

# Fluorescence study on polar intramolecular exciplexes of (9-phenanthroxy)alkyl *p*-cyanobenzoates

Masahide Yasuda \*, Goro Kuwamura, Kensuke Shima

Department of Materials Science, Faculty of Engineering, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-21, Japan

Received 25 May 1994; accepted 9 August 1994

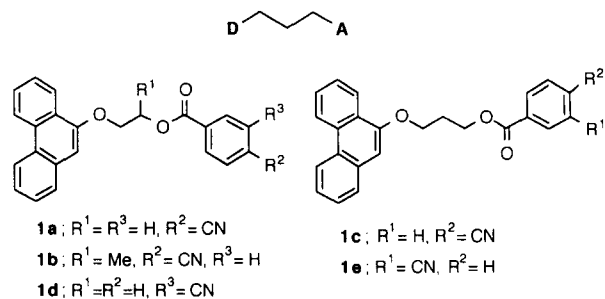
## Abstract

Intramolecular exciplex (EX)-formation system involving phenanthrene and cyanobenzoate moieties, (9-phenanthroxy)-alkyl cyanobenzoate (**1a–c**), were investigated in terms of emission maxima, lifetimes, and quantum yields of the emissions from the locally excited state and the EX state. The intense EX emissions of **1a–c** were observed in seven kinds of solvents from cyclohexane to dichloromethane. From the solvent effects on EX emission maxima, the dipole moments of the EX of **1a–c** were calculated to be 15–16 D. Moreover the deviation of the emission maxima in benzene and toluene from the Mataga–Lippert plots was observed, showing that the EX was stabilized by termolecular interaction of EX with these solvents.

**Keywords:** Fluorescence; Intramolecular exciplexes; Solvent effect

## 1. Introduction

The electronic structure of exciplexes (EX) has been elucidated by analysis of the decay profiles, the quantum yields, and the emission maxima of the EX emission. Especially, solvent effects on these parameters provide significant information to deduce the charge transfer character of EX [1]. In general, many of the exciplex systems do not show the EX emission in wide range of solvents from non-polar to polar solvents, because of poor stabilization energy of EX in non-polar solvents and of the dissociation of EX into ion radicals in polar solvents. We have designed the intramolecular exciplex formation system in order to observe the intense EX emission in wide range of solvent polarity. The electron donor–acceptor system linked by various bridges has been used for the investigation of the intramolecular exciplex formation systems [2–4], the long-range electron transfer [5], and the twisted intramolecular charge transfer [6]. The EX formation system of arene (ArH)-bridge-electron acceptor have been scarcely reported [7], although many ArH-bridge-electron donor systems, e.g. ArH-spacer-amines, have been investigated [3,5a,c,d]. Here, we report the solvent effect on an intramolecular exciplex-formation system involving



Scheme 1.

phenanthrene and cyanobenzoate moieties, (9-phenanthroxy)alkyl cyanobenzoate (**1**) (Scheme 1).

## 2. Experimental details

### 2.1. Instruments

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were taken on a Bruker 250P spectrometer. Mass spectra (MS) were obtained using a Hitachi 2000A spectrometer. Fluorescence spectra and UV spectra were measured on a Hitachi 850 spectrometer and a Hitachi 150-20 spectrometer, respectively. Fluorescence lifetimes were measured on a Horiba NAES 550 spectrometer by single-photon-counting method. Oxidation and reduction potentials were measured in acetonitrile

\* Corresponding author.

on a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator using Ag/AgNO<sub>3</sub> as a reference electrode.

## 2.2. Materials

Spectral grade solvents were used without the further purification. (9-Phenanthroxy)alkyl bromide was prepared from the reaction of 9-phenanthrol with di-bromoalkane in the presence of aqueous KOH and tetraethylammonium bromide. (9-Phenanthroxy)alkyl cyanobenzoates (**1a–e**) were prepared by the reaction of (9-phenanthroxy)alkyl bromide with *m*- and *p*-cyanobenzoic acids in the presence of Na<sub>2</sub>CO<sub>3</sub> and *n*-Bu<sub>4</sub>NBr. Purification was performed by repeated recrystallization from methanol. Spectral data are shown as follows:

2-(9-Phenanthroxy)ethyl *p*-cyanobenzoate (**1a**): melting point (m.p.) 143–144 °C (from MeOH). <sup>1</sup>H NMR δ 4.52 (2H, t, *J*=8.9 Hz), 4.85 (2H, t, *J*=8.9 Hz), 6.96 (1H, s), 7.46–7.74 (7H, m), 8.10 (2H, d, *J*=8.1 Hz), 8.35 (1H, d, *J*=7.9 Hz), 8.55 (1H, d, *J*=7.3 Hz), 8.61 (1H, d, *J*=8.0 Hz); <sup>13</sup>C NMR δ 64.01, 65.93, 103.06, 116.46, 117.94, 122.46, 122.54, 122.54, 124.61, 126.29, 126.50, 126.62, 127.02, 127.34, 130.17, 131.28, 132.18, 132.52, 133.58, 152.27, 164.93. Calc. for C<sub>23</sub>H<sub>17</sub>NO<sub>3</sub>: C; 78.46, H; 4.66, N; 3.81; Found C; 78.21, H; 4.71, N; 3.89.

3-(9-Phenanthroxy)-2-propyl *p*-cyanobenzoate (**1b**): m.p. 147.5–148.2 °C (from MeOH); <sup>1</sup>H NMR δ 1.62 (3H, d, *J*=6.5 Hz), 4.39 (2H, d, *J*=5.0 Hz), 5.68–5.77 (1H, m), 6.97 (1H, s), 7.47–7.74 (7H, m), 8.10 (2H, d, *J*=6.9 Hz), 8.3 (1H, d, *J*=7.9 Hz), 8.50–8.61 (2H, m). <sup>13</sup>C NMR δ 16.79, 70.09, 70.48, 103.03, 116.29, 117.89, 122.34, 122.46, 122.46, 124.50, 126.30, 126.42, 126.56, 126.92, 127.23, 127.23, 130.05, 131.23, 132.06, 132.52, 134.01, 152.26, 164.45. Calc. for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>: C; 78.72, H; 5.02, N; 3.67; Found C; 78.10, H; 4.81, N; 3.54.

3-(9-Phenanthroxy)propyl *p*-cyanobenzoate (**1c**): m.p. 153–154 °C (from MeOH). <sup>1</sup>H NMR δ 2.39–2.49 (2H, m), 4.38 (2H, t, *J*=5.9 Hz), 4.68 (2H, t, *J*=4.7 Hz), 6.96 (1H, s), 7.46–7.75 (7H, m), 8.08 (2H, d, *J*=8.5 Hz), 8.33 (1H, d, *J*=8.1 Hz), 8.56 (1H, d, *J*=7.3 Hz), 8.62 (1H, d, *J*=8.2 Hz); <sup>13</sup>C NMR δ 28.74, 63.08, 64.50, 102.74, 116.40, 118.04, 122.48, 122.60, 122.64, 124.48, 126.44, 126.44, 126.55, 127.03, 127.31, 127.31, 130.12, 131.32, 132.23, 132.79, 133.97, 152.49, 164.99. Calc. for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>: C; 78.72; H; 5.02; N; 3.69%. Found: C; 78.98; H; 5.03; N; 3.89%.

2-(9-Phenanthroxy)ethyl *m*-cyanobenzoate (**1d**): m.p. 134.0–135.0 °C (from MeOH) <sup>1</sup>H NMR δ 4.56 (2H, t, *J*=4.8 Hz), 4.88 (2H, t, *J*=4.8 Hz), 7.00 (1H, s), 7.48–7.80 (7H, m), 8.24–8.38 (2H, m), 8.38 (1H, s), 8.54–8.65 (2H, m); <sup>13</sup>C NMR δ 63.94, 66.00, 103.17, 112.97, 117.74, 122.43, 122.50, 122.50, 124.57, 126.31, 126.65, 126.96, 127.31, 127.31, 129.40, 131.14, 131.29, 132.51, 133.32,

133.68, 136.07, 152.27, 164.56; Calcd for C<sub>24</sub>H<sub>17</sub>NO<sub>3</sub>: C; 78.46, H; 4.66, N; 3.81; Found C; 78.20, H; 4.55, N; 3.73%.

3-(9-Phenanthroxy)propyl *m*-cyanobenzoate (**1e**): m.p. 127.5–128.2 °C (from MeOH), <sup>1</sup>H NMR δ 2.39–2.49 (2H, m), 4.38 (2H, d, *J*=5.9 Hz), 4.68 (2H, d, *J*=6.3 Hz), 6.97 (1H, s), 7.45–7.78 (7H, M), 8.19–8.34 (3H, m), 8.54–8.63 (2H, m); <sup>13</sup>C NMR δ 28.66, 62.94, 64.37, 102.69, 112.87, 117.82, 122.37, 122.46, 122.51, 126.34, 126.34, 126.46, 126.89, 127.16, 127.26, 129.33, 131.22, 131.38, 132.69, 133.14, 133.56, 135.89, 152.38, 164.53. Calc. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>: C; 78.72, H; 5.02, N; 3.67; Found C; 78.71, H; 4.87, N; 3.63%.

## 2.3. Measurement of fluorescence spectra

Measurements of the fluorescence spectra and fluorescence lifetimes were performed for a deaerated solution containing **1**, the concentration of which was adjusted for absorbance to be less than 0.05. Quantum yields for fluorescence were determined at room temperature for a solution containing **1**, using phenanthrene as an actinometer (the quantum yield is 0.13 in MeCN) [8].

## 3. Results

Fluorescence spectra of **1a–e** were measured in cyclohexane (CH), benzene (BZ), toluene (TL), dibutyl ether (BE), diisopropyl ether (PE), 1,2-diethoxyethane (DE), and dichloromethane (DM). The fluorescence spectra of **1a–c** showed an emission at 360, 370, and 390 nm independently on solvent polarity and an emission at a range from 420 to 527 nm dependently on solvent polarity. The former emission was similar to that of 9-methoxyphenanthrene (**2**), revealing that the emission came from the locally excited state (LE) of 9-phenanthroxy moiety (D) of **1a–c**. The latter one can be attributed to the emission from the exciplex (EX) formed between D and the *p*-cyanobenzoate moiety (A). The EX emissions were observed in seven kinds of solvents from CH to DM, but not observed in acetonitrile. As a typical example, Fig. 1 shows the fluorescence spectra of benzene solutions of **1a–c** compared with that of **2** in the presence of propyl *p*-cyanobenzoate where the fluorescence of **2** was efficiently quenched by propyl *p*-cyanobenzoate but showed very weak EX emission. Thus, the linking of D with A was effective to observe intense EX emission. However, remarkable EX emissions were not observed in the cases of **1d** and **1e** in various solvents, showing that *m*-cyanobenzoate moiety was not effective for the formation of EX. The EX emission maxima (λ<sub>max</sub>) of **1a–c** were summarized in Table 1.

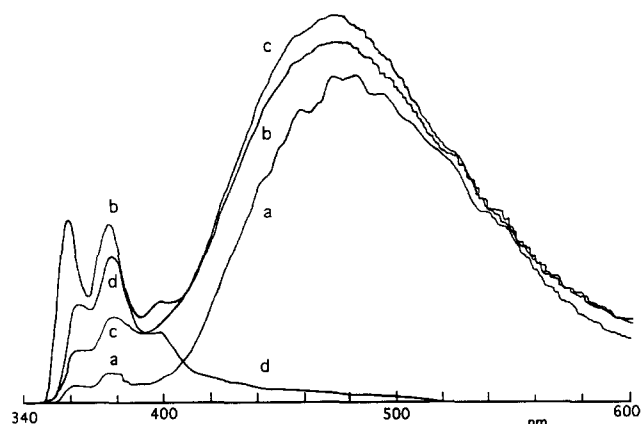


Fig. 1. Fluorescence spectra of benzene solutions of (a) **1a**, (b) **1b**, (c) **1c**, and (d) the fluorescence spectrum of **2** in the presence of propyl *p*-cyanobenzoate [ $7.5 \times 10^{-3}$  mol dm $^{-3}$ ] in BZ.

Table 1  
Emission maxima of **1a–c** in various solvents

Solvent <sup>a</sup>	$f(\epsilon, n)$ <sup>b</sup>	$\tau_M$ <sup>c</sup> (ns)	$\lambda_{\max}$ (nm) <sup>d</sup>		
			<b>1a</b>	<b>1b</b>	<b>1c</b>
CH	0.101	29	425	425	420
BZ	0.117	25	472	475	475
TL	0.127	26	477	475	475
BE	0.192	29	470	463	454
PE	0.237	29	474	468	468
DE	0.270	29	498	489	492
DM	0.320	13	520	527	527

<sup>a</sup> CH, cyclohexane; BZ, benzene; TL, toluene; BE, dibutyl ether; PE, diisopropyl ether; DE, 1,2-diethoxyethane; and DM, dichloromethane.

<sup>b</sup> Solvent polarity;  $f(\epsilon, n) = (\epsilon - 1)/(2\epsilon - 1) + (n^2 - 1)/(4n^2 + 2)$ .

<sup>c</sup> Lifetime of fluorescence of **2**.

<sup>d</sup> Exciplex emission maxima.

The lifetimes ( $\tau_{LE}$  and  $\tau_{EX}$ ) and the quantum yields ( $\Phi_{LE}$  and  $\Phi_{EX}$ ) for the fluorescences from LE and EX states were measured in seven kinds of solvents. The results are summarized in Table 2.

## 4. Discussion

### 4.1. Kinetic analysis

Scheme 2 shows EX formation system involving radiative and nonradiative decays from the LE and EX states. For kinetic analysis, **2** was used as a model compound for the analysis of the LE state without the interaction with A. The  $\tau_{LE}$  of **1** were much smaller than the fluorescence lifetimes ( $\tau_M$ ) of **2** which were measured to be 25–29 ns independently on solvent polarity except for DM (Table 1). The rate constants ( $k_{ex}$ ) for the exciplex formation between D and A of **1a–c** can be reduced by Eq. (1).

$$\tau_{LE}^{-1} = \tau_M^{-1} + k_{ex} \quad (1)$$

$$\Phi_{LE} = k_f / (k_f + k_d + k_{ex}) = k_f \tau_{LE} \quad (2)$$

$$k_f = \Phi_{LE} / \tau_{LE} \quad (3)$$

$$k_d = \tau_M^{-1} - k_f \quad (4)$$

$$\begin{aligned} \Phi_{EX} &= k_f^{ex} / (k_f^{ex} + k_d^{ex}) k_{ex} / (k_f + k_d + k_{ex}) \\ &= k_f^{ex} k_{ex} \tau_{LE} \tau_{EX} \end{aligned} \quad (5)$$

$$k_f^{ex} = \Phi_{EX} / (k_{ex} \tau_{LE} \tau_{EX}) \quad (6)$$

$$k_d^{ex} = \tau_{EX}^{-1} - k_f^{ex} \quad (7)$$

The rate constant ( $k_f$ ) for the radiative decay from LE state was calculated by Eq. (3) using  $\Phi_F$  and  $\tau_{LE}$ . The rate constant ( $k_d$ ) for the nonradiative decay from LE state was calculated by Eq. (4). Since  $\Phi_{EX}$  is represented by Eq. (5), the rate constants ( $k_f^{ex}$  and  $k_d^{ex}$ ) for the radiative and the nonradiative decays from the EX state were calculated by Eqs. (6) and (7) respectively. The nonradiative decay from EX involves the thermal decay, intersystem crossing to the triplet state, and the electron transfer from D to A. These rate constants were summarized in Table 2.

The  $k_f$  and  $k_d^{ex}$  of **1a–c** were nearly constant in solvents used except for DM which had heavy-atom effect. The  $k_f^{ex}$  gradually decreased as solvent polarity increased. The  $k_d^{ex}$  increased remarkably in DM probably due to the occurrence of electron transfer. The  $k_{ex}$  values of **1a** were almost same as that of **1c** irrespective the length of methylene bridge while  $k_{ex}$  values of **1b** were slightly lower than those for **1a**.

### 4.2. Electronic Structure of Intramolecular EX

The energy of EX ( $E_{ex}$ ) is represented by Eq. (8) where  $I_p$  and  $E_a$  are the ionization potential of D and the electron affinity of A, respectively,  $C$  is the Coulombic interaction energy between the cation radical of D and the anion radical of A,  $\mu$  is the dipole moment of EX, and  $\rho$  is the effective radius of the solvent cavity (Scheme 2). A summation of the half-peak of oxidation potential of D ( $E^{ox}$ ) and the half-peak of the reduction potential of A ( $E^{red}$ ) can be used instead of the summation of  $I_p$  and  $E_a$  in Eq. (8).

$$E_{ex} = I_p - E_a - C - \mu^2 / \rho^3 f(\epsilon, n) \quad (8)$$

$$f(\epsilon, n) = (\epsilon - 1) / (2\epsilon - 1) + (n^2 - 1) / (4n^2 + 2)$$

$$I_p - E_a = E^{ox} - E^{red}$$

$$h\nu = E_{ex} - E_{sol} \quad (9)$$

$$E_{sol} = \mu^2 / \rho^3 f(\epsilon, n)$$

$$\nu_{ex} (\text{cm}^{-1}) = \nu_0 - 2\mu^2 / (hc\rho^3) f(\epsilon, n) \quad (10)$$

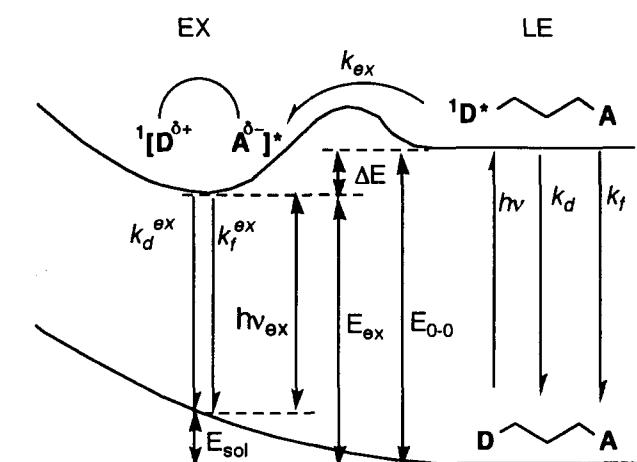
$$\nu_0 = (E^{ox} - E^{red} - C) / (hc)$$

$$\Delta E = E_{ex} - E_{0-0} \quad (11)$$

Table 2

Lifetime and quantum yield for fluorescence of **1a–c** in various solvents

<b>1</b>	Solvent	$\tau_{LE}$ (ns)	$(\Phi_{LE})^a$	$\tau_{EX}$ (ns)	$(\Phi_{EX})^b$	$k_{ex}^c$ ( $10^8$ s $^{-1}$ )	$k_f^d$ ( $10^6$ s $^{-1}$ )	$k_d^e$ ( $10^7$ s $^{-1}$ )	$k_f^{ex,f}$ ( $10^6$ s $^{-1}$ )	$k_d^{ex,g}$ ( $10^7$ s $^{-1}$ )
<b>1a</b>	CH	2.3	(nd) <sup>h</sup>	13	(0.038) <sup>i</sup>	4.0	–	–	–	–
	BZ	1.1	(0.002)	16	(0.045)	8.7	1.8	3.8	3.0	5.9
	TL	1.5	(0.009)	14	(0.036)	6.3	6.0	3.3	2.7	6.9
	BE	2.8	(0.007)	14	(0.023)	3.2	2.5	3.2	1.8	7.0
	PE	1.7	(0.005)	13	(0.042)	5.5	2.9	3.2	3.5	7.3
	DE	0.8	(0.005)	9.2	(0.012)	12.2	6.3	2.8	1.3	10.8
	DM	0.5	(0.005)	3.4	(0.003)	29.2	10.0	6.7	0.9	29.4
<b>1b</b>	CH	2.7	(nd) <sup>h</sup>	14	(0.021) <sup>i</sup>	3.4	–	–	–	–
	BZ	2.5	(0.007)	12	(0.024)	3.7	2.8	3.7	2.2	8.1
	TL	2.4	(0.009)	12	(0.026)	3.8	3.8	3.5	2.4	8.1
	BE	3.1	(0.009)	16	(0.034)	2.9	2.9	3.2	2.4	6.0
	PE	2.9	(0.005)	14	(0.025)	3.1	1.7	3.3	2.0	6.9
	DE	2.7	(0.005)	10	(0.017)	3.4	1.9	3.3	1.9	9.8
	DM	1.2	(0.004)	3.6	(0.002)	7.6	3.3	7.4	0.6	27.7
<b>1c</b>	CH	1.6	(nd) <sup>h</sup>	6.2	(0.073) <sup>i</sup>	5.9	–	–	–	–
	BZ	1.2	(0.018)	16	(0.057)	7.9	1.5	2.5	3.8	5.9
	TL	1.4	(0.017)	16	(0.030)	6.7	1.2	2.7	2.0	6.1
	BE	1.5	(0.014)	11	(0.029)	6.1	0.9	2.5	2.9	8.8
	PE	1.5	(0.013)	10	(0.033)	6.4	0.9	2.6	3.4	9.7
	DE	0.7	(0.012)	6.7	(0.007)	13.9	1.8	1.7	1.1	14.8
	DM	0.9	(0.009)	6.4	(0.007)	10.3	1.0	6.7	1.1	15.5

<sup>a</sup> Fluorescence lifetimes of LE state. The values in parenthesis are the quantum yield.<sup>b</sup> Fluorescence lifetimes of EX state. The values in parenthesis are the quantum yield.<sup>c</sup> Rate constant for the formation of the EX.<sup>d</sup> Rate constant for the radiative decay from LE state.<sup>e</sup> Rate constant for nonradiative decay from LE state.<sup>f</sup> Rate constant for the radiative decay from EX state.<sup>g</sup> The rate constants for the nonradiative decay from EX.<sup>h</sup> Not determined.<sup>i</sup> EX emission was not separated from LE emission.

Scheme 2.

Since the Franck–Condon ground state may be destabilized by the solvation energy ( $E_{sol}$ ), the emission maxima ( $\nu_{ex}$ ) can be represented by Eq. (9) [1]. Thus, the wavenumber of the emission maxima ( $\nu_{ex}$ ; in  $\text{cm}^{-1}$ ) is related to  $\mu$  by the Mataga–Lippert equation (Eq. (10)), where  $h$ , Planck constant;  $c$ , light velocity, and

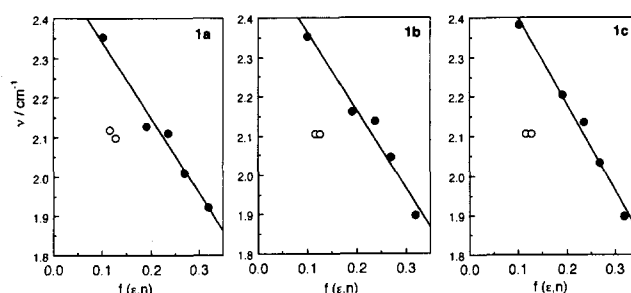


Fig. 2. Mataga–Lippert plots of EX emission maxima vs.  $f(\epsilon, n)$  in **1a–c**: The values (O) in BZ and TL deviate from the straight line.

$\epsilon$  and  $n$  are dielectric constant and refractive index of the solvent respectively [1,9]. Indeed Mataga–Lippert plots of  $\nu_{ex}$  of **1a–c** vs.  $f(\epsilon, n)$  gave good linear correlations except for the values in BZ and TL which deviated into shorter wavenumber from the straight lines, as shown in Fig. 2. The intercept of the Mataga–Lippert plot equals to  $(E^{ox} - E^{red} + C)/(hc)$ , thus giving the  $C$  value. Since  $\nu_{ex}$  values of **1** took almost identical values irrespective of the length of the methylene bridge, it is suggested that EX takes a sandwich-type structure. From the slope of the Mataga–Lippert plots which

Table 3  
Parameters for the EX state of 1a–c

	1a	1b	1c
$E^{\text{ox}}$ (V) <sup>a</sup>	0.98	0.98	0.94
$E^{\text{red}}$ (V) <sup>b</sup>	−1.96	−1.96	−2.02
Intercept ( $10^3 \text{ cm}^{-1}$ ) <sup>c</sup>	25.3	25.6	26.2
Slope ( $10^3 \text{ cm}^{-1}$ ) <sup>d</sup>	19.2	19.7	21.7
$E^{\text{ox}} - E^{\text{red}}$ (kcal mol <sup>−1</sup> )	67.8	68.3	68.3
$C$ (kcal mol <sup>−1</sup> ) <sup>e</sup>	−4.7	−4.9	−6.5
$\Delta E$ (kcal mol <sup>−1</sup> ) <sup>f</sup> CH	9.7	9.1	7.7
DM	15.7	15.2	14.5
$E_{\pi}$ (kcal mol <sup>−1</sup> ) <sup>g</sup> BZ	5.5	6.4	7.3
TL	5.6	5.8	6.7
$\mu$ (D) <sup>h</sup>	15.4	15.6	16.4

<sup>a</sup> Half-peak of oxidation potential.

<sup>b</sup> Half-peak of reduction potential.

<sup>c</sup> The intercept for Mataga–Lippert plots of Fig. 2.

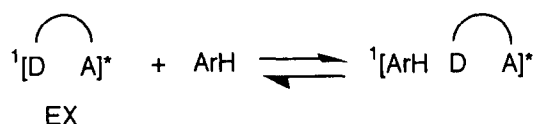
<sup>d</sup> The slope of Fig. 2.

<sup>e</sup> Coulombic interaction between the cation radical of D and the anion radical of A.

<sup>f</sup> Energy difference between LE state and EX state.

<sup>g</sup> Stabilization energy by  $\pi$ -chromophore.

<sup>h</sup> Dipole moments calculated from the slopes of Fig. 2 using  $\rho = 5 \text{ \AA}$ .



Scheme 3.

equal  $-2\mu^2(hc\rho^3)$ ,  $\mu$  are calculated to be 15.4–16.4 D for 1a–c by assuming  $\rho = 5 \text{ \AA}$ . These values of  $\mu$  for 1a–c are compatible to the values (15–16 D) reported for pure charge transfer state of the sandwich-type exciplexes [1]. The energy difference ( $\Delta E$ ) between LE and EX states calculated by Eq. (11) using 79.4 kcal mol<sup>−1</sup> of  $E_{0-0}$  are varied from 7.7–9.7 kcal mol<sup>−1</sup> for CH to 14.5–15.7 kcal mol<sup>−1</sup> for DM. The parameters described above are summarized in Table 3.

The deviations of the values in BZ and TL from the straight line of Fig. 2 are due to the stabilization by the termolecular interaction of EX with  $\pi$ -chromophore such as BZ and TL (Scheme 3). The stabilization energy ( $E_p$ ) of EX by these  $\pi$ -chromophores was calculated to be 5.5–7.3 kcal mol<sup>−1</sup> from Fig. 2.

## Acknowledgement

This work was supported by a Grant-in-Aid on Priority-Area Research, “Photoreaction Dynamics” from the Ministry of Education, Science and Culture, Japan, 06239109.

## References

- [1] N. Mataga, in M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975, p. 113.
- [2] J.W. Verhoeven, *Pure Appl. Chem.*, **62** (1990) 1585.
- [3] A.M. Swinnen, M. Van der Auweraer, F.C. De Schryver, T. Okada and N. Mataga, *J. Am. Chem. Soc.*, **109** (1987) 321; J.P. Palmans, A.M. Swinnen, G. Desie, M. Van der Auweraer, J. Vandendriessche, F.C. De Schryver and N. Mataga, *J. Photochem.*, **28** (1985) 419; A.M. Swinnen, M. Van der Auweraer and F.C. De Schryver, *J. Photochem.*, **28** (1985) 315; N.C. Yang, R. Gerald II and M.R. Wasielewski, *J. Am. Chem. Soc.*, **107** (1985) 5531; Y. Wang, M.C. Crawford, and K.B. Eisenthal, *J. Am. Chem. Soc.*, **104** (1982) 5874; T. Okada, M. Migita, N. Mataga, Y. Sakata and S. Misumi, *J. Am. Chem. Soc.*, **103** (1981) 4715; N.C. Yang, S.B. Neoh, T. Naito, L.-K. Ng, D.A. Chernoff and D.B. McDonald, *J. Am. Chem. Soc.*, **102** (1980) 2806; M. Migita, T. Okada, N. Mataga, Y. Sakata, S. Misumi, N. Nakashima and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **54** (1981) 3304.
- [4] R.M. Hermant, N.A.C. Backer, T. Scherer, B. Krijnen and J.W. Verhoeven, *J. Am. Chem. Soc.*, **112** (1990) 1214; M. Itoh, T. Mimura, H. Usui and T. Okamoto, *J. Am. Chem. Soc.*, **95** (1973) 4388.
- [5] (a) P. Frinckh, H. Heitele, M. Volk and M.E. Michel–Beyerle, *J. Phys. Chem.*, **92** (1988) 6584; (b) H. Oevering, M.N. Paddon–Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven and N.S. Hush, *J. Am. Chem. Soc.*, **109** (1987) 3258; (c) H. Heitele and M.E. Michel–Beyerle, *J. Am. Chem. Soc.*, **107** (1985) 8286; (d) G.F. Mes, J. van Ramesdonk and J.W. Verhoeven, *J. Am. Chem. Soc.*, **106** (1984) 1335; (e) P. Pasman, F. Rob, J.W. Verhoeven, *J. Am. Chem. Soc.*, **104** (1982) 5127; (f) H.E. Zimmerman, T.D. Goldman, T.K. Hirzel and S.P. Schmidt, *J. Org. Chem.*, **45** (1980) 3933.
- [6] I.A.Z. Al-ansari, *J. Photochem. Photobiol. A:Chem.*, **72** (1993) 15; W. Baumann, H. Bischof, J.-C. Frohling, C. Brittinger, W. Rettig and K. Rotkiewicz, *J. Photochem. Photobiol. A:Chem.*, **64** (1992) 49; J.L. Habbib and J.P. Soumilion, *J. Photochem. Photobiol. A: Chem.*, **64** (1992) 145.
- [7] T. Kanaya, Y. Hatano, M. Yamamoto and Y. Nishijima, *Bull. Chem. Soc. Jpn.*, **52** (1979) 2079; J. Kawakami, M. Iwamura and J. Nakamura, *Chem. Lett.* (1992) 1013.
- [8] S.L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.
- [9] N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **28** (1955) 690.