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N-bromosuccinimide-based Bromination and Subsequent Functionalization of Hydrogen-terminated Silicon Quantum Dots

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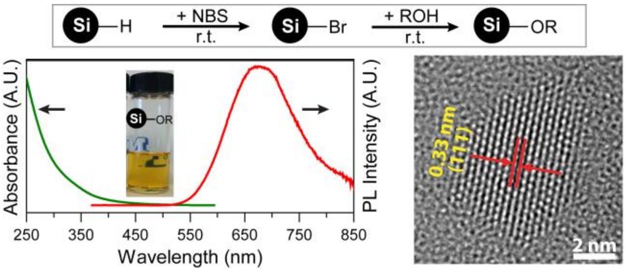
We report a mild, effective, room-temperature method for brominating and functionalizing colloidal hydrogen-terminated silicon quantum dots (H-SiQDs) using N-bromosuccinimide (NBS) as the bromination reagent. This post-synthesis bromination overcomes a long-standing challenge of producing emissive SiQDs through the functionalization of directly synthesized halogen-terminated colloidal SiQDs.



TOC Figure: N-bromosuccinimide based bromination is proven an effective and mild intermediate step to produce surface functionalized, red-emission, colloidal SiQDs.

Keywords: Silicon / Quantum Dots / Colloids / Bromination / Surface Functionalization

1. Introduction

Photoluminescent colloidal silicon nanocrystals below 10 nm are typically referred to as silicon quantum dots (SiQDs) due to the quantum confinement effect (QCE).[1] In the past two decades, SiQDs have attracted tremendous attention due to their promising applications in electronics,[2] tandem solar cells,[3] multi-exciton photovoltaics,[4] light emitting diodes (LEDs),[5] and biological labeling.[6] The realization of these applications requires highly-dispersed and well-passivated SiQDs, since they are prone to aggregation and oxidation, due to their high surface energies.[7] For selected applications, such as photovoltaics, the passivating ligands must possess optoelectronically-active functional groups in order to transport charges.[8,9] To date, there have been four major methods for synthesizing colloidal SiQDs: 1) direct colloidal synthesis via the reduction of silicon compounds,[10,11] 2) electrochemical etching of bulk Si,[12,13] 3) chemical vapor deposition (CVD) through decomposition of silanes,[14-19] and 4) sol-gel synthesis by calcining and reducing hydrogen silsesquioxane at high temperatures.[20,21] The first method produces halogenated SiQDs (X-SiQDs, X = Cl or Br) that can be further functionalized with –OR, $–NR_1R_2$, and –SR.[6,22-29] However, the obtained SiQDs do not emit at the expected wavelength as the QCE predicts; instead, they emit blue light regardless of particle sizes.[30] The origin of this mysterious phenomenon has been debated for a decade.[11,30] Recently, evidence has been shown that the blue emission is due to surface oxidation and amide passivation,[30] indicating a challenge in using the direct colloidal synthesis and amine passivation to produce functionalized SiQDs. The other three methods can produce QCE-governed SiQDs, terminated with hydrogen (H-SiQDs). These H-SiQDs, in contrast to X-SiQDs, are only suitable for grafting functional ligands via Si-C bonds through hydrosilylation reactions between the carbon-carbon bonds in 1-alkene (or 1-alkyne) molecules and the Si-H bonds on the H-SiQDs surfaces.[21,28] Thus, a fundamentally interesting question is whether it is possible to produce functionalized emissive SiQDs utilizing the versatility of X-SiQDs. The solution we propose is to halogenate the as-prepared H-SiQDs and functionalize the resultant X-SiQDs using non-amine ligands such as alcohols and silanols.

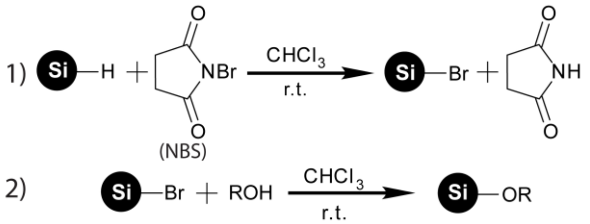
To date, there have been few publications on the halogenation of H-SiQDs,[7,31,32] despite many studies on the halogenation of Si wafers.[33-36] Rogozhiva *et al*. used chlorine gas (Cl_2) to chlorinate H-SiQDs that were synthesized by electrochemically etching H-SiQDs and then functionalizing the resultant Cl-SiQDs with n-butylamine.[31,32] Dasog *et al*. used phosphorous pentachloride (PCl_5) to chlorinate H-SiQDs that were made by the sol-gel method and then functionalized with allylamine.[7] In both cases, the resultant RHN-SiQDs (R = butyl or allyl) exhibited blue emission. Additionally, Cl_2 is very toxic and difficult to handle; PCl_5 is hygroscopic and insoluble in the solvent used (toluene). The Cl-SiQDs we prepared using PCl_5 showed serious aggregation, oxidation, and incomplete chlorination of the Si-H bonds (**SI-Fig. 1**). Other effective and user-friendly halogenation methods are needed.

This communication reports the use of ambient-stable N-bromosuccinimide (NBS) as the bromination reagent to produce 1-octanol (C_8OH), *tert*-butyldimethylsilanol (R_3SiOH), and 1-pyrenebutanol (PyOH) functionalized SiQDs with red emission. NBS is a common bromination reagent used in organic synthesis and can be handled in air without a problem.[34,37,38]

2. Experimental Section

Sol-gel Synthesis of H-SiQDs: H-SiQDs were synthesized by following the sol-gel method in the literature.[39] Details are provided in the Supporting Information (SI).

Bromination of H-SiQDs by NBS and Subsequent Functionalization (Scheme 1): Based on the bromination conditions for trialkylsilane (**SI-Figs. 2 and 3**), we developed the following conditions for brominating H-SiQDs. In a N_2-filled glove box, NBS (1.2 g), chloroform ($CHCl_3$, 80 mL) and H-SiQDs (~100 mg) were mixed in a 300-mL flask and stirred at room temperature for 24 hours. In the same flask, the resultant Br-SiQDs were then reacted with either 1-octanol (22.2 mmol), *t*-butyldimethylsilanol (7.6 mmol), or pyrenebutanol (3.1 mmol) and subsequently stirred overnight. Next, the solvent was removed through rotary evaporation outside of the glove box. The resultant mixture was dispersed in 30 mL of hexane and then centrifuged to remove excess NBS and succinimide by-product that are insoluble in hexane. After removing hexane using a rotovap system, the collected oily orange precipitate was further washed by repeating the following process three times: suspension in chloroform, precipitation with methanol, and separation from the supernatant with centrifugation. The purified product was dispersed in chloroform for further characterization.



Scheme 1. Illustration of H-SiQD bromination using NBS and the subsequent functionalization of the resultant Br-SiQDS with three types of HOR (C_8OH, R_3SiOH, and PyOH) ligands.

Measurements and Characterization: The characterization tools include X-ray diffraction (XRD, Philips X'Pert), Raman spectroscopy (Raman, WItech confocal), UV-Vis absorption spectroscopy (UV-Vis, Shimadzu UV-1800 probe spectrophotometer), fluorescence spectroscopy (PL, Photon Technology International, QuantaMaster 40), transmission electron microscopy (TEM, FEI Titan, 300 kV), Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 4700) with an attenuated total reflection (ATR) accessory, and nuclear magnetic resonance spectroscopy (NMR, JEOL ECA-500). XRD and Raman samples were made by drop-casting SiQDs solutions on glass substrates to form thin films. The UV-Vis and PL samples were diluted chloroform solutions in 3-mL cuvettes. The spectral resolution of these two techniques was 1 nm. All PL measurements utilized an excitation wavelength of 350 nm, a slit width of 3 nm and an integration time of 0.1 s. The TEM samples were prepared by dipping ultrathin carbon-coated copper grids (01824, Ted Pella) in C_8O-SiQDs reaction solutions. For FTIR, 32 scans at a resolution of 2 cm^{-1} were performed on the solution samples that were drop-cast and dried on an ATR crystal. The NMR samples were prepared by dissolving the functionalized SiQDs in $CDCl_3$ and loaded in quartz NMR tubes.

3. Results and Discussion

Sol-gel synthesis of H-SiQDs: The free standing H-SiQDs were characterized by XRD and Raman spectroscopy (**Fig. 1**). The diffraction peaks at 28.5°, 47.4°, and 56.0° in **Fig. 1A** were indexed to the (111), (220), and (311) planes of silicon, according to a silicon standard (the stick patterns in **Fig. 1A**). The peak broadening was assigned to small crystal sizes, confirming the formation of Si nanocrystals.[39,40] In the Raman spectrum (**Fig. 1B**), the peak at 517 cm^{-1} results from crystalline H-SiQDs, with a small blue shift versus the peak at 521 cm^{-1} from bulk silicon due to the size effect.[41] The peak at 493 cm^{-1} was assigned to the presence of amorphous silicon in the sample.[41] Thus the XRD and Raman data strongly suggest the synthesis of nanocrystalline silicon.

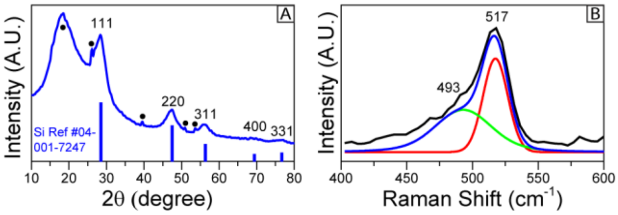


Fig. 1. Characterization of the synthesized H-SiQDs. (A) XRD profile, where the stick pattern is for the silicon reference (JCPSD 04-001-7247) and the dot-marked peaks arise from the glass substrate (**SI-Fig. 4**). (B) Raman spectrum, where the black line is the original data, the green and red lines are from the spectral deconvolution, and the blue line is the sum of green and red lines.

Bromination and functionalization of H-SiQDs: While NBS has been used to functionalize Si wafers and silane molecules,[33,34,37,38] the bromination of H-SiQDs has not been reported to our knowledge. As Si-X bonds are very reactive and difficult to directly characterize and isolate, the success of halogenation is typically confirmed by analyzing the derivatives after functionalization.[7,31] C_8OH was chosen as a functionalization ligand due to its long, linear carbon chain and wide use to functionalize the colloidal-synthesized Cl-SiQDs.[42,43] R_3SiOH was selected as a comparison ligand due to its short, branched carbon chain, stability of the resultant Si-O-Si bond, and novelty to functionalize SiQDs. As shown in **Fig. 2**, the obtained C_8O-SiQDs and R_3SiO-SiQDs present nearly identical UV-Vis absorption spectra (left), PL spectra (right), and visual appearance (inset image), comparable to the characteristics of colloidal SiQDs in the literature.[10,11] The PL peaks at ~680 nm are consistent with the observed red emissions under UV light. The slight difference in maxima of 675 nm for C_8O-SiQDs and 688 nm for R_3SiO-SiQDs can be ascribed to the different capability of the attached C_8O- and R_3SiO-ligands in confining excitons and/or the different SiQD sizes.[3,44,45] The full width at half maximum (FWHM) for the PL spectra of C_8O-SiQDs and R_3SiO-Si QDs are 150 nm and 145 nm, respectively. These values are at the high end of the 130 – 150 nm range reported in the literature for PL spectra with peak positions in the range of 650 – 690 nm (**SI-Fig. 5**).[18,19,21,28,46-50] While the possibility of low passivant surface coverage cannot be ruled out, the more likely reasons for the large FWHM are the wide size distributions (~20% relative standard deviation) and different SiQD shapes (supported by the TEM results). The shoulder at 800 – 850 nm is an artifact resulting from an instrumental correction that compensates for the insensitivity of the PMT (photomultiplier tube) detector beyond 800 nm. The transparency of the yellow solution indicates the high solubility of the colloidal functionalized SiQDs. These results strongly imply the successful bromination and subsequent functionalization.

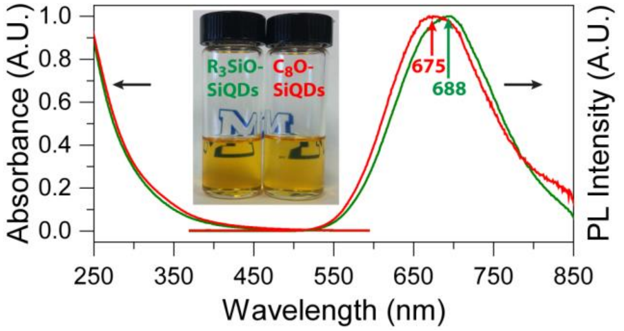


Fig. 2. Absorption spectra (left), PL spectra (right), and optical images (inset) of colloidal C_8O-SiQDs (red) and R_3SiO-SiQDs (green) solutions in chloroform. The excitation wavelength is 350 nm.

FTIR and NMR were employed to collect direct evidence for the bromination and the subsequent functionalization of H-SiQDs. In the FTIR spectrum of pristine H-SiQDs (**Fig. 3-i**), all characteristic peaks were observed: the stretching mode of ν(Si-H) at 2090 cm^{-1}, the scissoring of $\delta(SiH_2)$ at 907 cm^{-1}, and the bending mode of γ(Si-H) at 650 cm^{-1}.[51] The CH_x peaks at 2800 – 3000 cm^{-1} were from toluene, the solvent used to disperse the particles. After bromination and functionalization with C_8OH (**Fig. 3-ii**) and R_3SiOH (**Fig. 3-iii**), all peaks from Si-H disappeared, suggesting complete bromination. In the case of C_8O-SiQDs, the strong and broad peak centered at 1038 cm^{-1} was assigned to the newly-formed Si-O-C bond. In the case of R_3SiO-SiQDs, the newly-formed Si-O-Si bond was found at 1050 cm^{-1}.[17] The three sharp peaks at 1258 cm^{-1}, 838 cm^{-1}, and 784 cm^{-1} can be assigned to $Si\text{-}CH_3$.[52] The -OH stretching mode at 3300 cm^{-1} was ascribed to a small amount of free ligand.[52]

The ^1H NMR spectrum of C_8O-SiQDs (**Fig. 4-i**) provides the following positive evidence: 1) the signals from the C_8O-moiety were located at the expected positions of δ = 0.86 ppm (8), 1.25 ppm (4 - 7) and 1.55 ppm (2 and 3); 2) the methylene peak observed at δ = 3.75 ppm (1) was slightly shifted versus free C_8OH (■); and 3) all peaks are broadened, indicating the steric restriction of protons on the SiQD surfaces.[53] In the ^1H NMR spectrum of R_3SiO-SiQDs (**Fig. 4-ii**), two expected peaks from *t*-butyl and methyl can be found at δ = 0.2 ppm (1′) and 0.9 ppm (2′), respectively; the proton in the Si-OH moiety was absent at ~3.3 ppm, as expected.

In the ^{13}C NMR spectrum of C_8O-SiQDs (**Fig. 5-i**), eight peaks were observed at δ = 14.3 ppm (8), 22.9 ppm (7), 26.0 ppm (6), 29.6 ppm (4), 29.5 ppm (5), 32.0 ppm (3), 33.0 ppm (2), and 63.4 ppm (1). The 63.4 ppm peak was shifted by +0.1 ppm relative to that of C_8OH and can be assigned to the C_8O-moiety. In the ^{13}C NMR spectrum of R_3SiO-SiQDs (**Fig. 5-ii**), the *t*-butyl, quaternary, and methyl carbons originating from the R_3SiO-moiety were observed at the expected positions of δ = 25 ppm (3′), 18 ppm (2′), and -4 ppm (1′), respectively. The peak broadening was due to the steric restriction, indicating the attachment of R_3SiOH to the SiQD.[16] With the above analysis, we conclude that FTIR and NMR measurements provide strong evidence for the bromination with NBS as well as the subsequent functionalization with C_8OH and R_3SiOH.

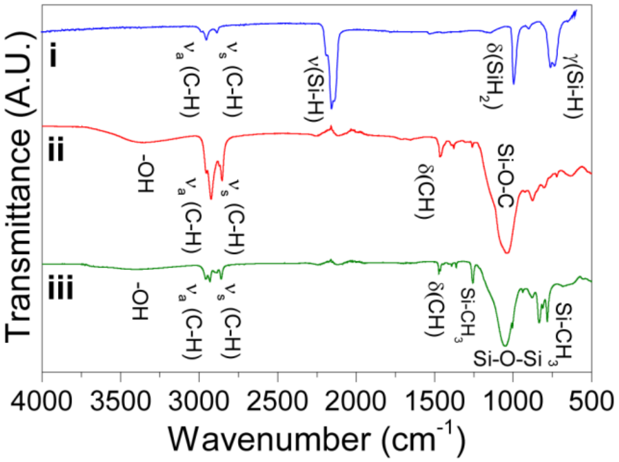


Fig. 3. FTIR spectra of H-SiQDs (i), C_8O-SiQDs (ii), and R_3SiO-SiQDs (iii) to assess the attachment of passivating ligands.

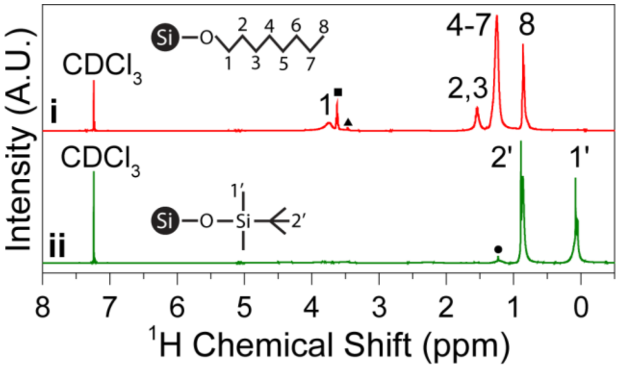


Fig. 4. ^1H NMR spectra of C_8O-SiQDs (i) and R_3SiO-SiQDs (ii) to assess the attachment of passivating ligands. The square (■) indicates free C_8OH, the triangle (▲) refers to the solvent methanol, and the circle (●) denotes an unknown impurity originating from the R_3Si-OH reagent.

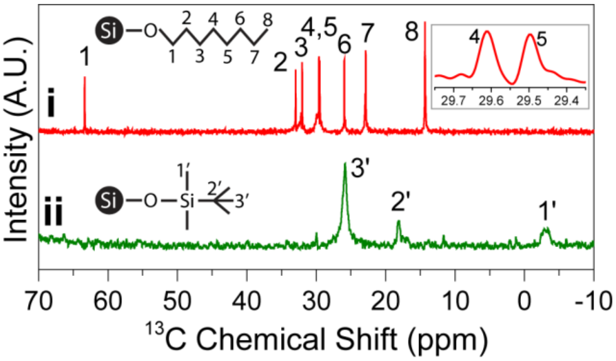


Fig. 5. ^{13}C NMR spectra of C_8O-SiQDs (i) and R_3SiO-SiQDs (ii) to assess the attachment of passivating ligands. The inset highlights peaks 4 and 5 in spectrum (i).

The obtained C_8O-SiQDs were then characterized using TEM (**Fig. 6**). The low-magnification image in **Fig. 6A** shows that the obtained C_8O-SiQDs were spherical and rod-like in shapes. The corresponding histogram (**Fig. 6B**) show that the average equivalent spherical diameter is 7.4 ± 1.5 nm. According to quantum confinement theory, the wavelength of maximum light emission from SiQDs of this size should be ~1000 nm.[54] The discrepancy may be ascribed to the decreased crystal sizes of the synthesized C_8O-SiQDs due to surface oxidation.[18,19,55,56] The selected area electron diffraction in (C) shows three characteristic diffraction rings of crystalline Si: (111), (220), and (311). High-resolution TEM images in (D) and (E) highlight one spherical and one rod-like SiQDs, respectively. The lattice fringes of 0.33 nm spacing throughout the entire particles indicate their single-crystalline nature.

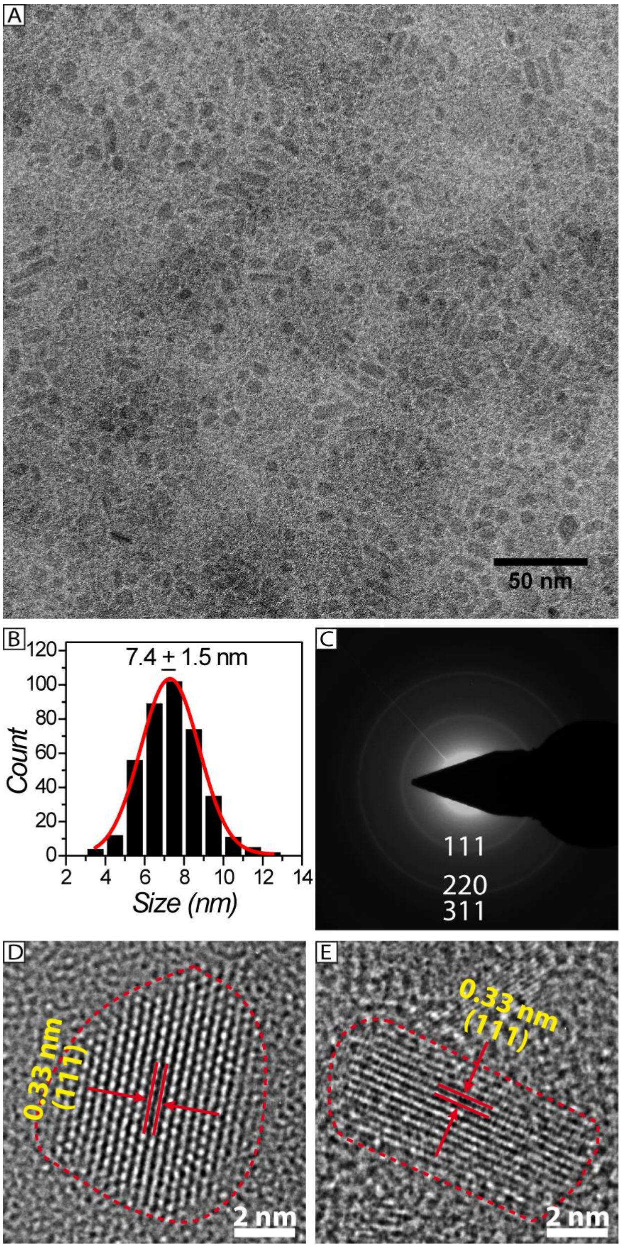


Fig. 6. TEM characterization of C_8O-SiQDs to analyze particle sizes, shapes, and crystallinity. (A) Low-magnification image; (B) histogram of the size distribution of the particles shown in (A); (C) selected area electron diffraction pattern of the particles shown in (A); (D) high-resolution image of a spherical SiQD; and (E) high-resolution image of a rod-like SiQD**.**

After the success of chemically attaching optically inactive ligands described above, we turn to PyOH, a fluorescent and aromatic molecule. The aim was to study whether it is possible to achieve energy transfer between the fluorophore ligands and SiQDs, an important process in optoelectronic applications of SiQDs, such as LEDs.[57] The UV-Vis absorption spectrum (Abs., blue in **Fig. 7**) shows the characteristic signal of the PyO-moiety at around 350 nm, superimposed on the absorption profile of SiQDs (refer to **Fig. 2**). The strong PL peak (red in **Fig. 7**) at 720 nm resulting from the SiQD-moiety versus the nearly-disappeared peak at 500 nm originating from the PyO-moiety (**SI-Fig. 6**) indicates the energy transfer from the PyO-moiety to the SiQD-moiety.[58] The significant redshift of the PL peak position versus those of C_8O-SiQDs and R_3SiO-SiQDs results from the delocalized excitons and different surface chemistry.[3,44,45] The photoluminescence excitation spectrum (PLE, black in **Fig. 7**) consisting of both the PLE feature of SiQDs at 400 nm and the absorption feature of PyOH at 350 nm (**SI-Fig. 6**) further confirms that the energy transfer herein follows the Förster resonance mechanism.[46,57,59,60] These results clearly demonstrate the feasibility of studying optoelectronic properties of SiQDs by functionalizing H-SiQDs with the respective fluorophores through pre-bromination.

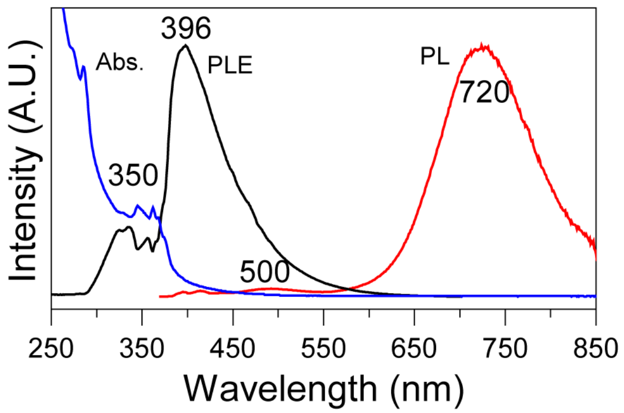


Fig. 7. Spectral characterization of the obtained PyO-SiQDs: absorption spectrum (Abs., blue); PL spectrum excited at 350 nm (red); and PL excitation spectrum (PLE, black) measured at 720 nm.

3. Conclusions

In conclusion, a room-temperature mild bromination of hydrogen-terminated silicon quantum dots (H-SiQDs) using N-bromosuccinimide has been proven an effective method to produce bromine-terminated SiQDs (Br-SiQDs). The prepared Br-SiQDs can then be in-situ functionalized with a variety of alcohols/silanols to prepare ambient stable and soluble red-emissive SiQDs. Three model systems using 1-octanol, *t*-butyldimethylsilanol, and 1-pyrenebutanol (PyOH) as surface ligands have been studied. A strong energy transfer from the PyO-moiety to the SiQD-moiety in PyO-SiQDs has been observed. This method circumvents two limitations: 1) only alkene and alkyne organic ligands can be directly grafted onto H-SiQDs through hydrosilylation; and 2) the directly synthesized halogen-terminated SiQDs do not present the quantum confinement effect. The generality of this method to other functional ligands and the application in photovoltaics are currently in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Extra synthesis and characterization details for chlorination of H-SiQDs with PCl_5, bromination of triethylsilane and the subsequent functionalization with 1-octanol]. See DOI: 10.1039/b000000x/

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