Supplementary Information

Photoluminescent Silicon Nanocrystals with Chlorosilane Surfaces – Synthesis and Reactivity

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Experimental Procedures

General Information

All reactants and reagents were purchased from Sigma-Aldrich and used without further purification if not stated otherwise. 1-Butenol and ethyl 6-hydroxyhexanoate and dodecyldimethylsilanol were dried over activated molecular sieve (3Å) prior to use. Dry toluene was obtained from a MBraun SPS 800 solvent purification system. Fourier transform infrared (FTIR) spectra were measured with a Bruker Vertex 70 FTIR using a Platinum ATR from Bruker. Nuclear magnetic resonance (NMR) spectra were measured on a ARX-300 from Bruker in deuterated chloroform at 300 K. Dynamic light scattering measurements were made with a Dyna Pro NanoStar from Wyatt with toluene as solvent. Photoluminescence (PL) spectra were taken with a AVA-Spec 2048 from Avantes using a Prizmatix (LED Current controller) as light source. Electron dispersive X-ray spectra (EDX) were measured with an Oxford Instruments SwiftED-TM coupled to a Hitachi Tabletop Microscope TM-1000. Transmission electron microscopy was performed using a JEOL-2010 (LaB 6 filament) electron microscope with an accelerating voltage of 200 keV. TEM samples of SiNCs were drop-casted onto a holey carbon coated copper grid (SPI supplies) and the solvent was evaporated in vacuum. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. A monochromatic Al Kα source (λ = 8.34 Å) was used to irradiate the samples, and the spectra were obtained with an electron takeoff angle of 90°.

Preparation of oxide-embedded silicon nanocrystals

Polymeric hydrogen silsesquioxane (HSQ) was prepared following a literature procedure. HSQ (7 g) was placed in a quartz reaction boat, transferred to a Nabertherm RD 30/200/11 oven with quartz working tube and heated from ambient to a peak processing temperature of 1100 °C at 18 °C min in a slightly reducing atmosphere (5% H₂/95% N₂). The sample was maintained at the peak processing temperature for 1 h. Upon cooling to room temperature, the resulting amber solid was ground into a fine brown powder using mortar and pestle to remove large particles. Further grinding was achieved via shaking the powder for 12 h with high-purity silica beads using a WAB Turbula mixer. The resulting SiNC/SiO₂ composite powder was stored in standard glass vials.

Liberation of SiNCs

Hydride-terminated SiNCs were liberated from the SiNC/SiO₂ composites using HF etching. First, 100 mg of the ground SiNC/SiO₂ composite was transferred to an ethylene-tetrafluoroethylene (ETFE) beaker equipped with a Teflon-coated stir bar. Ethanol (1.0 mL) and water (1.0 mL) were then added under mechanical stirring to form a brown suspension, followed by 1.0 mL of 49% HF aqueous solution. After 1 h of etching in subdued light, the suspension appeared yellow. Hydride-terminated SiNCs were subsequently extracted from the aqueous layer into ca. 30 mL of toluene by multiple (i.e., 3 × 10 mL) extractions. The SiNC toluene suspension was transferred to ETFE-centrifuge tubes, and the SiNCs were isolated by centrifugation at 5000 rpm.

Hydrosilylation of SiNCs with chlorodimethyl(vinyl)silane or trimethylvinylsilane

SiNC/SiO₂ composite (100 mg) was etched according the described procedure. After extraction and centrifugation, the resulting H-terminated SiNCs were resuspended in a mixture of 1 ml of dried toluene and chlorodimethyl(vinyl)silane (0.2 ml, 1.5 mmol) or trimethylvinylsilane (0.3 ml, 1.5 mmol) respectively. The dispersion was degassed via three freeze-pump-thaw cycles. Afterwards 4-
decylbenzene diazonium tetrafluoroborate (1.5 mg, 4.6 µmol) was added to start the hydrosilylation. After two hours, solvent and excess silane was removed \textit{in vacuo} to give the functionalized SiNC-SiCl/SiNC-SiMe. Since SiNC-SiCl are very sensitive towards hydrolysis and agglomeration via crosslinking in this state, they were used without further purification.

**Functionalization of SiNC-SiCl with alcohols and silanols**

The SiNC-SiCl were resuspended in toluene (1.0 ml) and the respective alcohol or silanol (0.5 mmol) was added followed by imidazole (2.0 mg, 0.03 mmol) and the reaction mixture was allowed to stir over night. Afterwards, the solution was filtered through a 0.45 µm Teflon-syringe filter and the functionalized SiNC-SiCl were precipitated with acetonitrile and centrifuged at 9000 rpm. The centrifugate was resuspended in a minimal amount of toluene and precipitated again with acetonitrile. This procedure was repeated three times in total. Finally, the functionalized SiNCs were suspended in toluene and stored in vials for further use.

**Functionalization of SiNC-SiCl and SiNC-SiMe with organolithium reagents**

The SiNC-SiCl or SiNC-SiMe respectively were resuspended in toluene (1 ml) and the organolithium reagents, phenyllithium (~1.9 M in dibutylether, 0.2 mmol, 0.1 ml), lithium phenylacetylide or 5-hexyl-2-thienyl)lithium respectively (~1 M in THF/hexane, 0.2 mmol, 0.2 ml) were added to the reaction mixture and allowed to stir over night. Afterwards the functionalized SiNC were precipitated with MeOH, acidified with conc. HCl and centrifuged, followed by two precipitation/centrifugation steps with pure methanol. The functionalized SiNCs were suspended in toluene, filtered through a 0.45 µm Teflon-syringe filter and stored in vials for further use.

**Synthesis of (5-hexyl-2-thienyl)lithium**

2-hexylthiophene was prepared following literature procedures.\(^2\) 2-hexylthiophene (0.84 g, 5.0 mmol) was dissolved in dry THF (2.1 ml) and cooled to -78°C. Afterwards \textit{n}-BuLi (2.5 M in hexanes, 2 ml, 5.0 mmol) was added slowly. The solution was warmed to room temperature and used without further purification.

**Synthesis of lithium phenylacetylide**

Phenylacetylene (0.51 g, 5.0 mmol) was dissolved in dry THF (2.1 ml) and cooled to -78°C. Afterwards \textit{n}-BuLi (2.5 M in hexanes, 2 ml, 5.0 mmol) was added slowly. The solution was warmed to room temperature and used without further purification.
Analytical Data

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR measurements of SiNC-SiCl functionalized with 3-buten-1-ol were conducted (Figure S1). The intermediate product, SiNCs functionalized only with dimethyl(vinyl)chlorosilane, is very instable towards hydrolysis and could therefore not be isolated.

The protons from the double bond of dimethyl(vinyl)chlorosilane (X, Y, Z) around 6 ppm are not found in the functionalized SiNC-SiCl since the double bond reacts in the hydrosilylation reaction. The two formed silicon bound methylene groups (M, N) should appear at around 0.5 ppm, however in this region, no signal is present. This observation was made by several other groups that worked with SiNCs in the size range of a few nanometers. A possible explanation is that the signals cannot be detected due to a broadening induced by the anisotropic surrounding and a prolonged relaxation time since the movement of the molecules is hindered on the SiNC surface. The protons of the two Si–Me groups of dimethyl(vinyl)chlorosilane at 0.5 ppm (A) are shifted upfield towards 0.1 ppm at the functionalized SiNC-SiCl, due to the absence of the electron withdrawing chlorine atom on the silicon.

The proton signals of 3-buten-1-ol (B-E) are all present when bound on the SiNC-SiCl with the exception of the OH-Proton (G) at 2.0 ppm which is consumed during the reaction with the chlorosilane surface.

Figure S1: NMR spectrum of dimethyl(vinyl)chlorosilane (top, blue), 3-buten-1-ol (middle, green) and SiNC-SiCl reacted with 3-buten-1-ol (bottom, red).
Energy Dispersive X-ray Spectroscopy (EDX)

EDX analysis of the functionalized SiNC-SiCl shows only small amounts of residual chlorine left on the particles (Table S 1).

Table S 1: EDX data of the functionalized SiNC-SiCl. The values are given as weight percent and were averaged from at least five different measuring spots. Only elements with a molecular weight higher than 23Na can be detected with the Oxford Instruments SwiftED-TM, therefore carbon and oxygen are not listed.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Si [wt%]</th>
<th>Cl [wt%]</th>
<th>I [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-buten-1-ol</td>
<td>99.1</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>73.6</td>
<td>1.2</td>
<td>25.2</td>
</tr>
<tr>
<td>ethyl 6-hydroxy hexanoate</td>
<td>99.2</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>triphenylsilanol</td>
<td>98.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>dodecyltrimethylsilanol</td>
<td>97.7</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>phenyllithium</td>
<td>99.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>lithium phenylacetylide</td>
<td>97.7</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

EDX results from SiNC-SiCl and SiNC-SiMe, functionalized with (5-hexyl-2-thienyl)lithium give with 0.16 to 0.06 a considerably higher silicon to sulphur ratio for the chlorosilane terminated SiNCs (Table S2).

Table S 2: EDX data of the functionalized SiNC-SiCl and SiNC-SiMe, functionalized with (5-hexyl-2-thienyl)lithium in weight percent.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Si [wt%]</th>
<th>S [wt%]</th>
<th>Cl [wt%]</th>
<th>S:Si (weight ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClVDMS</td>
<td>86.0</td>
<td>13.8</td>
<td>0.2</td>
<td>0.16</td>
</tr>
<tr>
<td>VTMS</td>
<td>94.1</td>
<td>5.9</td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure S 2: EDX spectrum of SiNC-SiCl (top) and SiNC-SiMe (bottom) functionalized with (5-hexyl-2-thienyl)lithium.
Photoluminescence Spectroscopy (PL)

PL spectra of SiNC-SiCl functionalized with various alcohols and silanols all have an intensity maximum around 690 nm (Figure S3).

![PL spectra of SiNC-SiCl](image)

**Figure S 3:** PL spectra of SiNC-SiCl under 365 nm UV radiation, functionalized with 3-buten-1-ol, 4-iodophenol, ethyl 6-hydroxyhexanoate, dodecyldimethylsilanol and triphenylsilanol.

SiNC-SiCl reacted with lithium phenylacetylide show PL with a lesser intensity (Figure S4 B) than SiNC-SiCl functionalized with phenyllithium and (5-hexyl-2-thienyl)lithium (Figure S4 A, C).

![SiNC-SiCl solutions](image)

**Figure S 4:** Solutions of SiNC-SiCl functionalized with phenyllithium (A), lithium phenylacetylide (B) and (5-hexyl-2-thienyl)lithium (C) under 365 nm UV radiation.
Dynamic Light Scattering (DLS)

The hydrodynamic radii of the functionalized SiNC are all in a size range for freestanding SiNCs therefore it can be assumed that no agglomeration of the SiNC takes place.  

Table S 3: DLS data of the functionalized SiNC-SiCl and SiNC-SiMe.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Nucleophile</th>
<th>Hydrodynamic radius [nm]</th>
<th>Polydispersity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIDMVS</td>
<td>3-buten-1-ol</td>
<td>2.6</td>
<td>42.1</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>4-iodophenol</td>
<td>4.2</td>
<td>45.7</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>ethyl 6-hydroxy hexanoate</td>
<td>4.0</td>
<td>46.9</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>triphenylsilanol</td>
<td>3.4</td>
<td>41.1</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>dodecyl(dimethyl)silanol</td>
<td>3.0</td>
<td>37.0</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>phenyllithium</td>
<td>2.6</td>
<td>26.2</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>lithium phenylacetylide</td>
<td>2.9</td>
<td>30.4</td>
</tr>
<tr>
<td>CIDMVS</td>
<td>(5-hexyl-2-thienyl)lithium</td>
<td>2.9</td>
<td>15.4</td>
</tr>
<tr>
<td>VTMS</td>
<td>phenyllithium</td>
<td>1.9</td>
<td>29.5</td>
</tr>
<tr>
<td>VTMS</td>
<td>lithium phenylacetylide</td>
<td>2.6</td>
<td>41.4</td>
</tr>
<tr>
<td>VTMS</td>
<td>(5-hexyl-2-thienyl)lithium</td>
<td>1.8</td>
<td>37.2</td>
</tr>
</tbody>
</table>

Transmission Electron Microscopy (TEM)

A TEM picture of SiNC-SiCl functionalized with (5-hexyl-2-thienyl)lithium shows the single SiNCs (Figure S6).

Figure S 5: TEM-picture of SiNCs-SiCl functionalized with (5-hexyl-2-thienyl)lithium.
References


