

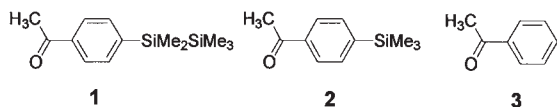
## Metal-Ion Induced Intramolecular Charge-Transfer Fluorescence of *p*-Pentamethyldisilanylacetophenone

Mitsuo Kira,\* Ramachandram Badugu, Tingxi Li, Wataru Setaka, Kenkichi Sakamoto, and Hisako Hashimoto  
 Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

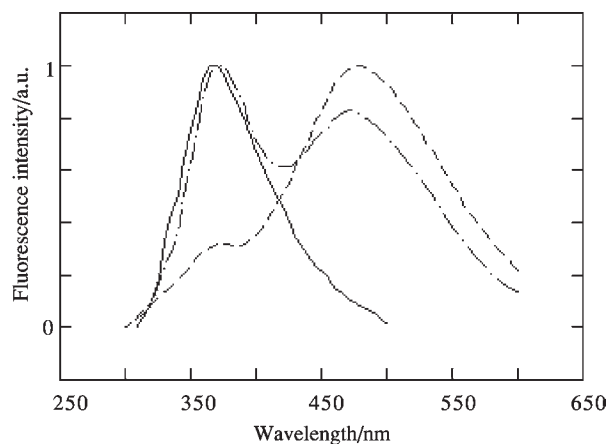
(Received November 13, 2001; CL-011143)

In the presence of  $\text{Lu}^{3+}$  and  $\text{Sc}^{3+}$  ions, *p*-pentamethyldisilanylacetophenone shows dual fluorescence, characteristic of a phenylpentamethyldisilane with an electron-accepting substituent on benzene ring, where the wavelengths of the LE (locally excited) and ICT (intramolecular charge transfer) band maxima and their relative intensity are dependent on the metal ions.

Since the discovery of the dual fluorescence in (*p*-dimethylamino)benzointrile (DMABN) in polar solvents, the intramolecular charge transfer (ICT) fluorescence is a well-established phenomenon.<sup>1-3</sup> We have recently investigated<sup>4-6</sup> in detail the dual fluorescence of arylpentamethyldisilanes discovered by Shizuka et al.<sup>7</sup> and found that the broad and structureless band in the longer wavelength region of an arylpentamethyldisilane is assigned to be the emission from the ICT excited state involving the SiSi  $\sigma$  system as an electron donor and the aromatic  $\pi$  system as an electron acceptor, while the regular shorter wavelength band as the emission from the aromatic locally excited (LE)  $\pi$ - $\pi^*$  state. The wavelength and intensity of the ICT fluorescence band increase by introducing an electron-withdrawing substituent such as trifluoromethyl<sup>5</sup> and cyano groups<sup>6</sup> on the benzene ring. In a recent study<sup>6</sup> we have found that jet-cooled (*p*-cyanophenyl)pentamethyldisilane shows the ICT emission from the isolated molecules, without any solvation. Since acetophenone is a good  $\pi$ -electron acceptor, we can expect the intense ICT fluorescence of *p*-pentamethyldisilanylacetophenone (**1**) as well. However, similarly to *p*-trimethylsilylacetophenone (**2**) and acetophenone (**3**), **1** is non-fluorescent in 3-methylpentane, THF, and acetonitrile, because of the efficient intersystem crossing from the lowest  $^1n$ - $\pi^*$  state to the  $^3\pi$ - $\pi^*$  state in these solvents. We wish herein to report that the fine-tuning of the relative energy levels of the  $n$ - $\pi^*$  and  $\pi$ - $\pi^*$  states in **1** is achieved in the presence of  $\text{Lu}^{3+}$  and  $\text{Sc}^{3+}$  ions to provide the dual fluorescence as expected for a phenylpentamethyldisilane with an electron-accepting substituent on benzene ring. The present results not only provide a proof for the ICT mechanism in arylidisilanes but also a new and elegant logic for controlling the unique electronic excited states of arylidisilanes.<sup>8</sup>



Compound **1**<sup>9</sup> shows dual fluorescence in 2-methyltetrahydrofuran (MeTHF), a 1 : 1 mixture of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{CN}$  in the presence of  $\text{Lu}(\text{OTf})_3$  as shown in Figure 1. The longer wavelength broad and structureless fluorescence band of  $\text{Lu}^{3+}$  complex of **1** shifted to red with increasing the solvent polarity. On the other hand, the shorter wavelength fluorescence band at around 375 nm showed no significant dependence towards



**Figure 1.** Fluorescence spectra of *p*-pentamethyldisilanylacetophenone (**1**) in various solvents in the presence of  $\text{Lu}(\text{OTf})_3$ : (—) in MeTHF,  $[\mathbf{1}] = 2.37 \times 10^{-3}$  M,  $[\text{Lu}(\text{OTf})_3] = 3.92 \times 10^{-3}$  M; (-·-) in  $\text{MeCN} : \text{CH}_2\text{Cl}_2$  (1 : 1),  $[\mathbf{1}] = 2.16 \times 10^{-3}$  M,  $[\text{Lu}(\text{OTf})_3] = 3.47 \times 10^{-3}$  M; (---) in  $\text{CH}_3\text{CN}$ ,  $[\mathbf{1}] = 1.48 \times 10^{-3}$  M,  $[\text{Lu}(\text{OTf})_3] = 4.94 \times 10^{-3}$  M.

the solvent polarity. The relative intensity of the former band to the latter increased with increasing solvent polarity; relative intensities of CT to LE fluorescence ( $I_{\text{CT}}/I_{\text{LE}}$ ) are 0.2, 0.8, and 4.0 in MeTHF,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1/1), and  $\text{CH}_3\text{CN}$ , respectively, as shown in Table 1. The longer wavelength emission band maximum of **1** (480 nm in  $\text{CH}_3\text{CN}$ ) is compared with the ICT band of *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{Si}_2\text{Me}_5$  at 412 nm in  $\text{CH}_2\text{Cl}_2$  and that of *p*- $\text{CNC}_6\text{H}_4\text{Si}_2\text{Me}_5$  at 437 nm in  $\text{CH}_2\text{Cl}_2$ .<sup>5,6</sup> Because  $\text{Lu}(\text{OTf})_3$  is insoluble in  $\text{CH}_2\text{Cl}_2$ , we cannot compare the emission energies in the same solvent among these substituted phenylpentamethyldi-

**Table 1.** Fluorescence band maxima of *p*- $\text{X-C}_6\text{H}_4\text{COCH}_3$  in various solvents in the presence of  $\text{Lu}^{3+}$  and  $\text{Sc}^{3+}$  Ions<sup>a</sup>

	Solvent	$\text{Lu}^{3+}$			$\text{Sc}^{3+}$		
		LE	CT	R.I. <sup>c</sup>	LE	CT	R.I. <sup>c</sup>
<b>1</b>	MeTHF	370	450	0.2	387	—	—
	$\text{CH}_2\text{Cl}_2/\text{AN}^b$	372	470	0.8	389	484	0.2
<b>2</b>	AN	375	480	4.0	391	495	0.8
	MeTHF	350	—	—	389	—	—
<b>3</b>	AN	389	—	—	427	—	—
	MeTHF	382	—	—	388	—	—
	AN	410	—	—	420	—	—

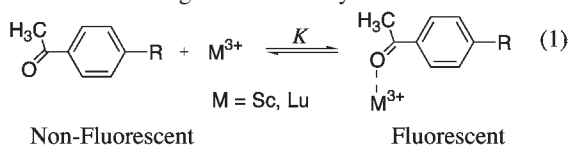
<sup>a</sup>MeTHF, 2-methyltetrahydrofuran; AN, acetonitrile. <sup>b</sup>The v/v ratio of  $\text{CH}_2\text{Cl}_2/\text{AN} = 1/1$ . <sup>c</sup>Relative intensity of CT to LE bands ( $I_{\text{CT}}/I_{\text{LE}}$ ).

silanes, but the longer wavelength emission of **1**-Lu<sup>3+</sup> complex should be assigned reasonably to the ICT band if the solvent shift from CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>3</sub>CN is taken into account; ICT band maximum of phenylpentamethylsilane was observed at 375 nm in CH<sub>2</sub>Cl<sub>2</sub> and 385 nm in CH<sub>3</sub>CN.

As shown in Table 1, the fluorescence spectral behavior of **1** in the presence of Sc(OTf)<sub>3</sub> is quite parallel to that in the presence of Lu(OTf)<sub>3</sub>, while the relative intensity (I<sub>CT</sub>/I<sub>LE</sub>) is less than unity even in polar CH<sub>3</sub>CN. The LE and ICT bands for **1**-Sc<sup>3+</sup> complex are red-shifted from those for **1**-Lu<sup>3+</sup> complex probably because of the stronger Lewis acidity of Sc<sup>3+</sup> than that of Lu<sup>3+</sup>.<sup>10</sup>

Since compound **1** is non-fluorescent in the absence of metal ions, the observed dual fluorescence of **1** in the presence of metal ions would be ascribed to the destabilization of the <sup>1</sup>n-π\* excited state as the result of the metal-ion binding to the carbonyl oxygen to yield a π-π\* state as the lowest singlet excited state. While the effects of the metal ions on the emission behavior of aromatic carbonyl compounds have been well established,<sup>11</sup> the present results support the existence of the channel from the π-π\* state to the ICT.<sup>12</sup>

Complexation of **1** with Lu<sup>3+</sup> and Sc<sup>3+</sup> in the ground state was confirmed by UV-vis spectroscopy. Compound **1** shows a structureless absorption band at around 269 nm (ε = 12000) in CH<sub>3</sub>CN, which appears at significantly longer wavelength than those of **2** (λ<sub>max</sub> 248 nm) and **3** (λ<sub>max</sub> 240 nm). When metal ions (5 × 10<sup>-3</sup>–2 × 10<sup>-2</sup> M) were added to **1** (ca. 1 × 10<sup>-4</sup> M) in acetonitrile, a new absorption band appeared in the differential absorption spectra at 305 and 315 nm for Lu<sup>3+</sup> and Sc<sup>3+</sup> ions, respectively, being indicative of the formation of the metal ion complexes of **1** (eq 1). The formation constants (K) were determined using the Benesi-Hildebrand equation<sup>13</sup> to be 6.1 and 13.9 for Lu<sup>3+</sup> and Sc<sup>3+</sup> ions, respectively. The red shift of the absorption maximum and the larger K value for Sc<sup>3+</sup> are in good accord with the stronger Lewis acidity of Sc<sup>3+</sup>.<sup>10</sup>



As expected, compounds **2** and **3** were also fluorescent in the presence of the metal ions. Interestingly, the fluorescence band maxima at around 400 nm for **2**-M<sup>3+</sup> and **3**-M<sup>3+</sup> (M = Lu and Sc) significantly depended on the solvent polarity. The solvent effects, broad and structureless features of these bands suggest that the emitting states of the complexes have significant charge-transfer nature. According to the configuration interaction theory,<sup>14,15</sup> the <sup>1</sup>B<sub>1u</sub> configuration of acetophenone is expected to mix strongly with the ICT configuration from benzene π to acetyl π, and hence, has polar nature. The emitting states of **2**-M<sup>3+</sup> and **3**-M<sup>3+</sup> may be the polar excited states instead of the <sup>1</sup>B<sub>2u</sub> states for normal weakly perturbed benzenes.

One of the authors (B.R.) thanks Japan Society for the Promotion of Science (JSPS) for the Postdoctoral Fellowship for Foreign Researchers.

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- While it remains open at present whether the adiabatic formation of the ICT state is achieved by the rotation around the C(Ar)-Si bond [OICT (orthogonal intramolecular charge-transfer) mechanism]<sup>4,5</sup> or other mechanisms. The OICT mechanism is a conceptually similar term to the TICT (twisted intramolecular charge transfer) mechanism<sup>2,3</sup> but is used to stress the orbital orthogonality rather than the twisting of the molecular frame at ICT states.
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