

π - π and σ - π Interactions in α,ω -Dinaphthyl and -Dianthryl Oligosilanes in Solution

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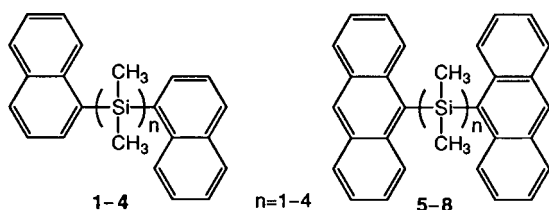
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The π - π and σ - π interactions in α,ω -di-1-naphthyl and -di-9-anthryl oligosilanes [Np-(SiMe₂)_n-Np (**1-4**), Ant-(SiMe₂)_n-Ant (**5-8**), n = 1-4] were investigated in solution. In nonpolar solvents such as cyclohexane, a strong excimer fluorescence is observed, which indicates a strong π - π interaction. In a polar solvent (CH₃CN), a charge-transfer (CT) emission is observed for **3** and **4** due to the σ - π interaction.

α,ω -Diaryl oligosilanes have attracted much attention because they have interesting photochemical characteristics compared to the carbon chain analogues.¹⁻⁴ The di-9-anthryldimethylsilane (**5**) is reported to produce unique [4+2] cycloadducts,¹ which are very similar to the photoadduct produced by the di-9-anthrylethylenes.⁵ The α,ω -di-3-pyrenyl oligosilanes are also reported to give excimer emission by photoexcitation.³ In that report, two pyrenyl groups are proposed to interact even in the ground state. In this report, we examined the photophysical nature of the α,ω -di-1-naphthyl and -di-9-anthryl oligosilanes [Np-(SiMe₂)_n-Np (**1-4**), Ant-(SiMe₂)_n-Ant (**5-8**), n = 1-4], in which there are π - π interactions between the two aryl groups and σ - π interactions between the aryl group and silicon chain unit. A compound with a carbon chain of length n = 3 has the highest ability to make an excimer (known as the Hirayama rule), however, for a carbon chain linked two 9-anthracenes, it does not give efficient excimer emission since the excimer is the key intermediate to give the [4+4] cycloadduct.⁶

Compounds **1-8** were prepared from 1-naphthyllithium and 9-anthryllithium (obtained from aryl bromide and 1.6 M *n*-butyllithium in hexane) and α,ω -dichloropermethyloligosilanes (Cl-(SiMe₂)_n-Cl). The 1,2-dichlorotetramethyldisilane (n = 2) was purchased from Tokyo Kasei, while the other dichlorotri- or tetrasilanes (n = 3, 4) were synthesized from dodecamethylcyclohexasilane and phosphorus pentachloride as previously reported.⁷

The absorption spectra of **1-4** and **5-8** are shifted about 15 nm to longer wavelength than that of naphthalene or anthracene. They are very similar to each other, which indicate neither a strong interaction between the two aromatic chromophores nor a dependence of the σ conjugation on the chain length. However, from the ¹H NMR analysis, compounds with n = 2-3 show weak interaction of overlapping two aromatic rings, which was indicated by the higher field shifts of the aromatic protons.⁸ Figures 1



and 2 show the fluorescence spectra of **1-4** and **5-8**, respectively, in cyclohexane and in acetonitrile. The compounds **1** and **5** gave only monomer-like fluorescence. However, a chain sili-

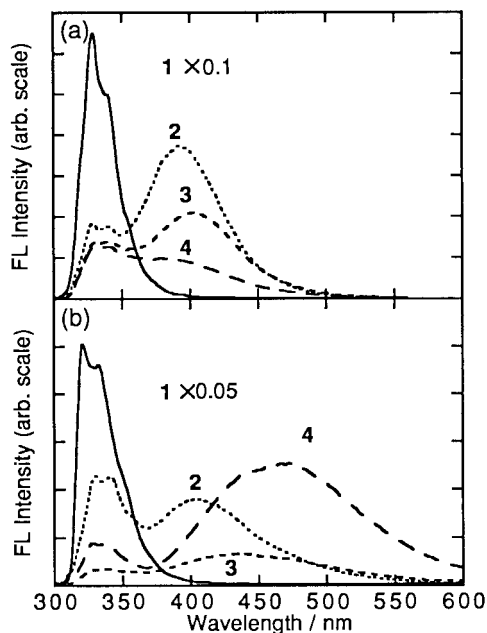


Figure 1. Fluorescence spectra of **1-4** in cyclohexane (a) and acetonitrile (b).

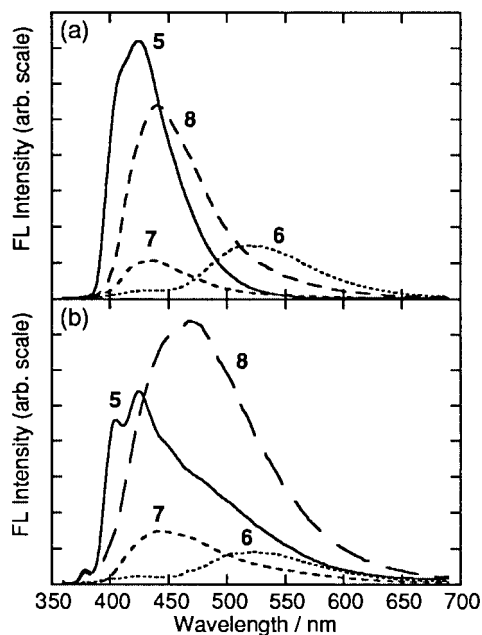


Figure 2. Fluorescence spectra of **5-8** in cyclohexane (a) and acetonitrile (b).

Table 1. Characteristics of fluorescence for 1-naphthyl and 9-anthryl oligosilanes

Compounds	in cyclohexane			in acetonitrile		
	$\lambda_{\max}^{\text{LE}} / \text{nm}^{\text{a}}$	$\lambda_{\max}^{\text{long}} / \text{nm}^{\text{b}}$	$\tau_s / \text{ns}^{\text{c}}$	$\lambda_{\max}^{\text{LE}} / \text{nm}^{\text{a}}$	$\lambda_{\max}^{\text{long}} / \text{nm}^{\text{b}}$	$\tau_s / \text{ns}^{\text{c}}$
1-(Me ₅ Si ₂)NP	(329 ^d)	—	(8.0 ^d)	(336 ^d)	(446 ^d)	no report
1	329	—	52.7	329	—	49.6
2	330	392	6.1 + 30.1	329	402	0.3 + 9.0
3	331	402	0.5 + 9.7 + 22.0	329	436	0.5 + 3.6 + 23.1
4	331	379	0.7 + 14.7	328	474	1.8 + 6.9
9-(Me ₅ Si ₂)ANT	(435 ^d)	—	(12.8 ^d)	no report	no report	no report
5	425	—	6.7(6.5 ^e)	406 + 425	—	6.9 + 11.1(9.5 ^e)
6	425(sh)	520	5.5 + 52.5	425	524	4.1 + 30.7
7	436	—	1.3 + 10.5	444	—	0.8 + 8.0
8	439	—	4.6+23.8	469	—	2.1 + 10.8

^a Emission from local excited state. ^b Emission from excimer or CT state. ^c Emission lifetime. ^d ref 12. ^e ref 1b.

con number more than 2 showed excimer emission. For **2–4**, the intensity of the excimer emission decreases with increasing chain length in cyclohexane. For **5–8**, the fluorescence behavior is somewhat different from that of **1–4**. Excimer emission with large Stokes shift was observed for **6** (Figure 2a). This shift ($\lambda_{\max} = 520 \text{ nm}$) is much larger than those observed for **7** and **8**, indicating a better stacking conformation of **6** in its excimer. A steric hindrance between the anthryl groups and dimethylsilane chain unit may interrupt the conformation to make better stacking for **7** and **8**. The λ_{\max} 's at 620, 570, and 460 nm of excimer emission were reported for anthracenophanes with 1, 2 and 3 phenyl rings in anthracene stacked face-to-face, respectively.⁹ In addition, there is the Hirayama-rule that an excimer is most stable with a three carbon chain unit, and especially, 1,3-di-9-anthrylpropane undergoes efficient [4+4] cycloaddition showing no excimer emission.¹⁰ In our case, **6** has unique characteristics such that the Si–Si bond length is longer than that of C–C bond, and the two anthracene rings make sandwich stacking which has a wide 9–9' position distance and also a more distant 10–10' length than that.¹¹ Therefore, it has a strong excimer emission without undergoing efficient photocyclization. This may be attributed to 1) an appropriate distance¹¹ between the two anthracene rings to make the excimer caused by the long Si–Si bond length, and 2) the gauche conformation of the central Si–Si bond restricted by the steric hindrance of the methyl substitutions on the Si atoms.

The λ_{\max} 's of the emission of **3** and **4** shifted to longer wavelength in acetonitrile than that in cyclohexane. These shifts were quite different from those observed for the excimer emission of **2**, **6**, and so on. There is an argument with the CT mechanism of aryl disilanes.^{2,12,13} In our experiment, the CT emission band was observed in the cases of naphthylsilanes with $n \geq 3$, but not in the case of anthrylsilanes for $1 \leq n \leq 4$ in polar solvent. These results are consistent with mechanism proposed by the $\sigma \rightarrow \pi^*$ OICT mechanism,¹³ where CT occurred from silane to aryl unit. The electron-donating ability of the silane unit increases with increasing in the chain length and electron-accepting ability of anthryl group is lower than that of naphthyl group. Another mechanism $2p\pi^* \rightarrow 3d\pi$ mechanism¹² seems to be not contradictory to the experimental result at a glance. The π^* -state energy level of naphthyl moiety is higher than that of anthryl moiety and energy of $3d\pi$ -state decreases

with increasing in silane chain length, however, the energy of $3d\pi$ -state of silane is expected to be higher than $2p\pi^*$ -state of naphthalene. These consideration proposes the mechanism of a CT from the silane unit to the aryl ring may occur, and it seems to obey the $\sigma \rightarrow \pi^*$ OICT mechanism¹³ in this case.

The fluorescence lifetime measurement by a single-photon counting method indicated that the compounds maintained the sandwich-like conformation even in the ground state because no rise-up components were observed just after the excitation. This result is consistent with the result of the ground state conformation obtained by the ¹H NMR mentioned above.

In conclusion, 1) for the **1–8** cases, the strongest excimer fluorescence was observed in the case of $n = 2$, and 2) CT emission indicated charge transfer from the naphthyl ring to the silane unit suggesting a $\sigma-\pi$ interaction for **3** and **4**.

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- 8) For example, Hs at the 2, 3, 4, 5, 6, 7, and 8 positions on a naphthalene ring were observed at 7.80, 7.20, 7.80, 7.57, 7.39, 7.39, 7.80 ppm for **2** and 7.84, 7.46, 7.84, 7.63, 7.46, 7.46, 7.98 ppm for 1-(pentamethyldisilyl)naphthalene, respectively.
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