Excited-state Property of 1-(4-Cyanophenyl)-2-(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane

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Diphenyldisilane derivative having electron-donating and -withdrawing groups in each phenyl group, 1-(4-cyanophenyl)-2-(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane was synthesized, and its excited-state property was studied. Intramolecular charge-transfer character through the disilanyl group was confirmed; the dipole moment of the excited-state has been estimated to be 28 debye.

It is well known that pentamethylphenyldisilane and its derivatives exhibit dual fluorescence: the fluorescence from the locally excited state in phenyl ring (LE fluorescence) and the intramolecular charge-transfer excited state (ICT fluorescence).[1–6] Its charge-transfer nature was intensively discussed by Shizuka et al.,[1–3] and Sakurai et al.,[4–6] and in the case of (4-cyanophenylethynyl)pentamethyldisilane it was concluded that the charge was transferred from the disilanyl group to 4-cyanophenyl group.[7] Dipole moments in the excited state of pentamethylphenyldisilane derivatives were estimated to be ca. 5–12 debye.[3]

Diphenyldisilane derivatives having electron-donating or -withdrawing groups in each phenyl group have been studied as one of functional materials with the nonlinear optical property because of their intramolecular charge-transfer (ICT) character of the excited state. Mignani et al. synthesized this kind of diphenyldisilane derivatives to study their nonlinear optical property and examined electronic absorption spectra and frequency-independent second-order polarizability.[8] Hutten and Hadziioannou also studied electronic absorption spectra and hyperpolarizability of diphenyldisilanes having the dimethylamino donor and perfluoroalkylsulfonyl acceptor in comparison with the results obtained by MO calculations.[9] However, they did not study the excited-state properties such as fluorescence property and excited-state dipole moment.

In this communication, we report the excited-state property of 1-(4-cyanophenyl)-2-(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane (abbreviated to be CMDSi), which has the electron-donating methoxy and -withdrawing cyano groups in each phenyl group as shown in Chart 1.

CMDSi was synthesized from 4-chloroanisole and 4-bromobenzonitrile and was identified by the spectroscopic methods and elementary analysis.[10]

Figure 1 shows the absorption (full line), fluorescence (broken line), and excitation spectra (dotted line) of CMDSi in acetonitrile (a), *n*-butyronitrile (b), chloroform (c), and cyclohexane (d), respectively. There are two absorption maxima in acetonitrile at ca. 270 and 240 nm with molar absorption coefficient of 10900 and 23800 $M^{-1}\,cm^{-1}$, respectively. The absorption spectrum observed in cyclohexane is very similar to that in acetonitrile, indicating that there is no significant solvent effect on the absorption process. This absorption spectrum can not be reproduced by the sum of the spectra of anisole, benzonitrile, and hexamethyldisilane, suggesting that there is some interaction between the donor and acceptor moieties. The spectrum can be explained by the calculated results shown by the stick spectrum in Figure 1d, which were obtained by TD-DFT approach using B3LYP/6-31G(d,p) for the optimized structure obtained by DFT using B3LYP/6-31G(d,p). The intense first and third bands are assigned to the transition from ψ_{ground} to $\psi_{\text{I}} = 0.695\Phi_{\text{HOMO}\rightarrow\text{LUMO}} + \cdots$ ($\lambda = 305$ nm, oscillator strength $f = 0.22$) and to $\psi_{\text{III}} = 0.641\Phi_{(\text{HOMO}-1)\rightarrow\text{LUMO}} + \cdots$ ($\lambda = 254$ nm, $f = 0.29$), respectively. As can be understood from the pictures of HOMO−1, HOMO, and LUMO shown in Figure 2, these two transitions have the ICT character from the donor 4-methoxyphenyl to acceptor 4-cyanophenyl moiety through the disilanyl group. Upon the excitation of CMDSi at 270 nm, fluorescence spectra were observed with a maximum at around 470 nm (a), 450 nm (b), 435 nm (c), and 410 nm (d), respectively, as shown in Figure 1. The Stokes shift between the first absorption maximum (ν_{abs}) and fluorescence maximum (ν_{fl}) increases with increase of solvent polarity as follows; 12600 cm^{-1} in cyclohexane (d), 14000 cm^{-1} in chloroform (c), 14800 cm^{-1} in *n*-butyronitrile (b), and 15800 cm^{-1} in acetonitrile (a): the latter is remarkably large and comparable with that observed for 4-(*N*,*N*-dimethylamino)benzonitrile (DMAB).[11] This solvent

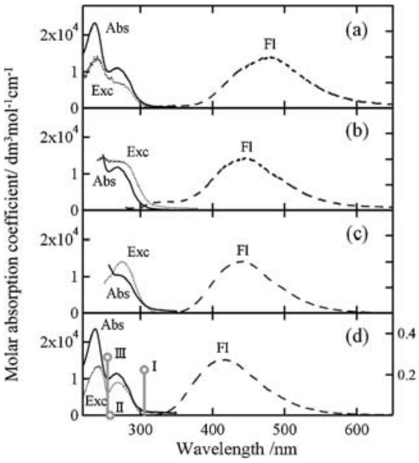

Figure 1. Absorption (full line), fluorescence (broken line), and excitation spectra (dotted line) of CMDSi in acetonitrile (a), *n*-butyronitrile (b), chloroform (c), and cyclohexane (d). Calculated transitions for CMDSi are shown as sticks in (d).

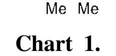

Chart 1.

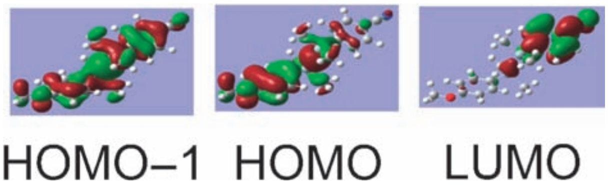

Figure 2. Molecular orbitals of CMDSi mainly related to the first and third transitions.

dependence of the Stokes shift supports that these fluorescence bands are of the ICT character from the 4-methoxyphenyl to 4-cyanophenyl moiety.

The Stokes shift ($\tilde{\nu}_{\mathrm{abs}} - \tilde{\nu}_{\mathrm{fl}}$) is related with the difference in dipole moments between the ground (μ_{g}) and emitting states (μ_{e}) by the Lippert–Mataga equation as follows;[12]

$$hc(\tilde{\nu}_{\mathrm{abs}} - \tilde{\nu}_{\mathrm{fl}}) = 2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2/(4\pi\varepsilon_0 a^3) \times (f_\varepsilon - f_{\mathrm{n}}) + \mathrm{const} \qquad (1)$$

where h, c, ε_0, and a are Planck's constant, velocity of light, permittivity of vacuum, and Onsager radius of the sample molecule, respectively. $f_\varepsilon = (\varepsilon - 1)/(2\varepsilon + 1)$ and $\mathrm{f_n} = (n^2 - 1)/(2n^2 + 1)$, where ε and n are dielectric constant and refractive index of the solvent, respectively. By plotting $hc(\tilde{\nu}_{\mathrm{abs}} - \tilde{\nu}_{\mathrm{fl}})$ against ($f_\varepsilon - f_{\mathrm{n}}$), a rather good linear relationship was obtained as shown in Figure 3. The slope and the intercept (const of eq 1) of this line were estimated to be 1.69×10^{-19} and 2.41×10^{-19} J, respectively. Assuming $\mu_{\mathrm{g}} = 6.4$ debye $= 1.5 \times 10^{-29}$ C m and $a^3 = 5.3 \times 10^{-28}$ m^3, as obtained by MO calculation on CMDSi, μ_{e} was estimated to be 28 debye. This value is greater than that determined for the ICT state of DMAB (23 debye).[11] It is noted that almost no LE emission was observed in the fluorescence spectrum, suggesting that the intramolecular charge-transfer process is very fast in CMDSi.

The fluorescence lifetime (τ_{f}) in cyclohexane was determined to be 3.4 ± 0.3 ns,[13] being a little longer than that of (4-cyanophenyl)pentamethyldisilane in pentane.[5] The lifetime in acetonitrile was determined to be ca. 100 ps. This solvent effect on the fluorescence lifetime has the same tendency as that observed for the "b emission band" observed for DMAB (τ_{f} is 1.84 ns in methylcyclohexane and shorter than 10 ps in acetonitrile).[14] It was also confirmed that CMDSi is much more stable for the 253.7-nm light photolysis in acetonitrile under Ar than the unsubsituted 1,1,2,2-tetramethyl-1,2-diphenyldisilane.

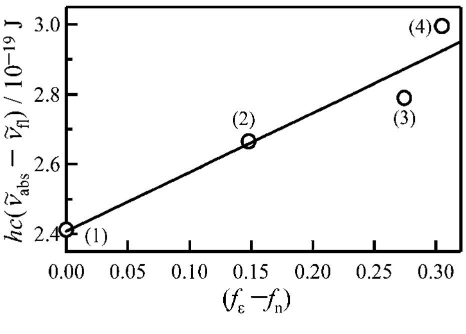

Figure 3. Plot of $hc(\tilde{\nu}_{\mathrm{abs}} - \tilde{\nu}_{\mathrm{fl}})$ versus ($f_\varepsilon - f_{\mathrm{n}}$) based on the Lippert–Mataga equation; cyclohexane (1), chloroform (2), *n*-butyronitrile (3), and acetonitrile (4). The correlation coefficient was 0.966.

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References and Notes

1 H. Shizuka, H. Obuchi, M. Ishikawa, M. Kumada, *J. Chem. Soc., Chem. Commun.* **1981**, 405; H. Shizuka, Y. Sato, M. Ishikawa, M. Kumada, *J. Chem. Soc., Chem. Commun.* **1982**, 439; H. Shizuka, K. Okazaki, M. Tanaka, M. Ishikawa, M. Sumitani, K. Yoshihara, *Chem. Phys. Lett.* **1985**, *113*, 89; H. Hiratsuka, Y. Mori, M. Ishikawa, K. Okazaki, H. Shizuka, *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1665.

2 M. Yamamoto, T. Kudo, M. Ishikawa, S. Tobita, H. Shizuka, *J. Phys. Chem. A* **1999**, *103*, 3144.

3 H. Shizuka, H. Hiratsuka, *Res. Chem. Intermed.* **1992**, *18*, 131.

4 H. Sakurai, H. Sugiyama, M. Kira, *J. Phys. Chem.* **1990**, *94*, 1837; M. Kira, T. Miyazawa, N. Mikami, H. Sakurai, *Organometallics* **1991**, *10*, 3793; H. Sakurai, J. Abe, K. Sakamoto, *J. Photochem. Photobiol., A* **1992**, *65*, 111.

5 M. Kira, T. Miyazawa, H. Sugiyama, M. Yamaguchi, H. Sakurai, *J. Am. Chem. Soc.* **1993**, *115*, 3116.

6 Y. Tajima, H. Ishikawa, T. Miyazawa, M. Kira, N. Mikami, *J. Am. Chem. Soc.* **1997**, *119*, 7400; H. Ishikawa, Y. Shimanuki, M. Sugiyama, Y. Tajima, M. Kira, N. Mikami, *J. Am. Chem. Soc.* **2002**, *124*, 6220.

7 K. A. Horn, R. B. Grossman, J. R. G. Thorne, A. A. Whitenack, *J. Am. Chem. Soc.* **1989**, *111*, 4809.

8 G. Mignani, A. Kramer, G. Puccetti, I. Ledoux, G. Soula, J. Zyss, R. Meyrueix, *Organometallics* **1990**, *9*, 2640; G. Mignani, A. Kramer, G. Puccetti, I. Ledoux, J. Zyss, G. Soula, *Organometallics* **1991**, *10*, 3656; G. Mignani, M. Barzoukas, J. Zyss, G. Soula, F. Balegroune, D. Grandjean, D. Josse, *Organometallics* **1991**, *10*, 3660.

9 P. F. van Hutten, G. Hadziioannou, R. Bursi, D. Feil, *J. Phys. Chem.* **1996**, *100*, 85.

10 The Grignard reagent of 4-chloroanisole was allowed to react at 0 °C with 1,2-dichloro-1,1,2,2-tetramethyldisilane to give 1-chloro-2-(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane. 4-Bromobenzonitrile was treated with *tert*-butyllithium in tetrahydrofuran at −100 °C to produce 4-lithiobenzonitrile, and into this solution 1-chloro-2-methoxyphenyl-1,1,2,2-tetramethyldisilane was added to prepare CMDSi (51% overall yield). Data for CMDSi: ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 6H), 0.32 (s, 6H), 3.79 (s, 3H), 6.85 (d, 2H, $J = 8.5$ Hz), 7.22 (d, 2H, $J = 8.5$ Hz), 7.40 (d, 2H, $J = 8.1$ Hz), 7.53 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (CDCl$_3$) $\delta - 4.3$, −4.0, 55.0, 111.8, 113.6, 119.2, 128.4, 130.8, 134.2, 135.1, 146.8, 160.2; ^{29}Si NMR (CDCl$_3$): $\delta - 22.1$, −20.6; MS: m/z (%) 325 (M$^+$, 50), 310 (10), 165 (100), 160 (13). Anal. Calcd for $C_{18}H_{23}NOSi_2$: C, 66.14; H, 6.99; N, 4.30%. Found: C, 66.41; H, 7.12; N, 4.30%.

11 E. Lippert, W. Lueder, H. Boos, in *Advances in Molecular Spectroscopy*, Pergamon Press, London, **1962**, p. 443.

12 E. Lippert, *Z. Naturforsch. A* **1955**, *10*, 541; E. Lippert, *Z. Electrochem.* **1957**, *61*, 962; N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690.

13 Fluorescence lifetime was determined by means of the time-correlated single photon-counting technique using an Edinburgh Analytical Instruments FL900CDT spectrometer system in the nanosecond time-region or a femtosecond laser system (Spectra Physics mode-locked Ti:sapphire laser; Tsunami) combined with a detector MCP-PMT (Hamamatsu R3809U-51) system in the picosecond time-region.

14 D. Huppert, S. D. Rand, P. M. Rentzepis, P. F. Barbara, W. S. Struve, Z. R. Grabowski, *J. Chem. Phys.* **1981**, *75*, 5714.