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Exciplexes in Perfluorohydrocarbon. Charge-Transfer Interaction between Exciplexes and Perfluorohexane

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The rate constants for photochemical processes of pyrene in perfluorohexane (PFH) and hexane containing *N*,*N*-dimethylaniline (DMA) have been determined by analyzing the rise and decay curves of the pyrene–DMA exciplex to study the interaction between electronically polar exciplex and an extremely nonpolar solvent, PFH. In PFH, the dissociation of the exciplex to the original pyrene in the excited singlet state and DMA was decelerated and the radiationless deactivation of the exciplex to the ground states was accelerated. In the case of the naphthalene–triethylamine exciplex system, the radiationless deactivation of the exciplex was also much faster in PFH than in hexane. These results suggest charge-transfer interactions between the polar exciplexes and PFH. The negative charges of the exciplexes may transfer to the strongly electronegative fluorine atom(s) of PFH. The deceleration of the back reaction and the acceleration of the radiationless deactivation seem to lead the efficient fluorescence quenching of pyrene and naphthalene by amines in PFH.

Solvation plays an essentially important role to dominate physical properties and chemical reactivities of molecules in solutions. Several studies have demonstrated very weak solute–solvent interactions in perfluorohydrocarbons. The absorption and fluorescence emission spectra of benzene in perfluorinated alkanes are very similar to those in vapor phase.[1–3] The vibronic bands of the electronic spectra of 9*H*-xanthene-9-thione and its related thiones in perfluorohexane (PFH) are well-resolved compared with those in 3-methylpentane glass at 77 K.[4,5] These spectral data clearly indicate a very weak perturbation of the electronic states of solute molecules by perfluorohydrocarbon solvents. The fluorescence intensities of the vibronic bands of the pyrene monomer are known to be sensitive toward solvent polarity. This probe molecule also indicates extremely weak dipole–dipole interaction between pyrene and perfluorohydrocarbons.[6,7] A Kamlet–Taft's π^* value is one of the measures of the ability of a solvent to interact with solute through dipole–dipole interaction.[8,9] Table 1 shows the π^* values of various perfluorohydrocarbons together with the dielectric constants (ε) and the refractive indexes (n_D). The Kamlet–Taft's π^* values of perfluorohydrocarbons are large and negative, indicating very weak solute–solvent interactions in these solvents. Fluorine atom is so electronegative that perfluorohydrocarbon solvents show extremely low polarizabilities leading to weak van der Waals interactions.

Table 1. Dielectric Constants (ε), Refractive Indexes (n_D), and Kamlet-Taft's π^* Values for Perfluorohydrocarbons

	ε	n_D	π^*
Perfluoro(dimethyldecalin)	1.94[a)]	1.312[a)]	−0.33[a)]
Tris(perfluorobutyl)amine	1.90[a)]	1.291[a)]	−0.36[a)]
Perfluorooctane	1.85[a)]	1.271[a)]	−0.41[a)]
Perfluoroheptane	1.765[a)]	1.258[a)]	−0.39[a)]
Perfluorohexane	1.679[b)]	1.251[c)]	−0.40[d)]

a) Ref. 9(b). b) This work. c) N. Ishikawa, *Petrotech*, **6**, 761 (1983). d) Ref. 8 e).

In spite of these physical aspects, we scarecely know chemical reactivities in perfluorohydrocarbons. Since perfluorinated alkanes are less active toward triplet carbonyl compounds than corresponding hydrocarbons, they are suitable solvents for phosphorescence measurements at room temperature.[10] Metal pentacarbonyls ($M(CO)_5$, M=Cr, Mo, and W) generated by the photolysis of the metal hexacarbonyls are very reactive toward carbon monoxide, cyclohexane, and nitrogen in perfluoro(methylcyclohexane) (PFMCH) because $M(CO)_5$ is free from solvation in PFMCH.[11] In some cases, perfluorohydrocarbons act as electron acceptors. The fluorescence emissions of triethylamine[12] and hydrocarbons such as cyclohexane, decalin, and 2,3-dimethylbutane[13] are quenched by perfluorohydrocarbons through charge-transfer interactions.

The present study deals with the solvent effects of perfluorohexane (PFH) on exciplex formation and dissociation. PFH shows the smallest ε and π^* values among the perfluorohydrocarbons listed in Table 1. The exciplex states have been well-known to be very sensitive toward solvent polarity because of their polar structures.[14] The exciplex, therefore, may be useful as a probe to study the interaction of polar solutes with extremely nonpolar solvents, perfluorohydrocarbons.

Experimental

Materials. Naphthalene was purified by sublimation. Pyrene was chromatographed on silica gel with cyclohexane and recrystallized from cyclohexane. Anthracene (Nakarai, 99.9%), triethylamine (TEA, Nakarai, reagent grade), and PFH (PCR Research Chemicals) were used without further purification. Reagent grade of *N*,*N*-dimethylaniline (DMA, Nakarai) was purified by distillation prior to use. Spectral grades of hexane and cyclohexane (Nakarai) were used.

Measurements. Fluorescence emission and excitation spectra were taken on a Hitachi 650—60 spectrofluorometer (emission and excitation bandwidths=2 nm). Fluorescence quantum yields of naphthalene and pyrene (Φ_X) were determined by measuring the corrected fluorescence spectra of very dilute sample solutions. The optical densities of the samples were arranged to be less than 0.05 at excitation wavelengths. We used the reported fluorescence quantum yields (Φ_{ST}) of naphthalene (0.21)[15] and pyrene (0.60)[6] in cyclohexane as standards. Both sample and standard solutions were excited at the same wavelength. Φ_X, therefore, can be represented as

$$\Phi_X = \Phi_{ST}(FA_X/FA_{ST})(A_{ST}/A_X)(n_X^2/n_{ST}^2), \quad (1)$$

where FA is the spectral area, A is the optical density at the excitation wavelength, and n is the refractive index. The fluorescence decay curves were taken using an Ortec-PRA single photon counting apparatus and analyzed by a Simplex method using an NEC 9801 microcomputer. All samples were degassed by five freeze-pump-thaw cycles.

Dielectric constant (ε) of PFH was kindly measured at 25 °C by Professor Shimizu and Mr. Tsuchihashi of this university by using a Shibayama dielectric constant measurement apparatus SS207-B.

Results

Figure 1 shows the fluorescence spectra of pyrene in PFH containing various amounts of DMA. Upon addition of DMA, the fluorescence intensities of the pyrene and anthracene monomers decreased and new broad fluorescence bands due to the exciplexes appeared at longer wavelengths in nonpolar solvents. The exciplex emission was also observed for the naphthalene–TEA system. The fluorescence maxima (λ_{max}) of these exciplexes are listed in Table 2. The peak of the fluorescence band of the anthracene–DMA exciplex was obscure in hexane and cyclohexane due to overlap with the monomer fluorescence band. In each system, the fluorescence maximum of the exciplex in PFH was observed at the shortest wavelength. A good linear relationship between the energy of the pyrene–DMA exciplex emission band (ν_E) and the solvent polarity parameter ($f(\varepsilon,n)$) was observed for the pyrene–DMA system:[16]

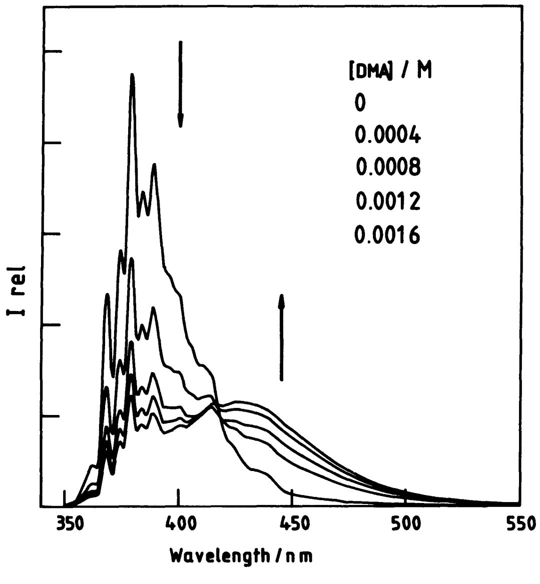


Fig. 1. Fluorescence spectra of pyrene (1×10^{-6} M) in degassed PFH in the absence and the presence of DMA at 25 °C. Pyrene was excited at 328 nm.

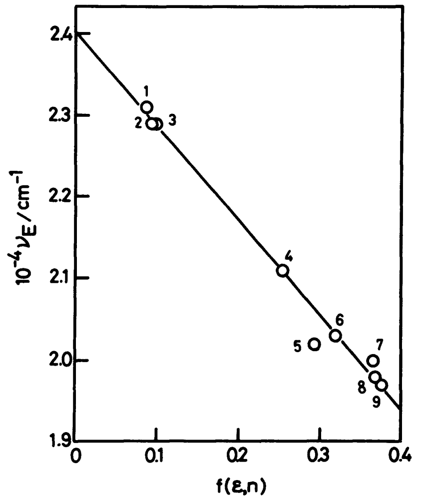


Fig. 2. Plot of the energy of the fluorescence maximum of the pyrene–DMA exciplex (ν_E) vs. the solvent polarity parameter $f(\varepsilon, n)$: 1: PFH, 2: hexane, 3: cyclohexane, 4: diethyl ether, 5: ethyl acetate, 6: dichloromethane, 7: isopropyl alcohol, 8: propyl alcohol, 9: ethanol.

Table 2. Fluorescence Maxima (λ_{max}) of Exciplexes of Pyrene and DMA, Anthracene and DMA, and Naphthalene and TEA in Various Solvents at 25 °C

	ε	λ_{max}, nm		
		Pyrene-DMA	Anthracene-DMA	Naphthalene-DMA
Perfluorohexane	1.679	432	458	402
Hexane	1.89	436	460—470	408
Cyclohexane	2.02	437	460—470	409
Ethyl acetate	6.12	494	516	473

Table 3. Fluorescence Quenching of Pyrene, and Naphthalene by DMA or TEA in PFH, Hexane, and Cyclohexane at 7 °C and 25 °C

Solvent	τ_0/ns	K_{SV}/M^{-1}	$10^{-9}\,k_q$/M^{-1} s^{-1}
	Pyrene-DMA (7 °C)		
Perfluorohexane	399	4940	12.4
Hexane	464	1014	2.2
	Pyrene-DMA (25 °C)		
Perfluorohexane	389	1827	4.7
Hexane	398	448	1.1
Cyclohexane	401	615	1.5
	Anthracene-DMA (7 °C)		
Perfluorohexane	7.1	244 (113)[a]	34.4 (15.9)[a]
Hexane	5.2	102	19.6
	Anthracene-DMA (25 °C)		
Perfluorohexane	7.0	156 (126)[a]	22.3 (17.9)[a]
Hexane	5.4	72	13.3
Cyclohexane	5.1	44	8.6
	Naphthalene-TEA (25 °C)		
Perfluorohexane	99	366	3.7
Hexane	120	132	1.1
Cyclohexane	117	187	1.6

a) The K_{SV} and k_q values in the parentheses were determined from the Stern-Volmer plots for fluorescence lifetime of anthracene.

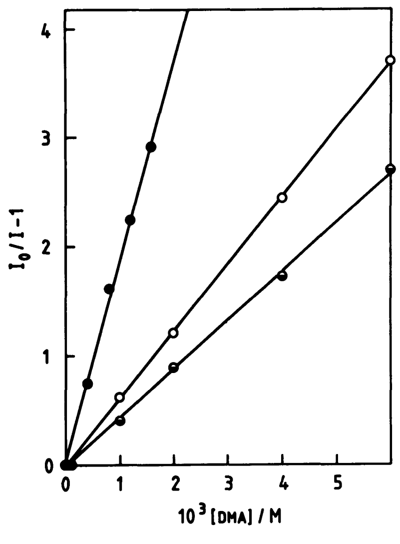
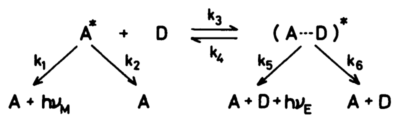


Fig. 3. Stern-Volmer plots for the fluorescence quenching of pyrene (1×10^{-6} M) by DMA in degassed PFH (●), hexane (◒), and cyclohexane (○) at 25 °C. Pyrene was excited at 328 nm in PFH, 334 nm in hexane, and 335 nm in cyclohexane. The fluorescence intensities (I) were followed at 378 nm in PFH and 382 nm in hexane and cyclohexane.

$$f(\varepsilon,\, n) = 2(\varepsilon-1)/(2\varepsilon+1) - (n^2-1)/(2n^2+1). \qquad (2)$$

The plot of ν_E vs. $f(\varepsilon,n)$ is shown in Fig. 2. A plot for PFH does not deviate from the straight line. The same linear relationship between ν_E and $f(\varepsilon,n)$ has been observed for the naphthalene-TEA system.[17]

A simple Stern-Volmer relationship could be applied for the fluorescence quenching of pyrene, anthracene, and naphthalene by amines (Fig. 3) and the results are summarized in Table 3. The fluorescence quenching parameters, the Stern-Volmer constants (K_{SV}) and the rate constants of fluorescence quenching (k_q), determined for the pyrene-DMA system in hexane and for the anthracene-DMA system in cyclohexane are in good agreement with those reported by Ware and his coworkers.[18,19] In each system, both K_{SV} and k_q values obtained for the fluorescence quenching in PFH were significantly larger than those in hexane and cyclohexane. In order to understand the reasons for very efficient fluorescence quenching in PFH, we determined the all rate constants of photochemical processes shown in the following scheme:



The fluorescence decays of monomer and exciplex can be written as Eqs. 2 and 3, respectively:[20,21]

$$I_M(t) = a_1\exp(-\lambda_1 t) + a_2\exp(-\lambda_2 t), \qquad (3)$$

$$I_E(t) = a_3[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)], \qquad (4)$$

where

$$\lambda_{1,2} = 1/2[k_1 + k_2 + k_3[Q] + k_4 + k_5 + k_6 \mp \{(k_1+k_2+k_3[Q]-k_4-k_5-k_6)^2+4k_3k_4[Q]\}^{1/2}]. \qquad (5)$$

From Eq. 3, linear correlations between ($\lambda_1+\lambda_2$) and $\lambda_1\lambda_2$ and [Q] can be expected:

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[\mathrm{Q}] + k_4 + k_5 + k_6 \tag{6}$$

$$\lambda_1\lambda_2 = (k_1+k_2)(k_4+k_5+k_6) + (k_5+k_6)k_3[\mathrm{Q}] \tag{7}$$

The k_3 and (k_5+k_6) values are determined from the slopes of the plots of $(\lambda_1+\lambda_2)$ vs. [Q] and of $\lambda_1\lambda_2$ vs. [Q], respectively. Since (k_1+k_2) can be obtained from the fluorescence decay of a fluorophore in the absence of quencher, k_4 is determined from the intercept of the plot of $(\lambda_1+\lambda_2)$ vs. [Q]. The k_1 and k_2 values are presented from the fluorescence lifetime (τ_0) and quantum yield (Φ_{M0}) of a fluorophore in the absence of quencher:

$$\tau_0 = (k_1+k_2)^{-1} \tag{8}$$

$$\Phi_{\mathrm{M0}} = k_1/(k_1+k_2) \tag{9}$$

In the presence of quencher, the ratio of the fluorescence quantum yield of exciplex to that of monomer $(\Phi_{\mathrm{E}}/\Phi_{\mathrm{M}})$ is represented as

$$\Phi_{\mathrm{E}}/\Phi_{\mathrm{M}} = (k_5/k_1)\{k_3[\mathrm{Q}]/(k_4+k_5+k_6)\}. \tag{10}$$

From the slope of the plot of $\Phi_{\mathrm{E}}/\Phi_{\mathrm{M}}$ vs. [Q], one can get k_5. We obtained $\Phi_{\mathrm{E}}/\Phi_{\mathrm{M}}$ value at each quencher concentration by measuring spectral areas of monomer and exciplex emissions:

$$\frac{\Phi_{\mathrm{E}}}{\Phi_{\mathrm{M}}} = \frac{\int I_{\mathrm{E}}(\nu)\mathrm{d}\nu}{\int I_{\mathrm{M}}(\nu)\mathrm{d}\nu} \tag{11}$$

The λ_1 and λ_2 values were determined from the fluorescence rise and decay curve of the exciplex. A typical example of the rise and decay curve of the pyrene–DMA exciplex in PFH is shown in Fig. 4. The plots of $(\lambda_1+\lambda_2)$ and of $\lambda_1\lambda_2$ vs. [DMA] are given in Figs. 5 and 6, respectively. The results shown in Figs. 5 and 6 were treated statistically by using a microcomputer to determine k_3 and (k_5+k_6). We had large experimental errors for determining λ_1 and λ_2 from the monomer fluorescence decay curve. The fluorescence quantum yields of naphthalene and pyrene in PFH

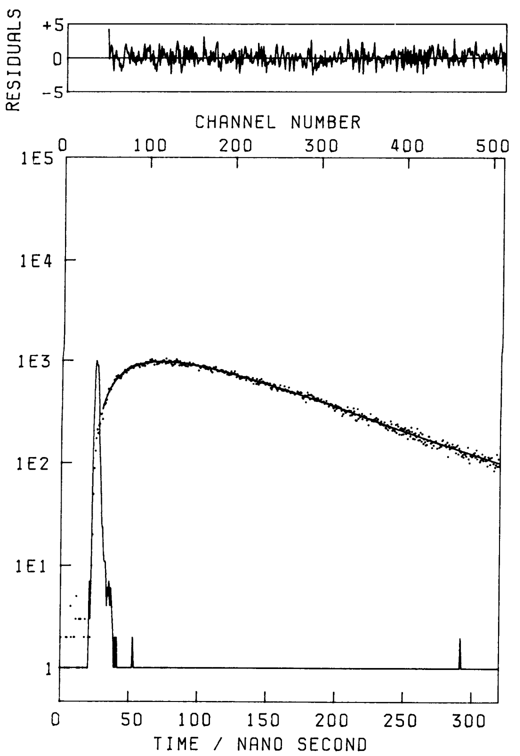


Fig. 4. Fluorescence decay curve of the pyrene–DMA exciplex in degassed PFH at 7 °C. The concentrations of pyrene and DMA were 1×10^{-6} and 1.5×10^{-3} M, respectively. Pyrene was excited at 328 nm and the exciplex emission was passed through a Toshiba glass filter VY-45 to eliminate the monomer emission. The best fit provided the rise and decay times of 29.5 and 91.8 ns, respectively ($\chi_\nu^2=1.09$).

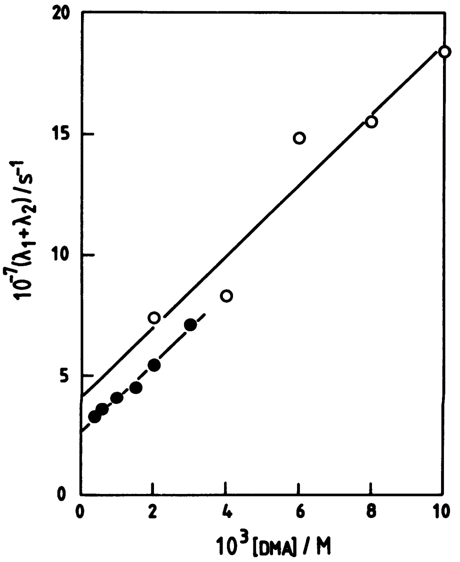


Fig. 5. Dependence of $(\lambda_1+\lambda_2)$ on the DMA concentration for the pyrene–DMA system in PFH (●) and hexane (○) at 7 °C.

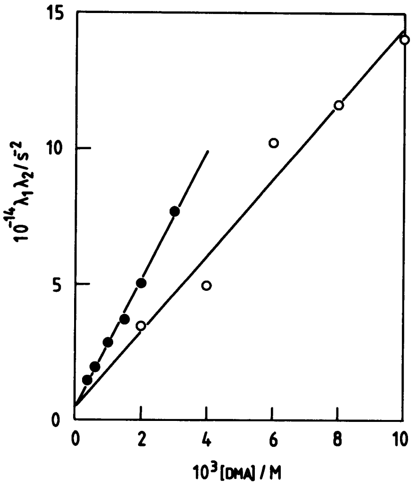


Fig. 6. Dependence of $\lambda_1\lambda_2$ on the DMA concentration for the pyrene–DMA system in PFH (●) and hexane (○) at 7 °C.

Table 4. Fluorescence Quantum Yields (Φ_{M0}) of Naphthalene and Pyrene in Degassed PFH and Hexane in Absence of Quencher

Fluorophore	Solvent	T/°C	Φ_{M0}
Naphthalene	Perfluorohexane	25	0.20
Naphthalene	Hexane	25	0.21
Pyrene	Perfluorohexane	25	0.33
Pyrene	Hexane	25	0.49
Pyrene	Perfluorohexane	7	0.35
Pyrene	Hexane	7	0.51

Table 5. Rate Constants for Photochemical Processes of Pyrene-DMA System in Degassed PFH and Hexane at 7 °C

	PFH	Hexane
$10^{-6} k_1$ s^{-1}	0.88±0.05	1.1±0.1
$10^{-6} k_2$ s^{-1}	1.6±0.1	1.1±0.1
$10^{-10} k_3$ M^{-1} s^{-1}	1.5±0.1	1.5±0.1
$10^{-7} k_4$ s^{-1}	0.69±0.17	3.0±1.6
$10^{-6} k_5$ s^{-1}	2.3±0.2	2.5±1.1
$10^{-6} k_6$ s^{-1}	13.0±1.0	7.0±2.0

and hexane are listed in Table 4. From the results listed in Tables 3 and 4, the k_1 and k_2 values were evaluated. The determined rate constants for the photochemical processes of the pyrene–DMA system are summarized in Table 5.

In the case of the naphthalene–TEA system, the rise time of the exciplex emission at 25 °C was so short that the λ_1 and λ_2 values could not be determined accurately. Although large errors might be included, we evaluated the $(k_4+k_5+k_6)$ values by extrapolating λ_2 to the zero TEA concentration. The λ_2 values were determined by fitting the experimentally obtained decay curves with trial single-exponential decay functions at larger t. Figure 7 shows the plots of λ_2 vs. [TEA] in PFH and hexane. The slope of the plot of Φ_E/Φ_M vs. [TEA] gives $(k_3k_5/k_1)/(k_4+k_5+k_6)$ (see Eq. 10). Since the k_1 value can be known from the fluorescence lifetime and quantum yield of naphthalene in the absence of quencher, the k_3k_5 value can be evaluated. The rate constant for fluorescence quenching is represented as

$$k_q = k_3(k_5+k_6)/(k_4+k_5+k_6). \tag{12}$$

From Eq. 12, we could get the k_3k_6 value. Table 6 summarizes the results.

Table 6. Rate Constants for Photochemical Processes of Naphthalene-TEA System in PFH and Hexane at 25 °C

	PFH	Hexane
$10^{-6} k_1$ s^{-1}	2.1	1.8
$10^{-6} k_2$ s^{-1}	8.5	6.6
$10^{-15} k_3k_5$ s^{-2} M^{-1}	2.5	1.6
$10^{-16} k_3k_6$ s^{-2} M^{-1}	7.2	0.94
k_6/k_5	29	6

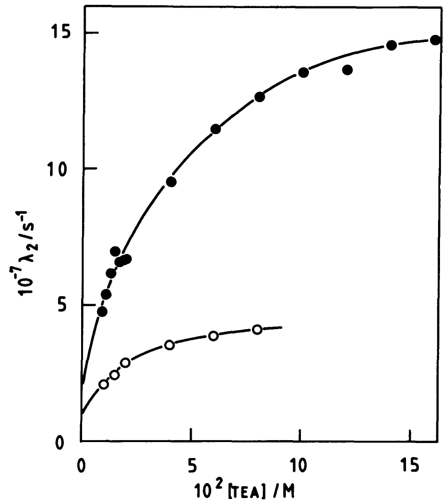


Fig. 7. Plots of λ_2 vs. [TEA] for the pyrene–DMA exciplex in PFH (●) and hexane (○) at 7 °C.

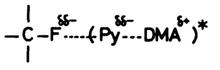
Discussion

The photochemical processes of the fluorophores such as pyrene, anthracene, and naphthalene in the presence of aromatic or aliphatic amines have been well known to be dependent on solvent polarity.[14] In nonpolar solvents, these fluorophores in the excited singlet states form the exciplexes in collision with amines while direct electron transfers from amines to photoexcited fluorophores occur without exciplex formation in strongly polar solvents. If an exciplex is fluorescent, the emission maximum of the exciplex shifts to longer wavelength with increasing solvent polarity because the exciplex having an electronically polar structure is solvated to a large extent by polar solvent. These characteristics of exciplex seem to be suitable for investigating the interaction between photoexcited solute and perfluorocarbon solvent. Especially, exciplexes may be very interesting probes for studing interaction of electronically polar solute with perfluorinated solvent, which has not been examined.

Fluorescence Quenching. The fluorescence quenching of pyrene and anthracene by DMA and of naphthalene by TEA was carried out in PFH, hexane, and cyclohexane. As indicated in Fig. 3 and Table 3, the fluorescence quenching in PFH proceeds much faster than that in hexane and cyclohexane. In the case of pyrene, the k_q values obtained at 7 °C are considerably larger than those at 25 °C. This should be due to the back reaction of the pyrene–DMA exciplex to the original precursors, pyrene in the excited singlet state and DMA in the ground state. The back reaction is accelerated at higher temperature.[18] Very efficient fluorescence quenching occurred in the anthracene–DMA system in PFH, the k_q values being $3.44\times10^{10}\,M^{-1}\,s^{-1}$ ($1\,M=1\,mol\,dm^{-3}$) at 7 °C and $2.23\times10^{10}\,M^{-1}\,s^{-1}$ at 25 °C. Since the viscosity (η) of PFH at 20 °C is 0.7 cP (1 P=0.1 Pas), the diffusion-controlled rate constant (k_{diff}) is calculated to be $1.4\times10^{10}\,M^{-1}\,s^{-1}$ using Stokes–Einstein–Smoluckowski's equation, $k_{diff}=8RT/(2000\eta)$. The k_q values are much larger than the calculated k_{diff} value. Then we measured the fluorescence lifetime of the anthracene monomer at each DMA concentration to obtain k_q for dynamic quenching. The Stern–Volmer plots for the fluorescence lifetimes provided the k_q values of $1.59\times10^{10}\,M^{-1}\,s^{-1}$ at 7 °C and $1.79\times10^{10}\,M^{-1}\,s^{-1}$ at 25 °C, which are very close to the calculated k_{diff} value. These results indicate the occurrence of a static quenching in this system. Although the mechanism of the static quenching is not clear, one possibility is the formation of ground-state aggregates of anthracene and DMA due to low solubilities of these solute molecules in PFH. In the case of the pyrene–DMA system, however, the fluorescence decay curve (see Fig. 4) indicates that the exciplex forms dynamically. The efficient fluorescence quenching of pyrene by DMA in PFH, therefore, cannot be interpreted in terms of the ground-state aggregates.

Pyrene–DMA System. We determined the rate constants for the photochemical processes of the pyrene–DMA system according to the procedures described in detail by Cheung and Ware.[18] The results are summarized in Table 5. Since the fluorescence rise time of the pyrene–DMA exciplex was so short in PFH at 25 °C that the measurements were undertaken at 7 °C. The exciplex formation for the pyrene–DMA system has been verified to be diffusion-controlled process.[18,22] The k_3 values in cyclohexane at 20 °C and in hexane at 7.6 °C have been reported to be 9.8×10^{9} and $1.37\times10^{10}\,M^{-1}\,s^{-1}$, respectively.[18,22] The k_3 value ($1.5\times10^{10}\,M^{-1}\,s^{-1}$) in hexane at 7 °C obtained in the present study is in good agreement with the reported value. The k_3 value in PFH is the same as that in hexane. As mentioned above, the Stokes–Einstein–Smolukowski's equation predicts that k_{diff} in PFH is $1.4\times10^{10}\,M^{-1}\,s^{-1}$ at 20 °C which is very close to k_3 obtained in this study.

The large difference between PFH and hexane was found in the k_4 and k_6 values. The fluorescence quenching rate constant, k_q, is represented as Eq. 12. The large k_q value in PFH, therefore, is ascribed to the smaller k_4 and larger k_6 values compared with the case in hexane. If the solute-solvent interaction in PFH is very weak as predicted from ε and π^* values (Table 1), the back reaction of the exciplex (k_4) in PFH should be faster than that in hexane because of the smaller stabilization of the pyrene–DMA exciplex in PFH. The experimental result, however, is opposite from the assumption. Therefore, we have to consider the interaction between the exciplex and surrounding PFH molecules. Alford et al. have found that the fluorescence of TEA is efficiently quenched by perfluorohydrocarbons such as PFMCH, octafluorocyclobutane, and perfluoro-2-butene in both vapor and liquid phases.[12] In cyclohexane, k_q for the fluorescence quenching of TEA by PFMCH is $1.3\times10^{10}\,M^{-1}\,s^{-1}$. Alford et al. assumed a charge-transfer (CT) interaction as the fluorescence quenching mechanism. Similarly, the fluorescence of hydrocarbons such as cyclohexane, decalin, and 2,3-dimethylbutane is also quenched by perfluorohydrocarbons such as PFMCH and perfluorodecalin.[13] Choi and Lipsky proposed a quenching mechanism involving charge transfer from photoexcited hydrocarbons to perfluorohydrocarbons.[13] In the case of pyrene, the fluorescence quantum yield (Φ_{M0}) and lifetime (τ_0) of the pyrene monomer in PFH without quencher are somewhat smaller than those in hexane (see Tables 3 and 4). Although CT interaction between photoexcited pyrene and PFH may be accounted for the smaller Φ_{M0} in PFH, the quenching by PFH was not so remarkable. Meanwhile, since the pyrenyl moiety of the exciplex is negatively charged and is expected to have a lower ionization potential compared with photoexcited pyrene, it can be expected to transfer the negative charge of the pyrenyl moiety to the strongly electronegative fluorine atom(s) of PFH:



$$-\overset{|}{\underset{|}{C}}-\overset{\delta\delta-}{F}\cdots\cdots(\overset{\delta\delta-}{Py}\cdots\overset{\delta+}{DMA})^*$$

The CT interaction between the exciplex and PFH may decelerate the back reaction of the exciplex and accelerate the radiationless deactivation of the exciplex leading to smaller k_4 and larger k_6. If the CT interaction stabilizes the exciplex, the fluorescence maximum of the exciplex may shifts to longer wavelength in PFH. No novel behavior of PFH, however, was observed in the plot of ν_E vs. $f(\varepsilon,n)$ as shown in Fig. 2. In the present stage, we do not have any experimental data to explain the fluorescence maximum of the pyrene-DMA exciplex in PFH. Presumably, the Franck–Condon ground state of the exciplex should be considered to answer this problem. The Franck–Condon ground state may still interact with PFH because PFH interacting with the exciplex can be regarded microscopically as a sort of a polar solvent. Another plausible mechanism for the smaller k_4 value in PFH is the self association of the exciplex. It can be assumed that the activation energy due to weak association of the exciplex causes the deceleration of the back reaction of the exciplex. However, this mechanism should be excluded by the fact that the fluorescence quenching of pyrene in PFH obeys a simple Stern–Volmer linear relationship (see Fig. 3).

Naphthalene–TEA System. In this system, we could not determined all rate constants for the photochemical processes because of a very fast rise of the exciplex emission intensity. However, we could evaluate the k_6/k_5 values as mentioned in the Results Section. As Table 6 shows, the k_6/k_5 value in PFH is much larger than that in hexane. Judging from the results obtained for the pyrene–DMA system, it may be reasonable to assume that the k_5 value for PFH does not differ largely from that for hexane. The radiationless deactivation of the exciplex in PFH, therefore, should be much faster than that in hexane as the case of the pyrene–DMA system. The CT interaction between the polar naphthalene–TEA exciplex and PFH may accelerate the radiationless deactivation.

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