.

GC-MS (toluene): 309 [M-CH<sub>3</sub>]<sup>+</sup>.

1.2.2.2. 1,1,1,3,3,-Pentamethyl-3-vinyldisiloxane

The synthesis is based on a literature known procedure.<sup>4</sup> 9.42 g sodium-trimethylsilanolate (84.0 mmol, 1.05 eq) are solved in 200 mL diethylether. A solution of 9.65 g chloro(dimethylvinylsilane) (80 mmol, 1.00 eq) in 50 mL diethylether is added dropwise. Afterwards, the reaction mixture is stirred for 3 h under reflux. After cooling to room temperature hydrochloric acid (aq. 2wt%) is added. The organic layer is then separated and the water phase extracted with diethylether. After drying of the organic phase with magnesiumsulfate, diethylether is removed in vacuum. Purification is achieved *via* column chromatography using silica gel and pentane ( $R^f = 0.63$ ). 5.72 g (41%) of the product are obtained as colorless liquid.

<sup>1</sup>**H-NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  (ppm) = 6.19 (dd, <sup>3</sup>J = 20.4, 14.8 Hz, 1H, CH=CH<sub>2</sub>), 5.91 (dd, <sup>2</sup>J = 3.9 Hz, <sup>3</sup>J = 14.8 Hz, 1H, CH=CH<sub>2</sub>), 5.76 (dd, <sup>2</sup>J = 3.9 Hz, <sup>3</sup>J = 20.4 Hz, 1H, CH=CH<sub>2</sub>), 0.19 (d, <sup>2</sup>J<sub>Si-H</sub> = 3.6 Hz, 6H, Si-CH<sub>3</sub>), 0.12 (d, <sup>2</sup>J<sub>Si-H</sub> = 3.0 Hz, 9H, Si-CH<sub>3</sub>).

<sup>13</sup>C-NMR (126 MHz,  $C_6D_6$ , 300 K):  $\delta$  (ppm) = 68.7, 60.7, -69.0, -70.5.

<sup>29</sup>Si-NMR (99 MHz,  $C_6D_6$ ):  $\delta$  (ppm) = 8.1, -4.0.

**GC-MS** (toluene): 171 [M]<sup>+</sup>.

#### 1.2.2.3. Triphenylvinylsilane

The synthesis is based on literature known procedures.<sup>5–7</sup> 3.89 g (0.16 mmol, 3.10 eq) magnesium powder are dispersed in 20 mL THF. The Grignard formation is started by the addition of 1/10 of a solution of 16.8 mL phenylbromide (25.1 g, 0.16 mol, 3.10 eq) in 20 mL of THF. After the reaction has started, the rest of the solution is added dropwise to the reaction mixture. After the addition, the reaction mixture is stirred at room temperature for 15 min previous to refluxing for 1 h. Afterwards, 6.56 mL trichlorovinylsilane (8.33 g, 51.6 mmol, 1 eq) are added dropwise at 0°C. Then, the mixture is warmed to room temperature and stirred overnight under reflux. After cooling to room temperature again, the reaction is quenched by the addition of saturated ammonium chloride solution. The organic layer is

separated and the water phase is extracted with THF. The combined organic phases are dried using magnesium sulfate and the solvent is removed under reduced pressure. 5.91 g of the product (40%) are obtained in form of colorless crystals after recrystallization from methanol.

<sup>1</sup>**H-NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  (ppm) = 7.57 – 7.52 (m, 6 H<sub>arom</sub>), 7.47 – 7.42 (m, 3 H<sub>arom</sub>), 7.42 – 7.35 (m, 6 H<sub>arom</sub>), 6.74 (dd, 3J = 20.2, 14.7 Hz, 1H, CH<sub>2</sub>), 6.35 (dd, 1H, 3J = 14.6, 3.6 Hz, CH<sub>2</sub>), 5.81 (dd, 1H, 3J = 20.3, 3.6 Hz, CH).

<sup>13</sup>C-NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ (ppm) = 137.3, 136.4, 134.7, 134.3, 130.1, 128.4.

<sup>29</sup>Si-NMR (99 MHz,  $CD_2Cl_2$ , 300 K):  $\delta$  (ppm) = -17.5.

GC-MS (toluene): 286 [M]+.

### 2. Analysis

#### 2.1. Characterization of SiNCs

For monitoring the decay of the Si-H bond by *in-situ* IR, SiNC grafting with the various monomers was performed based on the procedure for 400 mg ground composite (*vide supra*) and the success of functionalization was proven using various analytical methods. All substrates yield clear SiNC dispersions (Figure S3 a) and show PL at about 715 nm (Figure S3 b). Furthermore, we found freestanding nanocrystals in TEM and could prove crystallinity using HR-TEM (lattice fringe 0.32 nm; Figure S4). SiNCs have medium hydrodynamic radii from 2.8 - 3.8 nm with monomodal distributions (Table S3; Figure S5).

The FTIR spectrum of H-SiNCs shows clear Si-H bands at 2099 cm<sup>-1</sup> (stretching modes, v) and 909 cm<sup>-1</sup> (bending vibrations, δ). The spectrum of functionalized NCs still exhibits these bands, albeit at a lower intensity (Figure S6), as well as C-H stretching at 2900-2990 cm<sup>-1</sup>, bending at 1404 cm<sup>-1</sup>, the Si-CH<sub>3</sub> umbrella mode at 1247 cm<sup>-1</sup> and a signal assigned to Si-C stretching at 960 cm<sup>-1</sup>. These features are consistent with successful surface grafting of the target TMVS moiety. For 1-hexene and 1-dodecene mainly C-H stretches (2950 - 2834 cm<sup>-1</sup>) and C-H bending (1455 cm<sup>-1</sup>) could be observed (Figure S8). The spectra of DMPVS and TPVS (Figure S9) furthermore show aromatic C-H stretches (3086 – 3007 cm<sup>-1</sup>), C-H bending (687 cm<sup>-1</sup>), aromatic C=C stretches (1589 cm<sup>-1</sup>, 1465 cm<sup>-1</sup> 1424 cm<sup>-1</sup>), as well as aromatic overtones and combination bands (1957 cm<sup>-1</sup>, 1886 cm<sup>-1</sup>, 1824 cm<sup>-1</sup>, 1737 cm<sup>-1</sup>, 1668 cm<sup>-1</sup>). DMPVS functionalized SiNCs additionally show the Si-CH<sub>3</sub> umbrella mode at 1243 cm<sup>-1</sup>. Similarly, spectra obtained for DMEVS-SiNCs and TEVS-SiNCs describe several C-H stretching modes. More important, sharp Si-O-C stretching modes at around 1071 cm<sup>-1</sup> confirm the grafting with ethoxysilane. PMVDS-SiNCs and TTMSVS-SiNCs (Figure S 11) show strong Si-O stretching modes at 1032 cm<sup>-1</sup>.

High resolution X-ray photoelectron spectroscopy (XPS) of the Si 2p orbital of the functionalized SiNCs has been conducted to evaluate their composition (Figure S8). The dominant Si(0) feature at 99.3 eV arises from the silicon nanocrystal core. Higher energy oxide features (i.e., Si (I), Si (II) and Si (III)) are reasonably attributed to surface silicon sub-oxides (SiOx; 0 < x < 2), as well as organic silicon-carbon bonds tethering capping functionalities, consistent with TMVS-SiNCs being well functionalized. A weak Si (IV) component is also noted at 103.6 eV. As for TMVS-SiNCs, Si 2p XPS spectra of all the variously functionalized SiNCs show high amounts of Si(0) at 99.3 eV and less Si-suboxides and Si-C species (100.6, 101.8 and 102.7 eV). Si (IV) at 103.6 eV arising from surface oxidation is low (Figure S12 – S20).

Regarding the surface groups, NALDI measurements propose a low oligomerization degree, if not monolayer surfaces (Figure S8).<sup>8</sup> Hence, wt. losses in thermogravimetric analysis (TGA) arising from the surfaces are comparably low (22 - 41 wt%; Figure S 9, Table S4). Elemental analysis gives mainly comparative wt.% values of surface ligands (Table S 6), however some deviations to TGA have occurred from methodical differences (Table S6).

#### 2.2. Surface Coverage

To see the influence of monomer sterics on the degree of surface coverage, we used TGA (Figure S9; Table S4) and elemental analysis (C-H determination; Table S6) of the functionalized SiNCs. Furthermore, to calculate the substitution degree, the hydrogen amount of unfunctionalized and freeze dried SiNCs was determined to  $1.69 \pm 0.29$  wt% (18.8 µmol Si-H/mg SiNCs) by elemental analysis from three single measurements. Thus, we were able to calculate a hydride surface coverage of 140% based on the calculations of Avramov *et al.*<sup>9</sup> for 2.78 nm SiNCs (Table S7-S8). These results confirm, that due to surface defects,  $\equiv$ Si-H, =SiH<sub>2</sub> or SiH<sub>3</sub> species are present.

The TGA method to determine surface coverages has some drawbacks compared to elemental analysis, since the decomposition of some monomers does not occur quantitatively. Generally, the calculated surface coverage and hydride substitution increases with less steric bulkiness of the ligand (Table S7, S8).

As further characteristic number, we introduced the Si-H substitution degree as a quotient of the surface coverage of the ligands and the Si-H surface coverage (both obtained from elemental analysis; see main manuscript). This gives the basis for the calculation of the radical efficiency (*vide infra*).

#### 2.3. Determination of the Radical Efficiency

Initiator efficiencies are well known in polymer chemistry, describing the effective radical concentration. They are defined as the amount of initiator derived radicals that initiate polymerization reactions, divided by the amount of decomposed initiator.<sup>10</sup> In this context we defined radical efficiencies ( $f_R$ ) as a function of the calculated concentration of formed radicals (from  $t_{1/2}$ )<sup>11</sup>and the absolute concentration of substituted surface hydrides. In contrast to the polymer chemistry, where f may not exceed 1, we observed higher efficiencies arising from the low radical concentration and high initial surface hydride concentration, as can be seen in table S 9-11.

## 3. Figures



Figure S 1. **a**, IR spectrum of 1 mg/mL hydride terminated SiNCs dispersed in a 1.26 mM solution of TMVS in toluene; **b**, 3 dimensional illustration of the Si-H band in the reaction mixture; **c**, Time resolved decay of the Si-H band during the radical SiNC functionalization process with TMVS; **d**, *Time resolved in-situ IR trace* of SiNC functionalization using TMVS and AIBN with benzene as solvent at 70 °C for 50 min followed by 50 min at room temperature and a reheating step to 70 °C for another 50 min.



Figure S 2: UV-VIS transmittance measurement of hexyl-, TMVS- and TPVS-SINCs.



Figure S 3: **a**, SiNC dispersions under ambient and UV-light (365 nm): A) TMVS, B) EDMVS, C) TEVS, D) DMPVS, E) TPVS, F) PMVDS, G) TTMSVS, H) hexyl, and I) dodecyl; **b**, PL spectra of functionalized SiNCs.



Figure S 4: TEM and HR-TEM (inlet) images of functionalized SiNCs. White lines highlight 0.32 nm distances of lattice fringes.



Figure S 5: DLS data of functionalized SiNCs.



Figure S 6: ATR-IR spectrum of hydride terminated, hexyl-, dodecyl-, TMVS, TPVS, DMPVS, TEVS-SiNCs, DMEVS, TTMSV,S and PMVDS-SiNCs.



Figure S 7: XPS spectrum (left) and high resolution XPS spectrum of the Si 2p shell (right) of **a**, TMVS-SiNCs; **b**, hexyl-; **c**, dodecyl- **d**, DMPVS-; **e**, TPVS-; **f**, DMEVS-; **g**, TEVS-; h) PMVDS-SiNCs; **i**, TTMSVS-SiNCs.



Figure S 8: NALDI measurement of the **a**, background, **b**, TMVS-, **c**, TEVS-, **d**, DMPVS-, **e**, TPVS-, **f**, PMVDS-, **g**, TMSVS-, **h**, dodecyl-, and **i**, hexyl-SiNCs. Asterisks show background signals.



Figure S 9: TGA curves of functionalized SiNCs.

## 4. Tables

monomer	m <sub>Monomer</sub> [g]	V <sub>Monomer</sub> [mL]	V <sub>toluene</sub> [mL]	t [h]
TMVS	0.96	1.40	6.20	16
1-hexene	0.80	1.20	6.0	16
1-dodecene	1.60	2.12	5.08	16
DMPVS	1.58	1.76	5.46	16
TPVS	3.34	-	7.20	24
DMEVS	1.24	1.56	5.64	16
TEVS	1.82	2.02	5.18	16
PMVDS	1.66	2.12	5.08	23
TTMSVS	3.08	3.58	3.62	36

Table S 1: Reaction conditions of SiNC functionalization for characterization.

entry	monomer	n <sub>Monomer</sub> [mmol]	m <sub>Monomer</sub> [g]	V <sub>Monomer</sub> [mL]	V <sub>toluene</sub> [mL]	c <sub>AIBN</sub> [µmol]	m <sub>AIBN</sub> [mg]	Т [°С]
1-4	TMVS	4.78	0.48	0.70	2.90	24.4	4	70
	TMVS	4.78	0.48	0.70	2.90	164.4	24	70
1	TMVS	4.78	0.48	0.70	2.90	73.2.4	12	70
1	TMVS	4.78	0.48	0.70	2.90	6.1	1	70
	TMVS	4.78	0.48	0.70	2.90	24.4	0.6	70
	TMVS	4.78	0.48	0.70	2.90	24.4	4	50
2	TMVS	4.78	0.48	0.70	2.90	24.4	4	60
2	TMVS	4.78	0.48	0.70	2.90	24.4	4	85
	TMVS	4.78	0.48	0.70	2.90	24.4	4	100
	1-hexene	4.78	0.40	0.60	3.00	24.4	4	70
	1-dodecene	4.78	0.80	1.06	2.54	24.4	4	70
	DMPVS	4.78	0.79	0.88	2.72	24.4	4	70
2	TPVS	4.78	1.67	solid	3.6	24.4	4	70
3	DMEVS	4.78	0.62	0.78	2.82	24.4	4	70
	TEVS	4.78	0.91	1.01	2.59	24.4	4	70
	PMVDS	4.78	0.83	1.06	2.54	24.4	4	70
	TTMSVS	4.78	1.54	1.79	1.79	24.4	4	70
	TMVS	2.39	0.24	0.35	3.25	24.4	4	70
4	TMVS	9.56	0.96	1.41	2.19	24.4	4	70
	TMVS	24.5	2.45	3.6	0	24.4	4	70

Table S 2: Reaction conditions for SiNC functionalization performed in *in-situ* IR (1. AIBN variation, 2. Temperature variation,3. Substrate concentration variation, 4. Substrate structure variation).

	SiNCs	R <sub>h</sub> (nm)	Polydispersity (%)
1	TMVS	$3.8 \pm 1.0$	27.9
2	EDMVS	$3.2 \pm 0.6$	19.1
3	TEVS	$3.7 \pm 0.8$	22.8
4	DMPVS	$3.0 \pm 0.7$	22.9
5	TPVS	2.8±1.1	39.4
6	PMVDS	$3.8\pm0.9$	24.2
7	TTMSVS	$3.1 \pm 1.0$	31.1
8	Hexyl	$2.9\ \pm 0.7$	24.5
9	Dodecyl	$3.3\pm0.9$	25.9

Table S 3: Hydrodynamic radii and polydispersities of functionalized SiNCs.

Table S 4. Summarized total weight losses obtained from TGA.

	SiNCs-								
TMVS EDMVS TEVS DMPVS TPVS PMVDS TTMSVS Hexyl d						dodecyl			
wt. loss (%)	25	22	27	32	28	32	23	29	41

Table S 5: Elemental analysis of hydride terminated SiNCs.

SiNCs-H							
wt. [%]							
Н	$1.64^{a} \pm 0.29$						
<sup>a</sup> average of three single measurements							

Table S 6: Total C and H obtained from elemental analysis.

SiNCs-									
wt. [%]	TMVS	EDMVS	TEVS	DMPVS	TPVS	PMVDS	TTMSVS	hexyl	dodecyl
Н	4.9	2.3	2.6	4.5	3.4	5.2	3.4	4.6	6.3
С	22.4	11.2	13.0	35.6	42.6	23.0	14.1	27.1	36.1
O <sup>a</sup>	0	12.2	6.5	0	0	4.4	5.1	0	0
Si <sup>a</sup>	10.5	21.4	3.8	8.3	5.0	15.4	12.0	0	0
Σ	37.8	20.4	25.9	48.4	51.0	48.0	34.6	31.7	42.4

<sup>a</sup> calculated Si and O values are based on carbon and can be assigned to ligand.

	wt.loss	% Mole of	% Mole of Si	Number of	surface coverage <sup>d</sup>
monomer	(%)	ligand <sup>a</sup> X <sub>ligand</sub>	atoms <sup>b</sup> x <sub>Si</sub>	ligands per SiNC <sup>c</sup>	(%)
TMVS	25	0.246	2.66	56	28
EDMVS	22	0.169	2.76	37	18
TEVS	27	0.142	2.59	33	16
DMPVS	32	0.197	2.41	49	25
TPVS	28	0.0977	2.55	23	11
PMVDS	32	0.183	2.41	46	23
TTMSVS	23	0.0712	2.73	16	8
hexene	29	0.344	2.51	82	41
dodecene	41	0.244	2.09	70	35

Table S 7: TGA-based surface coverage calculated for 2.78 nm SiNCs.<sup>8</sup>

 $\label{eq:ligand_liga$ 

monomer	wt. (%)	% Mole of ligand <sup>a</sup> x <sub>ligand</sub>	% Mole of Si Atoms <sup>b</sup>	Number of Ligands per	surface coverage (SC) <sup>d</sup>	Si-H substitution degree (SD)	Substituted Si-H groups
		_	ASi	SiNC <sup>c</sup>	(%)	(%)	(µmol/mL)
Н	1.64	1.62	3.49	279	140	-	-
TMVS	37.4	0.373	2.22	101	50	36	6.8
DMEVS	20.4	0.157	2.82	33	17	12	2.3
TEVS	25.9	0.136	2.63	31	16	11	2.1
DMPVS	48.4	0.298	1.83	98	49	35	6.6
TPVS	51.0	0.178	1.74	61	31	22	4.1
PMVDS	48.0	0.275	1.84	90	45	32	6.0
TTMSVS	34.6	0.107	2.32	28	14	10	1.9
hexene	31.7	0.376	2.42	93	47	33	6.2
dodecene	42.4	0.252	2.04	74	37	27	5.1

Table S 8: Elemental analysis-based surface coverage and Si-H substitution degree calculated for 2.78 nm SiNCs.<sup>8</sup>

 $^{a}$  m<sub>Ligand</sub>/M<sub>Ligand</sub>.  $^{b}$  (1-m<sub>Ligand</sub>)/M<sub>Si</sub>.  $^{c}$  (x<sub>Ligand</sub>/ x<sub>Si</sub>600.  $^{d}$  (number of ligands/200) •100,  $^{e}$  SC<sub>ligand</sub>/SC<sub>Si-H</sub>.

Table S 9: Decomposition rates (k<sub>d</sub>), relative (1-I<sub>t</sub>) and absolute ( $[I]_0$ - $[I]_t$ ;  $[I]_0 = 6.8 \,\mu mol/mL$ ;  $[I]_t = I_t \cdot [I_0]$ ) amount of decomposed AIBN at the end point of the functionalization reaction with TMVS (Si- $H_{t,rel} \approx 0\%$ , main manuscript figure 3a, b) and calculated radical efficiency (f) at various temperatures.<sup>11</sup>

T (°C)	100	85	70	60	50
t <sub>1/2</sub> (s) <sup>a</sup>	0.12	0.70 <sup>b</sup>	4.81	21.0	89.1
$k_d (1/s)^c$	$1.60 \cdot 10^{-3}$	$2.75 \cdot 10^{-4}$	$4.00 \cdot 10^{-5}$	$9.15 \cdot 10^{-6}$	$2.16 \cdot 10^{-6}$
$1 - I_t^{d}$	0.63	0.50	0.40	0.26	0.14
[I] <sub>0</sub> -[I] <sub>t</sub> (µmol/mL)	4.3	3.4	2.8	1.8	0.95
$\mathbf{f}_{\mathbf{R}}^{\mathbf{e}}$	0.79	0.96	1.24	1.85	3.44

ln2

 $k_d = \frac{t_{1/2}}{t_{1/2}}$ , <sup>d</sup> obtained from Figure 3 A, <sup>a</sup>  $t_{1/2}$  of AIBN in toluene; <sup>b</sup>  $t_{1/2}$  in xylene <sup>c</sup> calculated from  $t_{1/2}$  using

 $f = \frac{SD_{ligand} \cdot 18.8 \,\mu mol/mL}{2 \cdot ([I]_0 - [I]_t) \,\mu mol/mL}$ 

Table S 10: Relative  $(1-I_t)$  and absolute  $([I]_0-[I_t]; [I]_t = I_t \cdot [I_0])$  amount of decomposed AIBN at the end point of 70 °C SiNC functionalization reaction with TMVS (Si-H<sub>t,rel</sub>  $\approx$  0%, main manuscript figure 3a, b) and calculated radical efficiency.

[I] <sub>0</sub> (μmol/mL)	45.7	20.3	6.8	1.7	1
1-I <sub>t</sub> <sup>a</sup>	0.24	0.24	0.42	0.80	0.86
[I] <sub>0</sub> -[I] <sub>t</sub> (µmol/mL)	11.0	4.9	2.9	1.4	0.86
f <sub>R</sub> <sup>b</sup>	0.30	0.67	1.14	2.39	3.81
	SD.	$188 \mu mol/ml$			

<sup>a</sup> obtained from Figure 3 **B**; <sup>b</sup>  $f = \frac{SD_{ligand} \cdot 18.8 \,\mu mol/mL}{2 \cdot ([I]_0 - [I]_t) \,\mu mol/mL}.$ 

Table S 11: Relative  $(1-I_1)$  and absolute  $([I_1]_{-}[I_1]_{-}[I_1]_{-}[I_1]_{-}[I_1]_{-}[I_1]_{-}[I_1]_{-}$  amount of decomposed AIBN at the end point of 70 °C SiNC functionalization reaction with various monomers (Si-H<sub>t,rel</sub>  $\approx$  0%, main manuscript figure 5 a-d) and calculated radical efficiency.

Substrate	TMVS	1- hexene	1- dodecene	DMEVS	TEVS	DMPVS	TPVS	PMVDS	TTMSVS
1-I <sub>t</sub> <sup>a</sup>	0.41	0.28	0.40	0.46	0.63	0.56	0.57	0.52	0.995
[I] <sub>0</sub> -[I] <sub>t</sub> (mol/mL)	2.8	1.9	2.7	3.1	4.3	3.8	3.9	3.5	6.77
SD <sup>b</sup>	0.36	0.33	0.27	0.12	0.11	0.35	0.22	0.32	0.10
f <sub>R</sub> <sup>c</sup>	1.19	1.60	0.92	0.35	0.23	0.83	0.52	0.82	0.13

	$SD_{ligand} \cdot 18.8  \mu mol/mL$
<sup>a</sup> obtained from Figure 5; <sup>b</sup> see table S 8; <sup>c</sup>	$T = \frac{1}{2 \cdot ([I]_0 - [I]_t)  \mu mol/mL}$

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