Silicon Nanoparticles with Surface Nitrogen: 90% Quantum Yield with Narrow Luminescence Bandwidth and the Ligand Structure Based Energy Law

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Supporting Information

ABSTRACT: Silicon nanoparticles (NPs) have been widely accepted as an alternative material for typical quantum dots and commercial organic dyes in light-emitting and bioimaging applications owing to silicon’s intrinsic merits of least toxicity, low cost, and high abundance. However, to date, how to improve Si nanoparticle photoluminescence (PL) performance (such as ultrahigh quantum yield, sharp emission peak, high stability) is still a major issue. Herein, we report surface nitrogen-capped Si NPs with PL quantum yield up to 90% and narrow PL bandwidth (full width at half-maximum (fwhm) ≈ 40 nm), which can compete with commercial dyes and typical quantum dots. Comprehensive studies have been conducted to unveil the influence of particle size, structure, and amount of surface ligand on the PL of Si NPs. Especially, a general ligand-structure-based PL energy law for surface nitrogen-capped Si NPs is identified in both experimental and theoretical analyses, and the underlying PL mechanisms are further discussed.

KEYWORDS: silicon nanoparticles, ultrabright fluorescence, narrow bandwidth, quantum dots, PL energy law

Gaining light from silicon has long been a dream for the scientific community. Silicon-based highly efficient light-emitting or amplifying materials would be of great significance not only for the development of the next technological frontiers—silicon photonics and optoelectronics—as silicon is the core of photovoltaics and microelectronics, but also to look for an alternative material for typical cadmium-based quantum dots and commercial organic dyes in light-emitting or bioimaging applications due to silicon’s intrinsic merits of least toxicity, low cost, and high abundance.1−7 Initially inspired by Canham’s discovery in the early 1990s that silicon can emit light at room temperature when made to be nanoporous,8,9 research on light-emitting silicon nanomaterials has since been ongoing for more than two decades, moving from initial porous silicon to recent free-standing colloidal silicon nanoparticles (NPs) or silicon quantum dots.8−21

However, improving Si NPs’ photoluminescence (PL) performance to achieve ultrahigh quantum yields (QYs) and narrow luminescence bandwidth is still a major target.5,22 High QYs up to 60% have been reported from plasma-based synthesis but only for large-size Si NPs, and the QYs drop significantly for those smaller sized NPs that emit visible light.23−25 Besides, previous Si NPs usually show broad PL bandwidths (full width at half-maximum (fwhm) 70−150 nm), which is probably a result of the electron−phonon effect and the inhomogeneous broadening from different sizes of Si NPs in the sample.26 Recently, a type of surface-modified and heavily oxidized Si NPs with a QY up to 75% in water has been reported by Li et al., but it still shows a broad emission (fwhm ~100 nm).27 To date, there has been no report of Si NPs simultaneously possessing ultrahigh QY and narrow PL bandwidth, which hinders Si NPs from being applied in many areas such as parallel detection in biolabeling or high color rendering index LEDs.

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Figure 1. Synthesis of yellow-emitting On-Si NPs with exceptional PL properties. (a) Scheme of the solution reduction synthesis and surface modification to make yellow-emitting Si NPs with ultrahigh quantum yield and narrow PL bandwidth. (b) Photograph of Si NPs in glyme under ambient light after the reaction. (c) TEM graph of On-Si NPs with an average diameter of 5.2 nm. Inset is the selected-area electron diffraction pattern of the On-Si NPs. Multiple rings are consistent with diamond lattice Si (111) at 3.1 Å and (220) at 2.0 Å. (d) PL, PLE, and Abs spectra of the On-Si NPs. The fwhm of the PL peak is very narrow (only 40 nm) (scale bar in TEM image: 20 nm).

On the other hand, a major question in the research area of Si NPs is the longstanding controversy regarding the association of optical spectroscopic results (in particular PL) with the structure of Si NPs. To date, it still lacks some general laws and theoretical models that can explain the reported PL of Si NPs made by different methods. Only those C- and H-terminated Si NPs made by pyrolysis of silane or thermal decomposition of hydrogen silsesquioxane were found to follow the quantum-confinement model. In recent years, the strong influence of surface on the PL of Si NPs has been reported by different groups. For example, Dasog et al. demonstrated in 2013 that surface doping with nitrogen would change Si NPs’ PL from the “slow red” quantum-confinement state to the “fast blue” charge-transfer surface state. DeBenedetti et al. found that this conversion can also be caused by passivating surface dangling bond defects with alcohol. Recently, various surface-modified Si NPs of the same size were demonstrated to exhibit distinct PL colors in the full visible range. However, it is still difficult to obtain some general laws for the relation between the surface structure and the PL energy of Si NPs made by different methods, which severely hampers the understanding of the mechanism of the PL from Si NPs.

Herein, we report surface nitrogen-capped yellow-emitting Si NPs with photoluminescence QY up to 90% and a narrow luminescence bandwidth of ~40 nm, of which the performance can compete with commercial dyes and typical quantum dots. The influences of particle sizes and ligands on the Si NPs’ PL have been comprehensively studied, which demonstrate that the structure of the ligand is critical for the ultrabright PL with narrow luminescence bandwidth. Femtosecond transient absorption spectroscopy reveals that this type of ultrabright and sharp yellow-emitting Si NPs has a surprising pure radiative decay with minimum nonradiative component, corresponding to the excellent PL performance. More importantly, a general ligand structure law on the PL energy is attained for the surface nitrogen-capped Si NPs experimentally and theoretically, and the underlying mechanism is discussed.

RESULTS AND DISCUSSION

The procedure to fabricate the Si NPs is shown in Figure 1a. Silicon tetrabromide (SiBr₄) is chosen as the precursor, rather than SiCl₄ as before. This is due to the better leaving tendency of −Br than the −Cl group, which promotes the subsequent nucleophilic substitution of a weak nucleophile such as 1,2,3,4-tetrahydrocarbazol-4-one (abbreviated as On), thus greatly reducing the reaction time. The as-synthesized Si NPs are termed On-Si NPs. It is worth noting that the On-Si NPs show excellent PL properties. As shown in Figure 1b, a surprisingly ultrabright yellow PL can be observed even under room light after the reaction of ~12 h. Figure 1c displays the TEM image of our On-Si NPs, and the inset is the corresponding selected-area electron diffraction pattern. The average size is determined to be 5.2 nm based on measuring more than 300 nanoparticles, and the size distribution is shown in Figure S1. The UV–vis absorption, PL, and PL excitation (PLE) spectra were measured after purification. As shown in Figure 1d, the PL is centered at ~555 nm with a rarely observed narrow peak (fwhm: ~40 nm). The PLE peak is around 520 nm, corresponding to the absorption (Figure 1d). The PL quantum yield was measured based on a relative method using rhodamine B (in water) as a reference. As shown in Figure S2, the QY was very high (~90%). The PL lifetime of the On-Si NPs (measured at PL maximum) is about 3 ns in methanol with a single-exponential decay (Figure S3). PL spectra under different excitation wavelengths are displayed in Figure S4, which show a consistent PL peak position at ~555 nm, suggesting a uniform fluorescent emitter in the sample. It should be noted that On-Si NPs show the same PL, PLE, and absorption spectra after surface-modification if SiCl₄ was used as the precursor in the synthesis, suggesting the precursor and the unreacted Si–Cl/Br bonds on the surface play negligible roles in the final optical properties of On-Si NPs. The merits of this type
of highly fluorescent On-Si NPs are as follows. First, the previously reported Si NPs or Si nanocrystals usually showed broad peak PLs (fwhm 70−150 nm), although recently He’s group reported biomimetic Si NPs with a 30 nm fwhm but only with a 15−20% QY. In our current work, the Si NPs possess simultaneously a narrow PL bandwidth and an ultrahigh QY, which can compete with the high-performance fluorescent dyes as well as typical quantum dots. Second, most of the previously reported Si NPs showed weak absorbance with no resolved absorption peak in the visible range. This is due to the indirect band gap transition of silicon, which leads to relatively weak absorbance below the first direct band gap (Γ−Γ, ~3.6 eV). The molar absorption coefficient of our On-Si NPs is determined to be ~6 × 10^4 M^{-1} cm^{-1} at 520 nm, which is significantly higher than that of conventional Si NPs in the visible range and similar to the values of typical quantum dots.

As the overall brightness of a fluorescent material is the product of PL quantum yields and the absorbance cross-section, our
current On-Si NPs have successfully overcome the two limitations in conventional Si quantum dots. This type of Si NPs emits strong fluorescence even under room light and holds great promise in future development of various applications.

The On-Si NPs were further characterized by X-ray photoemission spectra (XPS) and FTIR analyses. In the XPS analysis, the high-resolution spectrum of the Si 2p region (Figure 2a) shows the Si(0) peak at about 99.4 eV, which confirms the silicon core and is consistent with selected-area electron diffraction (SAED) results. The Si(II), Si(III), and Si(VI) signals arising from the surface Si–N and Si–O species can also be observed (Figure 2a). The peak at ~398.5 eV in the N 1s spectrum (Figure 2b) and the peak at ~532.9 eV in the O 1s spectrum (Supporting Figure S5) also confirm the formation of Si–N and Si–O–Si/ Si–O–H bonds, respectively, on the Si NP surface. Meanwhile, in the FTIR spectra (Figure 2c), the characteristic N–H stretch and bending modes (ca. 3100–3200 and 1626 cm⁻¹) of neat Oligands are absent in the spectrum of Si NPs, which is consistent with the amine group reacting with the silicon surface. In addition, oxidation of Si NPs can also be evidenced by the Si–O–Si stretch features at ~1100 cm⁻¹ and the broad Si–O–H stretch at 3300–3400 cm⁻¹ (Figure 2c); these peaks become much more pronounced if the solid sample on the KBr plate is exposed to air for several hours. The aromatic and alkyl C–H stretches at ca. 3047 and 2928 cm⁻¹ are also observed in all three spectra (Figure 2c). Taken together, the characterization results suggest that a crystalline silicon(0) core indeed exists in the On-Si NPs, and it is surrounded by a N-capped and oxidized surface with ligands attached through Si–N bonds (Figure 2d).

The influence of size on the On-Si NPs’ PL has been further studied. As shown in Figure 3, smaller sizes of On-Si NPs of 4.1 and 2.8 nm were also successfully obtained by reducing all the reactant concentrations two and three times in the reaction (Figures 3a,b and 3d,e). It is surprising that the PL positions of the 4.1 and 2.8 nm Si NPs (Figures 3c and 3f) are nearly the same compared with the above 5.2 nm Si NPs, and no blue shift can be observed. On the other hand, the QYs of these smaller Si NPs are still higher than 80%, and the fwhm slightly broadens to 43 and 53 nm as the size decreases. These results suggest that the ultrabright yellow PL from the On-Si NPs is different from the quantum-confinement-based size-dependent PL; the latter shows a distinct relationship between the PL energy and the particle size. In our case, the surface effect is so strong that a uniform surface center dominates the light-emitting process no matter what sizes the Si NPs are. This can also explain the narrower PL bandwidth of our On-Si NPs compared with conventional Si NPs, as there is no inhomogeneous broadening of emission from different sizes of NPs.

To further explain such ultrabright luminescence with narrow bandwidth, femtosecond transient absorption (TA) spectroscopy was carried out on our On-Si NPs. Figure 4a shows the time evolution of transient absorption spectra excited at 490 nm. Immediately after excitation, a strong ground-state bleaching (GSB) signal centered at 520 nm was observed, corresponding to the UV–vis absorption spectrum. In the following one picosecond, another negative peak centered at 550 nm rises accompanied by the decay of GSB at 520 nm, which should be ascribed to stimulated emission (SE) corresponding to the fluorescence of the Si NPs. To extract the excited-state species, global analyses (Figure 4b) were performed on the data, and three decay components (1.5 ps, 82 ps, 3.0 ns) were obtained. Since the pump (490 nm) is slightly higher in energy than the absorption peak (at 520 nm), the excess energy will be dissipated through vibrational relaxation before the excited-state carriers relax to the emissive state. Therefore, the first 1.5 ps component can be attributed to the vibrational relaxation from hot S₁ to S₀. The second (82 ps) and the third (3.0 ns) DAS (decay-associated spectra) components have a very similar spectral shape, so that they should be assigned to nonradiative conversion and radiative emission from S₁ to S₀. Kinetic traces at different wavelengths

Figure 4. Femtosecond transient absorption study of the On-Si NPs. (a) Time evolution of transient absorption spectra (excitation at 490 nm). (b) Decay-associated spectra (DAS) obtained from the global analysis (excitation at 490 nm). (c) DAS obtained from the global analysis (excitation at 350 nm). (d) Energy diagram of the On-Si NPs.
with the corresponding fittings by the above three time constants are shown in Figure S6. Compared with our previously reported Si NPs, the excited-state deactivation of On-Si NPs is much simpler and the emissive component has a much higher amplitude than the nonradiative decay component (Figure 4b). As is known, the complex nonradiative excited-state deactivation processes (e.g., vibrational cooling) are the main reason for the decreasing of QYs and broadening of PL peaks. The relatively simple excited-state deactivation and less nonradiative decay obtained from the TA spectra further explain the very high fluorescence quantum yield and narrow PL bandwidth of On-Si NPs. The TA spectra excited at 350 nm and the corresponding global analysis were also performed, and the results are shown in Figure 4c and Figures S7 and S8. When excited at 350 nm, the DAS obtained from the global analysis shows an extra ultrafast 0.2 ps component and the other three components (1.9 ps, 86 ps, and 3.1 ns) are nearly the same as the three components obtained when samples are excited at 490 nm. Since the excitation energy is around the intrinsic direct Γ−Γ band gap of silicon but still lower than the absorption onset of the On-ligand (start from 300 nm), the 0.2 ps component can be ascribed to the ultrafast surface carrier trapping of the electrons excited from the silicon core. The energy diagram of our On-Si NPs and the surface-state emission dynamics are shown in Figure 4d. In our Si NPs, the electrons can be excited through higher energy states, but the radiative recombination only happens on the surface state, which results in the ultrabright yellow PL.

As the PL is closely related with the structure of the ligand, different surface ligands were tried. Interestingly, a further red-shift of PLE and PL can be realized by other surface modifiers. Besides the previously reported aniline, it is found that other aniline derivatives can further narrow the band gap even to red. For example, the 4-aminoacetophenone-modified Si NPs (termed Aon-Si NPs) exhibit a PL maximum at about 600 nm and PLE maximum at 540 nm. The N-phenyl-1,4-phenylenediamine-modified Si NPs (termed Azo-Si NPs) gave rise to PL at about 640 nm and a PLE maximum at 480 nm.

![Figure 5. Ligand structure law on Si NPs’ PL energy. (a) PL of Si NPs with different surface ligands excited at 400 nm (blue: chlorine; cyan: carbazole; yellow: On; orange: 4-aminooctophenone; red: phenyl-1,4-phenylenediamine). (b) PL energies of various surface-modified Si NPs obtained from experiment. (c) Models of the nanoparticles with various ligands and HOMO and LUMO orbitals, respectively (left to right). (Azo stands for N-phenyl-1,4-phenylenediamine.)](image)

All types of nanoparticles are in organic solvents. Different sizes of these Si NPs have also been made, and no size-dependent difference of PL or PLE can be observed. On the other hand, different from arylamine, all the alkyamine-modified Si NPs show only blue PLs in the 400−480 nm range (examples are shown in Figure S11), which are similar to the previous results by the Veinot group. These experimental results show that the primary aryl amine ligand, with the ability to form two Si−N bonds with two surface Si atoms on the NPs, has a stronger red-shifting effect on the Si NPs PL than the secondary aromatic amine ligand, which can form only one Si−N bond on the Si NPs surface, and more delocalized groups on the ligands lead to further band gap narrowing (i.e., red-shifting of PL). Thus, together with our previous work, the solution-fabricated Si NPs with PL from deep blue to red can be realized and the relation of the PL energy and ligand structure can be generalized (Figure 5a and b). The QYs of all of the aromatic primary amine-modified Si NPs are very low (<1%), and their PL lifetimes are all less than 5 ns. NMR analysis was performed to confirm the attachment of ligands on the particle surface as opposed to free unbound ligands. As shown in Figures S12, 13, and 14, the characteristic peaks of neat ligands can also be observed in their corresponding ligand-modified Si NPs but with a dramatic broadening of NMR peaks, which suggests that the ligands are indeed attached on the surface and the peak broadening is caused by the restricted tumbling of surface-bound ligands compared to their free state. The surface coverage of ligands has also been estimated through a well-established literature procedure (details shown in the Methods section), which is estimated to be 59% from NMR analysis (Figure S15) and 62% from TGA results (Figure S16). It should be noted that although the organic ligands themselves show PL, PLE, and absorption, they are only in the UV range (Supporting Figures S17, S18, S19, and S20); therefore, the color-tunable PL of our Si NPs with the various ligands cannot arise from the ligands themselves. It should also be noted that a blank reaction using a mixture of glyme, Na naphthalide, and the capping agent alone has also been done under the same reaction conditions.
conditions, but only very weak UV-blue emission can be observed (Supporting Figure S21); therefore, the 550–650 nm PL originates from the Si NPs capped by various arylamine ligands, rather than from the impurities or byproducts.

Density functional theory (DFT) calculations are conducted to further qualitatively rationalize the effect of ligand on the PL band gap of the Si NPs. For simplicity and to reduce the computational cost, the Si NPs are modeled using the framework of Si$_{35}$H$_{35}$L (Figure S22). Results of the calculated HOMO–LUMO band gaps of various surface-modified Si NPs are compiled in Table 1. The relation of the HOMO–LUMO band gap and the ligand structure is in good agreement with the PL energy trend obtained from experimental results in Figure 5b. Figure 5c shows the electron density distribution of the HOMO and LUMO of Si NPs at the ground state. For the Cl-passivated case (Si$_{35}$H$_{35}$Cl) the HOMO and LUMO are delocalized throughout the nanoparticle. Attachment of all types of our aryl amine ligands results in localization of the HOMO on the ligand, while the LUMO remains delocalized through the core of the nanoparticle. Localization of the HOMO on the ligand should result in increment of the orbital energy, therefore leading to a smaller HOMO–LUMO gap compared to Si$_{35}$H$_{35}$Cl. In addition, DFT calculation results also show that an increase in the number of ligands on Si NPs slightly shifts the HOMO level to higher energies and notably increases the density of the HOMO (Figure 6a), indicating that covering of the Si NPs with more ligands can enhance the PL properties of the nanoparticles and further red-shifts the band gap (Table 2). This is also demonstrated by experimental results. The optical properties of On-Si NPs can be tailored by reducing the amount of added the –On ligand to 0.02 g in our reaction. (Calculations show that the molar amount of 0.02 g of the –On ligand equals ~1/10 of Si–Cl bonds on NPs’ surface.) As shown in Figure 6b, all the PL, PLE, and absorption of the Si NPs are blue-shifted, compared with the On-Si NPs modified by excess ligands. The PLE and absorption peak are blue-shifted to ~467 nm, and the PL to 543 nm.

The PL energies of surface nitrogen-capped Si NPs from our work and other recent studies are shown and compared in Figure 7a. It is very interesting that PL peak energies of surface nitrogen-capped Si NPs from different fabrication methods, though of different sizes, different degrees of crystallinity, different amounts of ligands on the surface, and different degrees of oxidation, can still be fit into a general ligand structure law. That is, arylamine shows a significant red-shift effect of PL, and more delocalized/conjugated groups on the ligands will lead to further band gap narrowing, while the PLs of allylamine-capped Si NPs remain in the blue range. In addition, all the surface nitrogen-capped Si NPs show a short lifetime in the nanosecond range, except for the work of He’s group, in which the PL lifetime was not reported. Thus, it can now be reasonably deduced that this kind of PL with a nanosecond lifetime arises from the surface nitrogen sites and the PL energy of Si NPs is determined by the structure of surface ligands (Figure 7b). This ligand-structure-based PL energy law is similar to the molecular structure law of organic dyes, but this type of surface PL is totally different from the quantum-confinement state in conventional silicon quantum dots (Figure 7c), which arises from the indirect X–L transition and shows a size-dependent band gap and microsecond lifetime.

More studies are still needed in the future to fully unveil the underlying mechanism of the PL from surface N-capped Si NPs. For example, where are the electrons exactly excited from: the silicon core or the exterior oxide/nitride layer? In our case, the PLE spectra also show a significant red-shift effect, and there are obvious overlaps between the PL and PLE spectrum. This indicates the electrons can be efficiently excited from the low-energy surface. However for those blue-emitting Si NPs, their electron excitations probably come from direct transitions of the

### Table 2. Calculated HOMO, LUMO, and Energy Band Gap (eV) for Si$_{35}$Cl$_{34}$xR$_1$R$_2$

<table>
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<tr>
<th>Entry</th>
<th>$-R_1$</th>
<th>$-R_2$</th>
<th>HOMO–LUMO</th>
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<tr>
<td>1</td>
<td>–Cl</td>
<td>–Cl</td>
<td>1.99</td>
<td>–6.20</td>
<td>–4.21</td>
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<tr>
<td>2</td>
<td>–On</td>
<td>–Cl</td>
<td>1.06</td>
<td>–5.24</td>
<td>–4.18</td>
</tr>
<tr>
<td>3</td>
<td>–On</td>
<td>–On</td>
<td>1.06</td>
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Figure 6. Influence of ligand amount on the optical properties of Si NPs. (a) Calculated electron density distribution of the HOMO and LUMO of the Si NPs with different amounts of On-ligand. (b) PL, PLE, and absorption spectra of the green-yellow-emitting On-Si NPs obtained by reducing the amount of added surface ligand during reaction.

8390

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silicon core, as the band gaps of surface SiO\(_x\)N\(_y\) and alkyl amine ligands are too large (4.5–8.0 eV).

CONCLUSIONS

In summary, ultrabright yellow-emitting Si NPs with a QY up to 90% and a narrow PL bandwidth (≈40 nm) have been obtained. Our work demonstrates that the PL performance of Si NPs after surface modification can compete with commercial dyes and typical quantum dots. The influences of particle size and ligand on the Si NPs’ PL have been comprehensively studied, which demonstrate that the structure of ligands is critical for the PL from the surface. A general ligand structure based PL energy law for surface nitrogen-capped Si NPs has been obtained both experimentally and theoretically, and the underlying mechanisms of PL from the Si NPs’ surface are also revealed.

METHODS

Chemicals. Silicon tetrabromide, silicon tetrachloride, glyme, sodium, naphthalene, 4-aminoacetophenone, and N-phenyl-1,4-phenylenediamine were purchased from Sigma-Aldrich. 1,2,3,4-tetrahydrocarbazol-4-one was purchased from TCI America.

Synthesis of Ultrabright-Yellow-Emitting On-Si NPs. In a typical synthesis of yellow-emitting On-Si nanocrystals (NCs), 0.51 g of sodium and 2.25 g of naphthalene were stirred in 15 mL of glyme for approximately 1 h to produce sodium naphthalide. Then, 0.7 mL of SiBr\(_4\) was added dropwise. The surface treatment was performed by adding excess 1,2,3,4-tetrahydrocarbazol-4-one to the as-synthesized Si NPs and stirring the mixture at room temperature for 24 h.

Synthesis of Orange- to Deep-Red-Emitting Si NPs. Generally, 0.17 g of sodium and 0.75 g of naphthalene were stirred in 15 mL of glyme for approximately 1 h to produce sodium naphthalide. Then, 0.20 mL of SiCl\(_4\) was added dropwise. The surface treatment was performed by adding excess 4-aminoacetophenone and N-phenyl-1,4-phenylenediamine to the as-synthesized Si NPs and stirring the mixture at room temperature for 24 h.

Synthesis of Green-Yellow-Emitting On-Si NPs. In a typical synthesis of yellow-emitting On-Si NCs, 0.51 g of sodium and 2.25 g of naphthalene were stirred in 15 mL of glyme for approximately 1 h to produce sodium naphthalide. Then, 0.7 mL of SiBr\(_4\) was added dropwise. The surface treatment was performed by adding 0.02 g of 1,2,3,4-tetrahydrocarbazol-4-one to the as-synthesized Si NPs and stirring the mixture at room temperature for only 24 h.

Computations. For the sake of simplicity and reduction of computational expenses, the silicon nanoparticles are modeled using a fully H-passivated nanoparticle, Si\(_{35}\)H\(_{36}\), which has T\(_d\) symmetry with a diameter of ≈1 nm. The nanoparticle was placed at the center of a cubic box of 35.0 Å × 35.0 Å × 35.0 Å. The geometry optimization at the DFT level was carried out using the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation and the projector augmented-wave (PAW) method. The kinetic energy cutoff was chosen to be 450 eV, and integration in the reciprocal space was carried out at the Γ-points of the Brillouin zone. To investigate the effect of surface modification by various ligands (L), one or two Cl/H atoms are replaced by the ligands. The resulting Si\(_{35}\)H\(_{35}\)L were next optimized using DFT. All the calculations were performed with the Quantum Espresso package.

Femtosecond Transient Absorption Experiments. In the transient absorption setup, a mode-locked Ti:sapphire laser/amplifier
were conducted for concentrated solutions of functionalized Si NPs in water using a PHI 5000C ESCA system. NMR measurements were performed using a Thermo/ATI/Mattson 60AR FTIR spectrometer. XPS measurements were measured with a time-correlated single photon counting technique; a spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-400 system (Spit; Spectra-Physics, Santa Clara, CA, USA) was used. The output of the amplifier of 1.5 mJ pulse energy, 100 fs pulse width, and 500 Hz repetition rate at 800 nm wavelength was split into two parts. The stronger beam was used to pump the optical Parametric amplifier and generate pump pulses at selected wavelengths, and the other 800 nm beam was used to generate the broadband white-light probe pulses in the 400–800 nm range by focusing it into a 2 mm thick sapphire plate. Both the white continuum pulse and pump pulse are focused on the sample and overlap with each other in space. The transient absorption data were collected by a fiber-coupled spectrometer connected to a computer. The group velocity dispersion of the transient spectra was compensated by a chirp program. All the samples were stored in a 1 mm cuvette for the TA experiments at room temperature. During the femtosecond experiments, the sample was stirred by a magnetic bar coated by Teflon, and no change in the UV–vis was observed before and after the experiments.

Characterization. The UV–vis absorption spectra were recorded in the range 190–1100 nm using a Hewlett Packard 8543 diode array spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-3 spectrophluorometer (Horiba Jobin Yvon). Fluorescence lifetimes were measured with a time-correlated single photon counting technique; a pulsed LED source (376 nm, 1.1 ns) was used as excitation source. The TEM and SAED measurements were performed on a JEOL-2000EX microscope operating at 200 kV. The FTIR spectrum was recorded on a Thermo/ATI/Mattson 60AR FTIR spectrometer. XPS measurements were conducted using a PHI 5000C ESCA system. NMR measurements were conducted for solution-functionalized Si NPs in DMSO-d$_4$ using a Bruker 300 MHz instrument. Thermogravimetric analysis (TGA) was conducted on a TGA Q500 thermal analysis system. Approximately 9 mg of the ON-Si NP sample was loaded onto a platinum pan and heated under a constant N$_2$ (UHP) atmosphere at a rate of 15 °C/min.

Estimation of Surface Coverage. To estimate the Si NP surface coverage of ligands, 7.0 mg of ON-Si NPs was dispersed in 1 mL of DMSO-d$_4$ with 0.05% (v/v) tetramethylethylene (TMS). The ratios of the integrated peak areas arising from the ligand protons to the peak from the TMS proton were determined from the H NMR spectra (see Figure S15). The surface coverage was also independently estimated by TGA assuming that the mass loss is due to the loss of grafted organic ligands (TGA result shown in Figure S16). A 4.0 nm Si NP contains a total of ~1600 Si atoms and ~500 surface Si atoms.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b03113.

Supporting Figures S1–S2 (PDF)

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The authors declare no competing financial interest.

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