Bull. Chem. Soc. Jpn., 57, 2700—2702 (1984) [Vol. 57, No. 10

Internal Heavy Atom Effects on the Exciplex Fluorescence: Anthracene-*N,N*-Dimethylaniline System

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(Received February 6, 1984)

Intrinsic fluorescence yields of exciplexes, ϕ_f^0, have been determined for halogenated systems of anthracene (A)-*N,N*-dimethylaniline (DMA) in cyclohexane. By the substitution of a chlorine atom for a hydrogen atom in either A or DMA, ϕ_f^0 is reduced to about 1/5, whereas by the bromine substitution it is reduced to about 1/80. When more than one halogen atom of the same kind are substituted in the A-DMA exciplex, the first substitution causes more prominent reduction in ϕ_f^0 than the subsequent substitution does. Although there is a remarkable irregularity in the fluorescence quantum yields of halogenated anthracenes which were used as the electron acceptors in the exciplexes, ϕ_f^0 varies regularly according to the kind and the number of the halogen substitutions. The internal heavy atom effect on ϕ_f^0 is explained by the enhancement of the intersystem crossing rate to the triplet state.

It has been well established that heavy atoms such as halogens affect many relaxation processes in excited molecules.[1] The fluorescence yields of benzene[2], naphthalene,[3,4] and phenanthrene[5] are reduced by the substitution of a halogen atom, demonstrating the internal heavy atom effect. On the other hand, fluorescence yields of halogen-substituted anthracenes are known not to exhibit such normal heavy atom effects. The fluorescence yields of anthracene, 9,10-dichloroanthracene, 9-bromoanthracene, and 9,10-dibromoanthracene have been reported to be 0.36 (in cyclohexane),[6] 0.55 (in cyclohexane),[6] 0.018 (in 2,2-dimethylbutane/pentane (8:3)),[7] and 0.094 (in cyclohexane).[8] The anomalous photophysical properties including "inverse heavy atom quenching" of halogenated anthracenes are explained by the small energy gap between the first excited singlet state (S_1) and the second excited triplet state (T_2) through which the nonradiative crossing occurs, and by the energy level inversion caused by the substitution between these two states.[9–11] In anthracene derivatives, which of the S_1 and T_2 states is higher than the other is governed critically by the kind(s) and position(s) of the substituent group(s).

Only a few studies have been made on the fluorescence of the halogen-substituted exciplex systems. For the exciplexes of benzo[*ghi*]perylene and dibenzo[*def, mno*]chrysene with *p*-chloro-*N,N*-dimethylaniline, Watkins has reported the reduction in the fluorescence yields of these exciplexes.[12,13] No exciplex fluorescence has been observed for the systems of some 9- or 9,10-substituted anthracene–bromobenzene derivatives.[14] In the case of the intramolecular charge-transfer states of 6-(arylamino)-2-naphthalenesulfonate derivatives, the fluorescence yields have been found not to be influenced by the halogen substitution.[15]

The aim of this work is to investigate systematically how the halogen substitution on the individual component constituting the exciplex affects the fluorescence yield of the exciplex. Anthracene–*N,N*-dimethylaniline, which is a typical exciplex,[16] was chosen as an unsubstituted parent exciplex.

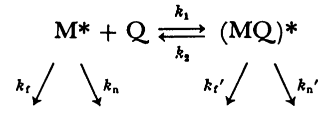
Experimental

Anthracene (A) was obtained from Wako, 1-chloroanthracene (CA) from Aldrich, 9,10-dichloroanthracene (DCA) from Tokyo Kasei, 9-bromoanthracene (BA) from Aldrich, and 9,10-dibromoanthracene (DBA) from Tokyo Kasei. Anthracene and its halogen derivatives were purified by column chromatography. *N,N*-Dimethylaniline (DMA) purchased from Tokyo Kasei was distilled under reduced pressure. *p*-Chloro-*N,N*-dimethylaniline (CDMA) was synthesized from *N,N*-dimethyl-*p*-phenylenediamine by the Sandmeyer reaction,[17] and recrystallized twice from ethanol. *p*-Bromo-*N,N*-dimethylaniline (BDMA) obtained from Fluka AG was recrystallized twice from cyclohexane. Cyclohexane, used as the solvent, was percolated through a silica-gel column.

Absorption spectra were measured with a Hitachi 124 spectrophotometer, and fluorescence spectra were recorded on a Shimadzu RF-501 spectrofluorophotometer equipped with a cooled EMI 9789 QA photomultiplier. Fluorescence was viewed at right angles to the direction of excitation. Fluorescence spectra were corrected for the spectral response of the detection system. The correction factor was obtained by the previously described method[18] employing a Rhodamine B quantum counter (below 600 nm) and a standard solution method[19] using 4-(dimethylamino)-4′-nitrostilbene (above 600 nm). Measurements were made on cyclohexane solutions of a fixed concentration of anthracene (2×10^{-5} mol dm^{-3}) or halogenated anthracene (1×10^{-5} mol dm^{-3}) and the varying concentrations of DMA derivatives. Samples for fluorescence measurements were nitrogen bubbled. 9.10-Diphenylanthracene in deaerated cyclohexane was used as a standard ($\phi_f=0.90$) for the fluorescence yield determinations.[20] All the measurements were made at 25±0.1 °C.

Results and Discussion

For every combination of the electron donor (DMA or its derivative) and the electron acceptor (A or its derivative) used in this work, the exciplex fluorescence was observed. As is usually the case the exciplex fluorescence is structureless and red-shifted from the monomer fluorescence of A or its derivative.[21] The positions of the fluorescence maxima of the exciplexes involving the same acceptor have been found to be independent of the kind of the donor to within ≈5 nm. In addition, the energy differences between the acceptor and its exciplex fluorescence have been found to be nearly constant, irrespective of the kind of acceptor. These results suggest that the geometrical structure and the potential energy curve of the halogen-substituted exciplex are similar to those of the unsubstituted exciplex A–DMA. The exciplex formation can be described by the following scheme:[22]



$$\begin{array}{ccc} M^* + Q & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & (MQ)^* \\ k_f \swarrow \quad \searrow k_n & & k_f' \swarrow \quad \searrow k_n' \\ M+h\nu_f \quad M & & M+Q+h\nu_f' \quad M+Q \end{array}$$

Here M* is anthracene (or its halogen derivative) in the excited singlet state, Q is DMA (or its halogen derivative), and (MQ)* is the exciplex formed between M* and Q. k_1, k_2, k_f, k_n, k_f', and k_n' are the rate constants for exciplex formation, exciplex dissociation, radiative transition of M*, nonradiative transition of M*, radiative transition of (MQ)*, and nonradiative transition of (MQ)*, respectively.

Under photostationary conditions, the relation between the intrinsic fluorescence yield of the exciplex, ϕ_f^0 $(=k_f'/(k_f'+k_n'))$, and the fluorescence yield of the exciplex, ϕ_f, at a given donor concentration [Q] is expressed by

$$\frac{1}{\phi_f} = \frac{1}{\phi_f^0} + \frac{(k_f+k_n)(k_2+k_f'+k_n')}{k_1 k_f'}\,\frac{1}{[Q]}.$$

The intrinsic fluorescence yield ϕ_f^0 can be evaluated from a plot of $1/\phi_f$ *vs.* 1/[Q]. As typical examples, plots for A–DMA, A–CDMA, and A–BDMA are displayed in Fig. 1. From the intercepts of the straight lines as shown in Fig. 1, the intrinsic fluorescence yields ϕ_f^0 for all the combinations of the donor and acceptor have been determined. They are listed in Table 1.[23] Also included in Table 1 are the fluorescence yields, ϕ_f(monomer), of anthracene and of its halogen derivatives.

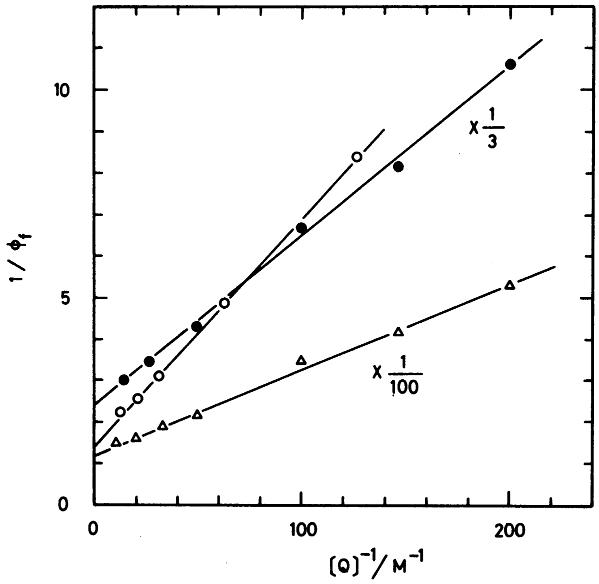


Fig. 1. Plots of $1/\phi_f$ *vs.* 1/[Q].
○: A–DMA, ●: A–CDMA, △: A–BDMA.

Table 1. Intrinsic fluorescence yields of exciplexes (ϕ_f^0) and fluorescence yields of their component acceptors (ϕ_f(monomer)) in cyclohexane

	ϕ_f(monomer)	ϕ_f^0		
		DMA	CDMA	BDMA
A	0.32	0.72	0.14	0.0083
CA	0.11	0.14	0.071	0.0053
DCA	0.60	0.087	0.080	0.0056
BA	0.013	0.0086	0.0075	0.0041
DBA	0.13	0.0047	0.0049	0.0038

It can be seen from Table 1 that the value of ϕ_f^0 in every row drops in going from left to right (with the increase in the atomic number of the heavy atom in the electron donor). The only exception for this trend is ϕ_f^0 of DBA–CDMA, which is the same as that of DBA–DMA within experimental uncertainties. The substitution of the chlorine atom in A–DMA decreases ϕ_f^0 to about 1/5, whereas the bromine substitution decreases ϕ_f^0 to about 1/80. Such regularity in ϕ_f^0 is further confirmed by looking at ϕ_f^0 in the columns of Table 1 (the exciplexes consisting of the same electron donor). As in the case of the rows (the exciplexes consisting of the same electron acceptor), ϕ_f^0 decreases in going from top to bottom. Table 1 also shows that the values of ϕ_f^0 do not depend on whether the halogen atom is substituted in the donor or acceptor component (*e.g.*, for the case of A–CDMA and CA–DMA *etc.*). When two halogen atoms of the same kind are introduced in the exciplex, ϕ_f^0 is further reduced by the second substitution of the halogen atom. However, the effect of the second substitution on ϕ_f^0 is much less than that of the first one.

The ratio of the exciplex fluorescence yield of the monosubstituted exciplex to that of the unsubstituted exciplex, *R*, is 0.19 for the chlorine-atom substitution (both for CA–DMA and A–CDMA), whereas *R* is 0.012 for the bromine-atom substitution (both for BA–DMA and A–BDMA). The ratio of the fluorescence yield of the halogenated aromatic monomer to that of the unsubstituted parent monomer has been reported to be 0.081 for chlorobenzene and <0.002 for bromobenzene at room temperature.[2] Moreover, these ratios have been found to be 0.080 and 0.017 for 1-chloronaphthalene and 1-bromonaphthalene, respectively.[4] Thus, both for chlorine and bromine substitution, the values of *R* for the A–DMA exciplex system are comparable with the reported values for benzene and naphthalene monomers, except for bromobenzene. It appears, therefore, that the internal heavy atom effect on the exciplex fluorescence is caused by a similar mechanism to that in the case of the aromatic monomer fluorescence, that is, by a normal heavy atom effect enhancing the rate of the intersystem crossing to the triplet state as the deactivation process.

The first excited singlet state of anthracene is lowered by 4200 cm^{-1} by virtue of the exciplex formation with DMA.[16] For the halogen-substituted exciplexes, almost the same stabilization energy is expected from their similar spectroscopic characteristics. On the other hand, laser photolysis studies on the systems of A–DMA and A–*N*,*N*-diethylaniline have revealed that the triplet state produced from the singlet exciplex is the triplet state of not the exciplex but of anthracene itself.[24,25] Although the energy level of the triplet exciplex is unknown, this fact indicates that the triplet state of the exciplex, to which the singlet exciplex decays, is dissociative.

On the basis of these facts, the result that ϕ_f^0 is regularly and stepwisely reduced by the halogen substitution in the A–DMA exciplex system may be explained as follows. In contrast to halogenated anthracene, no inversion of the energy level between the first excited singlet state and the second triplet state occurs in the halogenated exciplexes of the A–DMA systems. Therefore, the intersystem crossing rate to the triplet state, which immediately dissociates to the triplet state of the halogenated anthracene, is accelerated by the substitution of halogen.

With respect to the heavy atom effect for the triplet exciplex, detailed studies of Steiner and Winter were performed by flash spectroscopy.[26,27] They have determined the radical yields and rate constants in the quenching reaction of thionine triplet with the series of monohalogen substituted anilines.[26] The radical yield decreases with increasing the spin-orbit coupling constant of the halogen substituent. This result is explained in terms of the internal heavy atom effect on the T→S_0 intersystem crossing rate in the triplet exciplex.[26,27] The internal heavy atom effects in the singlet exciplexes of the A–DMA systems found in this study are thus qualitatively similar to those observed for the triplet exciplexes.

The author wishes to thank Professor Fumio Hirayama for his valuable discussion.

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