Electron-Accepting System of Si−Si Bond in Linear Framework by Combination with Strong Donor

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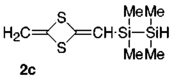
Organosilicon compounds have been widely utilized not only as various functional materials but also as valuable organic synthetic reagents owing to their unique chemical and physical properties.[1] There has been a remarkable growth in electro- and photochemistry of organosilicon compounds over the past two decades. Electronic state of cyclic and acyclic silicon catenates differs significantly from those of their carbon analogue. Low ionization potential (I_p) of a Si−Si bond leads to similar properties to a carbon−carbon double bond (electronic delocalization within the σ-bonded framework) and effective electron donating property.[2] Electron delocalization between the Si−Si σ bonds and π systems has been also conclusively established in various disilyl compounds containing unsaturated or aromatic groups,[3] which are important as semiconductors or conductors,[4] and light-emitting materials.[5] In this paper, we report the synthesis of disilyl-substituted thioketene dimers and demonstrate that effective $\sigma-\pi$ conjugations induce the unique charge transfer (CT) from the thioketene dimer to the Si−Si units, even though the Si−Si unit usually acts as an electron donor.

Scheme 1 shows the preparation of the thioketene dimers having silyl and disilyl moieties (**2**). Reaction of ethynyl compounds (**1**)[3d] with *n*-BuLi and sulfur yielded alkynyl thiolates in situ. Treatment with water generated unstable silylthioketenes, which rapidly dimerized to form **2** in excellent yields. The structures of the obtained dimer compounds **2** were supported by IR and ^{1}H and ^{13}C NMR spectra and elemental analysis. We first expected that the corresponding dithiole compounds should be obtained, since the usual results of this reaction, in the case of aromatic thioketenes, yield dithioles by [2 + 3] cycloaddition reaction between aldothioketenes and their alkynethiol tautomers.[6] However, all spectral data of **2** indicated the [2 + 2] cycloaddition of aldothioketenes to give 2,4-diylidene-1,3-dithietane structures.[7]

Calculation of HOMO and LUMO of disilyl-substituted thioketene dimer (**2c**) using the PM3 Hamiltonian was carried out.[8]



2c

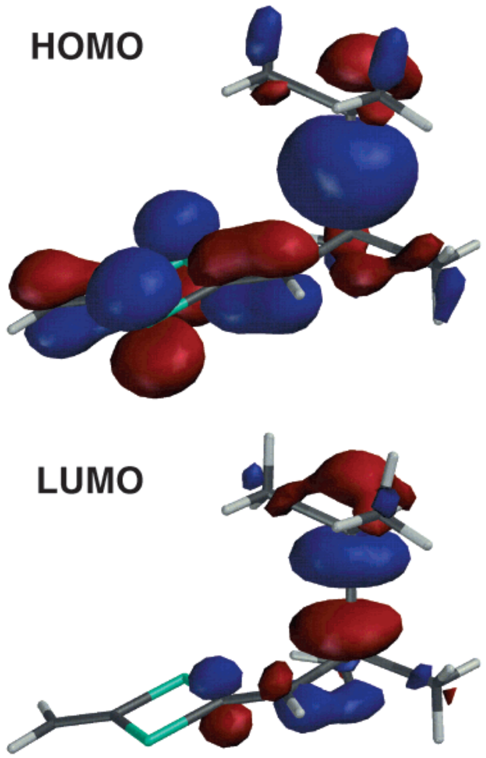
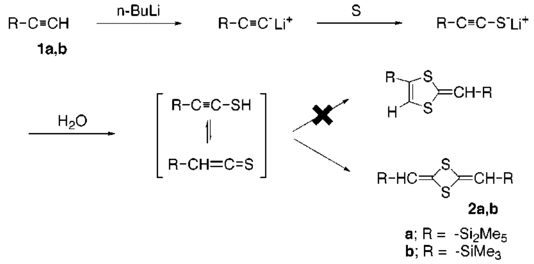


Figure 1. HOMO and LUMO density surfaces of **2c** calculated with the PM3 Hamiltonian. The density value is 0.002 electrons/au^3.

Scheme 1



The thioketene dimer and the Si−Si moieties bear the most of the electron density of the HOMO, while atomic coefficients of the LUMO are larger on the Si−Si fragment (Figure 1). Our recent report described that such a thioketene dimer unit shows a very strong electron-donating property.[7d] These results predicted that direct attachment of a strong donor such as the thioketene dimer to the Si−Si bond would lead to intramolecular CT from the donor to the Si−Si moiety. Interestingly, the Si−Si unit has been regarded as an electron donor thus far. The PM3 calculation of a thioketene dimer having one trimethylsilyl moiety showed no observation of the electron density of the LUMO on the silicon atom, suggesting less was available for CT. The CINDO/S calculation for the electron transition spectrum of **2a** suggested that a peak due to the HOMO−LUMO transition would appear at 429 nm.[9]

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(8) Calculation by use of the Spartan Package; Wavefunction, Inc., Irvin, CA. The molecular orbital surfaces were created after calculation of geometry optimization by PM3 semiempirical molecular orbital method.

(9) After the molecular structure of **2a** was optimized by PM3 semiempirical method, the electron transition spectrum of **2a** was calculated by the CINDO/S method implanted in the MOS-F, ver 4.2; Fujitsu Ltd.: Tokyo, Japan.

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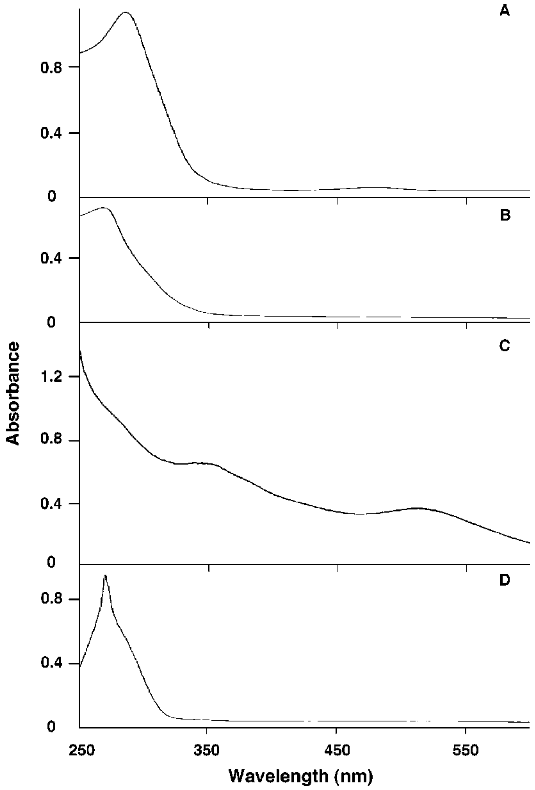
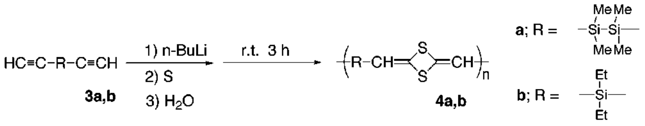


Figure 2. UV−vis spectra of thioketene dimers; (A) **2a** and (B) **2b** in $CHCl_3$, (C) **4a** and (D) **4b** in CH_3CN.

Scheme 2



In the UV−vis spectrum, the bis(silyl)-substituted thioketene dimer (**2b**) shows a peak due to the $\pi-\pi^*$ transition at 268 nm. The absorption maximum (282 nm) of the bis(disilyl)-substituted thioketene dimer (**2a**) moved to the direction of lower energy, indicating the presence of $\sigma-\pi$ conjugation. The spectrum of **2a** shows small but important absorption ($\epsilon = 530$) with a peak at 463 nm; however, **2b** shows no absorption in this region in $CHCl_3$ (Figure 2A and B). Since the peak intensity of the absorption in **2a** was proportional to the concentration of the sample solution, the absorption in the visible region of **2a** should be originated from the intramolecular CT interaction between the Si−Si and the thioketene dimer unit. The CT absorptions of **2a** showed interesting behavior in various solvents. The peak moved to shorter wavelength, with increasing the solvent polarity ($\lambda_{max} = 446$ nm in CH_3CN and 455 nm in acetone). This solvent-dependent shift is characteristic of negative-solvatochromism, which is clearly caused by the intramolecular CT interaction.[10] If, with increasing solvent polarity, the ground-state molecule is better stabilized by solvation than the molecule in the excited state, negative solvatochromism would result.[11]

We also carried out the polymerization by use of a disilanylene monomer **3a**[3d] aiming at preparation of a novel $\sigma-\pi$ conjugated polymer **4a** (39% yield, M_n= 7890, Scheme 2).[12] This polymer, unlike the low-molecular weight compounds **2**, shows a very large absorption ($\epsilon = 3310$) with a peak at 515 nm in CH_3CN (Figure 2C), which was located at a longer wavelength compared with that of **2a**. This fact indicates that extensive $\sigma-\pi$ delocalization enhanced the CT interaction between the units. The strong and broad absorption across the entire spectral region of **4a** is owing to the effective $\sigma-\pi$ conjugation, which overlaps with the CT transition in the visible range. The extinction of the CT band varied in accordance with Lambert−Beer law, also indicating the intramolecurar CT in **4a**. Similarly to **2a**, a clear negative-solvatochromism of the CT band of **4a** was observed ($\lambda_{max} =$ 488 nm in H_2O, 495 nm in MeOH, and 519 nm in acetone). Sunlight exposure decreased the intensity of the CT absorption of **4a** (Figure 3), suggesting that transformation of the Si−Si unit to a siloxane (Si−O−Si) or degradation of the polymer chain led to an inefficient CT interaction.[13] This short-time decrease of the absorption indicates the very low stability of **4a** against the light. A peak for Si−O−Si unit around 1100 cm^{-1} also appeared in the IR spectrum of **4a** after sunlight exposure.

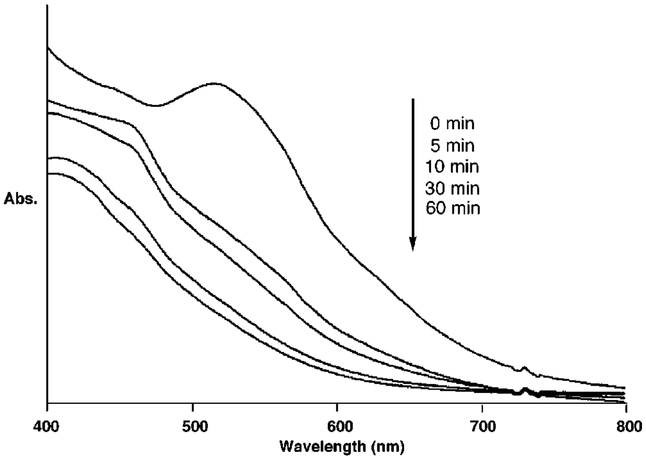


Figure 3. Time dependence of CT absorption of **4a** by sunlight exposure.

We also prepared a nonconjugated polymer **4b** by cycloaddition polymerization of bis-thioketene derived from diethynylsilane **3b** (Scheme 2). In contrast to **4a**, the obtained polymer **4b** (24% yield, M_n= 7100) had no absorption in the visible range (Figure 2D) in the UV−vis spectrum, suggesting no CT interaction between the thioketene dimer and the Si unit in the polymer. The fact that the absorption maximum of **4b** was same as that of **2b**, suggests that π-electrons on the thioketene dimer are hardly delocalized through the polymer chain.

A series of silyl-substituted thioketene dimers have been synthesized. The interesting fact of the CT from the thioketene dimer unit to the Si−Si bond was demonstrated. No intramolecular CT transition was observed in the systems of the thioketene dimers attached to the silyl or the silylene unit. To achieve the effective intramolecular CT interaction between the units, eventually, the $\sigma-\pi$ conjugation system would be required.

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Supporting Information Available: Synthetic procedures, analytical data for compounds and UV spectra in different solvents (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] The IR and NMR spectra of **4a** were similarly to those of CT complexes of **2** with strong acceptors, supporting the intramolecular CT structure of **4a**.

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