

The electronic structures of all *trans* form of permethyl-oligosilane radical cation with longer chain: A density functional theory study

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Abstract

Hybrid density functional theory (DFT) calculations have been carried out for neutral, radical cation and dication of permethyl-oligosilane, $\text{Si}_n(\text{CH}_3)_{2n+2}$ ($n = 4\text{--}30$), to elucidate the electronic structures at ground and low-lying excited states. It was found that a hole is distributed in both the Si–Si skeleton (main chain) and methyl group (side chain) in the case of shorter chain-lengths below $n = 6$, whereas the spin density (hole) in the methyl group becomes significantly smaller in longer chain-lengths ($n > 7$). The IR-band of radical cation were assigned on the basis of theoretical calculations.

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1. Introduction

Polysilane is one of the σ -conjugated one-dimensional polymers and has been extensively investigated because of their potential utility as hole and electron transport materials in organic multilayer light emitting diodes (LEDs), photo-resist materials, and high-density optical data storage materials [1–10]. These characteristic features are originated from high hole mobility of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a low-lying excited state of polysilanes at doped state, which correlates strongly with the electron and hole conductivities as an organic semi-conductor. Hence, determination of the electronic structures of ionic states at both ground and excited states is an important theme in development of new materials of silane systems.

The experimental works have been carried out by several groups. The electronic absorption spectroscopy is convenient technique to determine the electronic excited states of polysilanes. Transient absorption spectra of polysilanes in organic solvents after electron beam irradiation show that the radical ions (cation and anion) of polysilanes have a strong absorption band at UV region [11,12]. This band is assigned to an electronic transition of unpaired electron on Si–Si skeleton. Irie et al. [13,14] measured the transient- and steady state-absorption spectra of radical ions of polysilanes with aryl-group. They found that the radical ions has a near-IR band as well as the UV band. They assigned the near-IR band to a charge resonance band between two aryl groups. Ushida et al. [15] attributed the near IR band to a charge resonance between adjacent σ -conjugated polymer segments: namely, it is an intramolecular charge transfer band. Thus, the low-lying excited state of the ion radicals is still in controversy. In particular, origin of the near-IR band is not clearly understood.

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To elucidate the detailed electronic structure of the polysilane, an approach from “small-sized polysilane”, namely, “oligosilane” has been attempted by several groups. Irie and Irie [16] examined chain length dependence on the absorption spectra of the radical anion and cation of oligosilanes. The spectra have two peaks in UV and near-IR regions as well as those of polysilanes, and the maxima in both spectra are shifted to longer wavelengths with increasing chain length. Kumagai et al. [17,18] investigated absorption spectra of radical ions of permethyl-oligosilanes. They found that the radical ions of the oligosilanes possess UV and near-IR bands, as well as usual polysilanes.

The electronic states of neutral oligosilanes have been investigated mainly by ab initio calculations [19,20]. Michl and co-workers investigated conformers of n -Si₆(CH₃)₁₄ using ab initio, molecular mechanics (MM) and additive increment method [19a]. It was found that all transoid is the most stable conformer. Thus, information on the electronic structures of neutral oligosilanes have been accumulated from theoretical points of view. On the other hand, a few theoretical works have been carried out for radical ions of oligosilanes in spite of its importance.

In the previous works, we investigated the structures and electronic states of the polysilane radical anion [21] and cation [22] by means of semiempirical PM3-CI method. The permethyl-oligosilane Si_n(CH₃)_{2n+2} ($n = 8-20$) was chosen as a model of polysilane. We showed that excess electron and hole are fully delocalized along the skeleton of linear polysilane. The electronic excitation energy from the ground to first excited states was gradually red-shifted as a function of the number of chain Si atoms (n). Our previous studies suggested that the excess electron (hole) is not localized in the case of the regular all-*trans* form in the linear polysilane but is delocalized widely along the main chain. Also, mechanism of electron localization at finite temperature was investigated by means of MM2 molecular dynamics and PM3 methods [23].

Recently, Tada and Yoshimura have carried out SE-CI calculation for radical anion of oligosilane Si_nH_{2n+2} ($n = 2-6$) [24]. The ground state is composed of σ^* characteristics where unpaired electron occupies in σ^* orbital of Si-Si skeleton. The first electronic transition of (Si_nH_{2n+2})⁻ ($n = 2-6$) is assigned to Si-Si($\sigma^* \leftarrow \sigma$) transition. The π -character appears from third excited state. However, the radical anion (Si_nH_{2n+2})⁻ has been not observed experimentally, and the conclusion may be therefore limited only to the (Si_nH_{2n+2})⁻ system. Actual systems observed experimentally include alkyl groups (such as methyl- and ethyl-groups) in side-chain. Hence, studying of the electronic structures of methyl-substituted oligosilane is required to compare directly with the experiments.

In the present study, density functional theory (DFT) calculations have been carried out for neutral, radical cation and dication of the linear permethyl-oligosilane with long-chain Si_n(CH₃)_{2n+2} ($n = 4-30$) in order to determine the electronic structures.

2. Method of calculations

Almost all calculations were carried out at the DFT(B3LYP)/3-21G(d) level of theory. A linear oligosilane with methyl groups in side-chain, permethyl-oligosilane (Si_n(CH₃)_{2n+2}) ($n = 4-30$), was examined. First, the initial geometries of neutral oligosilanes were made by MM2 calculation. Using the optimized geometry of the MM2 calculation, the geometries of neutral, cation and dication of the oligosilanes were optimized at the DFT(B3LYP)/3-21G(d) level of theory. The excitation energies were calculated by means of time-dependent (TD)-DFT calculations. Six excited states were solved in TD-DFT calculations. All hybrid DFT calculations were carried out using GAUSSIAN 03 program package [25]. Note that this level of theory gives reasonable features for several molecular device systems [26–29].

3. Results and discussion

3.1. Ionization energies of oligosilanes ($n = 4-30$)

The structures of oligosilanes Si_n(Me)_{2n+2} ($n = 4-30$) with the regular all-*trans* form are fully optimized at the B3LYP/3-21G(d) level. As an example, the structure for $n = 20$ is illustrated in Fig. 1. Using the optimized struc-

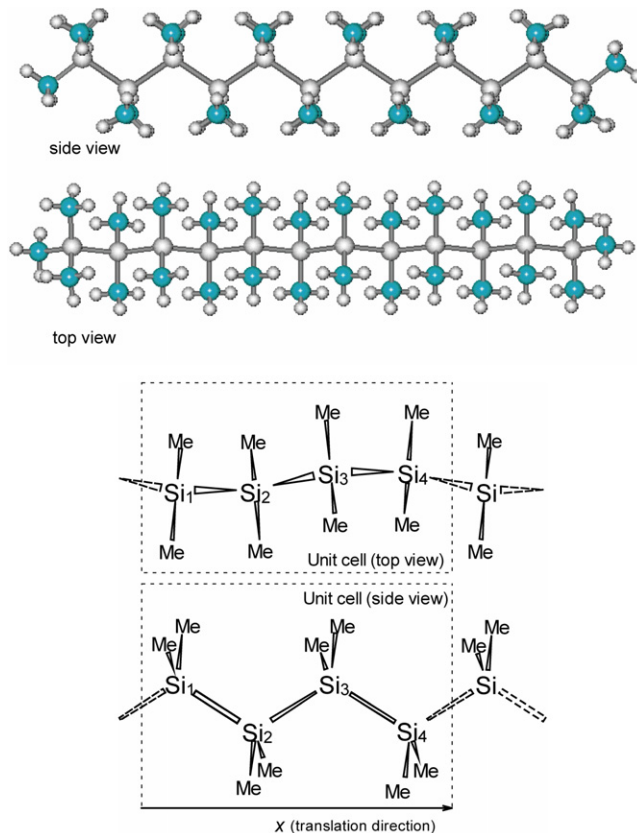


Fig. 1. Schematic illustration of (upper) a structure of permethyl-oligosilane, Si_n(CH₃)_{2n+2} ($n = 12$) with all-*trans* form, and (lower) the unit cell used in the calculation.

tures, vertical ionization energies, denoted by $E_{IP}(\text{ver})$, are calculated, and the results are plotted as a function of n in Fig. 2. $E_{IP}(\text{ver})$'s for $n = 4, 10, 20$, and 30 are calculated to be 7.45, 6.38, 5.88, and 5.67 eV, respectively, indicating that $E_{IP}(\text{ver})$ decreases gradually with increasing n . The experimental value of $E_{IP}(\text{ver})$ for $n = 4$ is measured to be 7.98 eV, which is in good agreement with the present value (7.45 eV) [30].

Next, the structures are further optimized at the cation state, and adiabatic ionization energies, denoted by $E_{IP}(\text{adv})$, are calculated. The results are plotted in Fig. 2a. $E_{IP}(\text{adv})$'s for $n = 4, 10, 20$, and 30 are calculated to be 6.93, 6.12, 5.73, and 5.58 eV, respectively. The difference between $E_{IP}(\text{ver})$ and $E_{IP}(\text{adv})$ for $n = 4, 10, 20$, and

30 are 0.52, 0.26, 0.15, and 0.09 eV, respectively. This result implies that the structural change of cation state becomes smaller in longer chains. The similar calculations are carried out for the second ionization energies. As shown in Fig. 2b, the second ionization energies decreases with increasing n . The second ionization energy is 12.9 eV even if $n = 30$. This high energy indicates that yield of the dication of oligo- and polysilanes is negligibly small in chemical doping.

3.2. Excitation energies of neutral, cation, and dication of oligosilanes ($n = 4-30$)

As mentioned in introduction, a low-lying excited state correlates strongly with the electron conductivity in organic semi-conductor. Hence, determination of the electronic structures at the excited states is important to elucidate the mechanism of electron and hole conductivities in oligosilanes. The first excitation energies of neutral, cation and dication of oligosilanes ($n = 4-30$) are given in Fig. 3 together with oscillator strengths. At the neutral state,

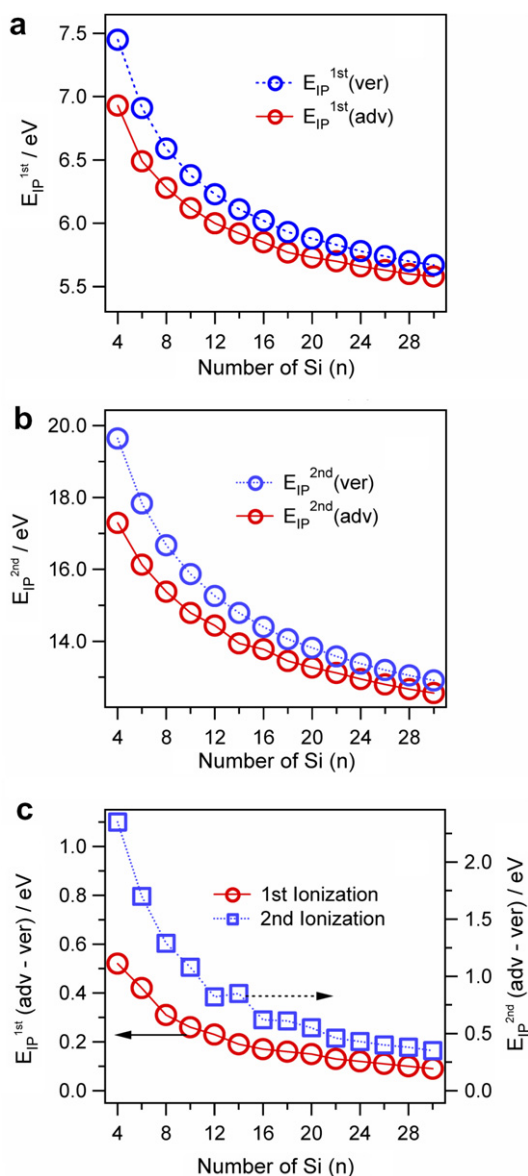


Fig. 2. Vertical and adiabatic ionization energies of oligosilanes plotted as a function of chain length (n): (a) first ionization energy, (b) second ionization energy, and (c) difference between the first and second ionization energies.

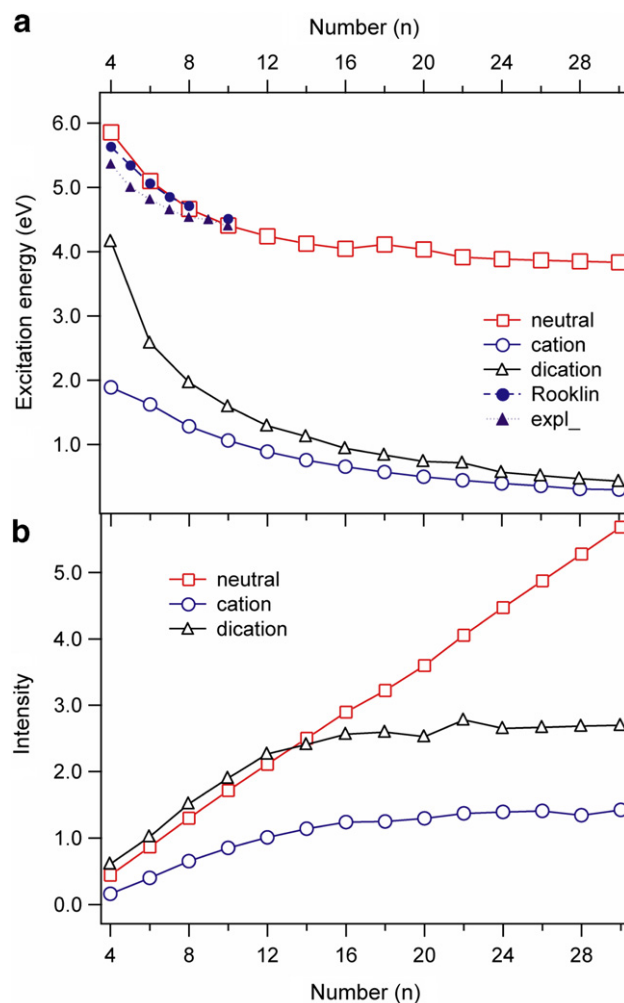


Fig. 3. (a) First excitation energies of neutral, cation and dication of oligosilanes plotted as a function of chain length and (b) intensities of excitation energies (in arb. unit).

the first electronic transitions for $n = 4, 10, 20,$ and 30 occur at 5.8, 4.4, 4.0, and 3.8 eV, respectively. The excitation energies decreased gradually with increasing chain length (n), and it reaches a limited value around $n = 16$. The oscillator strengths are linearly increased. The excitation energies, calculated by Rooklin et al. (TD-DFT(B3LYP/6-311G(d) level) and measured by Obata and Kira, are also plotted in Fig. 3. The present values are agreed well with previous excitation energies.

The radical cation has significantly lower excitation energies. The excitation energies for the first electronic transitions in $n = 4, 10, 20,$ and 30 are calculated to be 1.9, 1.1, 0.5, and 0.3 eV, respectively. The excitation energy of dication is slightly higher than that of radical cation, as shown in Fig. 3.

3.3. Comparison with the experimental absorption spectra of radical cation

Kumagai et al. and Irie et al. measured absorption spectra of radical cation of permethyl-oligosilanes with $n = 4-6$ and poly(methyl- n -propylsilane)s with $n = 8-21$, respectively. Therefore, we can compare directly our theoretical values with their experiments. Fig. 4 shows the calculated and experimental excitation energies of the radical cations. The B3LYP/6-311+G(d,p) values for $n = 4-6$ in our previous work [31] are also given in this figure. The present values calculated by B3LYP/3-21G(d) are in excellent agreement with the experimental values ($n = 4-6$) and those of B3LYP/6-311+G(d,p) ($n = 4-6$). Also, these are agreed well with the experiment with $n = 4-6$. At longer chain lengths ($n = 8-21$), the calculated values are also in reasonable agreement with the experiment of Irie et al., although the former is slightly deviated from the experi-

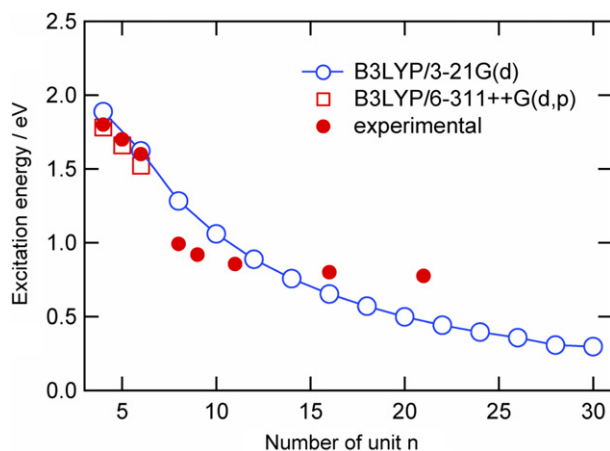


Fig. 4. Comparison of the calculated first excitation energies of radical cation of oligosilanes with experimental values. Experimental values are cited from Refs. [16] and [17].

mental values in longer region ($n = 22$). This slight difference may be caused by the effects of side-chain of oligosilane (methyl group in the present calculation vs. n -propyl group in the experiment). These results strongly indicate that B3LYP/3-21G(d) level would give a reasonable feature for the electronic structures of oligosilane at both ground and excited states.

3.4. Simulated absorption spectra of neutral and radical cation of oligosilane ($n = 4-28$)

Simulated absorption spectra of neutral and radical cation of oligosilane are illustrated in Fig. 5. In the plots of simulations, half width of spectrum is assumed to be 0.01 eV. For the neutral state, the peak of the absorption

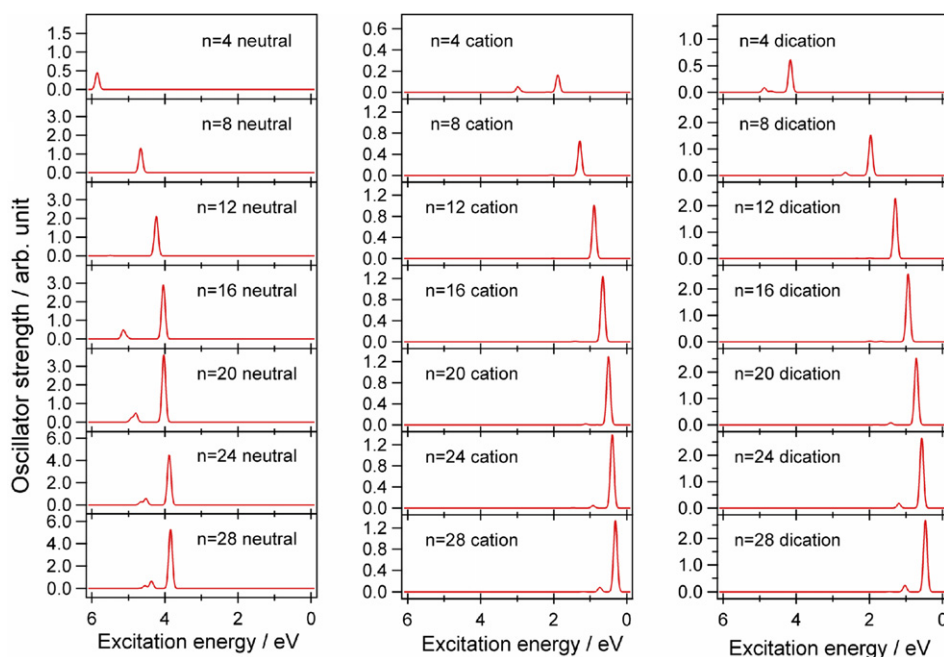


Fig. 5. Simulated absorption spectra of neutral, cation, and dication of oligosilanes.

spectrum is gradually red-shifted as a function of chain length, while the intensity is linearly increased. The peaks are appeared at ultraviolet region (3.80–5.90 eV). The coefficient of the main configuration $\phi(\text{HOMO} \rightarrow \text{LUMO})$ is calculated to be 0.626 ($n=28$) at the first excited state, and those of the other configurations are negligibly small, indicating that the excitation band is assigned to be the HOMO–LUMO transition of neutral oligosilane.

The simulated absorption spectra of radical cation show excitation band at lower energy region. The excitation energies for $n=4, 12, 20,$ and 28 are calculated to be 1.9, 0.9, 0.5, and 0.3 eV, respectively. The excitation band becomes significantly lower in longer chain-lengths and the intensity becomes stronger. For $n=28$, the band gap is only 0.3 eV, which is low in energy enough to thermal hopping of hole along the Si–Si backbone. Thus, it can be summarized that band structure of oligosilane is significantly changed by doping of positive hole. The new energy bands are appeared at very low energy region below 0.5 eV. In particular, it is predicted theoretically that new energy band with a strong transition probability is generated at low energy region. This is an origin of hole transport in oligo- and polysilanes.

3.5. Spin densities

To elucidate distribution of unpaired electron in oligosilanes, spin densities on the Si–Si backbone (main chain) and the methyl group (side chain) are calculated at B3LYP/3-21G(d) and B3LYP/6-311G(d,p) levels of theory, and the results are given in Fig. 6. The former and latter calculations are carried out for $n=4$ –30 and for $n=4$ –14, respectively. Both calculations give the similar spin densities. For $n=4$, the spin densities on the Si–Si backbone and methyl group are 0.82 and 0.18, respectively. The spin densities on the Si–Si backbone increases with increasing n , and it becomes ca. 1.0 above $n=10$.

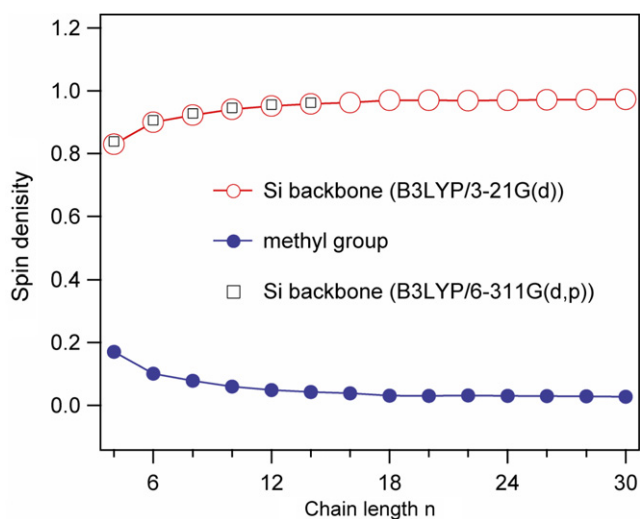


Fig. 6. Spin densities on Si–Si backbone (main chain) and methyl group (side chain) of oligosilanes plotted as a function of chain length (n).

Also, the spin densities on the side chain is close to zero. This result strongly implies that the hole is only localized in the Si–Si backbone, while the penetration of spin densities into the side chain is negligibly small in longer chain lengths.

3.6. Band structure of poly(dimethylsilane)s

To elucidate the electronic structures of neutral polysilane in details, a band structure is calculated at the B3LYP/3-21G(d) level of theory. We have used valence effective Hamiltonian (VEH) technique [32] to calculate the one-dimensional electronic band structure of the polymer. The optimized geometrical parameters are given in Table 1. The Si–Si bond lengths are calculated to be 2.3552 and 2.3589 Å. The result is plotted in Fig. 7. At the center of the Brillouin zone ($k=0$), the band gap is calculated to be 4.34 eV. On the other hand, the band gap becomes wider at the edge of the Brillouin zone ($k=\pi/a$). This result indicates that the doping is necessary to produce the carrier in the poly(dimethylsilane). Also, the band gap calculated by periodic condition (4.34 eV) is in good

Table 1

Optimized geometrical parameters obtained for an unit cell of poly(dimethylsilane)

| Parameters | HF/3-21G(d) | B3LYP/3-21G(d) |
|--------------------------|-------------|----------------|
| Si(1)–Si(2) | 2.3631 | 2.3552 |
| Si(2)–Si(3) | 2.3714 | 2.3589 |
| <Si(1)–Si(2)–Si(3) | 111.7 | 111.4 |
| <Si(2)–Si(3)–Si(4) | 111.7 | 111.6 |
| <Si(1)–Si(2)–Si(3)–Si(4) | 158.6 | 165.0 |
| Translation vector | 7.7956 | 7.7697 |

The unit cell is consisted of four Si atoms, expressed by Si(1)–Si(2)–Si(3)–Si(4). Bond lengths and angles are in Å and in °, respectively.

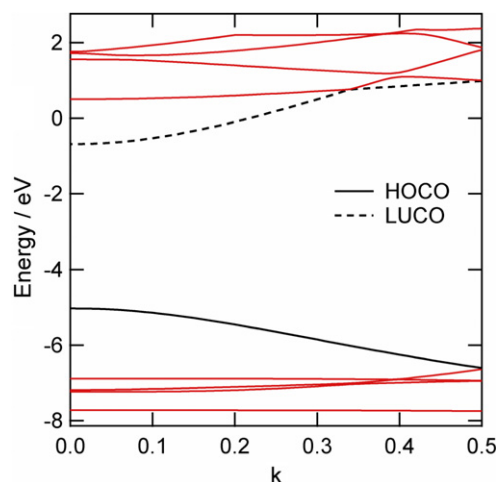


Fig. 7. Band structure of poly(dimethylsilane)s at neutral state calculated under the periodic boundary condition. HOCO and LUCO mean highest occupied crystal orbital and lowest unoccupied crystal orbital, respectively.

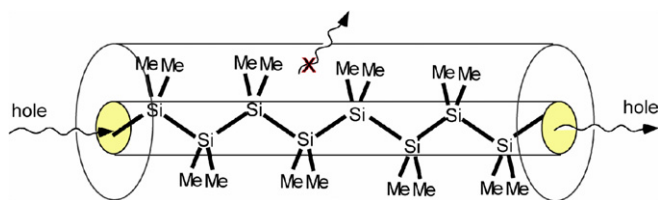


Fig. 8. Illustrations of model of hole transport in radical cation of permethyloligo- and polysilanes.

agreement with that of oligosilane ($n = 30$: 4.38 eV). This suggests that the longer oligosilanes around $n = 30$ exhibits the electronic properties of polysilanes. Crespo et al. calculated the band structure of poly(phenylsilane) using the VEH technique at the HF/3-21G(d) level. The present result is agreed well with previous calculations [32].

4. Discussion

The present calculations show that the hole is delocalized within the Si–Si skeleton, while the penetration of hole into the side-chain (methyl group) does not take place. On the basis of the present results, a model of hole transfer is illustrated in Fig. 8. In the case of polysilane with side-chain of methyl groups, hole is delocalized along the Si–Si chain. Also, the band gap of oligosilane is significantly low in cationic state [33]. Therefore, the hole is transferred along the Si–Si skeleton at thermal condition. Namely, in permethyl-oligosilanes and polysilanes, only intramolecular hole transfer is possible, but intermolecular hole transfer is significantly difficult. This is nature of hole transport in poly(dimethylsilane)s.

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