

**Low temperature radical initiated hydrosilylation of silicon quantum dots**

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Low temperature radical initiated hydrosilylation of silicon quantum dots.

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Abstract

The photophysics of silicon quantum dots (QDs) are not well understood despite their potential for many optoelectronic applications. One of the barriers to study and widespread adoption of Si QDs is the difficulty in functionalizing their surface, to make for example, a solution-processable electronically-active colloid. While thermal hydrosilylation of Si QDs is widely used, the high temperature typically needed may trigger undesirable side-effects, like the uncontrolled polymerization of the terminal alkene. In this contribution, we show that this high-temperature method for installing aromatic and aliphatic ligands on non-thermal plasma-synthesized Si QDs can be replaced with a low-temperature, radical-initiated hydrosilylation method. Materials prepared via this low-temperature route perform similarly to ones created by high-temperature thermal hydrosilylation when used in triplet fusion photon upconversion systems, suggesting the utility of low-temperature, radical-initiated methods for creating Si QDs with a range of functional behavior.

Introduction

Silicon is both non-toxic and earth-abundant, making it a highly attractive material for quantum-confined semiconductor structures. However, compared to direct gap chalcogenide quantum dots (QDs), the electronic states of silicon QDs remain a subject of sizable debate¹⁻⁵. This is not surprising as the electronic properties of QDs are greatly affected by their surface,⁶⁻⁹ yet surface functionalization of Si QDs is a key step in transforming these materials into solution-processable optoelectronics. The strong dependence of the electronic properties of Si QDs on their surface ligands stems from Si's ability to form strong, covalent bonds to surface-bound molecules. This is distinct from lead and cadmium-based QDs, which tend to ionically coordinate molecules to their surfaces. In principle, the covalent bonding nature of Si QDs surfaces creates the opportunity to rationally employ well-understood, widely-used organo-silicon chemistry to functionalize Si QDs to achieve a range of desired optical and electronic properties.

Thermal hydrosilylation is the most widely used method to functionalize Si QDs. Unfortunately, this reaction has many limitations, including use of high temperature (150–170 °C), substrate limitations due to the need to incorporate a terminal alkene, and the need for a large excess of reagents to complete functionalization in a reasonable timeframe. In particular, this need for a great excess of alkene or alkyne ligands is undesirable when designer ligands are to be incorporated on Si QD surfaces. As such, it is of practical interest to find conditions to hydrosilylate Si QDs at low temperatures in high yield to broaden the scope of ligands that can be attached to Si QD surfaces.

In this work, we examine a radical initiator commonly used for polymerization. While radical initiators have been explored to functionalize both porous and single crystal Si¹⁰⁻¹⁵, no systematic investigation has

been reported for Si QDs. Carroll et al. showed hydrosilylation of Si QDs can be achieved at 140 °C when initiated by 1,1'-azobis-(cyclohexanecarbonitrile) (ABCN) in neat alkene¹⁶. Similarly, 2,2'-azobis(2-methylpropionitrile) (AIBN)¹⁷⁻¹⁹ and 1,1'-azobis(cyclohexanecarbonitrile) (ACHN)²⁰ were used at lower temperatures. In all these cases, linear aliphatic molecules were bound to the Si QD surface, and the terminal alkene was used in great excess, usually as a neat solvent. The ability to extend this radical based method to forming covalent bonds between aromatic ligands and Si QDs, similar to forming Si-C bonds homogeneously in solution, will allow greater synergy between functional organic materials and Si QDs.

Here, we show that AIBN catalyzed hydrosilylation of Si QDs with aromatic ligands can be achieved at temperatures as low as 60 °C with aliphatic and aromatic alkenes. This is important for multi-excitonic processes like photon upconversion, where Dexter energy transfer occurs between the QD and surface-bound ligands²¹⁻²⁷. Since the efficiency of this short-range energy transfer decays exponentially with increasing distance between the QD donor and molecular acceptor, it is imperative to have both species within 1 nm of each other²⁸. We show here that the photon upconversion quantum yield (QY) with anthracene-functionalized Si QD light absorbers (Si:9EA) is comparable for larger Si QDs created by both thermal and radical-initiated hydrosilylation. For smaller Si QDs, the photon upconversion QY is ~3.3%, lower than that achieved with thermal methods²⁹.

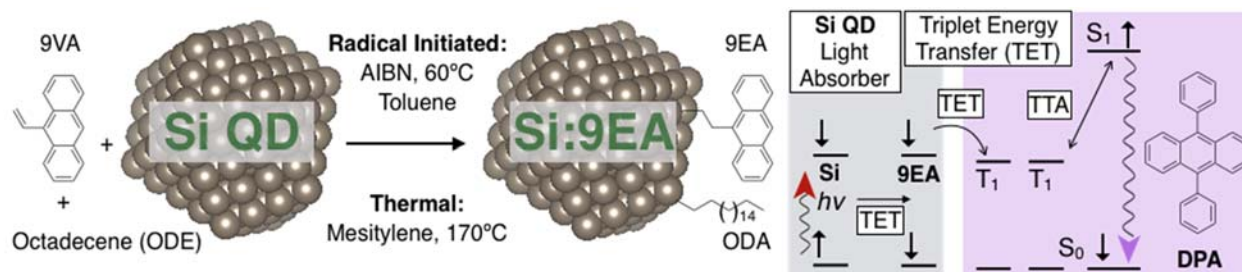


Figure 1. (Left) Non-thermal plasma-synthesized silicon quantum dots (Si QD) were hydrosilylated with 9-vinyl anthracene (9VA) and octadecene, to give Si QDs functionalized with 9-ethylanthracene (9EA) and octadecane (Si:9EA). (Right) Si:9EA can photosensitize triplet excited states in diphenylanthracene (DPA) via triplet energy transfer (TET). Photon upconversion occurs via triplet-triplet annihilation (TTA) between pairs of DPA molecules in their triplet excited state, producing violet light.

Results and discussion

Figure 1 shows our light harvesting scheme where non-thermal plasma synthesized silicon QDs are functionalized with octadecene (ODE) and 9-vinylanthracene (9VA) ligands under one of two conditions: (1) thermally at high temperature (170 °C), or (2) at relative low temperature (60 °C) with an AIBN radical initiator. In doing so, Si QDs functionalized with 9-ethylanthracene (9EA) and octadecane (ODA) are created, abbreviated Si:9EA. These Si:9EA QDs are colloiddally stable in non-polar solvents like toluene or hexane due to the presence of the solubilizing ODA groups. Excitation of Si:9EA QDs creates an excitonic state with triplet character that photosensitizes the surface bound 9EA molecules²⁹. This allows for triplet energy transfer (TET) between Si:9EA and diphenylanthracene (DPA) emitter molecules in solution. Photon upconversion is observed when DPA emits from its singlet state following triplet-triplet annihilation between two DPA molecules in their lowest excited triplet state, T_1 . Note that direct photoexcitation of a mixture of Si QDs and DPA with light comprised of photons with energy smaller than DPA's 3.2 eV optical gap, such as the 488 nm, 532 nm and 640 nm light used here, does not result in photon upconversion in the absence of surface-bound 9EA on the Si QDs.

Preparation of anthracene functionalized Si QDs

Table 1 outlines synthetic details. Non-thermal plasma synthesized Si QDs³⁰ were directly transferred into an air-free glove box to store under nitrogen for future use. Thermal hydrosilylation of Si QDs with 9VA and ODE was performed as previously reported²⁹. For the AIBN-initiated radical hydrosilylation of Si QDs, 0.21 mg of Si QDs were mixed with 0.5 mg of AIBN. Subsequently, either 0.2 or 1.0 mol equivalents of

ODE were added, corresponding to 0.03 and 0.144 mL respectively. As shown in **Table 1**, 9VA was added in different amounts by mole percentage, and the solution topped with toluene to a final volume of 0.56 mL. This solution was sealed, stirred and heated in a nitrogen glovebox at 60 °C for 15 hours. In **Table 1** and the remainder of this manuscript, Si QDs functionalized via radical-initiated or thermal hydrosilylation are labelled with R and T respectively. There are about 2-3 anthracene ligands per QD.

In the AIBN initiated hydrosilylation, the cloudy solution turned clear, indicating Si QD functionalization. Methanol was used to separate functionalized QDs from free 9VA precursor molecules. 1.7 mL of methanol were added to the reaction solution to precipitate out Si:9EA by centrifuging at 14,000 rpm for 20 mins. The precipitated Si:9EA was redispersed in 0.5 mL of toluene, followed by addition of 1.5 mL of methanol and centrifugation at 14,200 rpm for an additional 20 mins. This cleaning procedure was repeated three times in total. These cleaning steps result in full removal of free 9VA and ODE molecules in solution, as shown by UV-Vis absorption spectra of the supernatant which did not show any traces of anthracene. The second pellet was redispersed in toluene, split into two portions, and crashed out a third time with 0.75 mL of methanol. One portion was used for upconversion measurements by redispersing in 0.4 mL of 5.2 mM DPA solution in toluene, while the other portion was saved for characterization.

Figure 2 shows the electronic absorption and attenuated total reflection infrared (ATR-IR) spectra of Si:9EA colloids synthesized by the AIBN radical-initiated method after cleaning. There is no visible difference compared to the thermally hydrosilylated Si:9EA that we previously reported²⁹. For example, vibronic features corresponding to surface-bound anthracene molecules are observed following both synthetic methods. In **Figure 2b**, strong C-H absorption from ODA at $\sim 3000\text{ cm}^{-1}$ and C=C aromatic stretching bands from 1600 – 1700 cm^{-1} are observed, confirming covalent binding of 9EA and ODA to the Si QD surface.

Table 1. Synthetic conditions employed for radical-initiated hydrosilylation of Si QDs compared to conditions previously reported for thermal hydrosilylation. Photoluminescence (PL) spectra were measured in toluene at room temperature with an excitation source set to 532 nm. Photon upconversion measurements were performed with 5.2 mM DPA in toluene at room temperature. Upconversion QYs are reported using a 488 nm excitation source. The intensity of this source was set such that the upconverted emission scaled linearly with its intensity (i.e. molecular diffusion did not limit upconversion).

Synthesis	AIBN radical initiated: 60°C, 15 hrs						Thermal: 170°C, 3 hrs			
Sample	RI	RII	RIII	RIV	RV	RVI	T1.5	T2	T3	T4
ODE (mol eqv.)	0.2		1.0				4.6			
9VA/ ODE (%)	1.25	1.5	0.5	1.5	7.8	15.7	1.50	2.0	3.0	4.0
PL λ_{MAX} (nm)	776	777	774	792	800	804	771	776	784	785
PLQY (%)	12.0	18.3	4.5	2.1	8.4	3.1	11.8	10.4	6.9	5.0
Upconversion QY (%)	0.89	1.13	0.61	0.58	0.25	0.11	0.82	1.57	0.42	0.19

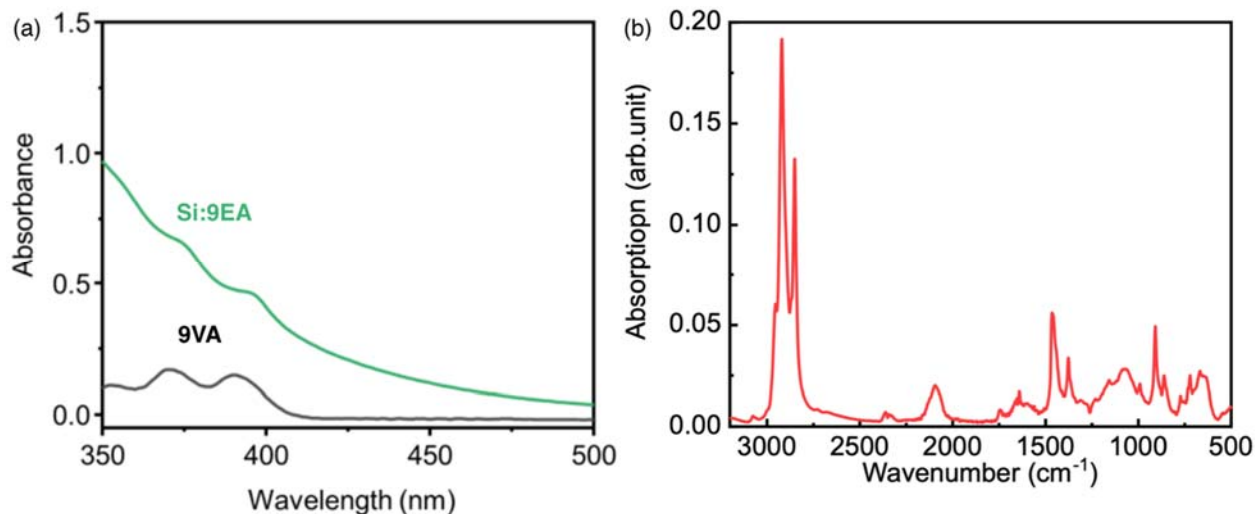


Figure 2. (a) Absorption spectra of 9VA and Si:9EA QDs hydrosilylated at 60 °C with the AIBN radical initiator (green). The vibronic features corresponding to the molecular absorption of the anthracene precursor are observed (black). (b) Attenuated total reflection infra-red (ATR-IR) spectra of Si:9EA shows that octadecane and 9-ethylanthracene (ODA and 9EA) are covalently bound to the surface of the Si QDs.

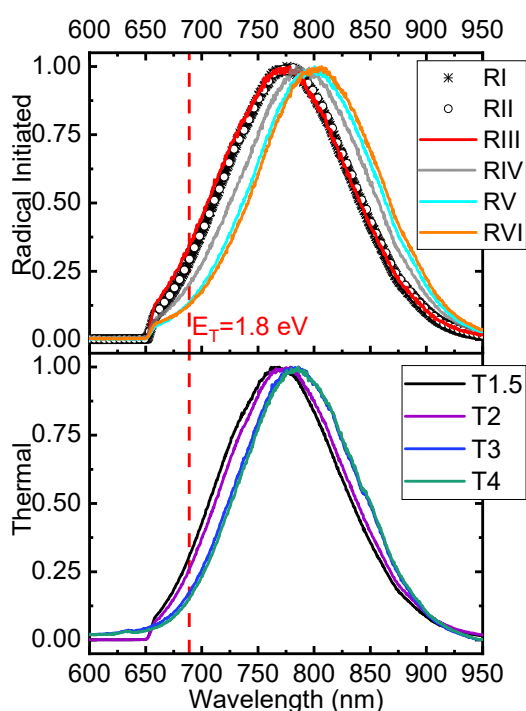


Figure 3. PL from Si QDs red shifts as the 9VA precursor is increased during hydrosilylation, independent of if it is initiated by AIBN (top) or thermally performed (bottom). See **Table 1** for sample information. Si:9EA was dissolved in toluene and excited by a 532 nm CW laser with a power density of 830 mW/cm² at the sample.

concentration is seen for the samples we have investigated. We note that both radical-initiated and thermal hydrosilylation lead to similar PL shifts with similar 9VA/ODE ratios.

An increase in the amount of 9VA during hydrosilylation bathochromically shifts the photoluminescence (PL) of the Si:9EA QDs. This is seen in **Figure 3**, which plots PL collected from Si:9EA in toluene following excitation with a 532 nm CW laser. In **Figure 3**, we have also highlighted the 9EA triplet energy of 1.8 eV, which falls on the high energy side of the Si QD PL spectrum. Thus, the bathochromic shift could stem from QD size heterogeneity as smaller QDs with a wider bandgaps will energetically favor triplet energy transfer to surface-bound anthracene, leading to a quenching of their emission. Consistent with this hypothesis, we observe a narrowing of the Si emission lineshape with increasing 9EA loading. Comparing T1.5 to T4, or the thermally hydrosilylated silicon QDs with 9VA at 1.5% and 4% respectively: the FWHM of Si QD PL decreases from 0.27 to 0.24 eV. Similarly, comparing the AIBN initiated radical hydrosilylation samples III to IV with 0.5 and 15.7 mol% of 9VA with respect to ODE, the FWHM decreases from 0.28 to 0.25 eV with 532 nm excitation as well. While the PL traces in **Figure 3** are normalized to their maxima, we also see a decrease in Si QD emission QY with increasing surface concentration of 9VA.

Table 1 shows that Si:9EA QD PL decreases by over a factor of two as the amount of surface-bound 9EA increases for the thermal hydrosilylation samples T1.5, T2, T3 and T4. The QY trend is less clear for the AIBN radical-initiated functionalization, possibly due to complication by other surface states, but a net QY decrease with increasing 9EA

Figures 4 and 5 (corresponding to samples T2 and RII respectively) show that the Si PL emitted by Si:9EA blue shifts as the power density of the CW 488 nm, 532 nm and 640 nm lasers increase. This trend is summarized in **Table 2**. This blue shift could again be attributed to the inhomogeneous size distribution. Gregorkiewicz et al. suggest that at high excitation density, smaller Si QDs preferentially emit light as larger Si QDs possess higher extinction cross-sections, making them more susceptible to absorption saturation³¹. Alternatively, there might be a possibility of bi-excitons formed on Si QDs³². The fact that blue-shifted emission with increasing excitation density is not observed in direct gap QDs may arise from the long $>500 \mu\text{s}$ lifetimes of Si QDs, compared to the short $\sim 10 \text{ ns}$ lifetime of cadmium chalcogenide QDs, or the $<10 \mu\text{s}$ for lead chalcogenide QD. Time-resolved experiments are needed to differentiate these and other possible scenarios.

Photon upconversion

As shown in **Table 1** and **Figure 6**, both thermal and radical-initiated hydrosilylation result in photon upconversion QYs between 1.3% and 1.5% for Si QDs whose emission peaks at 780 nm. This PL maxima was obtained for thermally hydrosilylated Si QDs with ODE only when excited with a 488 nm CW laser. Compared to the direct gap chalcogenide QDs, the indirect gap nature of Si QDs makes it impossible to index particle size by electronic absorption spectroscopy. On the other hand, the PL of Si QDs is affected by the synthetic methodology, thus in this work we compare Si QD size by comparing their PL when thermally hydrosilylated with ODE only. The photon upconversion QY was determined with a R6G standard as described previously²⁹. The photon upconversion QY for the samples in **Table 1** is not high as the large size of the Si QDs causes their bandgaps to be too small relative to the T_1 level of 9EA $\sim 1.8 \text{ eV}$ to allow efficient energy transfer. This makes triplet energy transfer (TET in **Figure 1**) a thermodynamically uphill process. Using Si QDs of a smaller size that emit maximally at 700 nm, a photon upconversion QY of 3.34 % was obtained. This is a factor of 2 lower than the value we previously reported²⁹. This suggests that the heating step at $170 \text{ }^\circ\text{C}$ may remove some surface states deleterious for triplet energy transfer.

Conclusions

We have shown that functionalization of non-thermal plasma-synthesized silicon QDs can be performed via a radical-initiated hydrosilylation at low temperature with a substantially lower concentration of ligands. The photon upconversion quantum yields here are a barometer of the efficiency of triplet energy transfer between the Si QD and the surface-bound anthracene, a measure of the quality of the organic-inorganic surface. For larger sizes of Si QDs, both hydrosilylation methods perform equally well. However, for the smaller QDs, the high-temperature thermal hydrosilylation method gives higher photon upconversion QYs compared to the low-temperature radical-initiated route, suggesting a size dependent surface reactivity. The functionalization of Si QDs needs be further developed to enhance electronic communication between the Si semiconductor core and conjugated ligands on its surface.

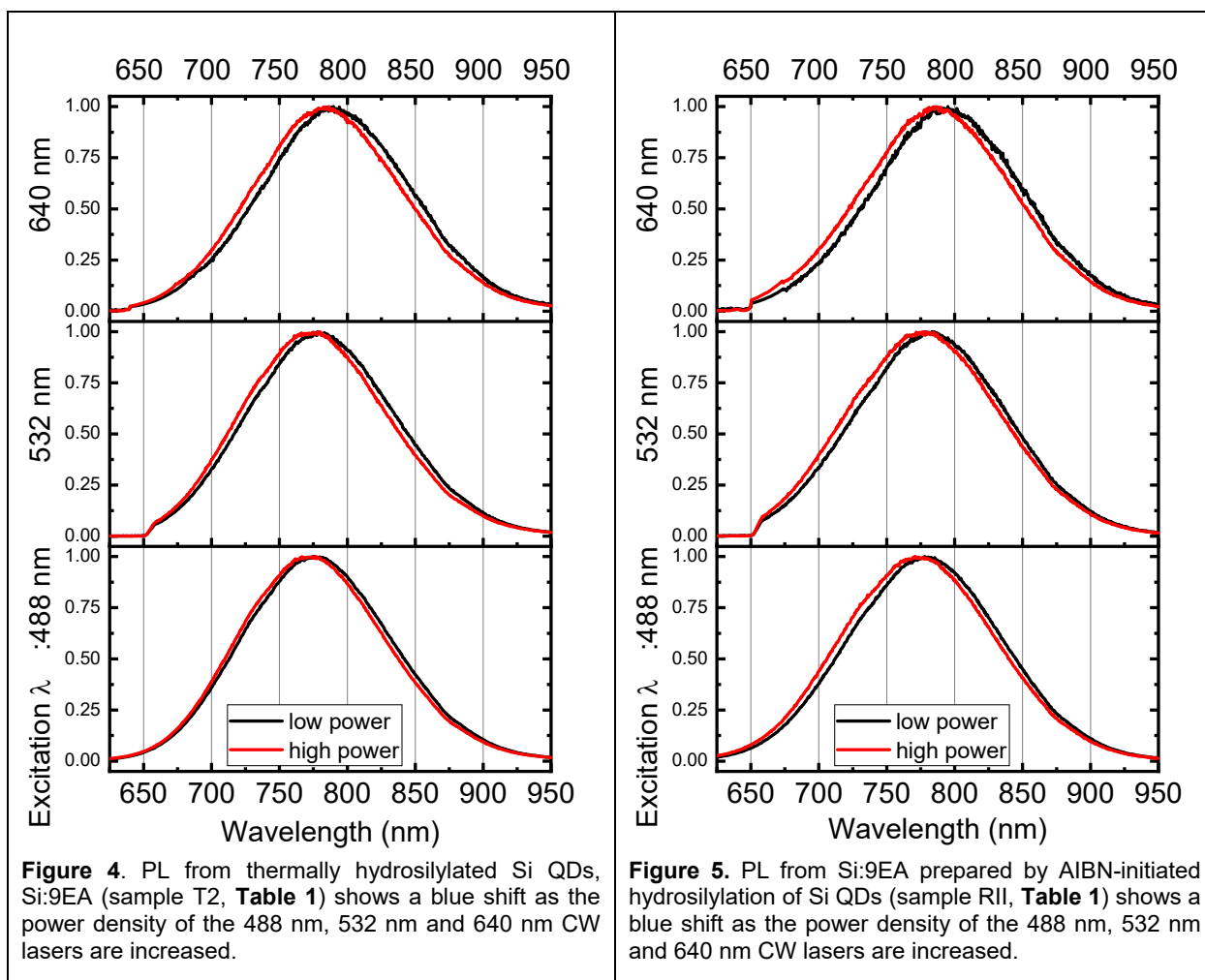


Table 2. As the excitation density of the CW lasers is increased by 10 \times , a slight blue shift of the PL of Si:9EA is observed for all excitation wavelengths. Sample T2 (**Figure 4**) and RII (**Figure 5**) are dissolved in toluene. All measurements were performed at RT.

Sample	λ_{EXC} (nm)	488		532		640	
	Power (mW/cm ²)	100	1800	85	830	18	130
RII	PLQY (%)	32.0	17.2	33.6	18.3	9.6	7.6
	PL λ_{MAX} (nm)	779	774	783	778	795	787
T2	PLQY (%)	16.0	9.9	21.8	11.8	21.2	13.0
	PL λ_{MAX} (nm)	778	774	781	776	791	785

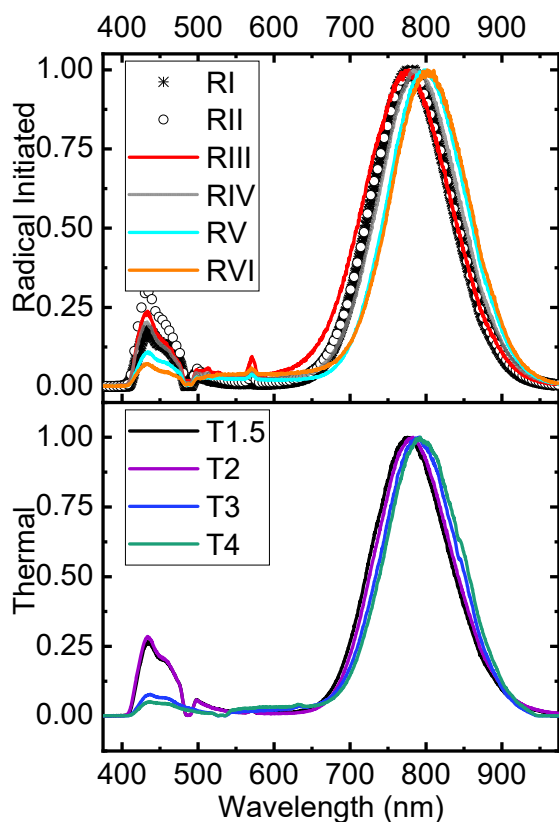


Figure 6. Photon upconversion is observed when Si:9EA colloids from **Table 1** are dissolved in 5.2 mM DPA and excited with a 488 nm CW laser.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table of Contents entry:

Non-thermal plasma synthesized silicon QDs are functionalized with aromatic and aliphatic ligands using a 2,2'-azobis(2-methylpropionitrile) AIBN radical initiator with hydrosilylation at 60°C for photon upconversion.

