and $CHCl_3$ with bimolecular rate contants[24] of (8.2 ± 0.8) and (1.4 × 0.1) × 10^7 M^{-1} s^{-1}, respectively (see Figure 2, insert).

In summary, the absorption spectrum observed following pulse radiolysis of CCl_4 has erroneously been assigned to dichlorocarbene.[4,5] The transient species has been identified as chlorine atom. A "clean" method (266-nm LFP) for direct study of the important reactions of chlorine atom, e.g., photochlorination reactions, is presented, and several absolute bimolecular rate constants for the reaction of chlorine atom in CCl_4 are reported.

Currently, the effect of other "inert" solvents on the reactivity of "free" chlorine atom are being pursued.

Registry No. CCl_4, 56-23-5; CCl_3^+, 27130-34-3; $\cdot O_2CCl_3$, 69884-58-8; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; $:CCl_2$, 1605-72-7; Cl, 22537-15-1; Cl_2, 7782-50-5; 2,3-dimethyl-2-butene, 563-79-1; methyl acrylate, 96-33-3; acetonitrile, 107-13-1; cyclohexene, 110-83-8; cyclohexane, 110-82-7; methanol, 67-56-1; triethylsilane, 617-86-7.

---

[24] No evidence of a radical chain depletion of Cl_2 was observed with these substrates.

Phosphorescence and Optical Detection of Magnetic Resonance Studies of Poly(methylpropylsilylene)

O. Ito, M. Terazima, and T. Azumi*

Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received April 27, 1989

The nature of the excited states of polysilylenes has attracted considerable attention.[1-4] Fairly intense fluorescence is observed at around 350 nm, and on the basis of the narrow spectral width of the fluorescence, the concept of a high degree of delocalization of the $^1(\sigma,\sigma^*)$ excited state of the polymers has been widely accepted.[3] Most previous studies on the excited states of polysilylenes are, however, limited to singlet states. Observation of the phosphorescence is scarce, except for polymers having aromatic pendants,[5] and the character of the triplet excited states of polysilylenes is not well elucidated. Michl et al.[1] recently reported that the fairly weak long-lived emission observed for poly(methylpropylsilylene), hereafter referred to as $(MePrSi)_n$, at 77 K was the phosphorescence. Harrah and Zeigler[2] also reported phosphorescence for several polysilylenes including $(MePrSi)_n$. The phosphorescence spectrum reported by Michl et al. is broad and structureless, whereas that reported by Harrah and Zeigler shows fine structure. Even though the two reported spectra are somewhat different in structure, they are both fairly broad (half-width of ~4500 cm^{-1}), and this broad feature is in sharp contrast to the narrow (half-width of ~400 cm^{-1}) fluorescence. Both groups of authors[1,2] attributed the broadness to the localized nature of the triplet excited state.

Most of the previous luminescence studies have been carried out at temperatures higher than 77 K. We have investigated the long-lived emission of $(MePrSi)_n$ at 4.2 K or below, and in this communication, we report the existence of the new phosphorescence which should be attributed to the emission from the delocalized triplet state.

$(MePrSi)_n$ was kindly synthesized by Dr. Fujino of NTT. The molecular weights of the synthesized polymer range from ~10^4 to ~10^6, and the main peak is located at molecular weight 2.0 × 10^4. There is another minor peak at molecular weight 1.7 × 10^6. The fluorescence and phosphorescence spectra were measured in a benzene solution and for a spin coated film on a SiO_2 substrate. Both samples give essentially identical spectra. The optical detection of magnetic resonance (ODMR) studies were carried out at 1.3 K for a benzene solution (concentration of 1.0 × 10^{-2} M/monomer repeat) with the apparatus described previously.[6-8] Light from an Ushio 500-W xenon lamp passed through a water filter was used for the excitation source.

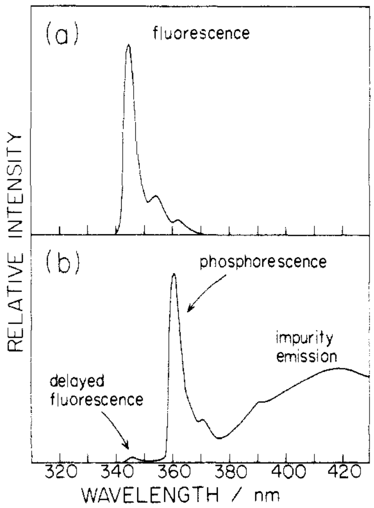


Figure 1. (a) Fluorescence spectrum and (b) long-lived emission of poly(methylpropylsilylene) (spin coated film) at 4.2 K. The assignments of the long-lived emission bands are also shown in b.

The fluorescence spectrum of $(MePrSi)_n$ observed at 4.2 K is shown in Figure 1a. The progression of the 740-cm^{-1} carbon–silicon stretching vibration is built on the intense 0,0 band at 345 nm as was previously observed by Kagawa et al.[3] Figure 1b shows the long-lived emission recorded by means of a phosphoroscope at 4.2 K in the time range of 1–4 ms after the excitation. An intense peak is located at 360 nm, and the vibrational progression of 740 cm^{-1} appears similar to the fluorescence. The quantum yield of the phosphorescence was not determined, but we estimate that it is of the order of ~10^{-4} or less. Besides this intense band, there exists a tiny band at 345 nm, exactly the same position as the fluorescence. For the reasons to be described below, we assign these two bands to phosphorescence and delayed fluorescence, respectively. The broad band at longer wavelengths (~420 nm) is due to an impurity[9] since the excitation spectrum differs from the absorption spectrum. The identification of the two newly observed bands as phosphorescence and delayed fluorescence is mainly due to (1) the decay analysis and (2) ODMR experiments, as discussed in the following sections.

The decays of the 360- and 345-nm bands are both nonexponential. The nonexponentiality is successfully analyzed in terms of a kinetic scheme involving the triplet–triplet annihilation process. If the singlet excited state (S_1) is generated by the annihilation of two triplet excited states (T_1), the populations of T_1 and S_1 should be expressed as follows:[10,11]

$$1/n_T(t) = [1/n_T(0) + k_{TT}/k_P] \exp(k_P t) - k_{TT}/k_P \quad (1)$$

$$[1/n_S(t)]^{1/2} = [\{1/n_S(0)\}^{1/2} + (k_F k_{TT}/f k_P{}^2)^{1/2}] \exp(k_P t) - (k_F k_{TT}/f k_P{}^2)^{1/2} \quad (2)$$

where k_P and k_F are respectively the first-order decay rate con-

---

[1] Michl, J.; Downing, W.; Karatsu, T.; McKinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakurmaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.

[2] Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987.

[3] Kagawa, T.; Fujino, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635.

[4] Ito, O.; Terazima, M.; Azumi, T.; Takeda, K.; Fujino, M.; Matsumoto, N. *Macromolecules* **1989**, *22*, 1718.

[5] Todesco, R. V.; Kamat, P. V. *Macromolecules* **1986**, *19*, 196.

[6] Yamauchi, S.; Azumi, T. *J. Chem. Phys.* **1977**, *67*, 7.

[7] Murao, T.; Azumi, T. *J. Chem. Phys.* **1979**, *70*, 4460.

[8] Asano, S.; Aita, S.; Azumi, T. *J. Phys. Chem.* **1983**, *87*, 3829.

[9] The origin of the impurity is unknown at present. The impurity emission does not increase upon light irradiation at liquid helium temperatures, and hence, it appears that the impurity is somehow introduced during the synthesis. It may be worth mentioning that the polymer synthesized by anionic polymerization (see: Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, N.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641) also shows similar but somewhat less impurity emission.

[10] Tanaka, Y.; Azumi, T. *Inorg. Chem.* **1986**, *25*, 247.

[11] Tanaka, Y.; Azumi, T. *Chem. Phys. Lett.* **1986**, *132*, 357.

0002-7863/90/1512-444$02.50/0

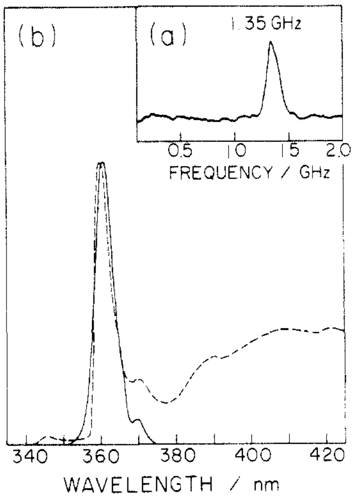


Figure 2. (a) ODMR spectrum of the phosphorescence of poly(methylpropylsilylene) (benzene solution) at 1.3 K. (b) The action spectrum of the ODMR signal (solid line) and the long-lived emission spectrum (broken line) shown in Figure 1b.

stants for T_1 and S_1 and k_{TT} is the rate constant for triplet-triplet annihilation. Further, f stands for the fraction of the annihilation rate constant yielding S_1. The decay curves of the 360- and 345-nm bands were successfully modeled by eqs 1 and 2, respectively, with the common k_P value of 200 s^{-1}. This kinetic analysis clearly shows that the 360- and 345-nm long-lived emissions are respectively the phosphorescence and delayed fluorescence.

In order to make the phosphorescence assignment more conclusive, we have made zero-field ODMR measurements at 1.3 K. As an example, the ODMR spectrum in the 0–2-GHz microwave range is shown in Figure 2a, which shows that the steady-state phosphorescence intensity increases by the application of 1.35-GHz microwave radiation. The ODMR action spectrum for the 1.35-GHz transition is shown in Figure 2b. The action spectrum well reproduces the phosphorescence spectrum without the perturbation of the impurity emission. Similarly, an ODMR transition is observed at 2.38 GHz, and its action spectrum again reproduces the phosphorescence spectrum. The other microwave transition is observed in the microwave induced delayed phosphorescence (MIDP) experiment (that is, the microwave is applied after the phosphorescence decays to a certain level) at 3.73 GHz, which agrees with the sum of the two transition frequencies. Thus, all three transitions among the three triplet sublevels are successfully observed. The finding that the ODMR action spectrum coincides with the phosphorescence very conclusively shows that the observed phosphorescence and ODMR spectra are genuine.

The observed zero-field splittings are relatively large as compared with those of carbon-based conjugated polymers such as polydiacetylene[12] (0.55, 1.11, and 1.66 GHz). The zero-field splittings of $(MePrSi)_n$ would be much smaller if they were governed solely by the spin-spin coupling. The relatively large zero-field splittings observed for the present polysilylene is most probably due to the large spin-orbit coupling.

The energy difference between the fluorescence and the newly observed phosphorescence is 1200 cm^{-1}. The smallness of the singlet-triplet splitting is in accord with the delocalized character of the excited states. Further, this singlet-triplet energy difference is almost in accord with the value 2000 cm^{-1} calculated recently by Takeda.[13]

Finally, the intensity of the phosphorescence strongly depends on temperature. The phosphorescence (except for the broad impurity band) is totally quenched at temperatures higher than 15 K. Unfortunately, the temperature dependence of the spectrum could not be measured between 4.2 and 15 K with our facilities at present. This thermal quenching, which, we surmise at this moment, is due to a mechanism proposed previously by one of the present authors,[14,15] is the main reason why the phosphorescence has not been detected so far.

Acknowledgment. We thank Dr. M. Fujino, Dr. K. Takeda, and Dr. M. Matsumoto of NTT for the gift of the polymer and for fruitful discussion. The present research was supported in part by Grant-in-Aid for Scientific Research No. 62430001 from the Ministry of Education, Science and Culture.

---

(12) Kollmar, C.; Ruhle, W.; Frick, J.; Sixl, H.; von Schutz, J. U. *J. Chem. Phys.* **1988**, *89*, 55.

(13) Takeda, K. Private communications.

(14) Azumi, T.; Nakano, Y. *J. Chem. Phys.* **1969**, *51*, 2515.

(15) Azumi, T. *J. Chem. Phys.* **1971**, *54*, 85.

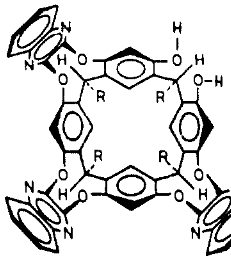
Host-Guest Complexation in the Gas Phase by Desorption Chemical Ionization Mass Spectrometry

Marco Vincenti,* Enrico Dalcanale,* Paolo Soncini, and Gianfranco Guglielmetti

Istituto Guido Donegani S.p.A.
Via Fauser, 4, 28100 Novara, Italy

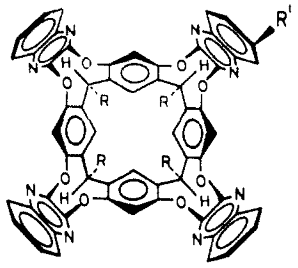
Received July 3, 1989

Cavitands are synthetic macrocycles capable of molecular recognition.[1] The structures and stabilities of supramolecular complexes formed by such hosts have been widely studied both in solution and in the solid state.[2] The few reports of gas-phase complexes in the literature refer to charged complexes formed in solution, which had been isolated and then evaporated.[3] We report the first study on the formation of caviplexes between gaseous reactants, wherein complexation occurs in the absence of solvation effects. Desorption chemical ionization[4] (DCI) mass spectrometry was used to evaporate the cavitand, provide an atmosphere of guest molecules, and ionize and analyze the reaction products.[5] Three differently shaped hosts of the same family were synthesized, namely, the cleft-shaped cavitand **1**,[7] the vessel-like cavitand **2**,[1c] and its derivative **3**,[7] in which a bulky menthoxy group perches on top of the cavity.[8]



1

R = C_6H_{13}



2 R' = H

3 R' = COO(-)Menthyl

---

* Authors to whom correspondence should be addressed.

(1) (a) Cram, D. J. *Science* **1983**, *219*, 1177. (b) Cram, D. J.; Weiss, J.; Hegelson, R. C.; Knobler, C. B.; Dorigo, A. E.; Houk, K. N. *J. Chem. Soc., Chem. Commun.* **1988**, 407. (c) Dalcanale, E.; Soncini, P.; Bacchilega, G.; Ugozzoli, F. *Ibid.* **1989**, 500.

(2) (a) Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 362 and references cited therein. (b) Cram, D. J. *Top. Curr. Chem.* **1981**, *98*, 43 and references cited therein. (c) Weber, E. *Ibid.* **1987**, *140*, 3.

(3) (a) Ashton, P. R.; Stoddart, J. F.; Zarzycky, R. *Tetrahedron Lett.* **1988**, *29*, 2103. (b) Laali, K.; Lattimer, R. P. *J. Org. Chem.* **1989**, *54*, 496.

(4) (a) Baldwin, M. A.; McLafferty, F. W. *Org. Mass Spectrom.* **1973**, *7*, 1353. (b) Cotter, R. J. *Anal. Chem.* **1980**, *52*, 1589A.

(5) DCI experiments were conducted on a Finnigan-MAT 8424 mass spectrometer (detailed experimental conditions are described in ref 6). Vapors of various guests were used as the CI reagent gas at uncorrected pressures of 0.3 mbar. The electron energy was set to 100 eV (positive ions) and 140 eV (negative ions). The magnet was scanned from 450 to 2100 Da in 1.3 s.

(6) Guglielmetti, G.; Dalcanale, E.; Bonsignore, S.; Vincenti, M. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 106.

(7) Dalcanale, E.; Du vosel, A.; Soncini, P.; Ugozzoli, F. Proceedings of Meeting on Macrocycles and Supramolecular Chemistry in Italy, 1988; p 91.