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Emission Spectra of $\sigma-\pi$-Conjugated Organosilicon Copolymers Consisting of Alternating Dimethylsilylene and Aromatic Units

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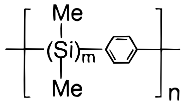
ABSTRACT: Emission measurements were performed on a series of $\sigma-\pi$ conjugated organosilicon copolymers, $-[(\mathrm{SiMe_2})_m\mathrm{A}]_n-$ ($m = 1, 2, 3, 4$, and 6), with alternating dimethylsilylene and π-conjugated units (A = phenylene, diphenylene, and anthranylene) in various solvents. The copolymers with $m \geq 2$ exhibit a broad emission ascribable to an intramolecular charge transfer (CT) excited state resulting from the charge transfer between the dimethylsilylene and aromatic units. The solvatochromism of the emission spectra was observed for the organosilicon copolymers, where the emission maximum shifted to longer wavelength in polar solvents. The influence of the dimethylsilylene chain-length and the π-conjugated unit on the CT emission was investigated. The molecular orbital calculations on a model compound suggest that the vibronically structured emission is attributed to the π-character of the aromatic unit, and the structureless broad emission is ascribed to the σ-character of the Si−Si bond in the excited states. The emission lifetime and the quantum yield also show the dimethylsilylene chain-length dependence.

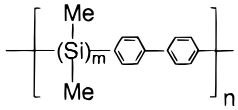
Introduction

The $\sigma-\pi$ conjugation between the Si−Si σ-bond and aromatic π-system in the ground state has been confirmed by the electronic absorption spectra.[1] The study of polymers having $\sigma-\pi$-conjugated systems along the polymer chain is an interesting subject in connection with their potential utility as electronically conducting, semiconducting, and emitting polymers.[2−5] The photochemical properties of silyl-substituted aromatic compounds are different from those of methyl- or methylene-substituted compounds.[6−11] One of the remarkable properties of silyl-substituted aromatic compounds in the excited state is the formation of an intramolecular charge transfer (CT) excited state resulting from the charge transfer between the Si−Si bond and the aromatic group.[6] A shorter wavelength emission ascribed to the π,π^* locally excited (LE) state and a longer wavelength emission ascribed to an intramolecular CT excited state have been reported.[6,7,10,11]

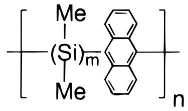
The photochemical properties of silyl-substituted aromatic compounds are well-established based on the excited-state behavior of various stereochemically designed compounds.[6−11] However, few studies have been reported on the excited-state properties of $\sigma-\pi$-conjugated organosilicon copolymers. In a previous paper we reported the spectroscopic properties and the thermochromism of $\sigma-\pi$-conjugated alternating silylene−phenylene, silylene−thienylene, silylene−acetylene, silylene−diphenylene, and silylene−anthranylene copolymers which have various dimethylsilylene chain lengths ($m = 1, 2, 3, 4$, and 6).[5] We demonstrated the enhancement of the $\sigma-\pi$-conjugation with an increase of the dimethylsilylene chain length m. In this work we report the results of the time-resolved emission of the $\sigma-\pi$-conjugated alternating silylene−phenylene (**1a**−**e**), silylene−diphenylene (**2a**−**e**), and silylene−anthranylene (**3a**−**e**) copolymers (Figure 1). The effects of the silylene chain length and solvent on the emission spectra will be discussed.



1a: m=1, **1b**: m=2, **1c**: m=3
1d: m=4, **1e**: m=6



2a: m=1, **2b**: m=2, **2c**: m=3
2d: m=4, **2e**: m=6



3a: m=1, **3b**: m=2, **3c**: m=3
3d: m=4, **3e**: m=6

Figure 1. Chemical structures of silylene−phenylene (**1a**−**e**), silylene−diphenylene (**2a**−**e**), and silylene−anthranylene (**3a**−**e**) copolymers.

Experimental Section

Materials. The $\sigma-\pi$-conjugated alternating silylene−phenylene (**1a**−**e**), silylene−diphenylene (**2a**−**e**), and silylene−anthranylene (**3a**−**e**) copolymers were prepared by the following procedures. The starting compounds, dibromoarenes, could be directly and quantitatively converted to dilithium derivatives by reaction with n-butyllithium, and quenching the solution with α,ω-dichloropermethylated oligosilanes, $\mathrm{Cl(SiMe_2)}_m\mathrm{Cl}$ ($m = 1, 2, 3, 4$, and 6), gives the desired copolymers. The detailed procedures are described elsewhere.[5] All copolymers are soluble in common organic solvents such as tetrahydrofuran, chloroform, and aromatic solvents. The molecular weight and the molecular weight distribution are summarized in Table 1.

Measurements. The emission spectra of organosilicon copolymers were recorded on a difference spectrofluorophotometer (Shimadzu RF-503A). The emission quantum yields of the organosilicon copolymers were determined by using quinine bisulfate in 0.1 N H_2SO_4 aqueous solution as a standard. The time-resolved emission spectra were measured

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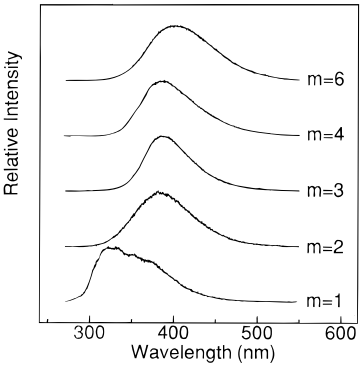

Figure 2. Emission spectra of 0.1 mM silylene−phenylene copolymers in dichloromethane at 22 °C; excitation wavelength, 250 nm.

Table 1. Characteristics of σ−π-Conjugated Organosilicon Copolymers

sample	yield (%)	M_w	M_w/M_n	sample	yield (%)	M_w	M_w/M_n
1a	49	2460	1.7	**2d**	27	9800	1.4
1b	28	2500	1.8	**2e**	31	10900	1.6
1c	35	2520	1.8	**3a**	20	6100	1.4
1d	26	2710	2.1	**3d**	21	7600	1.4
1e	21	3080	2.1	**3c**	20	8500	1.4
2a	21	7500	1.3	**3d**	22	9700	1.5
2b	20	8500	1.7	**3e**	24	10100	1.6
2c	25	9100	1.8				

using an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA), a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 11.5 ps fwhm) pumped by a pulse selector (Spectra-Physics, Model 3980), a harmonic generator (GWU-23PS), and a streak scope (HAMAMATSU, C4334-01, sweep repetition rate 2 MHz). In the measurements, by setting a threshold level for the A/D (analogue/digital) converted CCD (charge-coupled device) camera signal, the photoelectron image can be clearly separated from the noise. The system enables photon counting measurements at simultaneous multiple wavelengths. Typical instrument response function for this apparatus is 20 ps (fwhm) and the time resolution of the detection within 5 ps can be obtained by using the deconvolution technique. All of the sample concentrations were 0.1 mM at 22 °C.

Results

Emission Measurements. Emission spectra of silylene−phenylene copolymers **1a**−**e** in dichloromethane are shown in Figure 2. The copolymer **1a** having dimethylsilylene chain length $m = 1$ shows a vibronically structured emission with a maximum at 318 nm. On the other hand, copolymers **1b**−**e** exhibit broad, structureless emission spectra. The emission maximum shifts to longer wavelength with an increase of the silylene chain length. The shorter wavelength emission with a vibronic structure can be ascribed to the π,π^* LE (locally excited) state, and a longer wavelength broad emission can be attributed to an intramolecular CT excited state as reported for silyl-substituted aromatic compounds.[6,7,10,11] Since the concentration of polymer (0.1 mM) is low, the polymer chains are isolated from one another in solution and the intermolecular interaction is negligible. Similar dependence of emission spectra on the silylene chain length is observed for silylene−diphenylene copolymers **2a**−**e**, as shown in Figure 3. The emission spectra were measured by varying the emission wavelength from 250 to 300 nm, and no dependence of the emission spectra on the excitation wavelength was observed. The emission maxima of copolymers in dichloromethane are plotted against the silylene chain length *m* in Figure 4. The emission maximum of the intramolecular CT emission with $m \geq 2$ shifts to longer wavelength and exhibits the influence of the aromatic unit.

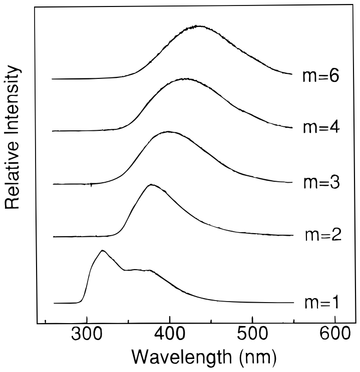

Figure 3. Emission spectra of 0.1 mM silylene-diphenylene copolymers in dichloromethane at 22 °C; excitation wavelength, 250 nm.

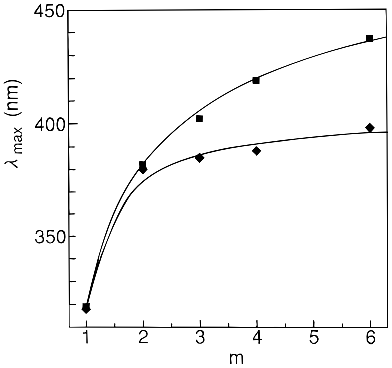

Figure 4. Plots of emission maxima against the dimethylsilylene chain length *m* for silylene−phenylene (◆) and silylene−diphenylene (■) copolymers in dichloromethane at 22 °C.

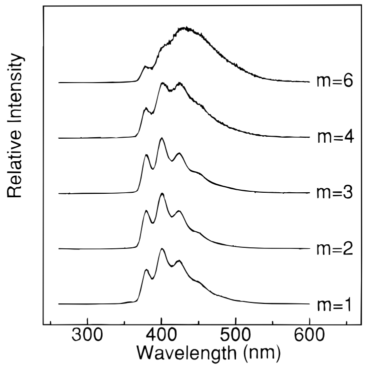

Figure 5. Emission spectra of 0.1 mM silylene−anthranylene copolymers in dichloromethane at 22 °C; excitation wavelength, 250 nm.

The influence of the aromatic unit is more significant for silylene−anthranylene copolymers. The emission spectra of silylene−anthranylene copolymers **3a**−**e** exhibit quite different features as shown in Figure 5. The copolymers **3a**−**c** ($m = 1$, 2, and 3) exhibit only a vibronically structured π,π^* LE emission which is ascribed to the anthranyl group. The overlap of this band with a structureless broad emission is observed for **3d** and **3e** ($m = 4$ and 6). Such differences in the intramolecular CT emission can be explained by considering the first ionization potential of the silylene chain and the aromatic unit, as discussed later.

Solvent Effects. The intramolecular CT emission of silyl-substituted aromatic compounds is sensitive to the solvent.[6,7,10,11] The CT emission maximum shifts to

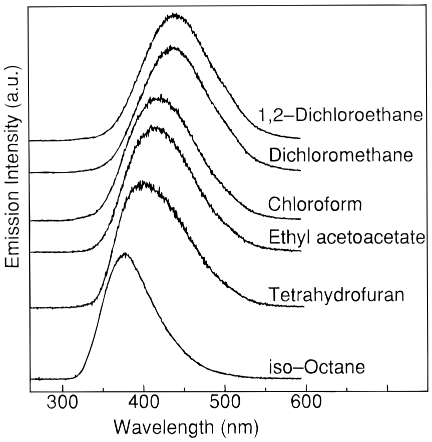

Figure 6. Emission spectra of the silylene–diphenylene copolymer **2e** in various solvents; excitation wavelength, 250 nm.

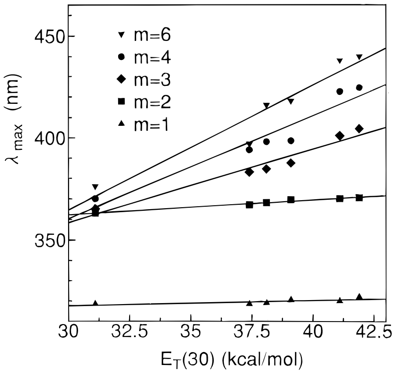

Figure 7. Plots of the emission maxima for silylene–diphenylene copolymers against the empirical parameter of the solvent polarity.

longer wavelength in polar solvents. On the other hand, a distinct dual emission from the π,π^* LE and the intramolecular CT state is observed in nonpolar solvents. The solvent dependence of the emission spectrum provides evidence for the intramolecular CT excited state. Figure 6 shows the emission spectra of the silylene–diphenylene copolymer **2e** ($m = 6$) in various solvents. The maximum of the broad, structureless emission shifts to longer wavelength with increasing the solvent polarity. In Figure 7, the emission maxima of silylene–diphenylene copolymers **2a**–**e** are plotted against the $E_T(30)$, which is an empirical parameter for the solvent polarity.[12] The silylene–phenylene copolymer **1a** ($m = 1$) shows little shift, even in a polar solvent. The CT emission shift to longer wavelengths in a polar solvent becomes significant with increase of the silylene chain length m.

Emission Lifetime and Quantum Yield. Conjugated polymers sometimes show nonexponential decays because of the rapid energy migration or transfer from higher to lower energy levels along the polymer chain.[13–16] The inhomogenities caused by variation in the conformation and the conjugated sequence length cause the distribution of the electronic levels and the excited-energy trapping sites. Although the emission decays of the organosilicon copolymers are essentially multiexponential because of the distribution, the decay analysis using the sum of two exponential decays can be applied for the qualitative investigation of the excited-state dynamics.[13,15] The emission lifetimes of silylene–phenylene (**1a**–**e**), silylene–diphenylene (**2a**–**e**), and silylene–anthranylene (**3a**–**e**) copolymers are summarized in Table 2. The lifetimes (τ_2) of organosilicon copolymers with the silylene chain length $m = 1$ (**1a** and **2a**) are longer than those with $m \geq 2$, since the former shows the π,π^* emission from LE state while the latter shows the CT emission. The negative lifetimes τ_1 of **1a** and **2a** correspond to the rise time of the emission after laser pulse excitation. The organosilicon copolymers ($m \geq 2$) show an increase of the lifetime with an increase of the silylene chain length. The π,π^* emission decays of silylene–anthranylene copolymers **3a**–**e** are fitted to a single exponential equation and do not show the influence of the silylene chain length.

Table 2. Emission Lifetimes of σ–π-Conjugated Organosilicon Copolymers in THF at 22 °C[a]

sample	τ_1^b(ps)	τ_2^c(ps)	sample	τ_1^b(ps)	τ_2^c(ps)
1a	−97[d]	1920	**2d**	194	900
1b	75	500	**2e**	228	1240
1c	102	540	**3a**	4860[e]	–
1d	118	600	**3b**	4690[e]	–
1e	167	880	**3c**	4790[e]	–
2a	−42[d]	1760	**3d**	4910[e]	–
2b	31	560	**3e**	4910[e]	–
2c	82	680			

[a] Excitation wavelength, 255 nm; Monitor wavelength, 400 nm for **1a**–**e**, 420 nm for **2a**–**e**, and 404 nm for **3a**–**e**. [b] Fast component of emission lifetimes. [c] Slow component of emission lifetimes. [d] Minus indicates the rise time. [e] The decays of **3a**–**e** are fitted to a single exponential equation.

The emission quantum yields of organosilicon copolymers are summarized in Table 3 and are relatively large. There are two distinctive features in Table 3. The first is the excitation wavelength dependence of the emission quantum yield, which shows the larger value at longer wavelength excitation. The second is the influence of the silylene chain length. The copolymers **1a**, **2a**, and **3a** with dimethylsilylene chain length $m = 1$ have higher emission quantum yields compared with **1b**, **2b**, and **3b** ($m = 2$), respectively. The higher quantum yields of organosilicon copolymers with $m = 1$ correspond to the longer lifetimes τ_2 in comparison with those with $m = 2$. The decrease of the emission quantum yield may be due to the formation of a intramolecular CT excited state. When the emission quantum yields of organosilicon copolymers which show the intramolecular CT emission are compared, those with the longer dimethyl silylene chain exhibit the higher emission quantum yield.

Discussion

The emission spectra of organosilicon copolymers are influenced by the dimethylsilylene chain length and the type of the aromatic unit. There are three remarkable changes in the emission spectra attributable to the silylene chain length and the aromatic unit. First is the discontinuous change between copolymers with silylene chain length $m = 1$ and those with $m \geq 2$ for silylene–phenylene (**1a**–**e**) and silylene–diphenylene (**2a**–**e**) copolymers The former shows vibronically structured emission spectra assigned to the π,π^* LE state, while the latter shows broad, structureless emission spectra ascribed to the intramolecular CT excited state. The second is the shift of the emission maximum to longer wavelength with an increase of the silylene chain length. The third is the different behavior of silylene–anthranylene copolymers **3a**–**e** versus other copolymers, where the vibronic structure is observed even for the emission of **3e** ($m = 6$).

The silylene chain length dependence of the CT emission has been rationalized by considering the first

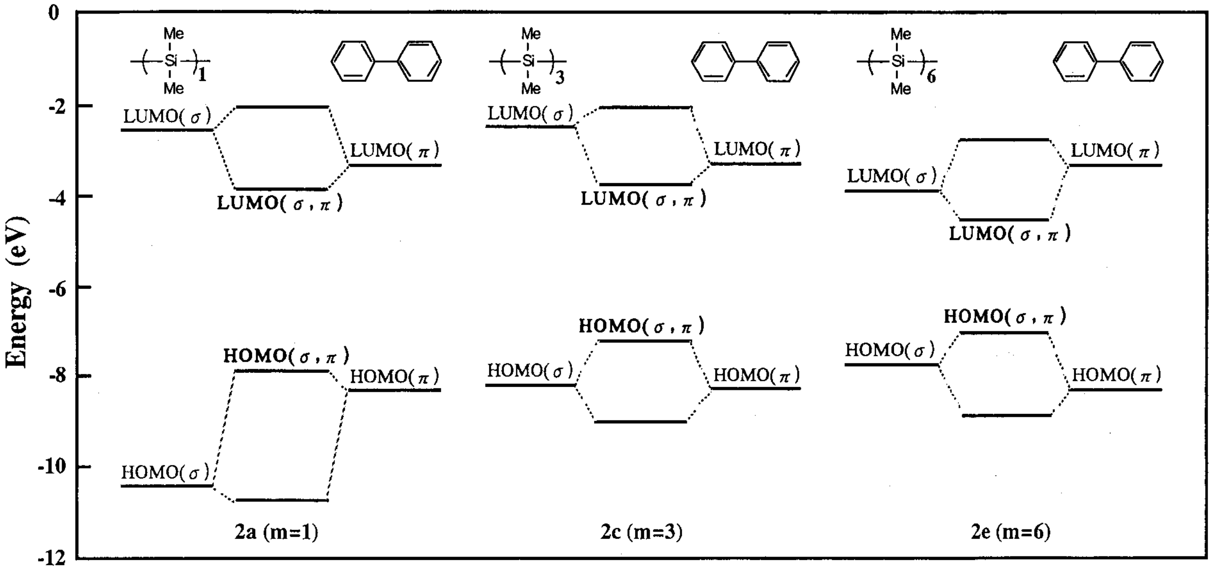

Figure 8. Schematic energy diagram for the HOMO and LUMO levels of permethylated oligosilanes and diphenyl.

Table 3. Emission Quantum Yields at Various Excitation Wavelengths (nm) of the σ–π-Conjugated Organosilicon Copolymers in THF at Room Temperature

	quantum yields											
sample	280	290	300	310	320	330	340	350	360	370	380	390
1a	0.061	0.194										
1b	0.027	0.103	0.162									
1c	0.047	0.151	0.309									
1d	0.091	0.262	0.406									
1e	0.141	0.337	0.460	0.524								
2a	0.315	0.551	0.874									
2b	0.023	0.041	0.073	0.128								
2c	0.042	0.081	0.120	0.159								
2d	0.050	0.088	0.127	0.173								
2e	0.062	0.098	0.137	0.185	0.258							
3a	0.067	0.107	0.141	0.162	0.197	0.226	0.223	0.259	0.284	0.306	0.470	0.662
3b	0.064	0.106	0.131	0.157	0.195	0.224	0.197	0.256	0.266	0.288	0.422	0.660
3c	0.065	0.115	0.137	0.170	0.209	0.240	0.240	0.267	0.296	0.336	0.461	0.725
3d	0.066	0.121	0.147	0.183	0.230	0.259	0.249	0.292	0.308	0.403	0.473	0.769
3e	0.076	0.123	0.168	0.191	0.247	0.263	0.267	0.303	0.340	0.422	0.500	0.840

ionization potentials of the individual σ- and π-units.[7c,10] In the explanation, the formation of the intramolecular CT excited state resulting from the electron transfer from the σ Si–Si unit to the vacant level of the photoexcited arene is assumed.[7c,10] The extent of the charge transfer from the Si–Si bond to the photoexcited arene was estimated by considering first ionization potentials.

Here we propose another explanation for the influence of the dimethylsilylene chain length on the emission spectra. We ask the question, is it possible to describe the unique excited state properties of silyl-substituted aromatic compounds by considering molecular orbitals (MO)? In the MO calculation, the first ionization potential is estimated from the negative of the energy level of the highest occupied molecular orbital (HOMO). On the basis of the first ionization potentials of permethylated oligosilanes and arenes,[7,10,17] the HOMO and the lowest unoccupied molecular orbital (LUMO) energy levels are depicted for individual σ- and π-units of silylene–diphenylene copolymers in Figure 8, where the HOMO–LUMO energy gaps were estimated from the absorption maxima of permethylated oligosilanes and diphenyl. Because the absorption maximum of tetramethylsilane ($SiMe_4$) occurs below 180 nm, the HOMO–LUMO energy gap is larger than that illustrated in Figure 8. The absorption maxima of permethyltrisilane ($Me(SiMe_2)_3Me$) and permethylhexasilane ($Me(SiMe_2)_6Me$) are 215 and 260 nm, respectively. In Figure 8, the HOMO and LUMO of the σ-unit are denoted as HOMO(σ) and LUMO(σ), respectively, while HOMO(π) and LUMO(π) denote those for the π-unit. The interaction between σ- and π-energy levels and the formation of new hybrid energy levels, HOMO(σ,π) and LUMO(σ,π), should be considered here. The MO character of the HOMO(σ,π) and LUMO(σ,π) can be estimated by the energy levels of the individual σ- and π-units. As indicated in Figure 8, the π-character of the HOMO(σ,π) and LUMO(σ,π) are expected for **2a** (*m* = 1) because the HOMO(π) is much higher in energy than the HOMO(σ) and the LUMO(π) is lower than the LUMO(σ) (case I). On the basis of the similar arguments, the increased σ-character of the HOMO(σ,π) and π-character of the LUMO(σ,π) are expected for **2c** (*m* = 3) because the HOMO(σ) is higher than the HOMO(π) and the LUMO(π) is lower than the LUMO(σ) (case II). When the silylene chain length is longer (e.g., *m* = 6), the HOMO(σ) is higher than the HOMO(π) and the LUMO(σ) is lower than the LUMO(π) (case III). The σ-character of the HOMO(σ,π) and LUMO(σ,π) are expected for **2e** (*m* =6). The decrease of the HOMO–LUMO gap is expected for silylene–diphenylene copolymers with increasing silylene chain length, as illustrated in Figure 8. This must be the reason for the shift of the emission maximum to longer wavelength with an increase of the silylene chain length.

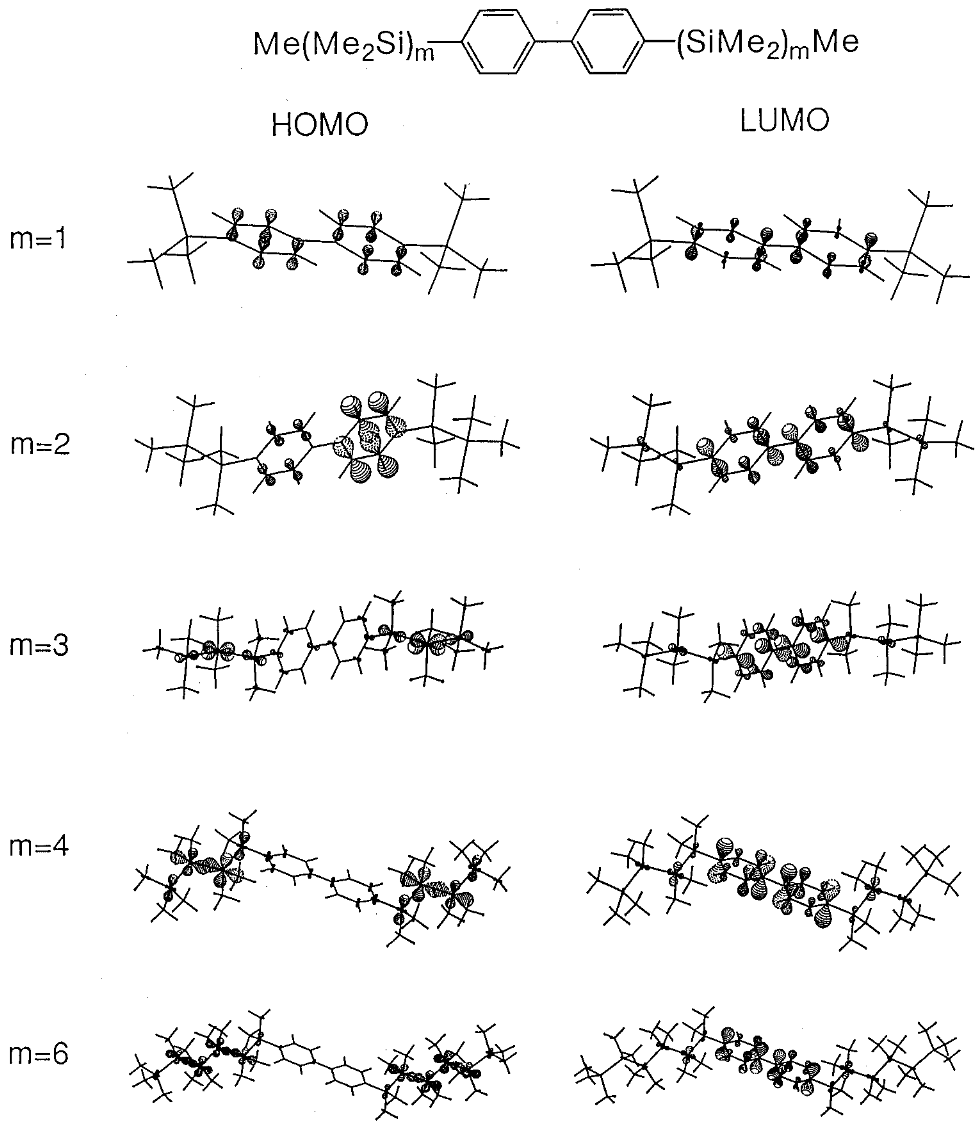

Figure 9. The HOMO and LUMO for silylene–diphenylene oligomer models calculated by MNDO calculations.

These qualitative expectations can be checked by MO calculation for the model compounds $Me(SiMe_2)_m$-$(C_6H_4)_2(SiMe_2)_mMe$. While an *ab initio* calculation is an exact method to estimate the MOs, it is not practical for the large molecules discussed here. Therefore, the HOMOs and LUMOs for the model compounds ($m = 1$, 2, 3, 4, and 6) were calculated using the semiempirical MNDO method and are illustrated in Figure 9. The HOMO and LUMO of the model compound ($m = 1$) exhibit primarily the π-character of the aromatic unit. The σ-character of the HOMO ($m \geq 3$) is demonstrated in Figure 9. These are in agreement with the expectations based on the perturbed energy levels of the individual σ- and π-units as shown in Figure 8. The HOMOs of the model compounds with the silylene chain length $m \geq 3$ each suggest significant σ-interaction, which is consistent with the predictions of the silylene chain-length dependence based on the first ionization potentials of the individual σ- and π-units. Similar results were obtained using MNDO calculations for the model compounds of silylene–phenylene copolymers.[5d] Although the LUMOs of the model compounds ($m \geq 2$) show mainly π-character, the contribution of the σ-character of the Si–Si unit is clear in contrast to the monosilane-substituted model compound ($m = 1$). It is evident that the vibronically structured emission is attributed to the π-character of the aromatic unit and the structureless, broad emission is ascribed to the σ-character of the Si–Si bond in the excited states.

Judging from the molecular orbitals in Figure 9, the selective excitation of the π-unit for **2c**–**e** is difficult because of the extension of conjugation of the σ-Si and π-electrons over the dimethylsilylenes and π-units. With increasing silylene chain length, the photoexcitation of the σ-electron becomes more dominant. The excitation wavelength-dependence of the emission spectra was investigated for **2e** ($m = 6$) in the region of the excitation wavelength from 250 to 300 nm. An influence of the excitation wavelength on the spectral shape of the emission was not observed.

The molecular orbitals in Figure 9 are calculated for the ground state using the closed-shell restricted Hartree–Fock (RHF) method. The MO calculations for model compounds of silylene–diphenylene copolymers $Me(SiMe_2)_2(C_6H_4)_2(SiMe_2)_2Me$ ($m = 2$) were carried out by the ZINDO method using the closed-shell RHF and the open-shell RHF. The former gives the information on the ground state while the latter describes the first singlet excited state. In the MO calculations, two conformations were adopted: One is the conformation with the C–C(diphenyl ring)–Si–Si torsion angle of 90° (perpendicular structure). Another is the C–C(diphenyl ring)–Si–Si torsion angle of 0°, which corresponds to an orthogonal orientation between the Si−Si orbital and biphenyl π-orbital (planar structure). The HOMOs by the closed-shell RHF calculation suggest that the conformation with the torsion angle of 90° is more suitable for the $\sigma-\pi$-conjugation between the σ- and π-units in the ground state. The MO for the first singlet excited state of the model compound also exhibit σ-character in both conformations. The model compound in the ground and the excited states did not show significant difference of the electronic density corresponding to the intramolecular CT excited state. The introduction of an effect of solvent polarity into the MO calculation may be necessary to discuss the solvent effect on the emission spectra and the intramolecular charge transfer excited state.

Vibronic structured LE emission spectra of silylene−anthranylene copolymers were observed even for the emission of **3e** ($m = 6$). The ionization potential of anthracene (7.37 eV) is lower than those of benzene (9.25 eV) and biphenyl (8.27 eV). The HOMO−LUMO gap of anthracene is also lower than those of benzene and biphenyl judging from the absorption spectra. The HOMO level of the anthranyl group is higher than those of permethylated organosilanes, and the HOMO−LUMO gap is lower than those of permethylated organosilanes. Therefore, the π-character of the HOMO and LUMO are expected for silylene−anthranylene copolymers. Declercq et al. have reported that the transition in pyrene−substituted dimethylsilylene oligomers ($m <$ 6) is predominately π,π^*. When $m = 6$, however, a polar charge transfer state was observed in the emission spectrum.[18] The silylene−anthranylene copolymers **3d** and **3e** (m = 4 and 6) also show a CT emission overlapped with a vibronically structured π,π^* LE emission.

Nonexponential emission decays have been reported for π- and σ-conjugated polymers.[13−16] The energy migration along the conjugated chain from the shorter to longer conjugated sequences causes the non-single-exponential emission decays, while the random conformation of the polymer chain in solution causes the distribution of energy levels. The lower energy levels act as energy trapping sites. In a previous work, we investigated the energy migration of silylene−diphenylene copolymers on the basis of the time-resolved emission anisotropic studies.[19] The extremely fast depolarization within 100 ps suggests the efficient energy migration along the $\sigma-\pi$-conjugated polymer chain. The $\sigma-\pi$-conjugation is also demonstrated using the MO calculation of model compounds, as shown in Figure 9. The energy migration along the $\sigma-\pi$-conjugated chain having inhomogeneous electronic levels causes the nonexponential emission decay. As an energy trapping site, the intramolecular CT excited state should be considered. The emission lifetime will depend on the density of the energy trapping sites. It has been reported that there is a suitable conformation to form the intramolecular CT excited state.[6,7c] The random conformation of the polymer in solution and the restriction of the conformational change of the macromolecule cause the distribution of the energy levels for the intramolecular CT excited states.

The excited states migrate toward the most stable CT excited state along the polymer chain accompanying the nonradiative deactivation. The degree of the nonradiative deactivation is more significant when the energy migration pathway from the higher to the lower energy levels is longer. The shortest pathway is the direct excitation at the absorption band tail. This is the reason for the wavelength dependence of the emission quantum yield in Table 3. Such features are characteristics of semiconducting materials having an amorphous band structure.[16]

Conclusions

The emission spectra of silylene−phenylene, silylene−diphenylene, and silylene−anthranylene copolymers are influenced by the dimethylsilylene chain length and the type of aromatic unit. The semiempirical MO calculations on the ground and excited states suggest that the vibronically structured emission is attributed to the π-character of the aromatic unit, and the structureless, broad emission is ascribed to the σ-character of the Si−Si bond in the excited states. The emission decay and the quantum yield of organosilicon copolymers suggest $\sigma-\pi$-conjugation along the polymer chain.

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