Modification of thermal property and LUMO level of disilane by phenyl-substitution

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Received 28 October 2004; accepted 1 April 2005

Available online 21 June 2005

Abstract

Thermal, optical and electrochemical properties of phenyl-substituted disilanes have been investigated. Phase-transition temperature increased with increasing the number of phenyl substitutents. σ–π Conjugation effect by the introduction of phenyl-substitutents also strongly affected LUMO levels of disilanes with slight change of their HOMO levels.

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Keywords: Phase transitions; Other conjugated; Conducting polymers; UV–Vis-NIR absorption; Electrochemical methods

1. Introduction

Polysilanes have been attracting great attention as a novel class of photo- and electroactive materials [1]. In studying the properties of conjugated polymers, corresponding oligomers with well-defined structures are often synthesized as model compounds. In some cases, these oligosilanes show even superior properties to the corresponding polymers, and their applications as photo- and electroactive materials are suggested in field-effect transistors, Schottky diodes, electroluminescent, electrochromic, and photovoltaic devices [2].

Although there are numerous reports on their synthetic methods, photochemical, thermal, spectroscopic and electrical properties of oligosilanes with well-defined structures as model compounds of σ-conjugated poly-silanes, their optical and electrochemical properties are little reported [3]. We have been studying the thermal, optical, electrochemical, and electrical properties of oligosilanes with well-defined structures, and found that the band gap energies and oxidation potentials of permethylated oligosilanes increased with decreasing chain length and that the HOMO level of hexamethyldisilane (P00) became as low as 6 eV [4], which is much lower than those of typical π-conjugated materials used in EL devices, such as N,N’-bis(3-methylphenyl)-N,N’-diphenylbenzidine (TPD, 5.10 ± 0.1 eV) and aluminum tris(8-hydroxyquinoline) (Alq3, 5.57 ± 0.1 eV) [5]. This HOMO value suggests that P00 can act as a hole-blocking material in the EL devices. However, P00 is a liquid material and its LUMO (<1 eV) is too high, and it is difficult to use P00 itself in EL devices.

To improve thermal property and LUMO level of disilanes as the hole-blocking material, phenyl-substituents were introduced into disilane structure. It is expected that phenyl group can act as both the bulky substituent for the improvement of thermal property, and the π-electron system to modify of electronic property due to the σ–π conjugation effect [6]. In this paper, series of phenyl-substituted disilanes (Fig. 1) are synthesized, and their thermal, optical and electrochemical properties are investigated related with the number and position of phenyl groups.

2. Experimental

Oligosilanes were synthesized according to the literature [7].
Morphological changes of disilanes were examined by differential scanning calorimetry (Seiko Instruments Inc., EXSTAR6000, DSC6200).

Electronic absorption spectra were measured by JASCO V-570 UV/VIS/NIR spectrometer. Cyclic voltammetry was carried out as acetonitrile solution (1.0 × 10⁻³ mol dm⁻³) of oligosilanes containing tetra- n-butylammonium tetrafluoroborate (1.0 × 10⁻¹ mol dm⁻³) as a supporting electrolyte in a cell equipped with platinum working and counter electrodes and a Ag/Ag⁺ (1.0 × 10⁻² mol dm⁻³) reference electrode.

### 3. Results and discussion

Properties of phenyl-substituted disilanes are summarized in Table 1. As expected, phase-transition temperature of disilanes increased with increasing number of phenyl groups. Asymmetric disilanes (P10, P20, P21, and P31) tended to show glass-transition temperature and some of them did not show any crystallization temperature at all. Interestingly, disilanes having three phenyl groups on one silicon atom (P30 and P33) showed only sublimation temperature.

**Table 1**

| Disilanes | Number of phenyl groups | T_g [°C]d | T_c [°C]e | T_m [°C]f | T_s [°C]g | E_g [eV]h | E_ox,th [V]i | HOMO [eV]j | LUMO [eV]k |
|-----------|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| P00       | 0                      | 9      |        | −54    | −87    | 5.88   | 1.32   | 6.1     | 0.2     |
| P10       | 1                      | −121   | −80    | −87    | −54    | 4.87   | 1.24   | 6.0     | 1.2     |
| P11       | 2                      | 31     |        | 4.92   | 1.24   | 6.0     | 1.3    |
| P20       | 2                      | −80    |        | 4.92   | 1.29   | 6.1     | 1.3    |
| P21       | 3                      | −59    |        | 4.72   | 1.24   | 6.0     | 1.3    |
| P30       | 3                      | 106    |        | 4.86   | 1.31   | 6.1     | 1.3    |
| P31       | 4                      | 142    | 84m    | 4.70   | 1.27   | 6.1     | 1.3    |
| P32       | 5                      | 146n   |        | 4.67   | 1.30   | 6.1     | 1.4    |
| P33       | 6                      | 357    |        |        |        |        |        |

- a In N₂, heating rate: 10 degree min⁻¹.
- b Cyclohexane solution.
- c Acetonitrile solution.
- d Glass-transition temperature.
- e Crystallization temperature.
- f Melting temperature.
- g Sublimation temperature.
- h Band-gap energy.
- i Threshold value of electrochemical oxidation. These data are internally calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) (E_ox,th = 9.7 mV vs. Ag/Ag⁺).
- j HOMO was estimated by the comparison with ferrocene (4.8 eV) [7].
- k LUMO = HOMO − E_g.
- ℓ 2nd heating.
- m 1st heating.
- n Slight weight loss due to sublimation was observed.
- o Insoluble in organic solvents.
Electronic absorption spectra of P00, P10, P11, and P20 are shown in Fig. 2 and the electronic absorption edges ($E_g$) of all disilanes are summarized in Table 1. New absorption at 230–260 nm was observed by the electrochemical oxidation process. The comparison of electrochemical oxidation processes of disilanes are also affected by the thermal stability.

Fig. 2. Electronic absorption spectra of P00 (solid), P10 (dash), P11 (dash-dot), and P20 (dash-dot-dot). Solvent: Cyclohexane.

Electronic absorption spectra of P00, P10, P11, and P20 are shown in Fig. 2 and the electronic absorption edges ($E_g$) of all disilanes are summarized in Table 1. New absorption at 230–260 nm was observed by the introduction of phenyl group, which is not observed in the spectrum of P00. This new peak is ascribed to the electron transition due to the $\sigma-\pi$ conjugation [6]. The absorption of P11 showed red-shift compared with P10, which suggests the expansion of $\sigma-\pi$ conjugation. However, the absorption of P20 was observed at similar wavelength with P10, while the molar absorption coefficient of P20 increased almost twice than that of P10. Similarly, disilanes having phenyl groups on both silicon atoms showed smaller $E_g$s than those of disilanes having phenyl groups on one silicon atom.

Cyclic voltammograms of P00, P10, P11, and P20 are shown in Fig. 3 and the threshold voltages ($E_{ox,th}$) are summarized in Table 1. All disilanes showed irreversible electrochemical oxidation processes. The comparison of P00 with P10 suggests that $E_{ox,th}$ decreases due to the $\sigma-\pi$ conjugation effect on the introduction of phenyl group into disilanes. P11 showed lower $E_{ox,th}$ than that of P10 due to the further expansion of $\sigma-\pi$ conjugation. However, P20 showed slightly higher $E_{ox,th}$ than that of P10. Each phenyl ring on one silicon atom may disturb their configuration suitable for $\sigma-\pi$ conjugation because of their steric hindrance. P30 showed higher ox,th because of larger steric effect than that of P20. $E_{ox,th}$s of P11, P21, P31 and P21, P22, P32 showed similar trends.

From these data, HOMO and LUMO levels are estimated and are summarized in Table 1. HOMO levels were correlated to ferrocene (4.80 eV) [8]. LUMO levels are calculated by $\text{LUMO} = \text{HOMO} - E_g$. LUMO levels of phenyl-substituted disilanes are much lower than P00 by about 1 eV, but do not change so much once phenyl-group is introduced into disilane structure. Contrary to this, changes of HOMO levels are very small, although $E_{ox,th}$s showed some differences due to the $\sigma-\pi$ conjugation and steric effects. Thus, $\sigma-\pi$ conjugation effect can strongly affect to the LUMO level of disilanes rather than the HOMO levels. This result indicates that phenyl-substituted disilanes are better than P00 for the hole-blocking material in the EL devices.

4. Conclusions

Thermal, optical, and electrochemical properties of phenyl-substituted disilanes have been investigated. The thermal transition temperature of disilanes increased with increasing the number of phenyl groups. The introduction of phenyl group strongly affected the electronic absorption spectra due to the $\sigma-\pi$ conjugation effect between Si–Si $\sigma$-electron system and phenyl $\pi$-electron system. Electrochemical oxidation processes of disilanes are also affected by the $\sigma-\pi$ conjugation, but its effect is not so large. Thus, it is concluded that introduction of one or two phenyl groups is enough from the viewpoint of hole-blocking property, but that the larger number of phenyl groups is good to improve the thermal stability.

At the present state, LUMO levels of phenyl-substituted disilanes are still high to inject the electron from the electrode. For the further improvement of hole-blocking nature, stronger electron-withdrawing $\pi$-electron systems than phenyl group should be introduced.

Acknowledgements

This work was supported in part by grants for Basic Science Research Projects from the Sumitomo Foundation and for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japanese government (16205016 and 17750177).
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