

Supplementary Information

Photoluminescence Through In-gap States in Phenylacetylene Functionalized Silicon Nanocrystals

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1. General Information

1.1. Chemicals

All reactants and reagents were purchased from Sigma-Aldrich and used without further purification if not stated otherwise. Phenyllithium was bought as a 1.8 M solution in dibutyl ether, *n*-hexyllithium as 2.3 M solution in hexane, *n*-butyllithium as 2.5 M solution in hexane. Dry toluene and THF was obtained from a MBraun SPS 800 solvent purification system.

1.2. Instruments and Measurement Details

FTIR spectra were measured with a *Bruker Vertex 70 FTIR* using a *Platinum ATR* from *Bruker*. **Photoluminescence (PL) spectra** were taken with an *AVA-Spec 2048* from *Avantes* using a *Prizmatix (LED Current controller)* as light source. Samples were excited with a 365 nm source.

HR-TEM measurements were performed on a *JEM-2200FS TEM* with 200 kV field emission gun. Samples of SiNCs were drop-casted onto a lacey carbon grid and the solvent was evaporated in vacuum.

UV-Vis Spectroscopy was performed with a *Varian Cary 50 Scan Spectrometer*. (Wavelength region: 200-800 nm.)

PL life-time decay measurements were performed by a 445 nm CW diode laser, sent through an *Isomet IMDD-T110L-1.5 acousto-optic modulator (AOM)* operated at a frequency of 200 Hz. The PL lifetime decays were collected by a *Becker-Hickl PMC-100* photon-counting PMT.

For **STM measurements**, SiNCs were spin cast from a toluene solution onto atomically flat flame-annealed Au(111) substrates. All measurements were performed at room temperature, using Pt-Ir tips. Tunneling current-voltage (I-V) characteristics were acquired after positioning the STM tip above individual NCs, realizing a double barrier tunnel junction (DBTJ) configuration¹ and momentarily disabling the feedback loop. In general, care was taken to retract the tip as far as possible from the NC, so the applied tip-substrate voltage would fall mainly on the tip-NC junction rather than on the NC-substrate junction whose properties (capacitance and tunneling resistance) are determined by the layer of organic capping ligands that cannot be modified during the STM measurement. This protocol reduces the voltage division induced broadening effects, and thus the measured gaps and level separations in general better correspond to the real SC gaps, although broadening on the order of 10% are still expected.¹⁻⁴ The dI/dV -V tunneling spectra, proportional to the local tunneling density of states (DOS), were numerically derived from the measured I-V curves. We have acquired the topographic images with a set sample-bias, V_s , of 2.2 V and set current $I_s = 0.2$ nA. This bias value ensures tunneling to states well above the conduction band edge, where the DOS is rather large, thus the measured SiNC height corresponds well to the real height. The tunneling spectra (on the NCs) were measured with lower set bias, of $V_s \cong 1.2$ -1.5 V, and $I_s \cong 0.1$ -0.3 nA. These V_s values still ensure tunneling above the band edge (before disconnecting the feedback loop), yet being sensitive to the details of the DOS around the band edge. I_s was reduced as much as possible, to the lowest value that still allowed acquisition of smooth tunneling spectra, in order to retract the tip as much as possible from the NC (thus reducing the voltage division factor).

2. Synthetic Procedures

2.1. Preparation of Oxide-Embedded Silicon Nanocrystals

Polymeric hydrogen silsesquioxane (HSQ) was synthesized as described in a literature known procedure.⁵ 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 kept 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 a mortar and pestle to remove large particles. Further grinding was achieved via shaking the powder dispersed in

ethanol for 24h with high-purity silica beads using a *WAB Turbula mixer*. The resulting SiNC/SiO₂ composite was dried in vacuo and the powder stored in glass vials.

2.2. Liberation of Hydride Terminated SiNCs

Hydride-terminated SiNCs were obtained by etching the SiNC/SiO₂ composite using HF. First, 300 mg of the ground SiNC/SiO₂ composite was transferred to a ethylene-tetrafluoroethylene (ETFE) beaker equipped with a Teflon-coated stir bar. Ethanol (3 mL) and water (3 mL) were then added, and it is stirred to form a brown suspension, followed by addition of 3 mL of 49% HF aqueous solution. After 30 min 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 9000 rpm for 5 mins. To remove any residual water/ethanol, extracted particles dispersed in 5 ml dry toluene and centrifuged again.

2.3. Synthesis of Lithium Phenylacetylide

Phenylacetylene (1.53 g, 15 mmol, 1 eq.) is dissolved in 9 ml THF and *n*-butyllithium (4.8 ml, 2.5 M in hexanes, 12 mmol, 0.8 eq.) is added to the reaction flask drop wise in 30 minutes at -78°C. Upon the completion of the addition, the reaction mixture is stirred for 15 more minutes, then it is brought to room temperature. The product is obtained as a clear yellow/orange solution. The solution is degassed and stored in a schlenk flask in a cool place.

2.4. Functionalization of SiNCs with Organometallic Reagents

Hydride terminated Si-NCs, obtained by etching 300 mg Si/SiO₂ composite, are dispersed in 2 ml of a degassed solution of the organolithium reagents. The organolithium reagents used for this study are diluted with toluene to form 0.1 M solutions. The mixture is stirred for overnight. The reaction was terminated by precipitating functionalized SiNCs in 5 ml 1:1 ethanol-methanol mixture, acidified with HCl conc. (0.2 ml). Obtained SiNCs are centrifuged at 9000 rpm for 10 min and the sediment is redispersed in minimum amount of toluene. The precipitation-centrifugation-redispersion step is performed two more times from ethanol-methanol and toluene. Finally, functionalized SiNCs are dispersed in toluene and filtered through a 0.45 μm PTFE syringe filter.

3. Analytical Data

3.1. PL Decay Lifetime

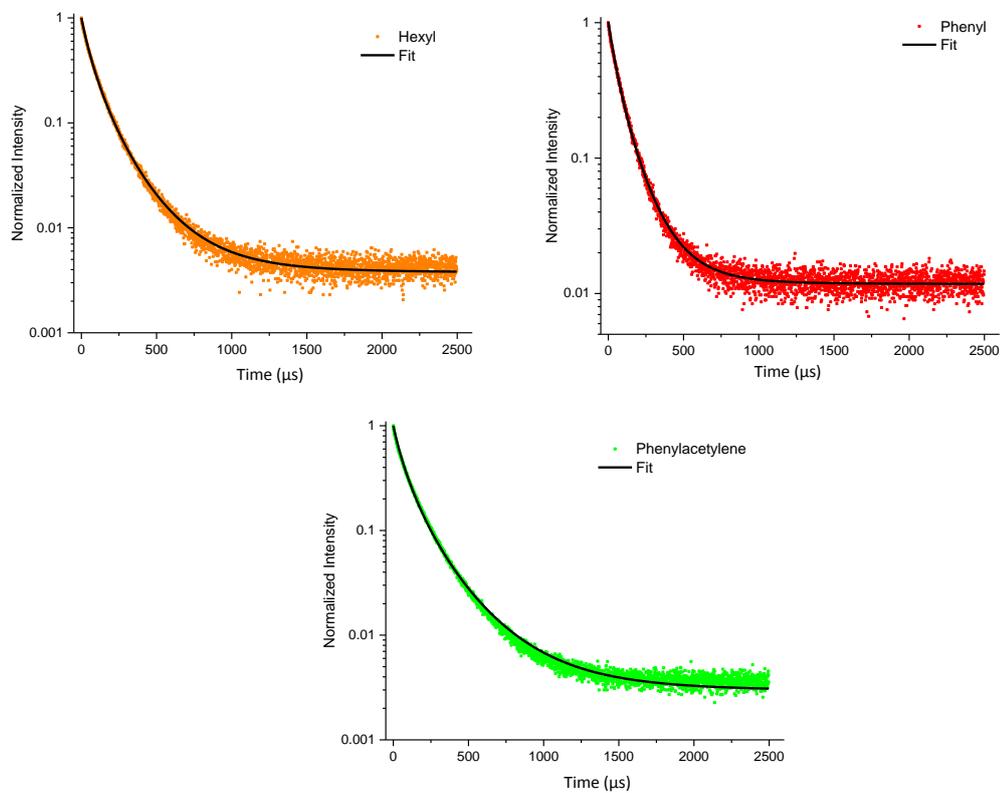


Fig. S1 PL decay curves of SiNCs functionalized with *n*-hexyllithium (orange), phenyllithium (red) and lithium phenylacetylide (green). Black curves show the fitted curve with lognormal function.

3.2. HR-TEM

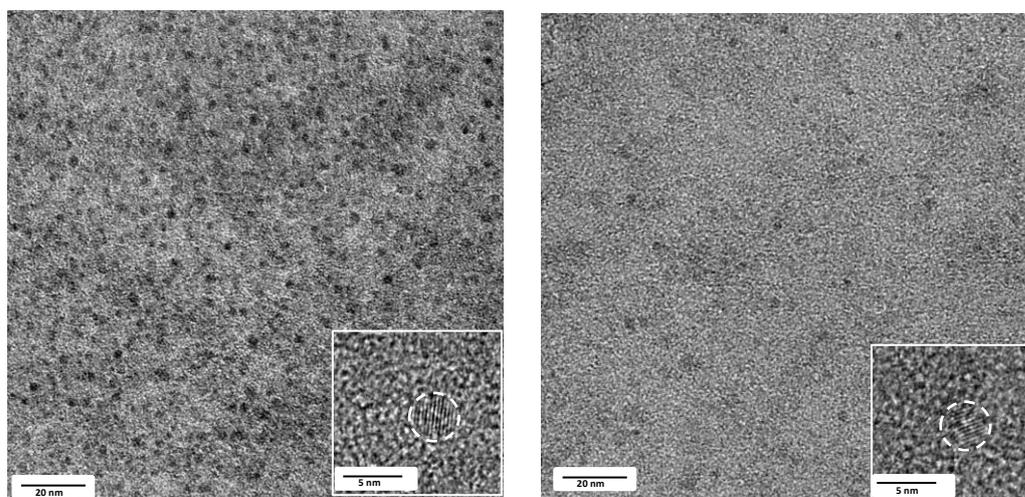


Fig. S2 TEM image of SiNCs functionalized with phenyllithium (left) and lithium phenylacetylide (right). HR-TEM images showing crystal fringes are shown in insets.

References

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