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Fluorescence Quenching of Perfluoronaphthalene by Triethylamine

Koji Kano,* Masaru Yanagimoto, Hisashi Uraki, Bin Zhou, and Shizunobu Hashimoto
Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto 602

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The relatively fast fluorescence quenching of perfluoronaphthalene by triethylamine as well as the lack of the exciplex emission of this system has been interpreted in terms of the electron transfer from triethylamine to photoexcited perfluoronaphthalene, where the electron donor-acceptor pair takes a loose geometric configuration.

Some hydrocarbons have been known to yield exciplexes through a charge-transfer interaction with aromatic or aliphatic amines.[1] In some cases, the exciplexes show broad fluorescence bands at longer wavelengths in nonpolar solvents.[2] The possibility of a direct electron transfer which yields a solvent-separated ion pair has been accounted for the absence of exciplex emission in strongly polar solvents.[3] The exciplex formation is also affected by the structures of amines as electron donors. Although aromatic amines such as *N*,*N*-dimethyl- and *N*,*N*-diethylanilines form the exciplexes with hydrocarbons with diffusion-controlled rates,[4] the rates of exciplex formation for aliphatic amines are smaller by one order of magnitude.[5] The conformational change of aliphatic amine from pyramidal to planar is required for exciplex formation. Such geometric requirement causes larger activation energy for exciplex formation.[5] Some hydrocarbons such as pyrene and naphthalene are known to form the fluorescent exciplexes with aliphatic amines.[5,6]

The present study deals with the effects of the fluorine substituents attached to the naphthalene ring on photoinduced electron transfer and exciplex formation. The results suggest an electron transfer from triethylamine (TEA) to perfluorinated naphthalene in the excited state prior to exciplex formation.

Experimental

Materials. Octafluoronaphthalene (perfluoronaphthalene, PFN, Tokyo Kasei) was recrystallized from cyclohexane. Naphthalene (Nakarai) was purified by sublimation. 1-Fluoronaphthalene (1-FN, Tokyo Kasei), triethylamine (TEA, Nakarai), and perfluorohexane (PFH, PCR Research Chemicals) were purchased and used without further purification. All solvents used were analytical or reagent grades.

Measurements. The absorption spectra were taken on a Shimadzu UV-200S spectrophotometer. The fluorescence emission and excitation spectra were measured on a Shimadzu RF-540 or a Hitachi 650-60 spectrofluorometers whose cell compartments were thermostated at 298 K. The phosphorescence spectra were taken on a Hitachi 650-60 spectrofluorometer using an attachment 650-0175 for phosphorescence measurement at 77 K. The fluorescence spectra at 77 K were measured on a Shimadzu RF-540 spectrofluorometer using a Dewar vessel described previously.[7] The fluorescence lifetimes were determined by using an Ortec-PRA single-photon counting appratus.[8] The fluorescence quantum yields were determined by measuring the corrected fluorescence spectra on a Hitachi 650-60 spectrofluorometer and using quinine sulfate as a standard.[9]

Results and Discussion

Absorption and Fluorescence Spectra. Introduction of the fluorine substituents into the naphthalene ring causes red shifts of the ^1L_a and ^1L_b bands, broadening of the vibronic structures of these bands, and increase in the intensities of the ^1L_b bands. The extinction coefficients of the 0–0 bands of naphthalene, 1-FN, and PFN in cyclohexane are 274 $M^{-1} cm^{-1}$ at 311.5 nm, 631 $M^{-1} cm^{-1}$ at 317 nm, and 2367 $M^{-1} cm^{-1}$ at 323 nm, respectively.

The fluorescence maxima in hexane are 313(sh), 323, 332(sh), 336, and 344(sh) nm for naphthalene, 317, 321(sh), 332, 336(sh), and 348 nm for 1-FN, and 348 nm for PFN. PFN shows a structureless fluorescence in solutions at 25 °C. The fluorescence quantum yield (Φ_f) of 1-FN determined in degassed hexane (0.23±0.010) is the same as that of naphthalene (0.22±0.010) and Φ_f of PFN (0.10±0.015) is about half of those of naphthalene and 1-FN. The fluorine substituents introduced to the naphthalene ring markedly reduce the fluorescence lifetimes (τ_f), the τ_f values of naphthalene, 1-FN, and PFN being 120, 42.5, and 3.1 ns, respectively. The rate constants for the emission process ($k_f = \Phi_f/\tau_f$) increased in the order of naphthalene ($1.8 \times 10^6 s^{-1}$), 1-FN ($5.4 \times 10^6 s^{-1}$), and PFN ($3.2 \times 10^7 s^{-1}$). The S_0–S_1 transition of naphthalene is orbital symmetry forbidden. For PFN, however, this transition may be partially allowed.

Fluorescence Quenching. The fluorescence of naphthalene, 1-FN, and PFN were quenched by TEA and the data could be treated by a simple Stern-Volmer equation. The rate constants for fluorescence quenching (k_q) determined from the plots of I_0/I vs. [TEA] are listed in Table 1, where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively.

As the TEA concentration increased, the broad exciplex emissions appeared at longer wavelengths in the cases of naphthalene and 1-FN when ethyl acetate, cyclohexane, hexane, and PFH were used as the solvents. The emission maxima of the exciplexes are shown in Table 1. Of course, no exciplex emission was observed in polar solvents such as ethanol and

Table 1. Rate Constants for Fluorescence Quenching ($10^{-9}k_q$, $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$) of Naphthalene, 1-FN, and PFN by TEA and Fluorescence Maxima (λ_{max}, nm) of Exciplexes of These Naphthalene Derivatives and TEA in Various Solvents at 298 K

Solvent	Naphthalene		1-FN		PFN	
	k_q	λ_{max}	k_q	λ_{max}	k_q	λ_{max}
Acetonitrile	5.5	a	8.7	a	10.8	a
Ethanol	1.0	a	1.5	a	3.5	a
Ethyl acetate	4.9	473	6.9	482	10.8	a
Cyclohexane	3.4	413	4.8	417	10.1	a
Hexane	1.0	413	5.8	418	14.3	a
Perfluorohexane	5.7	402	7.6	417	19.0	a

a) No exciplex emission was observed.

acetonitrile. Interestingly, PFN did not show the exciplex emission in any solvents used in spite of the quenching of the monomer fluorescence by TEA. Van and Hammond reported the dipole moment of the naphthalene–TEA exciplex to be 11.1 D,[6] which has been determined from a plot of energies of exciplex emission maxima vs. solvent polarity parameters ($f(\varepsilon,n)$).[10] The same plot provided a dipole moment of an exciplex of 1-FN and TEA to be 11.6 D. Since an electron transfers almost completely from donor to acceptor in the exciplex system, no effect of a fluorine substituent of the acceptor molecule seems to be observed.

As Table 1 shows, the fluorine substituents introduced to the naphthalene ring enhanced the fluorescence quenching. In agreement with the results obtained by Van and Hammond,[6] the rate of fluorescence quenching of naphthalene by TEA in each nonpolar solvent was smaller than the diffusion-controlled rate, which may be attributed to the higher activation energy for forming exciplexes because of a conformational change of aliphatic amines to form exciplexes.[5] By the way, relatively large k_q values were obtained for the quenching in acetonitrile. In strongly polar solvents, electron transfer is known to occur from loose electron donor–acceptor pairs prior to exciplex formation.[3] A major factor which dominates the k_q values in strongly polar solvents including acetonitrile, therefore, may be the diffusion rates of both donor and acceptor molecules. The fluorescence quenching of 1-FN by TEA occurred more efficiently than that of naphthalene. Extremely fast fluorescence quenching proceeded in the case of PFN where the k_q value in each solvent is very close to the diffusion-controlled rate constant. In the system where an exciplex needs forming upon fluorescence quenching, the quenching should be accelerated by substituent(s) if the substituent(s) can stabilize the exciplex state. This may be the case for the fluorescence quenching of 1-FN in nonpolar solvents. A fluorine substituent, a strongly electronegative substituent, should stabilize an anionic form of the naphthalene moiety in the exciplex leading to lowering of the activation energy for exciplex formation. The situation of PFN seems to be different from those of naphthalene and 1-FN because no exciplex emission was detected in this system. No ground-state interaction between donor and acceptor molecules was suggested for all cases by means of the absorption spectroscopy.

Irreversible photoreactions of PFN (1×10^{-4} mol dm^{-3}) took place in both hexane and acetonitrile solutions containing TEA (1×10^{-3} mol dm^{-3}) under anaerobic conditions. Upon irradiation with an Hg lamp, a photoproduct having absorption maximum at around 380 nm was generated. Although we did not determine the reaction product(s) in the present study, the radical ion pairs of PFN and TEA should be generated as the intermediates. Dehalogenation is the most plausible photoreactions.[11]

Fluorescence at 77 K. In methylcyclohexane matrices at 77 K, the relative fluorescence intensity of the naphthalene derivatives decreased in the order of 1-FN, naphthalene, and PFN and weak phosphorescence emissions of these naphthalene derivatives were observed at longer wavelengths (Fig. 1). The difference in the fluorescence and phosphorescence yields between these naphthalene derivatives is appreciable, but not very large.

In glassy TEA at 77 K, the relatively strong monomer fluorescence emissions of naphthalene and 1-FN were observed along with the weak exciplex fluorescence and monomer phosphorescence emissions (Fig. 2). The monomer fluorescence of PFN, however, was quenched almost completely and very weak exciplex emission centered at 420 nm was observed in neat TEA at 77 K. The exciplex emissions of naphthalene and 1-FN in the TEA matrices decayed multiexponentially without rise (the data are not shown), suggesting that several exciplex states are formed immediately upon photoexcitation. Some of the naphthalene and 1-FN molecules may make pairs with TEA molecules which have preferable geometric configurations for exciplex formation. Large amounts of the naphthalene and 1-FN molecules seem to exist without any interaction with surrounding TEA molecules. In the case of PFN, however, most of the PFN molecules were quenched by surrounding TEA molecules, whose mobility was strictly restricted. It is reasonable, therefore, to assume a

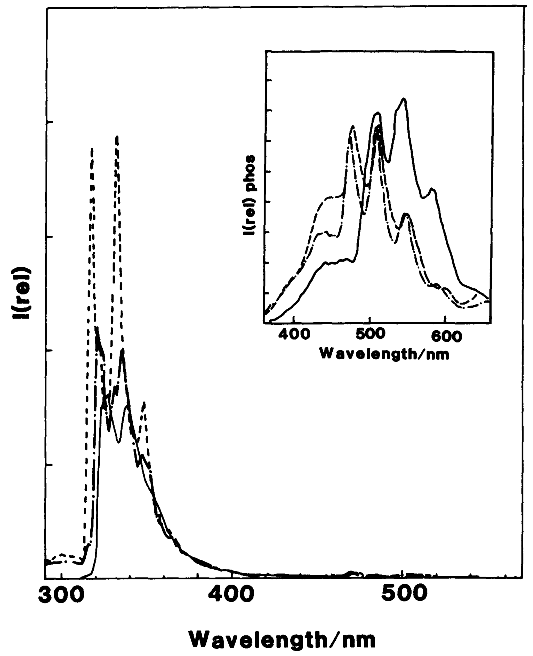

Fig. 1. Fluorescence and phosphorescence spectra of naphthalene (—·—), 1-FN (---), and PFN (——) in methylcyclohexane at 77 K. Naphthalene, 1-FN, and PFN (1×10^{-5} mol dm^{-3}) were excited at 278, 281, and 290 nm, respectively. The insert shows the phosphorescence spectra.

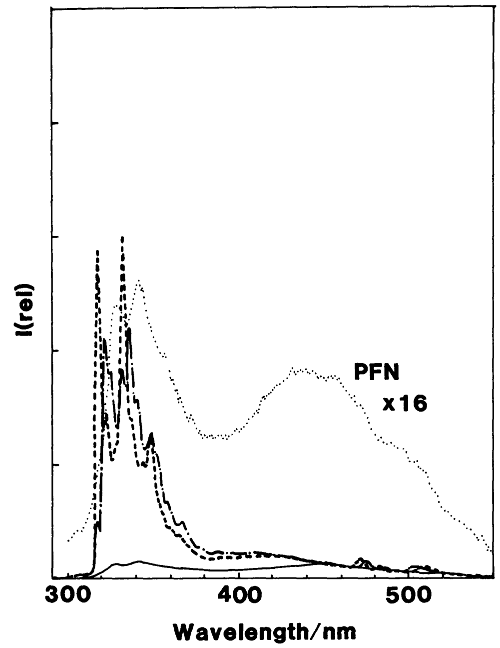

Fig. 2. Fluorescence spectra of naphthalene (—·—), 1-FN (---), and PFN (——) in TEA at 77 K. Naphthalene, 1-FN, and PFN (1×10^{-5} mol dm^{-3}) were excited at 279, 282, and 290 nm, respectively.

long-distance interaction between PFN and TEA. It is noteworthy that the exciplex emission for the PFN–TEA system is observed only in the TEA matrix. PFN can form a fluorescent exciplex with TEA if these two molecules take an appropriate configuration for forming an exciplex. In fluid organic solvents, however, no exciplex emission of this donor-acceptor pair was observed at any TEA concentrations. These observations strongly suggest the fluorescence quenching of PFN by TEA prior to the exciplex formation.

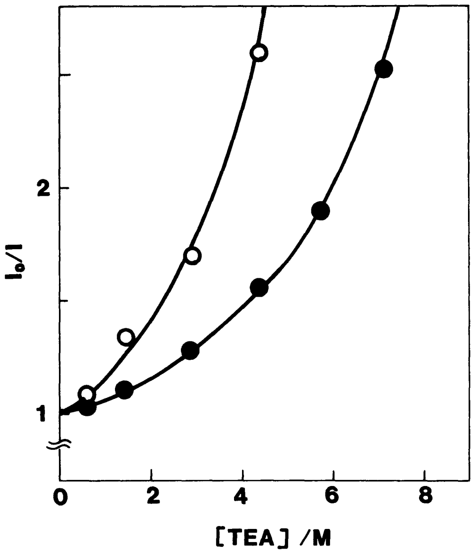

Fig. 3. Plots of I_0/I vs. [TEA] for the fluorescence quenching of naphthalene (●) and PFN (○) in EPA at 77 K.

Figure 3 shows the plots of I_0/I vs. [TEA] for the fluorescence quenching of naphthalene and PFN in the EPA (diethyl ether:isopentane:ethanol=5:5:2) matrices at 77 K. Although a Stern–Volmer linear relationship was observed in fluid media, the plots were deviated upward from the straight lines for the fluorescence quenching in the rigid matrices. Since both fluorescer and quencher molecules cannot move freely in glassy EPA, only donor–acceptor pairs within an interaction radius can participate in fluorescence quenching. The fluorescent state of PFN was quenched more efficiently than that of naphthalene at each quencher concentration in rigid medium. This clearly indicates that an interaction radius for the PFN–TEA system is larger than that for the naphthalene–TEA system. The data shown in Fig. 3, therefore, support a long-distance electron transfer via a loose donor-acceptor pair in the PFN–TEA system.

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