PCCP

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

Dynamic Article Links ►

ARTICLE TYPE

The Effects of Electronic Coupling between Capping Molecule and Quantum Dot on the Light Absorption and Emission in Octyl, Styryl, and 4-Ethynylstyryl Terminated Silicon Quantum Dots

Thu-Huong Le and Hyun-Dam Jeong[*]

Optical properties of silicon quantum dots (Si QD) are greatly influenced by their size and surface chemistry. We report micro-emulsion synthesis of hydrogen terminated Si QD, with the modification of quenching the remaining reducing agent LiAlH$_4$, by CuSO4. Subsequent functionalization was carried out
10 with different capping molecules, including 1-octene, phenylacetylene, and 1,4-diethynylbenzene, to give octyl, styryl, and 4-ethynylstyryl terminated silicon quantum dots, respectively. The optical properties of the three kinds of Si QD synthesized, with extending conjugation length, were examined. The effects of surface chemistry on the optical properties of the Si QD, obtained from ultraviolet-visible absorption spectroscopy and photoluminescence spectroscopy, were compared to the extension of electron and hole
15 wave functions into the capping molecules, which was estimated from modified particle in a box calculation. The observed quantum yield increased from 2 % to 2.5 % and 9.0 %, and the average lifetime decreased with increasing conjugation length of the octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD, were ascribed to the effect of electronic coupling between the capping molecules and the Si QD. A tentative model in which the strong electronic interaction through covalent bonding induced more direct
20 band gap character for light emission was proposed by tuning of the ground state wave functions of the electron and hole in wave vector space.

Introduction

Semiconductors quantum dots (QD), whose radii are smaller than the bulk exciton Bohr radius, exhibit distinct quantum mechanical
25 properties. In a QD, the electron motion is confined in all spatial directions, resulting in a discrete energy level as opposed to a continuous energy level of bulk material, with an additional alteration in the band gap.[1,2] Hence, the size-dependent electronic and optical properties of QDs make them a useful material for
30 physics, chemistry, and materials science, with various applications in light-emitting diodes,[3] bio-imaging,[4] solar cells,[5] and lasers.[6] However, due to environmental issues arising from compound II-VI and III-V semiconductor QDs (e.g., CdS, CdSe, which are often highly poisonous), production using alternative
35 materials, such as silicon quantum dots (Si QD), is urgently needed. Si QD with visible light emission has attracted much attention as a promising replacement, due to the properties of being non-toxic, earth-abundant, and environmentally friendly, as well as the ease of integration into well-established industrial
40 silicon processes.[7,8] Therefore, recent achievements in the synthesis of colloidal Si QD in terms of controlling the particle size, size distribution, and achieving surface modifications make the Si QD even more promising for application.[9,10,11] Modifying the surface chemistry through attachment of organic molecular
45 ligands on the surface of the Si QDs is performed to stabilize the

QD surface, and gives rise to their chemical functionality and solubility in solvent.[12] In addition, the chemical modifications of the surface of Si QD induces tuning of the optical properties and quantum yield, and also allows an ultrafast charge transfer across
50 the surface through the organic conjugated capping molecule.[13,14] To investigate the effects of surface chemistry on the optical properties of Si QD, our groups adopted the micro emulsion approach to synthesize hydrogen terminated Si QD using CuSO$_4$ for the quenching of LiAlH$_4$,[15,16] with subsequent
55 functionalization with three different capping molecules, viz. 1-octene, phenylacetylene, and 1,4-diethynylbenzene to give octyl capped Si QD, styryl Si QD, and 4-ethynylstyryl Si QD, respectively. In particular, the newly introduced molecular 1,4-diethynylbenzene is very promising for capping on the Si QD
60 surface, since the free functional group (-C≡C-H) attached to the benzene ring is expected to give a strong quantum yield which would be very useful in solar cell and light-emitting diode applications. Interestingly, the ultra-violet absorbance spectroscopy (UV-vis) and photoluminescence (PL) spectroscopy
65 of 4-ethynylstyryl Si QD showed an extension into the longer wavelength region compared to the octyl Si QD and styryl Si QD. The quantum yield increased from 2% to 2.5% and 9 %, with increasing conjugation lengths of the octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD, while the average lifetime of the
70 excited state of the QDs decreased. Based on these results, we

suggest that there is a strong electronic coupling between the Si QD and the 4-ethynylstyryl group. In other words, significant orbital interactions between some molecular orbitals of the Si QD and the π orbitals of the capping group occurred, providing dramatic changes in the optical properties of 4-ethynylstyryl Si QD in comparison with octyl Si QD and styryl Si QD.

Experimental section

Synthesis was performed in a glove box filled with Ar gas, for which the process is summarized in Figure 1 A and explained in detail in the supporting information. Hydrogen-terminated silicon quantum dots (H-Si QDs) were synthesized by the mini-emulsion method reported by Tilley *et al.*,[15] with the modification that the remaining reducing agent, LiAlH₄, was quenched by CuSO4 instead of methanol.[16] Finally, three Si QD samples were obtained: octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD.
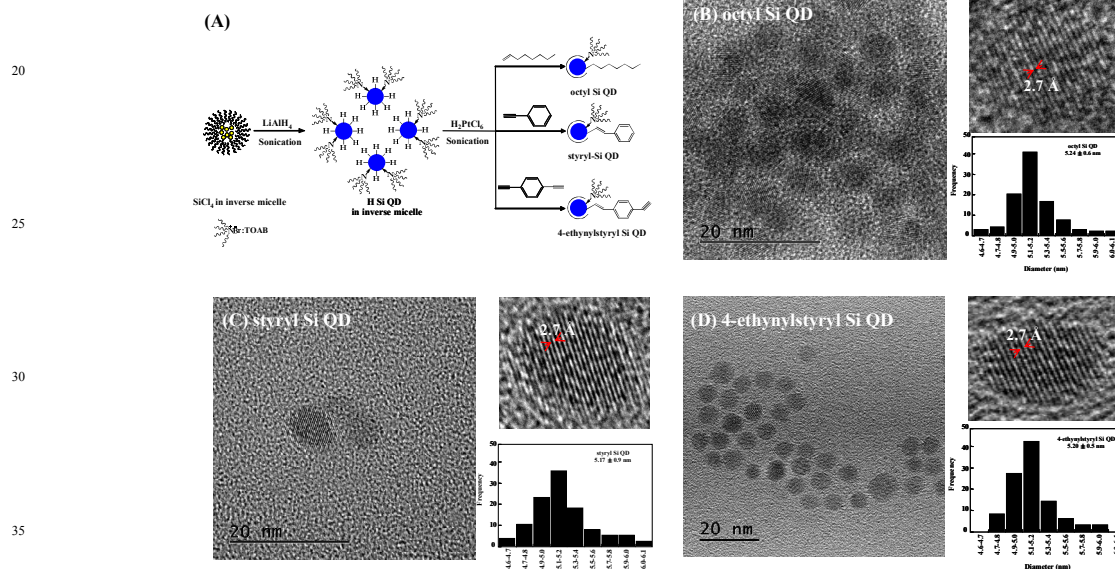

Figure 1. Synthetic procedure and chemical structure of octyl Si QD, styryl Si QD, 4-ethynylstyryl Si QD samples (A), and TEM micrographs for the octyl Si QD (B), styryl Si QD (C), and 4-ethynylstyryl Si QD (D).

DFT calculations were performed to obtain orbital energies and electronic distribution of wave functions, hence determining the barrier height and width for electron or hole relaxations. All calculations were conducted using the B3LYP, 6-31G (d, p) basis set available in the Gaussian 03 package. The numerical calculations were carried out using the Numerov method, in Microsoft Excel 2003.

All chemical reagents, including silicon tetrachloride (SiCl4, 99.998%), tetraoctylammonium bromide (TOAB, 98%), lithium aluminum hydride solution (LiAlH4, 2M in THF), 1-octene (98%), phenylacetylene (98%), 1,4-diethynylbenzene (96%), N-methylformaide (99%), chloroplatinic acid (H₂PtCl₆, 99.98%), CuSO₄, toluene (anhydrous, 99.8%), 99.5%, and silica-gel (SiO₂, 40-63 μm) were purchased from Sigma-Andrich. UV-vis absorption spectra were obtained on an S-3150 UV-vis spectrometer (SCINCO, Korea). Photoluminescence spectroscopy was performed on a Flourolog-3 spectrometer with a 2-nm slit width for excitation monochromators. FT-IR spectroscopy was performed on a Spectrum 400 (PekinElmer, U.S.A) to obtain the IR spectra of the Si QDs. A 300 MHz FT-NMR spectrometer (Varian Inc, Palo Alto, CA) was used to obtain the 1H-NMR spectra of octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD. High-resolution transmission electron microscopy (HR-TEM) was performed with a JEOL JEM-2100F operated at 200 kV. Photoluminescence spectroscopy was performed using a He-Cd (Kimmon Electric Co., IK3501R-G, Japan) light source at 325 nm, with 50 mW power and an intensified photodiode array detector (IRY1024, Princeton Instrument Co., U.S.A.) to investigate the quantum yield of Si QD, determined by comparison with quinine sulfate, whose quantum yield is known to be 55% in 0.05 M H₂SO₄.[17] Photoluminescence life time of the three Si QD samples in dichloromethane solvent was analyzed by time resolved fluorescence confocal microscope (MicroTime-200, PicoQuant, Gemany). Each sample was excited using an excitation laser at 375 nm (20MHz).

Results and discussion

In Figure 1 (B), (C), and (D) shows the transmission scanning electron microscopy (TEM) images of octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD. The TEM images of three samples clearly showed highly spherical dots with average sizes of 5.24±0.6 nm (Figure 1B), 5.17±0.9 nm (Figure 1C), and 5.20±0.5 nm (Figure 1D), respectively. As shown in the TEM images, a characteristic lattice spacing of 2.7Å corresponding to the (200) plane was found, indicating the diamond crystal structure of the octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD samples.[16] The similarity in the average sizes of the three kinds of Si QD indicates that the changes of optical properties observed, mentioned in the following sections, was not due to size variation, but is attributed to another physical origin.
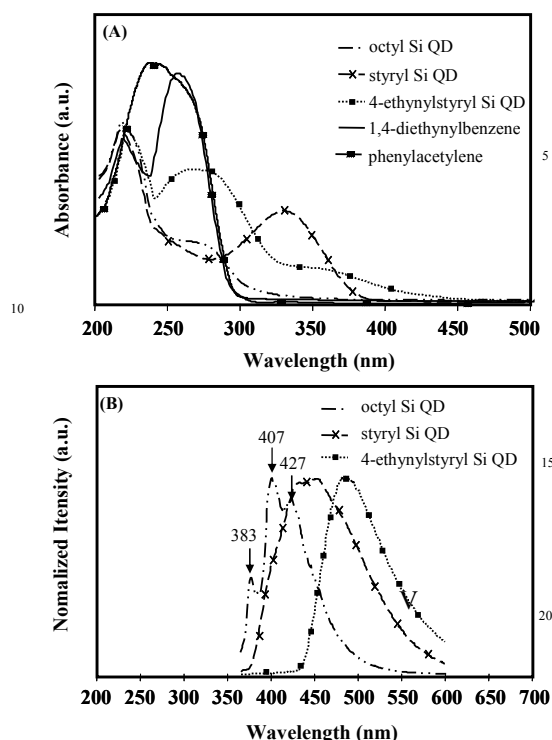
Figure 2. UV-vis spectra (A) of octyl Si QDs, styryl Si QDs, and 4-ethynylstyryl Si QDs compared with 1,4-diethynylstyryl and phenylacetylene in dichloromethane and PL spectra (B) of octyl Si QDs, styryl Si QDs, and 4-ethynylstyryl Si QDs at an excitation wavelength of 360 nm in dichloromethane solvent.

Figure 2 (A) shows the UV absorption spectra of the octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD (dashed lines), in comparison with 1,4-diethynylbenzene molecule and phenylacetylene molecule (solid line) in dichloromethane. First, while the phenylacetylene molecule and 1,4-diethynylbenzene molecule (solid line) have absorbance under 300 nm, the styryl Si QD and 4-ethynylstyryl Si QD have absorbance above 320 nm and above 350 nm, respectively. Second, distinct differences in the optical properties, that is, an enhancement of the UV absorbance can be seen in Figure 2 (A). It is well known that Si QD usually have a featureless UV absorption spectrum with low absorbance near onset point (around 300 nm) due to their indirect band structure,[16,18] as could be seen with octyl Si QD. Addition, the absorption spectrum of octyl Si QD also exhibits two main peaks at 230 nm (5.3 eV), 270 nm (3.4 eV) which are attributed to the direct transition.[19,18] On the other hand, the absorbance above 320 nm is enhanced for styryl Si QD sample and above 350 nm in the case of 4-ethynylstyryl Si QD, which expect to be from strong conjugation between the Si QD and styryl, and 4-ethynylstyryl groups. The increase in UV absorbance matches well with the increase in the length of the π-conjugated capping groups, despite similarity in the average sizes of the three kinds of Si QD.

In Figure 2B and Figure S3, the PL spectra of three Si QD samples shows strong red-shift of luminescence as the conjugation length increase. This trend is very similar to that deduced from the UV absorption spectra (Figure 2A). There have previously been suggestions that the origin of the red-shift of luminescence observed in Si QDs is due to size-dependent

properties, or surface chemistry.[20,21] In particular, Hessel *et al.* observed size-dependent PL of Si nanocrystals,[20] while Kovalev *et al.* similarly suggest that the PL peak energy was a function of size.[22] In contrast, Warner *et al.* observed differences in the optical response of two Si nanocrystals capped with different molecules (1-heptene and allyamine). The 1-heptene capped Si nanocrystal solution displayed emission with higher energy than the allyamine capped Si nanocrystal solution for the same excitation wavelength. Since both solutions contained an identical size distribution of the Si nanocrystals, the difference in the PL spectra must be attributed to the effect of the surface capping molecules.[21] Furthermore, Wang and Yang *et al.* demonstrated the effects of alkenes and alkyne ligands on the HOMO-LUMO gap of Si NC (1.4 nm) by using the density functional theory (DFT). The HOMO-LUMO gap decreased in the case of Si NCs terminated by conjugated alkyne groups, compared to Si NCs terminated by alkene groups.[23] Therefore, we propose that the red-shift of emission wavelength is due to the effect of surface chemistry.

Second, the PL spectra of octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD exhibit blue spectra region, which is incongruent with TEM data. There have been some suggestions that such a blue PL of the Si QDs originates from their defect states in surface.[24,25] In particular, Dasog and Veinot *et al.* demonstrated that the blue luminescence can be induced by contaminating red-luminescent Si QD that even follows quantum confinement effect, by introducing nitrogen impurities on the QD surface under oxidative air condition. Dasog and Veinot *et al.* concluded that the nitrogen impurities probably give surface defect states acting as trap states for the exciton, resulting in the blue luminescence, and low quantum yield.[24] Furthermore Fuzell and Larsen *et al.* studied the exciton dynamics of the blue luminescence-directed Si QD from the red-luminescent Si QD, in relation to the trap states using ultrafast transient absorption spectroscopy.[25] In this report, we believe that the nitrogen (N) atoms from TOAB still remaining in the surface of Si QD obtained from SiCl$_4$ reduction (Figure 1 (A)). The existence of nitrogen on surface of Si QD could give surface defect states lead to blue emission. Addition, the different in PL spectra may be related strong electronic interactions between Si QD and the π-conjugated molecules, or variation in the size of QD, or surface defect states from nitrogen on surface of Si QD. However, the three kinds of Si QD samples were synthesized from the same mother H-Si QD solution. The variation in the size of QD and effect of surface defect states from nitrogen on surface of Si QD on strong red-shift of luminescence can be excluded. Therefore, the strong electronic interactions between Si QD and the π-conjugated molecules was suggested that provoking the significant changes observed in the above light absorption properties and emission of styryl Si QD or 4-ethynylstyryl Si QD, in comparison with octyl Si QD.

The PL quantum yield (QY) of the octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD were determined by comparison with quinine sulfate, whose quantum yield is known to be 55% in 0.05 M H$_2$SO$_4$ to be as low as 2%, 2.5%, to 9%, respectively. The existence of nitrogen on surface of Si QD could give surface defect states, which is cause of low quantum yield.[24] Even though quantum yield of three kinds of Si QD are low, the quantum yield

still increasing from 2% to 2.5% and 9 %, with increasing conjugation lengths of Si QD. Based on these results, we suggest that there is a strong electronic interaction between the Si QD and highly conjugated molecule through covalent bond induces more direct band gap character, which correspond to more recombination of electron and hole, or an increase in quantum yield.

Third, PL spectra of the octyl Si QD sample shows a sub-band structure, while the PL spectra of styryl Si QD, 4-ethynylstyryl Si QD samples does not show sub-band structure (Figure 2B and Figure S4). In Figure 2B, the energy different between two adjacent peaks of octyl Si QD sample is about 0.13 eV (or 1048 cm^{-1}). The value of 0.13 (corresponding to 1048 cm^{-1}) is almost equivalent to the Si-O vibration as discussed in detail in the supporting information (Figure S1). As, Martin *et al.* suggested that, for surface oxidized silicon nanocrystals, strong electron-phonon coupling between the excitons and the LO-phonon of the Si-O-Si vibration could generate the vibration feature (0.13-0.17 eV) in the emission spectra.[26] Here, we propose that the vibrational PL feature observed with octyl Si QD sample is due to electron-phonon coupling between excitons and Si-O vibration phonon. However, Martin *et al.* also reported that the electron-phonon coupling is base on the Fröhlich coupling between an electric field generated by a nonuniform charge density distribution and an electric field created by lattice phonon. If the electron and hole wavefunctions are delocalized over the whole QD, the electric field generated by the delocalized electron and hole usually decrease with increasing size.[26] In Figure 2B, the PL spectra of styryl Si QD, 4-ethynylstyryl Si QD samples does not show sub-band structure due to i) electron and hole wavefunctions are delocalized over the whole QD lead to electron-phonon coupling decrease with increasing size, ii) In the FT-IR results (Figure S1) of styryl Si QD, and 4-ethynylstyryl Si QD samples does not show Si-O vibration. Therefore, the styryl Si QD, and 4-ethynylstyryl Si QD samples does not show vibration structure in emission spectrum.
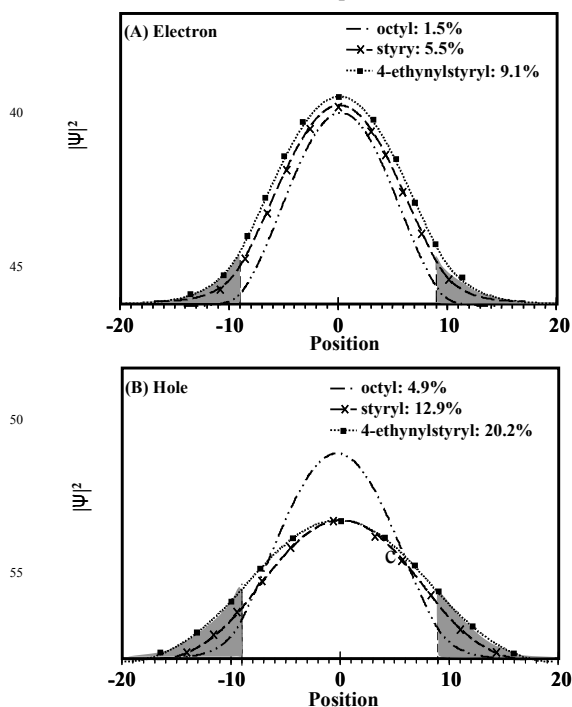

Figure 3. Probability densities ($|\Psi|^2$) for electron (A) and hole (B). The indicated values represent the percentage of electrons (A) and holes (B) at the capping layer.

As previously introduced by our group,[16] we modelled the Si QD as a typical core-shell structure, then calculated the carrier's probability at the capping layer. The probability densities ($|\Psi|^2$) of finding the electron and the hole along the x axis were solved numerically, using the Numerov method. The probability densities for the electron and hole increased with extending conjugation lengths, as shown in Figure 3 (A-B). However, the calculated values could be far from the values in real systems, because the diameter of the Si QD core was set at 1.8 nm while the real Si QD core size was 5.2 nm. Nevertheless, the increasing trend in the carrier's probabilities at the capping layer with the increasing conjugation length suggests a simple method to confirm the effect of the surface chemistry on the charge transfer from the QD.
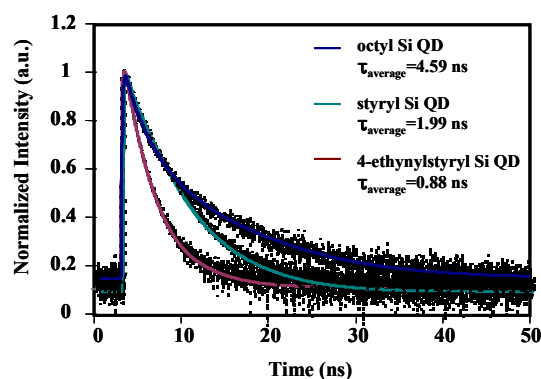

Figure 4. Time-resolved photoluminescence spectroscopy of octyl Si QDs, styryl Si QDs, and 4-ethynylstyryl Si QDs.

The average lifetime values of the three Si QDs generated from time resolved in photoluminescent reduced in order from 4.59 ns for octyl Si QD, to 1.99 ns for styryl Si QD, and 0.88 ns for 4-ethynylstyryl Si QD, as shown in Figure 4. Alternatively, the radiative transition rate (k_f) values increased from $0.43 \times 10^7 s^{-1}$ to $1.25 \times 10^7 s^{-1}$, and $10.22 \times 10^7 s^{-1}$ with extending conjugation length, as estimated in Table 1. Wang. R *et al.* reported that radiative recombination was sensitive to the surface chemistry of the Si nanocrystals. They demonstrated that the radiative recombination rates were 1-2 orders of magnitude lager for Si NCs hydrosilylated with conjugated alkynes than for those hydrosilylated with nonconjugated alkynes. This observation may be attributed to the excellent overlap of the LUMO-HOMO in the ligands derived from conjugated alkynes.[23] Dohnalova and *et al.* also demonstrated that the radiative rate of C-terminated Si QD enhanced by about 10^2-10^3 times compared to that of H- or O-terminated Si QD, and about 10^5 times compared to bulk Si, due to the direct band gap.[27] Meanwhile, Dasog and Veinot *et al.* concluded that the nitrogen impurities on the Si NC surface obtained from SiCl$_4$ reduction probably give an alternative relaxation pathway lead to short nanosecond excited state lifetime (*i.e*, τ=4 ns).[24] Therefore, the average lifetime of three kinds Si QD at a 1nanosecond level may be related to direct band gap character due to strong electronic interaction of Si QD with organic molecules, or surface defect states from the nitrogen impurities on the Si QD surface. Addition, the different of

average lifetime can suggest that the strong electronic interaction of Si QD with highly conjugated molecules through covalent bonds induces more direct band gap character, which corresponds to a decrease in the average lifetime, or an increase in the radiative transition rate.

Samples	$\tau_{average}$ (ns)	Quantum Yield	k_f (s^{-1})*10^7
octyl Si QD	4.59	2%	0.43
styryl Si QD	1.99	2.5%	1.25
4-ethynylstyryl Si QD	0.88	9%	10.22

Table 1. Summary of the average lifetime, quantum yield, and radiative transition rate of octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD.

The discussed effect of the strong electronic interaction of Si QD with highly conjugated molecules is summarized in Figure 5. The hole and electron density in k-space $|\psi(k)|^2$ in the lowest excited state for Γ-X direction for the three Si QDs with different caps, including octyl-, styryl-, and 4-ethynylstyryl-, and the wave functions were determined for the bulk Si indirect band gap structure, as shown in Figure 5. According to the schematic illustration of the dominant radiative in the Figure 5, the strength conjugations allows the wave function of the excited state to penetrate into the region with a wave vector near the Γ-point, leading to more recombination of electron and hole with extended conjugation, and an increased quantum yield from 2%, 2.5%, to 9% with increasing conjugation length in the order octyl Si QD > styryl Si QD > 4-ethynylstyryl Si QD. Therefore, we can assert that the strong electronic interactions of Si QD with highly conjugated molecules through covalent bonds induces more direct band gap character for light emission, which needs to be further confirmed by DFT calculations based on plane wave or molecular orbitals.
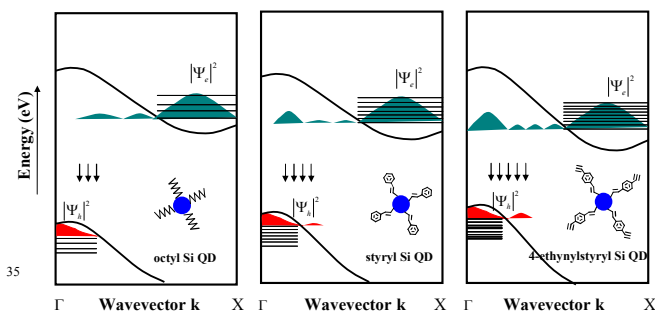

Figure 5. Illustration of the dominant radiative transition in octyl Si QD, styryl Si QD, and 4-ethynylstyryl Si QD, proposing a tentative model in which the strong electronic interaction through covalent bonding induces more direct band gap character for light emission. The wave functions were determined for the bulk Si indirect band gap structure. Hole and electron density in k-space $(|\Psi|^2)$ in the lowest excited stated for Γ-X direction are predicted in red and blue.

Conclusions

In conclusion, we have synthesized three Si QD samples of identical size (5.2 nm) and size distribution, by functionalizing H Si QD with 1-octene, phenylacetylene, and 1,4-diethynylbenzene, to give octyl, styryl, and 4-ethynylstyryl terminated silicon quantum dots, respectively. The newly introduced molecular 1,4-diethynylbenzene was especially promising for capping the Si QD surface, since the free functional group (-C≡C-H) attached at the benzene ring was expected to give a strong quantum yield, which is very useful for applications in solar cells and light-emitting diodes. Importantly, a tentative model by which the strong electronic interactions through covalent bonding induces more direct band gap character for light emission was proposed by tuning of the ground state wave functions of the electron and hole in wave vector space.

Notes and references

1. A. P. Alivisatos, *Science* , 1996, **271**, 933.
2. N. Shirahata, T. Hasegawa, Y. Sakka, and T. Tsuruoka, *Small*, 2010, **6**, 915-921.
3. A. L. Rogach, N. Gaponik, J. M. Lupton, C. Bertoni, D. E. Gallardo, S. Dunn, N. L. Pira, M. Paderi, P. Repetto, G. S. Romanov, C. O'Dwyer, M. C. S. Torres, and A. Eychmuller, *Angew. Chem., Int. Ed*,2008, **47**, 6538-6549.
4. X. Cheng, B. S. Lowe, J. P. Reece, and J. J. Gooding, J. *Chem. Soc. Rev*., 2014. **43**, 2680-2700.
5. V. P. Kamat, *J. Phys. Chem. C,* 2008, **112**, 18737-18753.]
6. H. J. Eisler, V. C. Sundar, M. G. Bawendi, M. Walsh, H. I. Smith, and V. Klimov, *Appl. Phys. Lett,* 2002, **80**, 4614–4616.
7. L. Pavesi, and R. Turan, *Silicon Nanocrystals: Fundamentals, Synthesis and Applications*, WILEY-VCH Verlag Gmbh & Co. KgaA, Weinheim, Germany, 2010.
8. J. G. C. Veinot, *Chem. Commun,* 2006, 4160.
9. L. M. Mastronardi, M. F. Flaig, D. Faulkner, J. E. Henderson, C. Kübel, U. Lemmer, and A. G. Ozin, *Nano Lett*, 2012, **12**, 337-342.
10. S. D. English, E. L. Pell, Z. Yu, F. P. Barbara, and B. Korgel, *Nano Lett*, 2002, **2**, 681-685.
11. N. Shirahata, D. Hirakawa, and Y. Sakka, *Green Chem*., 2010, **12**, 2139-2141.
12. N. Shirahata, *Phys. Chem.Chem. Phys*., 2011, **13**, 7284-7294.
13. C. Cimpean, V. Groenewegen, V. Kuntermann, A. Soomer, and C. Kryschi, *Laser Photonics Rev*, 2009, **3**, 138 – 145.
14. A. Sommer, C. Cimpean, M. Kunz, C. Oelsner, J. K. Kupka, and C. Kryschi, *J. Phys. Chem. C,* 2011, **115**, 22781 –22788.
15. R. D. Tilley, J. H. Warner, K. Yamamoto, I. Matsui, and H. Fujimori, *Chem. Commun.,* 2005, **14**, 1833.
16. X. D. Mai, D. T. Dao, J. Sohee, and D. J. Hyun, *Chem. Asian J*, 2013, **8**, 653-664.
17. M. A. Brouwer, *Pure Appl. Chem*., 2011, **83**, 2213-2228.
18. J. P. Wilcoxon, G. A. Samara, and P. N. Provencio, *Phys. Rev. B,* 1999, **60**, 2704.

19. D. Tan, J. Ma, B. Xu, Y. Dai, G. Ma, Min. He, Z. Jin, and J. Qiu, *Phys. Chems. Chem. Phys,* 2011, **3**, 20255-20261.

20. M. C. Hessel, D. Reid, G. M. Panthani, R. M. Rasch, W. B. Goodfellow, J. Wei, H. Fujii, V. Akhavan, and A. B. Korgel, *Chem. Mater*, 2012, **24**, 393-401.

21. H. W. Warner, R. H. Dunlop, and D. R. Tilley, *J. Phys. Chem. B*, 2005, **109**, 19064.

22. D. Kovalev, J. Diener, H. Heckler, G. Polisski, N. Kunzner, and F. Koch, *Phys. Rev. B,* 2000, **61**, 4485−4487.

23. R. Wang, X. Pi, and D. Yang, *J. Phys. Chem. C,* 2012, **116**, 19434 – 19443.

24. M. Dasog, Z. Yang, S. Regli, T. M. Atkins, A. Faramus, M. P. Singh, E. Muthuswamy, S. M. Kauzlarich, R. D. Tilley, J. G. C. Veinot, *ACS Nano* 2013, **7**, 2676.

25. J. Fuzell, A. Thibert, T. M. Atkins, M. Dasog, E. Busby, J. G. C. Veinot, S. M. Kauzlarich, D. S. Larsen, *J. Phys. Chem. Lett* 2013, **4**, 3806.

26. J. Martin, F. Cichos, F. Huisken, C. Borczyskowski, *Nano Lett*. 2008, **8**, 656-660.

27. K. Dohnalova, N. A. Poddubny1, A. A. Prokofiev, D. W. Boer, P. C. Umesh, MJ. J. Paulusse, H. Zuilhof, and Gregorkiewic, *T. Light: Science & Application*, 2013, **2**, e47.