Electronic Coupling in $\pi$-Conjugated Molecule-Bridged Silicon Quantum Dot Clusters Synthesized by Sonogashira Cross-Coupling Reaction

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Supporting Information

ABSTRACT: $\pi$-Conjugated molecule-bridged silicon quantum dot (Si QD) clusters were first synthesized by Sonogashira cross-coupling reaction between 4-ethynylstyryl and octyl co-capped Si QDs (4-Es/Oct Si QDs) and 2,5-dibromo-3-hexylthiophene. The formation of Si QD clusters was confirmed by field emission transmission electron microscopy. The electronic coupling between the QDs in the Si QD cluster is significantly enhanced as compared with that for 4-Es/Oct Si QDs, which is verified from the red shift in ultraviolet–visible absorption and photoluminescence spectra of the Si QD cluster with the possibility of exciton transport, the increased charging effect found in the core-level photoemission spectra, the shift to lower binding energy of the valence band photoemission spectrum, and more decisively, the increase in electrical conductance of the Si QD cluster thin film. To investigate the physical origin of the temperature dependence of the electrical conductance, we have merged the microscopic viewpoint, Marcus theory, on the electron transfer ($W$) between the adjacent QDs, with macroscopic concepts, such as the conductance ($G$), mobility ($\mu$), and diffusion coefficient ($D$). The effective reorganizational energies of charge transfer between the neighboring Si QDs in 4-Es/Oct Si QD and Si QD cluster thin films are estimated to be 170 and 140 meV, respectively, while the ratio of the effective electronic coupling of the latter to that of the former is determined to be 7.3:1.

INTRODUCTION

The size-dependent electronic and optical properties of semiconductor quantum dots (QDs) give them great potential for thin-film optoelectronics applications, such as light-emitting diodes,1,2 solar cells,3–6 photodetectors,7,8 and optoelectronic synaptic devices.9,10 Because most device applications of semiconductor QDs are not based on isolated QDs but on the assembly of QDs, understanding the optoelectrical properties of the assembly of QDs is necessary to improve device performance. It is known that the optoelectrical properties of QD molecular or solid-like assembly are influenced by interdot interactions.11–13 In addition, Koole et al have investigated the interaction of homonuclear CdTe QD molecules and have indicated wave function overlap in QD molecules,14 where the signature of electronic coupling has been reported for colloidal QD molecules with organic interconnections. Recently, our group has reported that the thermal cross-linking of 4-ethynylstyryl capping groups at curing temperatures of 250 and 350 °C to generate $\pi$-conjugated molecule linkage between two neighboring silicon QDs (Si QDs) decreases the width and height of the energy barrier between neighboring QDs, which allows the expansion of the wave functions of individual Si QDs and more resonant interaction with the neighboring QDs.15 We have also reported that the revelation of electronic coupling between the Si QDs in QD solids induces significant changes in the valence band photoemission spectral, optical, and electrical properties.15

Recently, we have initiated research on the Si QD-based functional materials, aggressively utilizing the phenomena of electronic coupling observed in our previous study for Si QD solids.15 Under such direction, we have considered that the most urgent matter is to check whether a $\pi$-conjugated molecule bridge inserted between the Si QDs by the use of a $\pi$–$\pi$-cross-coupling interaction reaction provides the possibility of controlling the electronic coupling. If this is revealed, the diversity of C–C cross-coupling reactions is sure to open huge opportunity for developing novel Si QD functional materials—appropriately responding to the material property requirements of the various applications. In this study, we focus on the investigation on electronic coupling in $\pi$-conjugated molecule-bridged Si QD clusters (Si QDs each covalently connected to one another by $\pi$-conjugated molecule bridges). The first synthesis of the Si QD clusters has been attempted by Sonogashira cross-coupling reaction between 4-ethynylstyryl...
and octyl co-capped (4-Es/Oct) Si QDs and 2,5-dibromo-3-hexylthiophene, as shown in Scheme 1a, after the previous syntheses of $\pi$-conjugated soluble poly(aryleneethynylene) (PAE)-type polymers were referenced. Field emission transmission electron microscopy (FE-TEM) of 4-Es/Oct Si QDs shows the image of an isolated particle with an average diameter of $(5.4 \pm 0.6)$ nm, whereas that of the Si QD clusters shows the image of mixtures of a dimer, trimer, tetramer,
The effect of C–C cross-coupling on the optical properties of Si QDs is investigated by ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectroscopy. The valence-band photoemission spectrum of the Si QD cluster thin film is obtained by high-resolution photoemission spectroscopy with the photon energy at 130 eV, which is compared with that for a 4-Es/Oct Si QD thin film. The results demonstrate remarkably increased electronic coupling in the π-conjugated molecule-bridged Si QD clusters. In addition, the temperature dependences of the current–voltage (I–V) curves for the Si QD cluster and 4-Es/Oct Si QD thin films are compared and analyzed in terms of the microscopic model of electron transfer between adjacent Si QDs, based on Marcus theory.

RESULTS AND DISCUSSION

π-Conjugated molecule-bridged Si QD clusters were first synthesized by Sonogashira cross-coupling reaction between 4-Es/Oct Si QDs and 2,5-dibromo-3-hexylthiophene, as shown in Scheme 1a,b, where adjacent Si QDs are covalently connected with considerably short linkages of vinyleneethylene-(3-hexyl)thiophene-ethynylene-vinylene (VPE-T-EPV). On the basis of the detailed explanations in the Experimental Section on the purification process (Scheme 1b) and TEM results (Figure 1) and the discussions in the Supporting Information on the H nuclear magnetic resonance (NMR) data (Figure S2a,b of the Supporting Information) and the UV–vis absorption spectra (Figure S3 of the Supporting Information) of P.1 and P.2, we conclude that P.2 is the main product containing Si QDs and P.1 is a byproduct of high fraction of a very long π-conjugated polymer chain. The dominant product in the P.2 is Si QD cluster (A) containing the considerably short VPE-T-EPV linkage. This is because its TEM image shows the distance between the QDs to be smaller than 2.5 nm (Figure 1b–d), implying no additional involvement of 1,4-diethynylbenzene molecules, which remained not completely consumed in the previous hydrosilylation reaction step. We name the main product of Si QD (P.2) as “Si QD cluster”, by considering the morphology of the cluster, confirmed by the following TEM results.

Figure 1 shows the transmission scanning electron microscopy images of 4-Es/Oct Si QD and Si QD clusters (A; P.2). First, the TEM images and selected area electron diffraction (SAED) patterns of 4-Es/Oct Si QD clearly show highly spherical dots, diamond structure, and isolated QDs with average sizes of (5.4 ± 0.6) nm (Figure 1a), whereas the TEM images of the Si QD cluster show aggregated QDs, in other words, a QD cluster (Figure 1b). Second, multiple TEM images (Figure 1b) reveal that the Si QD clusters are a mixture of monomer, dimer, trimer, tetramer, pentamer, and nonamer Si QDs, in which the monomer, dimer, and trimer are the main clusters with the count fractions of 34, 32, and 20% (Figure 1c), respectively. Finally, in the Si QD dimer, which is one of the clusters, the interparticle distance between two Si QDs (23 Å) obtained from the TEM images of the Si QD clusters is quite similar to the length (24.1 Å) of the π-conjugated molecule bridge originated from one thiophene ring and two ethynyleneethylenevinylene fragments directly anchored on two Si QDs, which is estimated from the geometry optimized in density function theory (DFT) calculations (Figure 1d). This implies that the synthesis of the Si QD cluster (A; P.2), our main product, is not involved with free diethynylbenzene molecules which remained, not completely consumed in the previous hydrosilylation reaction step. In addition, Fourier transform infrared spectroscopy (FT-IR) results (Figure S4 of the Supporting Information) indicate that 4-Es/Oct Si QD and 2,5-dibromo-3-hexylthiophene are C–C cross-coupled together in the Si QD cluster (A; P.2). This is very reasonable because most of the Si QD clusters (B, B’) additionally associated with free diethynylbenzene molecules in the
Sonogashira cross-coupling reaction were discarded in the purification process.

The optical properties of the Si QD cluster compared to 4-Es/Oct Si QD were characterized by UV–vis absorption and PL emission spectroscopy. Figure 2 shows the UV–vis absorption spectra of the 4-Es/Oct Si QD and Si QD cluster in chloroform. The new, broad peak around 340 nm is attributed to the change of the electronic structure of the Si QD upon clustering. Concretely, it is surely generated from the extension of the conjugation length with the thiophene ring and adjacent Si QDs after the C–C cross-coupling reaction. This is related to the reduction in the optical gap of Si QDs due to electronic coupling between the adjacent Si QDs. On the other hand, an absorption peak for the thiophene ring was rarely observed for our Si QD clusters, unlike a very broad, strong absorption peak at 390 nm (Figure S3) was observed for PAE containing a thiophene ring or the absorption peak of polythiophene at 443.6 nm was reported in a previous study. This means that light absorption due to the thiophene ring in our Si QD clusters is greatly suppressed. This is due to the relatively small cross section of the thiophene ring for the light absorption process, as compared to a huge volume of Si QDs.

A similar trend was also observed on comparing their PL spectra obtained under an excitation wavelength at 380 nm (Figure 2a). While an emission peak was observed at 490 nm for 4-Es/Oct Si QD, a very broad emission peak is observed at 540 nm for Si QD clusters. The emission peak wavelength of 490 nm for a 4-Es/Oct Si QD of 5.4 nm is significantly smaller, even if the difference in capping groups is considered, as compared with 750 nm for a 5.8 nm Si QD and 770 nm for a 5 nm Si QD of high quality reported in previous studies. This is because the Si QD synthesized by our group is still in part oxidized, which has been mentioned in detail in our previous paper. Although there may be a little issue in the quality of the Si QD, we think that it is possible to focus on the effect of clustering on the optical and electrical properties of the Si QD and the related physical chemistry. The broad peak at 540 nm could be divided into three components at 490, 520, and 567 nm, as shown in Figure 2b. The emission component at 490 nm is originated from the monomer of 4-Es/Oct Si QD itself that still exists in the Si QD cluster solution. The existence of the monomer was confirmed in the above TEM investigation. The emission component at 530 nm is ascribed to the Si QD itself in the Si QD clusters, such as the dimer, trimer, and so on. The red shift from 490 to 530 nm is due to the extension of the conjugation length with the thiophene ring and adjacent Si QDs, which is well-consistent with the above absorption result. This is related to the reduction in the optical gap of Si QDs due to electronic coupling between the adjacent Si QDs. The emission component of 567 nm is attributed to the thiophene ring when considering very large similarity with the PL emission peak at 573 nm of polythiophene and its asymmetric tail of more than 700 nm.

It is very interesting that in the Si QD cluster solution, its PL due to the thiophene ring is present, although its absorption feature is not observed. We tentatively suggest the possibility of exciton transport from the Si QD to the thiophene ring through the vinylene-phene-thienylene linkage because this can be indirect evidence of electron coupling through the conjugated molecule bridge between Si QDs. As shown in Figure 2c,d, excitation at 380 nm on Si QD clusters generates an electron–hole pair (i.e., exciton) in the Si QD. The electron and hole in excitons, in part, will fall down...
into lower energy levels through electronic and vibrational relaxations in the Si QD. They then recombine to emit a photon near 530 nm in the Si QD. The other parts of excitons can transport to the thiophene ring through the vinylenephenyleneethynylene linkage and their electron and hole can recombine to emit a photon near 567 nm after some electronic and vibrational relaxation mechanisms are generated in the aromatic molecular structure. The exciton migration from the Si QD to the ligand molecules has been studied in both experimental and theoretical works on Si QDs.\textsuperscript{20,21} The exciton transport through ethynylenephenyleneethynylene (−C≡C−Ph−C≡C−) linkage, very similar to our vinylenephenyleneethynylene linkage in terms of high degree of \( \pi \)-conjugation, has been well-known in fluorescence studies of poly(p-phenyleneethynylene)\textsubscript{s} (PPE)s,\textsuperscript{22,23} where the exciton diffusion length of PPE was found to be ca. 140 (Ph−C≡C−) units. When considering this large exciton diffusion length in the ethynylenephenyleneethynylene (−C≡C−Ph−C≡C−) linkage system, we can never deny the possibility of fast exciton transport from the Si QD to the thiophene ring through vinylenephenyleneethynylene (−C≡C−Ph−C≡C−) linkage of a very short transport pathway. This exciton transport is possible by the formation of conducting channels, that is, conduction and valence bands, upon QD clustering with \( \pi \)-conjugated molecule linkages. In view of quantum mechanics, this is very relevant to the enhancement of electronic coupling between adjacent Si QDs due to \( \pi \)-conjugated molecule linkage. This is further supported with following photo-emission spectroscopy and temperature dependence of electrical conductivity.

4-Es/Oct Si QD and Si QD cluster thin films were fabricated by conventional spin-coating and a curing process at 150 °C for 4 h under argon. After being filtered through 0.2 μm polytetrafluoroethylene (PTFE) membranes, 2 wt % solutions in toluene for 4-Es/Oct Si QD and the Si QD cluster were poured onto Si wafer substrates, followed by spinning at 500 rpm for 5 s and subsequently at 2500 rpm for 25 s. The thin films on the Si wafers were then cured at 150 °C for 4 h under argon in a tube vacuum furnace. Figure 3a shows that the thickness of films were found to be 70 and 60 nm, respectively, from the vertical cross-sectional images in secondary electron microscopy.

High-resolution photoemission spectroscopy was performed to investigate the chemical environment of the silicon element and the valence band edge position of 4-Es/Oct Si QD and Si QD cluster thin films. Figures 4 and S5a–c of the Supporting Information show the binding energies (BEs) of the Si 2p, C 1s, O 1s, and S 2p peaks. As for the C 1s spectra (Figure S5a of the Supporting Information) at the photon energy of 630 eV, charge calibration in data analysis is not performed to directly show the different extent of charging for the two thin films, while the other peaks are calibrated by positioning the C 1s peaks at 285.0 eV. The BEs of the C 1s peak for 4-Es/Oct Si QD and Si QD cluster thin-films are 288.2 and 286.2 eV, respectively. This indicates that both films experience charging phenomena upon photon irradiation. The lower charging effect in the Si QD cluster thin film, as compared to that in the 4-Es/Oct Si QD thin film, implies that the electrical conductivity of the former is larger than that of the latter. This is thought to be related to more significant electronic coupling for the Si QD cluster, which was suggested in the above UV–vis absorbance spectroscopy and PL spectroscopy analyses.
The valence band spectra of the Si QD cluster and 4-Es/Oct Si QD thin films cured at 150 °C were recorded at photon energies of 130 eV (Figure 4c). The valence band spectra of Si QD cluster thin films shift to a lower BE of 4.1 eV, as compared with 5.0 eV of 4-Es/Oct Si QD thin films. The lower BE means the increase in the energy of occupied valence orbitals of the valence band, which gives rise to the reduction of the highest occupied molecular orbital−lowest unoccupied molecular orbital gap or band gap. Recently, Koole et al proposed that the electronic coupling of the band edge orbitals from neighboring CdTe QD molecules is responsible for the observed reduction of the band gap. Then, we consider that the lower BE of 4.1 eV in the valence band spectra of the Si QD cluster thin films also originated from the enhanced electronic coupling. This is in good agreement with the above arguments that the red shift in the UV−vis absorbance spectra and PL spectra of Si QD clusters is ascribed to the reduction in the optical band gap due to significant electronic coupling between the neighboring Si QDs.

Recently, we have reported in our previous studies for Si QD solids that the electronic coupling-invoked thermal cross-linking has an effect on not only their optical properties but also their electrical properties. Thus, for more in-depth understanding of the effect of electronic coupling on the electrical properties of the Si QD cluster thin films, we investigated the electron transport of the Si QD cluster thin films compared to that of the 4-Es/Oct Si QD thin film using a metal−insulator−metal (MIM) device (Figure 3b), as shown in the current−voltage (I−V) measurements and analyses of Figure 5. To make an efficient interpretation for the temperature dependence of the I−V data, we introduce the microscopic theoretical framework, Marcus theory, on the electron transfer between the adjacent QDs and explain how to merge it with macroscopic concepts, such as conductance ($G$),
mobility ($\mu$), and diffusion coefficient ($D$). Then, we build up a very useful simple equation, where the natural log of $G$ is expressed as a function of the reciprocal of the absolute measurement temperature, allowing the investigation of microscopic phenomena, such as comparison of the electronic coupling and activation energy (or reorganization energy) for the 4-Es/Oct Si QDs and Si QD cluster thin films.

Figure 6. Current–voltage curves in the low-voltage range (−100 to 100) mV at various temperatures of the (a) 4-Es/Oct Si QD thin film and (b) Si QD cluster thin film cured at 150 °C. (c) Slope of the plot of $\ln G - 3/2 \ln(1/T)$ as a function of $1/T$ for five points from (213 to 293) K in the 4-Es/Oct Si QD thin film. (d) Slope of the plot of $\ln G - 3/2 \ln(1/T)$ as a function of $1/T$ for five points from (213 to 293) K in the Si QD cluster thin film. (e) Effective activation energies ($E_a$) for electron transfer between adjacent Si QDs in 4-Es/Oct Si QD and Si QD cluster thin films.
Chen et al. suggested that the carrier transport mechanism in thin films of alkyl ligand-terminated Si QDs corresponds to nearest-neighbor hopping (NNH) throughout the measured interval of temperature.27 The carrier transport via the NNH was also reported in a benzonitrile-treated Si nanocrystal (NC) thin film.7 Then, the charge transport mechanism in 4-Es/Oct Si QD and Si QD cluster thin films is assumed to be the NNH mechanism. In addition, the hopping transport of QD thin films is described by Marcus theory.27 Within Marcus theory, the charge transfer rate \(W\) between neighboring two Si QDs is given by the following equation27

\[
W = \frac{2\pi}{\hbar} \left( \frac{1}{4k_B T \lambda^2} \right)^{1/2} \exp \left\{ - \frac{(\Delta G_0 + \lambda)^2}{4k_B T} \right\}
\]

where, \(V\) is the electronic coupling between QDs, \(\lambda\) is the reorganization energy, \(\Delta G_0\) is the free-energy difference between the two electronic origins, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature, as depicted in a model for the energetics of the electron transfer reaction in Scheme 2a.

The relationship between the reorganization energy \(\lambda\) and activation energy \(E_a\) is defined as

\[
E_a = \frac{(\Delta G_0 + \lambda)^2}{4\lambda}
\]

For a charge hopping process in the Si QD cluster and 4-Es/Oct Si QD thin films, the donor and the acceptor are the same kind of Si QD. Then, if we ignore the small difference of electronic energy due to QD size variation, the free-energy difference approximates zero \((\Delta G_0 \approx 0)\). The organization energy \(\lambda\) is obtained as

\[
\lambda = \frac{E_a}{4}
\]

Substituting eq 3 into eq 1, we obtain the charge transfer rate \(W\) between neighboring two Si QDs in the hopping transport of Si QD thin films, such as

\[
W = \frac{2\pi}{\hbar} \left( \frac{1}{16k_B T \pi E_a} \right)^{1/2} \exp \left\{ - \frac{E_a}{k_B T} \right\}
\]

We then need to make the mathematical relationship between the conductance \(G\) in our MIM device and the electron transfer rate \(W\) between the adjacent Si QDs in the sandwiched thin film. As a first step, we use the following relationship between the conductance \(G\) and the electron diffusion coefficient \(D\) with cross-sectional area \(A\), thickness \(l\) of the thin film, and elementary charge \(e\), whose derivation is explained in detail in the Supporting Information

\[
G = \left( \frac{Ane^2}{4k_B T} \right) D
\]

The key route to relate \(G\) to the microscopic, Marcus-type electron transfer rate \(W\) between the neighboring Si QDs is the adoption of the NNH model used in organic semiconductors,23,24,25,26 where \(D\) is proportional to \(W\).

\[
D = \frac{1}{2d} \sum_i q_i W_i P_i
\]

where \(d = 3\) is the dimensionality for our three-dimensional system. As shown in Scheme 2b, we build up a closest-packed layer of QDs, where there are 6 nearest neighbors in a single layer, but a total of 12 nearest neighbors including the above 3 neighbors and the below 3 neighbors, mimicking the hexagonal close-packed (hcp) structure or the cubic close-packed (ccp) structure in inorganic chemistry.28 As shown in Scheme 2b, the index \(i\) covers all the hopping pathways out of a particular Si QD with \(r_i\) being the corresponding hopping distance, which is usually expressed as the interdot center-to-center distance and \(W_i\) being the electron transfer rate. \(P_i\) is the relative probability to choose the \(i\)th pathway

\[
P_i = \frac{W_i}{\sum_i W_i}
\]
We tentatively assume, for 4-Es/Oct Si QD thin films, that all \( r_i \) and \( W_i \) can be represented by \( r_{i, mono}^* \) and \( W_{i, mono}^* \) respectively. Then, this is very reasonable if we imagine the closest-packed QD lattice of Scheme 2b. Then, the diffusion coefficient \( D_{mono} \) can be computed simply from the representative interdot center-to-center distance \( r_{mono}^* \) and interdot electron transfer rate \( W_{mono}^* \).

\[
D_{mono} = \frac{1}{6} (r_{mono}^*)^2 W_{mono}^* 
\]

As shown in Scheme 2c, we also build up a closest-packed layer of QDs for Si QD cluster thin films. Here, owing to the diversity of the kinds of cluster (with different numbers of Si QD), there are large structural variations deviating from the standard closest packing, though, we also assume, for Si QD cluster thin films that all \( r_i \) and \( W_i \) can be represented, in an average sense, with \( r_{cluster}^* \) and \( W_{cluster}^* \) respectively. This assumption is unavoidable to make the following quantitative arguments. However, because the \( r_{cluster}^* \) and \( W_{cluster}^* \) values are effective, representative ones to consider all structural variations, and even for Si QD cluster thin films, there is a closest-packed QD solid with very short molecular bridges, we can utilize the representative values for comparison in the following discussion.

\[
D_{cluster} = \frac{1}{6} (r_{cluster}^*)^2 W_{cluster}^* 
\]

After inserting eqs 8 and 9 into eq 5 and using eq 4, as explained in very detail in the Supporting Information, we can obtain the simple equation, where the natural log of \( G \) is expressed as a function of the reciprocal of absolute temperature with the electronic coupling (\( V_{mono} \) for the 4-Es/Oct Si QD thin film, \( V_{cluster} \) for the Si QD cluster thin film), activation energy (\( E_{a, mono} \) for the 4-Es/Oct Si QD thin film, \( E_{a, cluster} \) for the Si QD cluster thin film), and an appropriate constant \( B \).

\[
\ln(G_{mono}) = \frac{3}{2} \ln \left( \frac{1}{T} \right) \cong B_{mono} - \frac{E_{a, mono}}{k_B} \left( \frac{1}{T} \right) \quad (10a) 
\]

\[
B_{mono} = B + \ln \left[ \frac{2\pi}{h} \left( V_{mono} \right)^2 \left( \frac{1}{16k_B \pi E_{a, mono}} \right)^{1/2} \right] \quad (10b) 
\]

\[
\ln(G_{cluster}) = \frac{3}{2} \ln \left( \frac{1}{T} \right) \cong B_{cluster} - \frac{E_{a, cluster}}{k_B} \left( \frac{1}{T} \right) \quad (11a) 
\]

\[
B_{cluster} = B + \ln \left[ \frac{2\pi}{h} \left( V_{cluster} \right)^2 \left( \frac{1}{16k_B \pi E_{a, cluster}} \right)^{1/2} \right] \quad (11b) 
\]

The activation energies of the Si QD cluster and 4-Es/Oct Si QD thin films are obtained by measuring the temperature dependence of conductance. The current–voltage (I–V) characteristics of the Si QD cluster and 4-Es/Oct Si QD thin films were recorded in a probe station in a nitrogen-filled chamber at different temperatures in the range from 133 to 293 K using an HP4145B semiconductor parameter analyzer. The current–voltage (I–V) curves in the low-bias regime of (−100 to 100) mV for 4-Es/Oct Si QD (Figure 5a) and Si QD cluster thin films are obtained (Figure 5b) at different temperatures from 133 to 293 K. During these measurements, the thin films were placed in the dark and under vacuum at a pressure of 10⁻³ Torr. The values of activation energy (\( E_{a, mono} \) and \( E_{a, cluster} \)) and \( B_{mono} \) and \( B_{cluster} \) are obtained by measuring the slope of the natural log plot of the electrical conductances (\( G \)) at several points, as shown in Figure 5c,d. Figure 5c shows two different slopes, one in the range from 133 to 193 K and the other in the range from 213 to 293 K. In addition, Figure 5d shows different slopes, one in the range from 133 to 193 K and the other in the range from 213 to 293 K. Here, we take the graphs and their slopes of the higher temperature range for the following two reasons. The first reason is that in the high-temperature range, the NNH process exactly matching with our Marcus-type charge transfer is favored, whereas in the lower temperature range, a variable range hopping process is preferred. The second reason is that the equation is well-applied for explaining carrier mobility at room temperature in organic semiconductor thin films. From the slope of the higher temperature plot, we can obtain the activation energy value \( E_{a, mono} \), and \( E_{a, cluster} \) for the 4-Es/Oct Si QD thin film, which is larger than the activation energy value \( E_{a, cluster} = 34 \) meV for the Si QD cluster thin film (Figure 5c). In other words, the reorganization energy for 4-Es/Oct Si QD and Si QD cluster thin films is calculated to be 170 and 140 meV, respectively, using eq 3. The reorganization values could be of those for hole or electron transfer, even though in our study the carrier is temporarily assigned to an electron, for simplicity in building up the theoretical formulation. These reorganization energy values are compared to those calculated for the Si QD thin film in ab initio calculations. The reorganization energies of Si₁₃H₃₅O DB QD (fully passivated), Si₁₃H₃₅DB QD (dangling bond), and Si₃₅H₃₄O (doubly bonded oxygen defect) for hole transfer were calculated to be 270, 830, and 390 meV, respectively, whereas those for electron transfer were 170, 1170, and 850 meV, respectively. In addition, the larger molecule tends to give smaller reorganization energy, as confirmed in a study on hopping transport in conductive heterocyclic oligomers. Then, the smaller reorganization energies in our Si QD system, as compared with the referenced Si QDs whose number of silicon are 35, are surely due to the larger QD diameter (5.4 nm for our synthesized Si QDs vs ca. 1 nm for Si₁₃H₃₅O DB QD, and Si₃₅H₃₄O). From the activation energies and \( B_{mono} \) and \( B_{cluster} \), we obtain the electronic coupling ratio between the Si QD cluster \( V_{cluster} \) and 4-Es/Oct Si QD \( V_{mono} \) thin films using eqs 10b and 11b.

\[
\frac{B_{cluster} - B_{mono}}{B_{cluster}} = \ln \left[ \frac{\sqrt{V_{cluster}}}{\sqrt{V_{mono}}} \left( \frac{E_{a, mono}}{E_{a, cluster}} \right)^{1/2} \right] = 4.1 \quad (12) 
\]
\[ \frac{V_{\text{cluster}}}{V_{\text{mono}}} = 7.3 \]  

On the other hand, we can obtain eq 14 from eqs 10a and 11a and substitute the conductance values at 293 K, electronic coupling, and activation energy values into the equation

\[ \frac{G_{\text{cluster}}}{G_{\text{mono}}} \approx \left( \frac{V_{\text{cluster}}}{V_{\text{mono}}} \right)^{2} \left( \frac{E_{\text{a,mono}}}{E_{\text{a,cluster}}} \right)^{1/2} \exp \left( -\frac{(E_{\text{a,cluster}} - E_{\text{a,mono}})}{kT} \right) \]  

\[ \frac{5.7 \times 10^{-6}}{7.4 \times 10^{-6}} = 77 \cong 53 \times 1.1 \times 1.3 \]  

Equations 14 and 15 show that the increase in conductance of the Si QD cluster thin film compared with that of the 4-Es/Oct Si QD thin film is almost exclusively due to the enhanced electronic coupling rather than the thermal factor.

Here, it is very necessary to keep in mind that the electronic coupling and reorganization energy for charge transfer in 4-Es/Oct Si QD and Si QD cluster thin films are contributed by those for all hopping pathways under all structural variations and randomness schematically depicted in Scheme 2b,c. In other words, the above values for our Si QD systems are not determined from a particular hopping pathway but just act as representative ones to effectively consider all hopping pathways, as confirmed by the derivation of eqs 8 and 9 with defining \( r_{\text{mono}} \), \( W_{\text{mono}} \), \( r_{\text{cluster}} \), and \( W_{\text{cluster}} \). This is why we can tentatively call them the “effective” coupling and “effective” reorganization energy, respectively. Their effectiveness and representability are more necessary for the Si QD cluster thin film, as compared with the 4-Es/Oct Si QD thin film. This is because, as shown in Scheme 2b,c, the structural variation of the nearest QDs around a Si QD with an electron (or a hole) is much more serious for the Si QD cluster thin film. In our previous study, we provided a unique Si QD thin film where all Si QDs are connected covalently through a \( \pi \)-molecular bridge by thermal cross-linking.\(^{15} \) The dramatic increase by 4 orders of magnitude in current density observed for the cross-linked Si QD thin film, surely giving rise to huge increases in conductance values as compared to those of 4-Es/Oct Si QD thin films, is due to the approximately single chemical environment around Si QDs experiencing strong electronic coupling through the \( \pi \)-molecular bridge. To confirm the possibility of huge electronic coupling in the thermal cross-linked Si QD thin film of complete \( \pi \)-molecule interconnection, the investigation of its temperature dependence will be again performed under the theoretical framework—merge of the microscopic viewpoint, Marcus theory, with the electron transfer (W) between the adjacent QDs with macroscopic property, such as the electrical conductance (G), introduced in this study. In addition, we want to mention that the physical origin of the higher conductivity of our Si QD cluster thin film is distinctively different from that for phenylpropyl ligand-terminated Si QDs—\(^{5} \)the former is originated from the enhanced electronic coupling through the \( \pi \)-molecular bridge and the latter is due to the benzene ring-induced \( \pi-\pi \) stacking in phenylpropyl ligands of adjacent Si QDs.

The electrical conductivity of our Si QD cluster thin film is calculated to \( 1.7 \times 10^{-9} \) S cm\(^{-1} \), which is very poor compared to that of a typical organic semiconductor [undoped poly(3-hexylthiophene): ca. \( 2 \times 10^{-4} \) S cm\(^{-1} \)].\(^{40} \) The reason for such poor conductivity of the Si QD cluster thin film is that there are a lot of interfaces of no molecular bridge because there are still a lot of monomers of 4-Es/Oct Si QDs, although dimers and trimers are dominant clusters. This means that in our Si QD cluster thin film, electronic coupling between Si QD clusters (not between Si QDs) would be relatively very small compared to that between polymer chains in an organic semiconductor. On the other hand, for the Si QD thin film cured at 350 °C in our previous study,\(^{15} \) the completely \( \pi \)-molecule-bridged QD network over the entire thin film exhibited 4 orders of magnitude higher conductivity compared to that of Si QD solids of no \( \pi \)-molecular bridges. Thus, we now believe that chemical control at interfaces between Si QD clusters is crucial to further increase the electrical conductivity of the Si QD cluster thin film in the future.

### CONCLUSIONS

In this article, for the first time, we synthesized a \( \pi \)-conjugated molecule-bridged Si QD cluster by Sonogashira cross-coupling reaction, which is sure to open huge opportunity for developing novel functional materials owing to the diversity of C–C cross-coupling reactions and bridged molecular structures. The enhanced electronic coupling through the \( \pi \)-conjugated molecule bridge in the Si QD cluster was verified by the red shifts in UV–vis absorption and PL emission with the possibility of exciton transport, the increased charging effect found in the core-level photoemission spectra, the shift to lower BE of the valence band photoemission spectrum, and the increase in electrical conductance of its thin film. For the first time, in the field of QD solids, we developed a theoretical framework which merges the microscopic viewpoint, Marcus theory, on the electron transfer (W) between the adjacent QDs, with macroscopic concepts, such as the conductance (G), mobility (\( \mu \)), and diffusion coefficient (D), to investigate the physical origin of the temperature dependence of the electrical conductance of a Si QD cluster thin film. We also, for the first time, demonstrated that, in the Si QD thin film, its electrical conductivity is almost exclusively governed by electronic coupling rather than the thermal factor.

### EXPERIMENTAL SECTION

**Chemicals and Materials.** Toluene (anhydrous, 99.8%), methanol (anhydrous, 99.8%), borane—tetrahydrofuran complex solution 1 M in tetrahydrofuran (BH\(_3\)OC\(_4\)H\(_8\), 1 M in tetrahydrofuran), 1,4-diethynylbenzene (C\(_8\)H\(_6\), 96%), 1-octene (C\(_8\)H\(_{16}\), 98%), silica-gel [(40–63) mm], magnesium sulfate (MgSO\(_4\), anhydrous, >99.0%), 2,5-dibromo-3-hexylthiophene (97%), bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh\(_3\))\(_2\)Cl\(_2\), 98%), copper(I) iodide (CuI, >98.0%), and triethylamine (TEA) (N(C\(_2\)H\(_5\))\(_3\), 99.0%) were purchased from Sigma-Aldrich. Ethanol (C\(_2\)H\(_5\)OH, 99.5%), n-hexane (C\(_{20}\)H\(_{46}\) 95%), methanol (CH\(_3\)OH, 99.5%), and chloroform (CHCl\(_3\), 99.7%) were purchased from Dae-Jung (South Korea), and hydrofluoric acid [(48–51)%] was purchased from J.T. Baker.

**Synthesis of Si QD Clusters.** Scheme S1a–c of the Supporting Information summarizes the synthesis of silica (SiO\(_2\)) nanoparticles, silicon NCs embedded in silicon oxide phase (Si NCs@SiO\(_2\)), and 4-Es/Oct Si QD. Especially, the synthesis of the 4-Es/Oct Si QD was performed in the same way we had used in our previous paper.\(^{3} \) The Sonogashira cross-coupling reaction has been employed in organic synthesis to form carbon–carbon bonds between a terminal alkyne...
(RC≡C−H) and aryl or vinyl halide (R′−X).16,41 Thus, to connect isolated 4-Es/Oct Si QD by π-conjugated molecule linkers, we performed Sonogashira cross-coupling reaction, as shown in Scheme 1a. The C–C cross coupling reaction between 4-Es/Oct Si QD and 2,5-dibromo-3-hexyl-thiophene was carried out in the argon atmosphere by using the standard Schlenk line technique. The 4-Es/Oct Si QD (0.1 g), Pd(PPh₃)₄Cl₂ (20 mg), and CuI (8 mg) were dispersed in a mixture of anhydrous toluene (6 mL) and TEA (3 mL) and then added to a 100 mL two neck flask equipped with a condenser that was connected to a Schlenk line filled with argon. The solution was stirred for 5 min at room temperature. 2,5-Dibromo-3-hexyl-thiophene (0.2 g) and anhydrous toluene (6 mL) were added to the mixture, and the reaction mixture was stirred at 110 °C for 2.5 h to obtain a brown solution. After cooling the reaction mixture, methanol (MeOH) was added into the reaction mixture to precipitate Si QD clusters and then centrifuged at 15 000 rpm for 5 min to obtain a brown powder. This powder was washed with MeOH repeatedly (three times) to remove the catalyst. As mentioned in the X-ray diffraction (XRD) result (Figure S1 of the Supporting Information), the removal of the remaining conjugating molecules, 1,4-diethynylbenzene, is not completed because of the interaction between 4-Es/Oct Si QD and 1,4-diethynylbenzene through C≡C–H···π–C hydrogen bonding.42 The 4-Es/Oct Si QDs were obtained as a yellow powder including the remaining conjugating molecules, 1,4-diethynylbenzene. Because of the remaining 1,4-diethynylbenzene molecule, as shown in Scheme 1a, the synthesis of Si QD clusters is performed not only by cross-coupling between 4-Es/Oct Si QD and 2,5-dibromo-3-hexylthiophene to generate a molecule (relatively smaller molecular weight part: A, relatively larger molecular weight part: A′) but also by cross-coupling between 4-Es/Oct Si QD, 1,4-diethynylbenzene and 2,5-dibromo-3-hexylthiophene to a generate molecule (relatively smaller molecular weight part: B, relatively larger molecular weight part: B′). Hence, we suggest that the product of the Sonogashira cross-coupling reaction is a mixture of two kinds of product groups ((A, A′), (B, B′)) (Scheme 1b). Some powder products did not completely dissolve in toluene. There are some soluble parts (A, B) because of relatively smaller molecular weight and some insoluble parts (A′, B′) because of relatively larger molecular weight. Hence, the products in toluene solvent were separated by filtering through 0.2 μm PTFE membranes (Scheme 1b). The remaining solution of A and B was dried by using a rotary evaporator to give powder product. The powder of the soluble part was further purified by a precipitation method with toluene as a solvent and methanol as an antisolvent, in which the Si QD clusters (A) with considerably short linkage of VPE-T-EPV were precipitated, whereas the Si QD hybrid polymer of very long chain of (3-hexyl)thiophene-ethylenephenyleneethynylene units (B) remained soluble. After centrifugation, the Si QD clusters (A′) were obtained as a yellow powder (P.2), while the soluble hybrid polymer of higher organic fraction (B) was taken as a solution (P.1). The dominant product in the P.2 is the Si QD cluster (A) containing the considerably short VPE-T-EPV linkage because its TEM image shows the distance between the QDs to be smaller than 2.5 nm (Figure 1b–d), implying no additional involvement of the 1,4-diethynylbenzene molecules, which remain not completely consumed in the previous hydrosilylation reaction step.

Thin-Film Fabrications. 4-Es/Oct Si QD and Si QD cluster thin films were fabricated by a conventional spin-coating method. After being filtered through 0.2 μm PTFE membranes, 2 wt % solutions in toluene for 4-Es/Oct Si QD and the Si QD cluster (A; P.2) were poured onto Si wafer substrates, followed by spinning at 500 rpm for 5 s and subsequently at 2500 rpm for 25 s. The thin films on the Si wafers were then cured at 150 °C for 4 h under argon in a tube vacuum furnace.

Theoretical Calculations. The optimized geometries of the π-conjugated molecule bridge (Figure 1d) were obtained using the MP3 semiempirical method in the HyperChem 8.0 package. The geometries were further optimized using DFT at B3LYP level and the 6-31G** basis set in Gaussian 16.43

Characterizations. FE-TEM was performed using a JEM-2100F electron microscope (JEOL, Japan) with an accelerating voltage of 400 kV. For TEM sampling, a solution of 0.05 wt % of 4-Es/Oct Si QD and Si QD clusters in toluene was dropcast onto a carbon-coated copper grid, and the solvent was evaporated in a vacuum. NMR data were collected on superconducting FT-NMR 300 MHz (Varian Inc., Palo Alto, California, USA). Chemical shifts are reported in parts per million (ppm) in a solvent of chloroform-d (99.8 atom % D).

FT-IR measurements were conducted by a Nicolet 380 spectroscopy system (Waltham, MA, USA) operated in the mid-IR range of (4000–400) cm⁻¹, with spectra obtained at a spectral resolution of 8 cm⁻¹ in transmission mode. SCINCO S-3150 spectroscopy (Scinco Co., Ltd., Korea) was used to obtain the UV–vis absorption spectrum of the 4-Es/Oct Si QD and Si QD cluster solution of 0.01 wt % in chloroform.

HR320 Hiroba spectroscopy (Hiroba, Japan) with 3 nm slit width for emission monochromators was used to perform PL spectroscopy of 4-Es/Oct Si QD and Si QD clusters.

Photoemission Spectroscopy. The 4-Es/Oct Si QD and Si QD cluster thin films were cured at 150 °C under an Ar atmosphere. Each sample was introduced into an ultrahigh vacuum chamber and pumped down to the base pressure reaching 5 × 10⁻¹⁰ Torr. The O 1s, C 1s, S 2p, and Si 2p core-level spectra of the samples were recorded at the photon energy of 630 eV with a total resolution of 200 meV at the 8A2 HRPES beam line at the Pohang Accelerator Laboratory (PAL) equipped with an electron analyzer (Scienta 2002). As for the C 1s spectra at the photon energy of 630 eV, the charge-calibration in data analysis is not performed to directly show the different extent of charging for the two thin films. The BEs of Si 2p, O 1s, and S 2p for the photon energy of 630 eV were calibrated by positioning the C 1s peaks at 285.0 eV. Valence-band spectra were recorded at the photon energy of 130 eV. Si 2p core-level spectra were also measured at the photon energy of 130 eV. As for the photon energy of 130 eV, all spectra were calibrated by positioning SiO2 peaks at the corresponding ones for the photon energy of 630 eV. All spectra were obtained in the normal emission mode. The O 1s, C 1s, and Si 2p photoemission spectra were fitted by using a standard nonlinear least-squares fitting procedure with Voigt functions.

Electrical Property Measurement of Thin Films. MIM device structures of Al electrode–thin film–p⁺ Si wafer (resistivity <0.005 Ω cm) were fabricated to investigate the temperature dependence of conductance for the 4-Es/Oct Si QD and Si QD cluster thin films, which were cured at 150 °C under an Ar atmosphere. Current–voltage (I–V) characteristics were obtained in a probe station in a nitrogen-filled chamber at different temperatures in the range from 133 to 293 K using an HP4145B semiconductor parameter analyzer.
The current passing through the film was measured while the applied voltage was swept from −100 to 100 mV. All measurements were carried out in the dark and under vacuum at a pressure of 10−3 Torr.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03459.

Synthesis procedure of SiO2 NPs and Si NC@SiO2; synthesis procedure of the ethynylstyril and octyl cocapping Si QD; synthesis procedure of π-conjugated PAE; XRD patterns of 4-Es/Oct Si QD with 1,4-diethynylbenzene; H NMR spectra of P.1 and P.2 (Si QD clusters) compared to PAE, 4-Es/Oct Si QD, and 2,5-dibromo-3-hexylthiophene; UV−vis absorption spectra of P.1 and P.2 (Si QD cluster) compared with 4-Es/Oct Si QD and PAE in chloroform; FT-IR spectra of the 4-Es/Oct Si QDs and Si QD clusters; and C 1s, O 1s, and S 1s photoemission spectra for 4-Es/Oct Si QD and Si QD cluster thin films at the photon energy of 630 eV (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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