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Electronic states of radical cations of all-*trans* oligo[methyl(phenyl)silane]

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Abstract

The electronic states of radical cations of oligo[methyl(phenyl)silane] (OMPSi$^+$) with all *trans* form ($n = 2$–8, where n is number of monomer unit of OMPSi) have been investigated by means of density functional theory (DFT) calculation to shed light on the mechanism of hole-transport in oligosilanes with phenyl group in the side chain. For the shorter oligomers ($n < 3$), the hole (unpaired electron) was widely distributed equivalently in both the Si main and side chains (55% for the Si main chain and 45% for the side chain). The distribution of hole on the chains was largely changed as a function of chain lengths (n). Ratios of the hole distribution on the main and side chains became almost constant at $n = 7$–8: 70% of spin density was distributed on the Si-main chain and 30% on the side-chain, which is much different from that of oligo(dimethyl)silane (the spin density on the methyl side chain was less than 3% of spin density). From these results, it was concluded that the hole in OMPSi$^+$ can transfer by the mechanism for both intermolecular and the intrachain hole-transfer processes.

Keywords: Oligosilane; Radical cation; DFT; Ab initio; Spin density; Excitation energy

1. Introduction

Recently, polysilanes have been extensively utilized as hole and electron transport materials in organic multilayer light emitting diodes (LEDs), one-dimensional semi-conductors, photo-resist materials, and high-density optical data storage materials [1–10]. These characteristic features are originated from high hole mobility of 10^{-4} cm^2 V^{-1} s^{-1} and a low-lying excited state of polysilanes at doped state. Therefore, determination of the electronic structures for ionic states at both ground and excited states is an important theme in development of new materials of silane systems.

Charge transport in charge-injected polysilane has been investigated extensively using time-of-flight [11,12] and time resolved microwave conductivity techniques [13–17]. These experiments indicate that thermal activation and field-assistance enhance the hole mobility in polysilanes.

To elucidate mechanism of hole and excess electron transfers in polysilanes, several experiments have been carried out. In particular, the effects of substitution of side-group on the charge conductivity of oligo- and polysilanes have been investigated from experimental points of view. Seki et al. have recently measured [16] the transient absorption spectra of radical cations of a variety of substituted polysilanes by means of pulse radiolysis technique. They suggested that phenyl ring bonded to the Si–Si skeleton plays an important role in hole transport process. If the side chain is only composed of alkyl groups, the hole mobility is significantly slower than that of the phenyl group. As a reason for the high hole mobility in the polysilane with phenyl groups in side-chain, two reasons have been considered as follows: (1) σ–σ conjugation along the Si–Si backbone is more favorite in the polysilane with phenyl ring than that with alkyl group because the

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structural conformation of the former polymer is well aligned by steric effect. The other reason is (2) the electronic states of polysilane are changed by the substitution of phenyl group in the side-chain. However, details of the hole transport mechanism is still not clearly understood.

From theoretical points of view, several ab initio and density functional theory (DFT) calculations have been carried out to elucidate the structures and electronic states of radical ions of oligo- and polysilanes. Recently, Toman et al. [18] performed a conclusive investigation for ion radicals of oligo[methyl(phenyl)silane] (OMPSi). They assigned explicitly infrared (IR) band of $MPSO^+ \rightarrow OMPSi^+$ using DFT calculation. In previous papers, we investigated theoretically the electron transfer process in radical cation of oligo(dimethyl)silane [19] at the ground and excited states. The intermolecular electron transfer between oligomer chains does not occurred at the ground state, whereas it takes place at the excited states.

In the present study, density functional theory (DFT) calculations were applied to the neutral and radical cations of OMPSi to elucidate the mechanism of hole transport in oligosilane radical cations with the phenyl group. As be known, the first excitation band plays an important role in electron conductivity of semi-conductor. Hence, the excitation energies are calculated as a function of chain length (n). For comparison, the electronic states of oligo-(dimethyl)silane (ODMSi) were investigated with the same matter.

2. Method of calculations

The geometries of neutral, radical cations and dications of OMPSi ($n = 2$–8) with all *trans* form were fully optimized at the DFT(B3LYP)/3-21G(d) level of theory. The end-groups were capped by the hydrogen atoms. We assumed syndiotactic structure throughout for the oligomers. All *trans* forms were only treated for the initial structures throughout in the present study. The spin densities and hyperfine coupling constants were calculated at the B3LYP/6-311+G(d) level. Using the optimized geometries, the excitation energies were calculated by means of time-dependent (TD)-DFT method. Six excited states were solved in the TD-DFT calculations. All hybrid DFT and ab initio calculations were carried out using Gaussian03 program package [20]. Note that the similar levels of theory give reasonable features for several molecular device systems [21–23].

3. Results

3.1. Structures of neutral and radical cation of OMPSi

First, the geometrical structures of neutral OMPSi with all-*trans* form ($n = 2$–8) are fully optimized at the B3LYP/3-21G(d) level. Definition of geometrical parameters is given in Fig. 1, and the selected optimized parameters for $n = 2$–8 are listed in Tables 1 and 2. The bond lengths of Si–Si atoms of neutral OMPSi are distributed in the range 2.34–2.37 Å. When OMPSi is ionized, the bond lengths are slightly elongated because the electron is removed from the Si–Si bonding orbital of OMPSi. For example, the bond length of Si(1–2) for $n = 8$ is changed from 2.3583 to 2.3786 Å by the ionization. This change is larger in shorter oligosilanes.

The dihedral angles of OMPSi are also changed by the ionization of OMPSi. The angles are distributed in the range 145–180°, indicating that the oligomers have transoid forms. Four dihedral angles of neutral OMPSi for $n = 7$ are calculated to 154.0°, 156.1°, 144.5°, and 157.9°, whereas those of $OMPSi^+$ are be 156.6°, 156.6°, 154.9° and 155.8°.

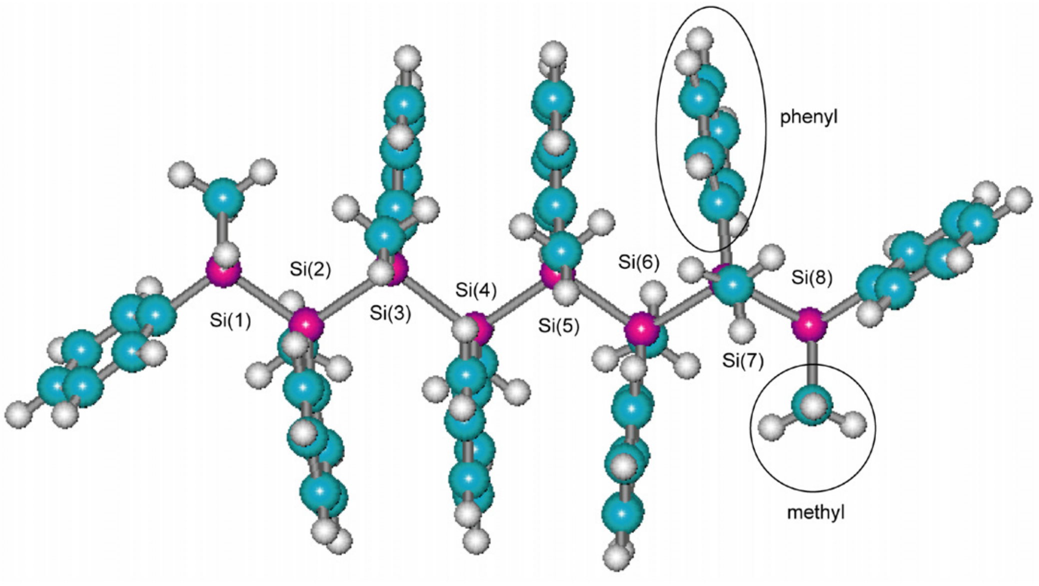

Fig. 1. Schematic illustration of structure of oligo[methyl(phenyl)silane] (OMPSi, $n = 8$).