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Nanoparticles Surface-Modified with Organic Molecules via
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Complete List of Authors:	Miyano, Mari; Hokkaido University, Faculty of Engineering Kitagawa, Yuichi; Hokkaido University, Faculty of Engineering Wada, Satoshi; Hokkaido University, Faculty of Engineering Kawashima, Akira; Hokkaido University, Faculty of Engineering Nakajima, Ayako; Hokkaido University, Faculty of Engineering Nakanishi, Takayuki; Hokkaido University, Faculty of Engineering Ishioka, Junya; Hokkaido University, Faculty of Engineering Shibayama, Tamaki; Hokkaido University, Faculty of Engineering Watanabe, Seiichi; Hokkaido University, Graduate School of Engineering Hasegawa, Yasuchika; Hokkaido University, Faculty of Engineering

Photophysical Properties of Luminescent Silicon Nanoparticles Surface-Modified with Organic Molecules via Hydrosilylation

Mari Miyano, Yuichi Kitagawa*, Satoshi Wada, Akira Kawashima, Ayako Nakajima, Takayuki Nakanishi, Junya Ishioka, Tamaki Shibayama, Seiichi Watanabe, and Yasuchika Hasegawa*

Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, Hokkaido 060-8628,
Japan

Author information

Corresponding Authors

Tel & Fax: +81-11-706-7114

y-kitagawa@eng.hokudai.ac.jp (Y. Kitagawa)

hasegaway@eng.hokudai.ac.jp (Y. Hasegawa)

Faculty of Engineering, Hokkaido University

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Abstract: Luminescent silicon nanoparticles have attracted considerable attention for their potential uses in various applications. Many approaches have been reported to protect the surface of silicon nanoparticles and prevent their easy oxidation. Various air-stable luminescent silicon nanoparticles have been successfully prepared. However, the effect of interactions of the π -electron system with the silicon surface on the excited state properties of silicon nanoparticles is unclear. In this study, we have successfully prepared silicon nanoparticles protected with three organic compounds (styrene, 1-decene, and 1-vinyl naphthalene) and have examined their photophysical properties. The ligand π -electron systems on the silicon surface promoted the light harvesting ability for the luminescence through a charge transfer transition between the protective molecules and silicon nanoparticles and also enhanced the radiative rate of the silicon nanoparticles.

1. Introduction

As novel luminescent materials, quantum dots (QDs) have attracted considerable attention for their potential use in applications such as light-emitting diodes, solar cells, biosensors, and photodynamic therapy.¹⁻¹² Because of the quantum size effect, the energy gap in QDs can, in general, be manipulated by controlling the particle size, making it possible to control the luminescence wavelength from near ultraviolet (UV) to near infrared.¹³⁻¹⁴ At present, various nanoparticles and their luminescence properties have been reported. Shirahata reported the size tunable luminescence for Ge nanoparticles.¹⁵ Tanaka reported the aggregation of EuS nanoparticle through the interdigitation of protective molecules induced red-shifted luminescence band.¹⁶ Balaz reported the size dependent circular polarized luminescence for CdSe nanoparticles.¹⁷ In particular, silicon nanoparticles have major advantages such as being non-toxic, abundant natural resources, and inexpensive.¹⁸

The visible red luminescence of silicon nanoparticles after UV irradiation was first reported by Canham in 1990.¹⁹⁻²¹ The luminescence of silicon nanoparticles is based on a quasi-direct electronic transition, which comes from the direct recombination of excited electrons and positive holes, based on the wavefunction overlap in the nanometer range, i.e., the quantum confinement effect.²² To observe quantum confinement and size effects in silicon nanoparticles, we need to prepare the silicon nanoparticles with diameters of less than 6 nm. The luminescent properties of silicon nanoparticles with this size are strongly affected by the large numbers of Si atoms with dangling bonds on the surfaces of the particles. These Si atoms can be rapidly oxidized, which induces low luminescent quantum yields.²³ Therefore, the creation of air-stable luminescent silicon nanoparticles requires a surface protection method.

At present, various types of approaches to the surface protection of silicon nanoparticles have been reported, including termination strategies using chlorides²⁴, amines²⁵, and esters²⁶. Recently, we reported prepared luminescent silicon nanoparticles using a photochemical reaction of styrene molecules with Si-H bonds on the surface in a deoxidizing atmosphere.²⁷ We also induced large

chiroptical properties in silicon nanoparticles modified by chiral molecules.²⁸ However, the effect of the resulting π -electron system with the silicon surface on the excited states properties of silicon nanoparticles is unclear, although the control of the excited properties of silicon nanoparticles with protective molecules is very important.

In this paper, we report the photophysical properties of silicon nanoparticles that have protective molecules bonded to surface Si atoms via hydrosilylation. These surface-modified silicon nanoparticles using three protective organic molecules were prepared (Figure 1). The light harvesting abilities of the silicon nanoparticles were obtained by the π -electron system on their surface. Based on the light harvesting properties, we found that the nanoparticles provide luminescence related to their effective quantum size. This quantum size was observed via transmission electron microscopy (TEM) images. We found the π -electron systems on the silicon surface not only promote the light harvesting ability for the luminescence using a charge transfer transition between organic compounds and silicon nanoparticles, and but also enhance the radiation rate of silicon nanoparticles.

2. Experimental section

2.1 Materials.

Tetra-ethoxysilane ES40 as a source for silicon was purchased from COLCOAT CO.LTD. Phenol resin SR-101 as a source of carbon was obtained from AIR WATER INC. Aqueous solution of maleic acid (70 %) as a catalyst was purchased from Nippon Shokubai. These materials were starting materials for a synthesis of silicon nanoparticles. Hydrofluoric acid HF (48 %) was purchased from Wako Pure Chemical Industries, Ltd. Nitric acid HNO₃ (62%) and styrene (Sty) were purchased from Kanto Chemical Co., Inc. Chloroform was purchased from Wako Pure Chemical Industries, Ltd. 1-Decene and 1-vinylnaphtharene (Nap) were purchased from Sigma-Aldrich. Polyethylene filter was obtained by Japan Entegris Inc. All other chemicals and solvents were reagent grade and were used without further purification.

2.2 Apparatus

UV light source (wavelength at 365nm) was used a LED365-SPT/L (Optocode Corp) for observation of acid-etching process. UV cross-linker, as a photo-assisted reactor (Funakoshi Co.) was used for the photo-chemical reaction of each organic compound with silicon surface. TEM measurements were performed by 200 kV FE-TEM (JEOL JEM-2010F) with multi-scan CCD camera (Gatan Co.).

2.2.1 Acid-etching process of silicon nanoparticles for control of particle size

Silicon nanoparticles were synthesized from tetra-ethoxysilane, phenol resin and aqueous solution of maleic acid by using the same method as previous reported.²⁷⁻²⁸ The silicon nanoparticles (8 mg) and methanol (4 ml) were placed into a polypropylene container with the simultaneous addition of 10 mL of 48% HF and 1 mL of 68% (HNO₃). Acid etching of the silicon nanoparticle was performed under ultrasonication at room temperature. The acid etching process was monitored by observation of the silicon nanoparticle luminescence under excitation with UV light (365 nm). The acid etching process was stopped by the addition of mixed solvent (water: methanol = 3:1 v/v, 20 ml) to the solution. After the acid etching process, the solution was filtered using a polyethylene filter (20 nm mesh) and the residue (silicon nanoparticles) was washed with 5 mL of 2% HF to eliminate the thin surface oxidation layer, followed by rinsing twice with 5 mL of purified water to completely wash off the acid. This filter with silicon nanoparticle capped by hydrogen was cut into three equal parts carefully. These three pieces were put in glass vessels and vacuum-dried at room temperature for 60 min to completely remove water.

2.2.2 Surface Protection

The three different organic compounds (Figure 1a, 2mL) were placed into each glass vessel including silicon nanoparticles and PE filter. We carried out freeze-thaw cycles to remove oxygen from glass vessels. The dispersion of silicon nanoparticles was moved to Teflon resin container and 0.3ml-HF (2%) was added. These dispersions were agitated using a magnetic stirrer under irradiation with UV light ($\lambda = 365$ nm) for hydrosilylation on the surface of the silicon nanoparticles. The irradiation times are 20, 50, and 10 minutes for Sty, Dec, and Nap, respectively. In order to remove HF for each resultant solution, we carried out vacuum-dry. The resultant solution was centrifuged (4000 rpm) for 60 min.

2.2.3 Optical measurements

Electronic absorption was measured with a JASCO V-670 spectrophotometer. Photoluminescence (PL) and excitation spectra were measured using a Horiba FluoroLog®3 spectrofluorometer. The luminescence lifetimes were measured using the third harmonic ($\lambda_{\text{ex}} = 355$ nm) of a Qswitched Nd:YAG laser. Luminescence quantum yields were measured using FP-6300 spectrofluorometer with an integration sphere. The yields were calculated as the ratio of the number of photons emitted from sample as fluorescence to the number of photons in the excited light absorbed ($\lambda_{\text{ex}} = 380$ nm).

2.2.4 Calculation methods

The DFT and TD-DFT calculations were carried out with the Gaussian 09W D.01 employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP).²⁹⁻³⁰ The LANL2DZ basis set was used for Si atoms and the 6-31G(d) basis set was used for all other atoms.

3. Results and discussion

3.1 TEM images of silicon nanoparticles with organic compounds

TEM images of prepared silicon nanoparticles with organic compounds are shown in Figure 2. We

observed these silicon nanoparticles with clear lattice fringes and the quantum size. These lattice spacing are estimated to be about 0.31 nm from TEM image, which is consistent with the typical spacing value of the Si (111) plane (0.312nm).

3.2 Electronic absorption properties of silicon nanoparticles with organic compounds

The electronic absorption spectra of organic compounds (Sty, Dec, and Nap) are shown in Figure 3. The absorption peaks were observed for Sty (282 nm, 291 nm) and Nap (298 nm). On the other hand, that of Dec couldn't be observed at wavelength longer than 250 nm. These differences can be well explained by the effects of π -conjugation length and substituents using TD-DFT calculations (The detailed explanations are shown in the Electronic Supplementary Information). These differences can be well explained by the effects of π -conjugation length and substituents using TD-DFT calculations (The detailed explanations are shown in the Electronic Supplementary Information). The lowest excited states (S_1) of Sty and Nap are composed of two electronic configurations.³¹ For the S_1 states, the weak band for Sty and intense band for Nap can be explained by the differences between the configuration interaction degrees (Table S1 and S3). S_1 state of Dec was expressed as a single electronic configuration, whose energy is higher than the extended π -conjugated molecule such as Sty and Nap (Table S2).

On the other hand, the intense absorption bands of surface modified silicon nanoparticles were blue-shifted (Si-Sty, Si-Dec, and Si-Nap) (Figure 3). The blue shifted bands originate from the decrease of π -conjugation length of the organic compounds, which indicate the formation of the new electronic states due to the covalent bonds with the surface silicon atoms.

3.3 Luminescence properties of silicon nanoparticles with organic compounds

Luminescence spectra of surface-modified silicon nanoparticles (Si-Sty, Si-Dec, and Si-Nap) were shown in Figure 4. We observed luminescence at around 700 nm for Si-Sty, Si-Dec, and Si-Nap. In the previous report, the aggregation of EuS nanoparticle through the interdigitation of protective

molecules induced red-shifted luminescence band.¹⁶ On the other hand, the luminescence band of silicon nanoparticle was also slightly red-shift and broadened after four days (Figure S6, Si-Sty: 692 nm \rightarrow 721 nm, FWHM: 3880 cm⁻¹ \rightarrow 3990 cm⁻¹). The characteristic red-shift band may reflect the aggregation of silicon nanoparticles through the interactions between protective molecules as previously reported.¹⁶

In the excitation spectra (Figure 5, $\lambda_{em} = 690$ nm), the intense signals were observed in the ultraviolet regions. The band at 300 nm for Si-Nap is assigned to $\pi-\pi^*$ transition of Nap moiety. The characteristic shoulder bands were also observed for Si-Sty (300 nm) and Si-Nap (330 nm), respectively. These shoulder peaks can't be explained by the direct-band gap transition of silicon nanoparticles, because the absorption wavelengths are completely different from the theoretical prediction value.³² These bands are the CT transitions between silicon nanoparticles and protective molecules. This interpretation is consistent with the experimental fact that these bands are broad (FWHM: Si-Sty: 8860 cm⁻¹, Si-Nap: 9860 cm⁻¹), and supported by TD-DFT calculations of silicon cluster with Sty in the Electronic Supplementary Information (Figure S4-S5, Table S4). This calculation suggests that the oscillator strength of the charge transfer bands is much larger than that³² of direct-band gap transition of silicon nanoparticles, in spite of the small overlapping orbitals between organic compounds and silicon nanoparticles. These facts indicate that the control of the coupling scheme and the orientation between the organic moieties and silicon nanoparticles may be one of the key factor in enhancing the light harvesting ability for the luminescence. In addition, the orientations induced the transition between the nonplanar orbitals³³ of the aromatic compounds and silicon nanoparticles, which is consistent with the previous results of the large chiroptical properties with the CT transitions between chiral organic compounds and silicon nanoparticles.²⁸ Therefore, the control of the CT transition is expected to be an important factor for not only the enhancement of light harvesting ability for the luminescence and but also a creation of a new photo-functional materials.

In order to study the influence of the protective molecules to the excited states properties of silicon nanoparticles, the luminescence quantum yields and time-resolved luminescence decays (Figure 6) were measured for the red-luminescent silicon nanoparticles (Si-Sty, Si-Dec, and Si-Nap). The luminescence quantum yields of Si-Sty and Si-Nap were estimated to be 4.3% and 4.4%, respectively ($\lambda_{\text{ex}} = 380 \text{ nm}$). These quantum yields are based on both the excitations corresponding to CT transitions and the direct transitions of silicon nanoparticles (Figure 5). On the other hand, the smaller luminescence quantum yield was observed for Si-Dec excited by the direct transitions of silicon nanoparticles. The luminescence decay profiles of silicon nanoparticles exhibit multiexponential decay curves (Figure S10). The lifetimes are summarized in Table 1. Although the multiexponential decays indicate the presence of distinct populations of emitting nanoparticles, which may originate from distinct nanoparticles size or the ratio of organic compounds on the surface to silicon nanoparticles, the results indicate that the calculated lifetimes of Si-Dec are longer than those of Si-Sty and Si-Nap.

These results indicates the radiation rate of Si-Dec is slower than those of Si-Sty and Si-Nap. We consider that surface modification by π -electron system as Sty or Nap promotes the enhancement of the radiation rate of silicon nanoparticle. The detail analysis of specific interaction of π -electron orbitals and silicon orbitals are now in progress.

4. Conclusions

We successfully prepared silicon nanoparticles with three organic compounds, and examined their photophysical properties. The π -electron systems on the silicon surface promote the light harvesting ability for the luminescence and enhance the radiation rate. The results indicate that luminescent silicon nanoparticles with a π -electron system are expected to be an important factor for creating strongly luminous silicon nanoparticles.

Acknowledgements

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Table 1. Luminescence quantum yields and lifetimes of surface-modified silicon nanoparticles in CHCl_3 .

	$\phi^a / \%$	$\tau^b / \mu\text{s}$
Si-Sty	4.3	9.7(57%), 24.4(43%)
Si-Dec	< 0.5	11.5(58%), 61.1(42%)
Si-Nap	4.4	8.2(54%), 21.3(46%)

^a $\lambda_{\text{ex}} = 380 \text{ nm}$. ^b $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$.

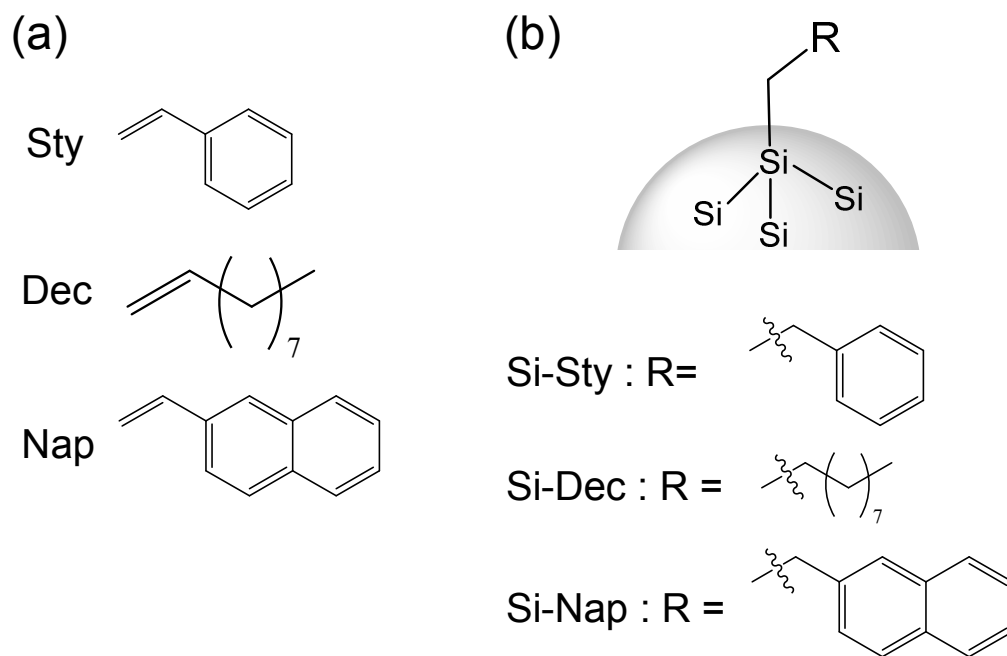


Figure 1. Structures of organic compounds (a) and surface-modified silicon nanoparticles (b).

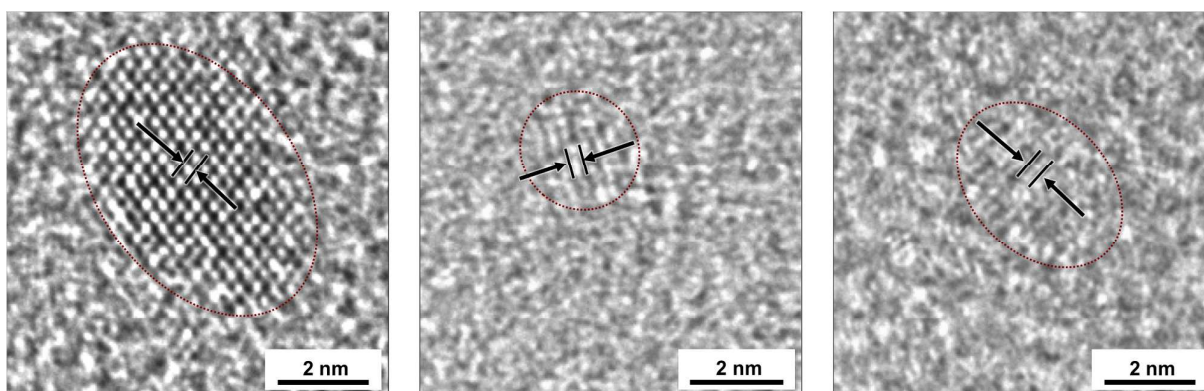


Figure 2. TEM images of Si-Sty (a), Si-Dec (b), and Si-Nap (c).

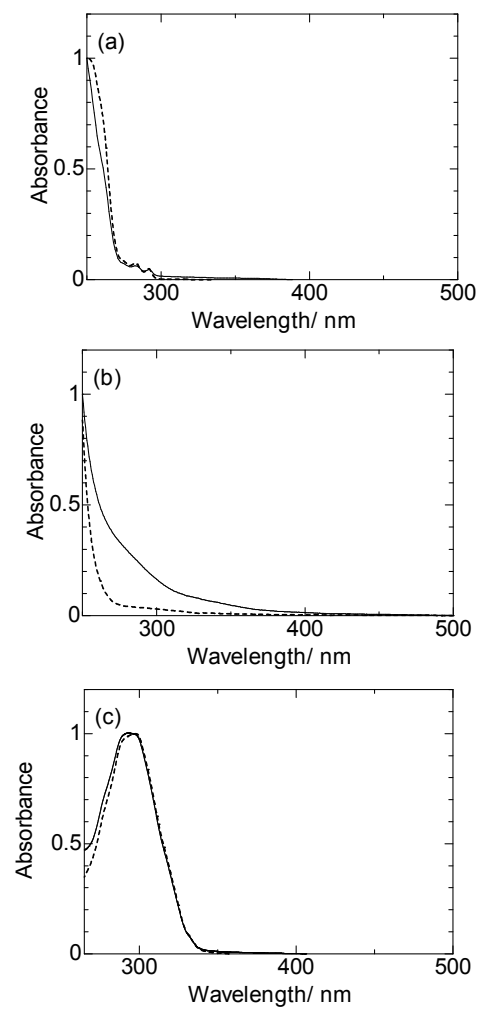


Figure 3. Electronic absorption spectra of organic compounds (broken line; a: Sty, b: Dec, c: Nap) and surface-modified silicon nanoparticles (solid line; a: Sty, b: Dec, c: Nap) in CHCl_3 . The spectra were normalized at the intense maxima (Sty: 2.0×10^{-3} M, Dec: 1.4 M, 5.1×10^{-5} M).

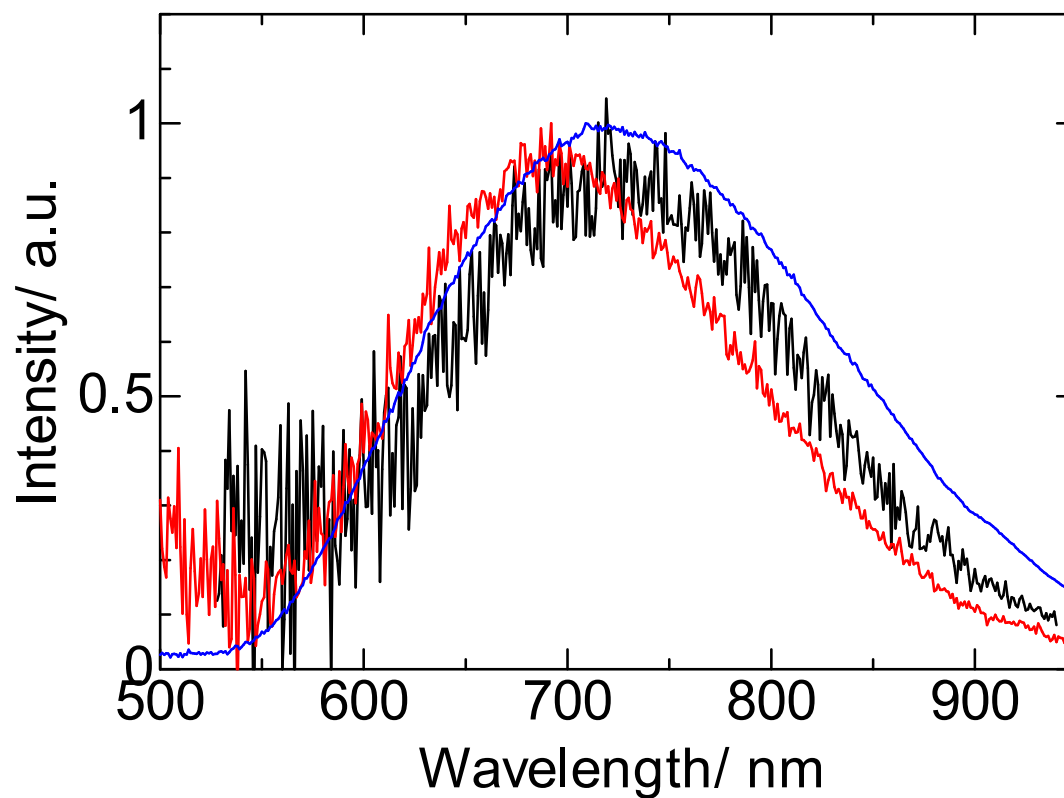


Figure 4. Luminescence spectra of surface-modified silicon nanoparticles in CHCl_3 (Si-Sty: black line, Si-Dec: red line, Si-Nap: blue line) (Si-Sty, Si-Dec: $\lambda_{\text{ex}} = 260 \text{ nm}$, Si-Nap: $\lambda_{\text{ex}} = 380 \text{ nm}$). The spectra were normalized at the intense maxima.

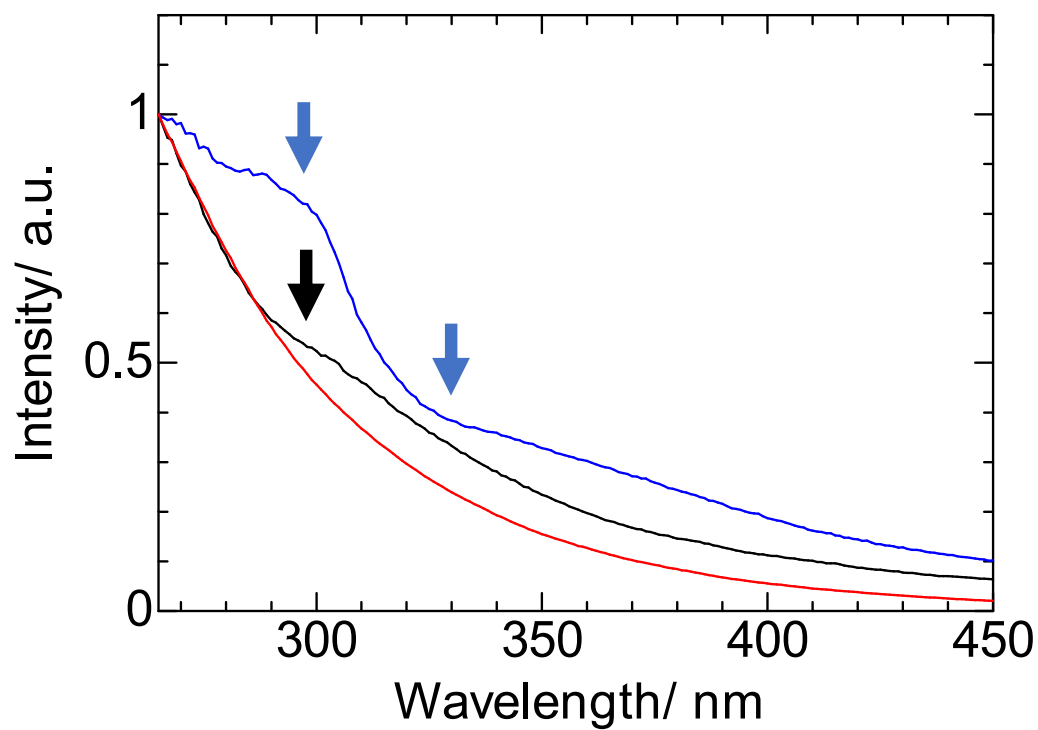


Figure 5. Excitation spectra of surface-modified silicon nanoparticles in CHCl_3 (Si-Sty: black line, Si-Dec: red line, Si-Nap: blue line) ($\lambda_{\text{em}} = 690 \text{ nm}$). The spectra were normalized at the intense maxima.

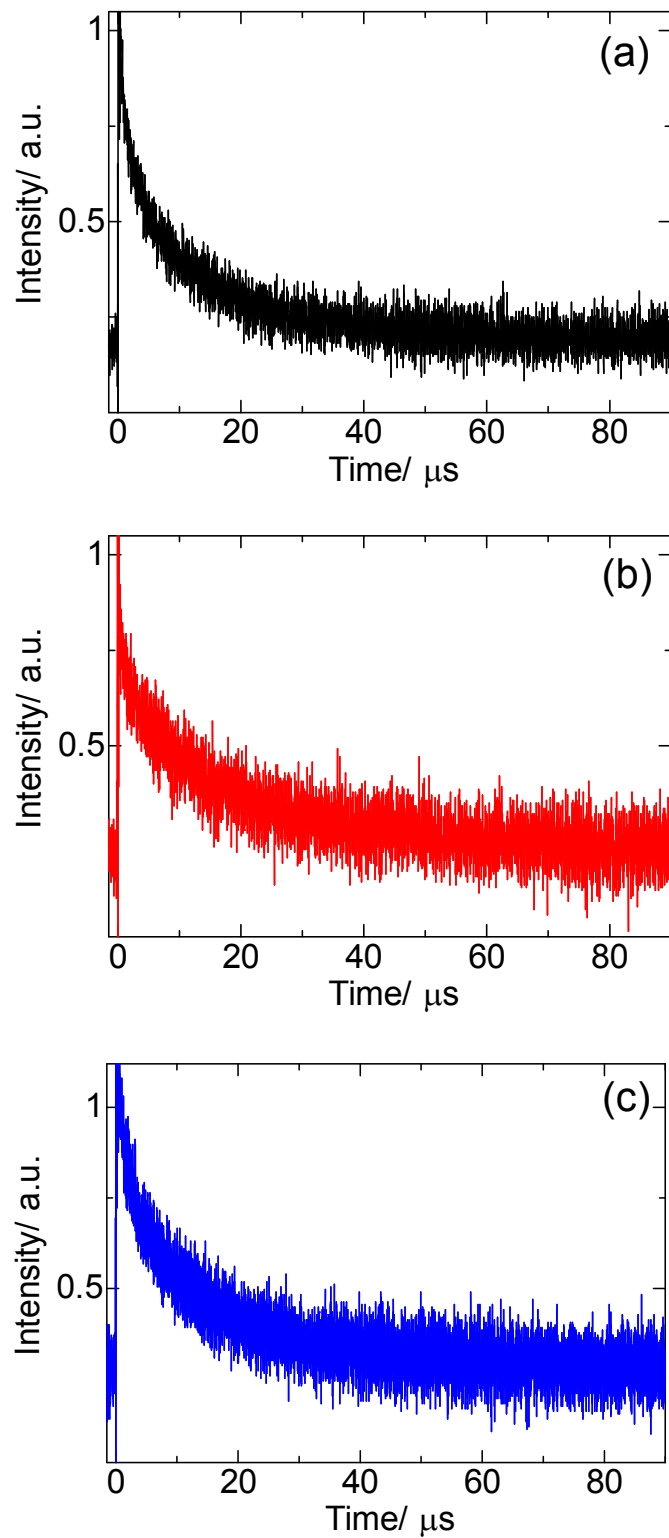


Figure 6. Luminescence decay profiles of surface-modified silicon nanoparticles in CHCl_3 (Si-Sty: black line, Si-Dec: red line, Si-Nap: blue line).

Luminescent silicon nanoparticles with a π -electron system are expected to be an important factor for creating strongly luminous silicon nanoparticles.

