ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 29-34

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Intramolecular charge transfer and exciplex formation in anthracene bichromophoric compounds

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Abstract

A binary compound containing strong electron donor and acceptor groups, (*N,N*-dimethylanilino)-CH_2-9-cyanoanthrace ne (**II**), was synthesized, and its photophysical behaviour was studied. Intramolecular exciplex emission was observed in non-polar and moderately polar solvents, but not in polar solvents. Exciplex formation in non-polar and moderately polar solvents accounts for the exothermic electron transfer reaction and/or the efficient coupling of the amine lone pair with 9-cyanoanthracene π orbitals; in polar solvents, the molecular structure corresponds to a solvent- separated radical ion pair formed by intermolecular electron transfer, where the energy is dissipated via back electron transfer (BET) without fluorescence emission. A new, blue- shifted emission at 510 nm appears in the region of the local emission band for compound **II** at 77 K, which may originate from a ground state, charge transfer (CT) conformer. The dependence of exciplex formation on the solvent and temperature is discussed by comparison with the compound (*N,N*-dimethylanilino)-CH_2-anthracene (**I**), and a simplified energy diagram showing intramolecular charge transfer and exciplex formation in compounds **I** and **II** is described.

Keywords: Intramolecular charge transfer; Exciplex formation; Anthracene bichromophoric compounds

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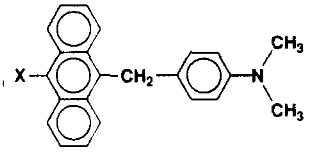
1. Introduction

Photoinduced intramolecular charge transfer is a complex phenomenon. It is strongly influenced by the molecular structure, nature and length of the chain of the molecule and the solvent polarity, viscosity and temperature [1-5]. Several valence-linked arene–amine systems have previously been reported to exhibit exciplex emission in non-polar solvents [4b,5]. The formation of fluorescent intramolecular exciplexes in moderately polar and strongly polar solvents, but not in non- polar solvents, has also been reported for a number of arene–amine systems [3]. In general, when no carbon chain is present ($n=0$), a twisted intramolecular charge transfer (TICT) state [6] is favourable. With longer chains, it is possible to form planar sandwich-like exciplexes. Compounds with one carbon chain ($n=1$), e.g. (*N,N*-dimethylanilino)-CH_2-anthracene (**I**), form exciplexes only in polar solvents due to the solvent-induced change in the electronic state during the lifetime of the excited state [3].

In this paper, the results of an investigation into the intramolecular charge transfer and exciplex formation of (*N,N*-dimethylanilino)-CH_2-9-cyanoanthracene (**II**) are reported and compared with those of compound **I**. In non-polar solvents, intramolecular exciplex emission of compound **II** was observed, but no exciplex emission of compound **I**. In addition, charge transfer (CT) emission for compound **II** was observed at 77 K. The effects of the solvent and temperature on exciplex formation for compounds **I** and **II** were investigated.



X = H (I)
CN (II)

2. Experimental details

2.1. General methods

Absorption spectra were measured using a Hitachi-330 UV spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian 300 MHz instrument. IR spectra were recorded on a Perkin–Elmer 983 G IR spectrophotometer. Mass spectra (MS) were obtained on a Finnigan GC-MS 4021 C spectrophotometer. Fluorescence spectra were obtained using a Hitachi MPF-4 fluorescence

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SSDI 1010-6030(95)04156-7

spectrophotometer. The samples were purged with nitrogen for 20 min before measurement.

2.2. Materials

2.2.1. Compound I

Compound I was prepared by the reported procedure [3a]. Melting point (m.p.), 132–134 °C (133–134 °C [3a]). ^{1}H NMR (CDCl$_3$): δ 2.90 (s, 6H), 4.95 (s, 2H), 6.60–6.65 (d, 2H), 7.00–7.10 (d, 2H), 7.40–7.50 (m, 4H), 8.00–8.10 (m, 2H), 8.25–8.35 (m, 2H), 8.45 (s, 1H). IR: 2880, 1610, 1557, 1518, 1352, 815 cm^{-1}. MS *m/e* (relative intensity): 311 (M$^+$, 100).

2.2.2. 9-Bromomethyl-10-bromoanthracene

Bromine (0.83 ml, 16.1 mmol) was added slowly to a refluxing mixture of 9-methylanthracene (1.5 g, 7.8 mmol) and 20 ml of carbon tetrachloride for 1 h. After another 8 h of refluxing, the reaction mixture was cooled and the resultant precipitate was collected. Recrystallization of the crude product from carbon tetrachloride gave pale yellow crystals: 2.4 g (87.9%), m.p., 200–202 °C (198–200 °C [7]). ^{1}H NMR (CDCl$_3$): δ 5.50 (s, 2H), 7.56–7.74 (m, 4H), 8.21–8.33 (m, 2H), 8.52–8.64 (m, 2H).

2.2.3. p-(10-Bromo)anthrylmethyl-N,N-dimethyl aniline

A mixture of 9-bromomethyl-10-bromoanthracene (2.0 g, 5.7 mmol) and *N,N*-dimethylaniline (7.65 g, 6.3 mmol) was stirred overnight at 30 °C and for another 1 h at 50 °C. After the addition of 20 ml of methanol, the resultant precipitate was collected and washed with methanol. The precipitate was chromatographed on silica gel with chloroform as eluent to afford the product: yellow flakes, 1.7 g (76.3%), m.p., 209–211 °C. ^{1}H NMR (CDCl$_3$): δ 2.90 (s, 6H), 4.93 (s, 2H), 6.60–6.70 (d, 2H), 6.95–7.05 (d, 2H), 7.45–7.65 (m, 4H), 8.25–8.35 (d, 2H), 8.60–8.70 (d, 2H). IR: 2876, 1609, 1561, 1517, 1348, 1323, 828, 571 cm^{-1}. MS *m/e* (relative intensity): 391 (M$^+$, 86.80), 310 (100).

2.2.4. Compound II

A mixture of 9-bromomethyl-10-bromoanthracene (1.2 g, 3.08 mmol), cuprous cyanide (2.8 g, 30.8 mmol) and 20 ml of dried pyridine was stirred in a 110 °C oil bath for 2 days. After removing pyridine, the residue was treated with aqueous ammonia (20%–25%, 40 ml) and chloroform (3 × 50 ml). Compound II was obtained by chromatography on silica gel with chloroform as eluent (three times) and further purified by recrystallization from chloroform and methanol to afford yellow flakes, 150 mg (14.5%), m.p., 213–215 °C. ^{1}H NMR (CDCl$_3$): δ 2.87 (s, 6H), 4.98 (s, 2H), 6.58–6.65 (d, 2H), 6.92–7.00 (d, 2H), 7.53–7.75 (m, 4H), 8.30–8.52 (m, 4H). IR: 2214, 1609, 1557, 1518, 1352, 1334, 840 cm^{-1}. MS *m/e* (relative intensity): 336 (M$^+$, 100).

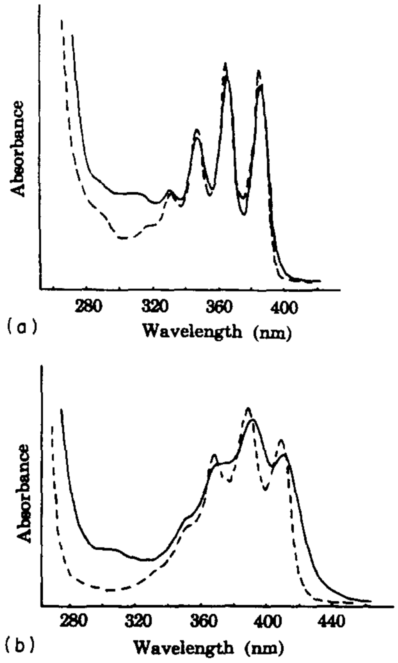


Fig. 1. (a) Absorption spectra of compound I (full line) and I + H$^+$ (broken line) in CH$_3$CN (2 × 10^{-5} M). (b) Absorption spectra of compound II (full line) and II + H$^+$ (broken line) in CH$_3$CN (2 × 10^{-5} M).

3. Results and discussion

3.1. Absorption spectra

Compounds I and II are typical donor–acceptor (D–A) compounds in which the donor and acceptor are separated by one methylene unit. The absorption spectrum of compound I in polar acetonitrile solution resembles the spectrum of a mixture of anthracene with *N,N*-dimethylaniline. In the region of 330–400 nm, an anthracene-like spectrum is observed, which exhibits no significant change in the presence of a trace of sulphuric acid to protonate the electron donor moiety *N,N*-dimethylaniline (Fig. 1(a)). For compound II, the absorption bands are broader and become anthracene-like in the region 340–440 nm (Fig. 1(b)) when a trace of sulphuric acid is added. This suggests that stronger CT interaction between the donor and acceptor exists in compound II than in compound I. Indeed, a CT conformation is involved in compound II at room temperature. Further support for a ground state CT conformation is provided in Section 3.2. No significant change in the absorption spectra of compounds I and II is observed in a variety of solvents (Table 1).

3.2. Fluorescence spectra

3.2.1. Solvent effect

The free energy changes involved in the electron transfer process for compounds I and II in non-polar (Eq. (1)) [8a] and polar (Eq. (2)) [8b] solvents were calculated. The results are listed in Table 2.

Table 1
Physical parameters of compounds I and II in solvents of different polarity

Compound parameter	C_6H_{12} (cyc.)	Et_2O	$CHCl_3$	CH_2Cl_2	CH_3CN
I					
λ_{max}^{ab} (nm) [a]	388	387	385	385	388
E_{max}^{ex} (nm)	–	490	503	540	612
$\nu_a-\nu_f$ (cm^{-1})	–	6047	6093	7459	9433
II					
λ_{max}^{ab} (nm) [a]	408	409	412	412	410
E_{max}^{ex} (nm)	452	590	600	640	–
$\nu_a-\nu_f$ (cm^{-1})	2386	7500	7605	8647	–

[a] 0 – 0 transition of the absorption spectrum.

Table 2
Redox potential, excitation energy and ΔG values

Compound	E_D^{ox} (V) [9]	E_A^{red} (V) [7]	E_s (eV) [7]	ΔG (eV)
Anthracene		– 1.82	3.28	
9-Cyanoanthracene		– 1.39	2.96	
N,*N*-Dimethylaniline	0.68			
Compound I				– 0.78 [a] (– 0.40) [b]
Compound II				– 1.21 [a] (– 0.83) [b]

[a] In polar solvent.
[b] In non-polar solvent.

$$\Delta G_1 = E_D^{ox} - E_A^{red} - E_s + 0.38 \text{ V} \quad (1)$$

$$\Delta G_2 = E_D^{ox} - E_A^{red} - E_s \quad (2)$$

E_D^{ox} is the oxidation potential of the donor, E_A^{red} is the reduction potential of the acceptor and E_s is the electronic excitation energy of the fluorescer.

All of the ΔG values shown in Table 2 are negative, which means that the electron transfer reactions are exothermic in both polar and non-polar solvents for compounds **I** and **II**, but the spacer with only one methylene unit prevents a parallel plane configuration which is the geometrical requirement for exciplex formation.

The solvent polarity plays a key role in the formation and properties of intramolecular exciplexes. The structure of fluorescent exciplexes changes from a compact geometry in non- polar solvents to a more extended geometry in polar solvents [3]. We investigated the fluorescence spectra of compounds **I** and **II** in a variety of solvents with different polarity (Fig. 2). The simplified energy diagram for intramolecular charge transfer and exciplex formation for compounds **I** and **II** is given in Scheme 1. The exciplex emission for compound **I** was not detected in non-polar cyclohexane (Fig. 2(a)), and only emission from the locally excited state (Scheme 1, step 2) was observed, which may reflect a relatively small driving force (Table 1) and/or an unfavourable geometry for exciplex formation. For compound **II**, strong exciplex emission (Scheme 1, step 4) in the region of the quenched local emission was observed (Fig. 2(b)) in non-polar solvent, possibly due to the fact that the 9-cyanoanthracene moiety in compound **II** bears a stronger electron acceptor with a larger π conjugated system than that of the anthracene unit in compound **I**. Therefore the driving force is relatively strong and the coupling of the amine lone pair with the 9-cyanoanthracene π orbital is more efficient than that in the case of compound **I**. In moderately polar solvents,

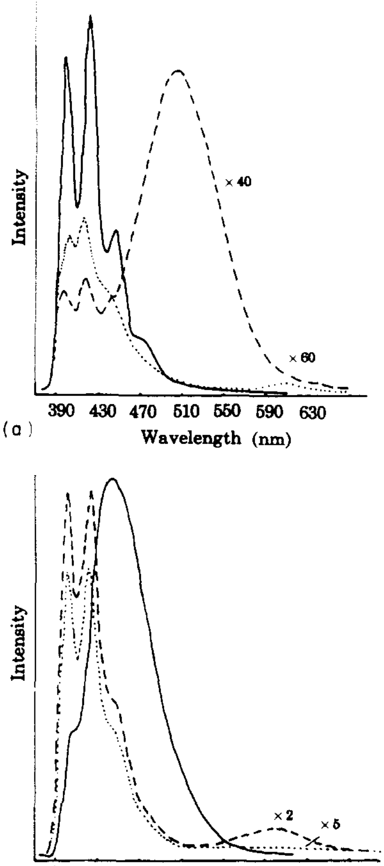
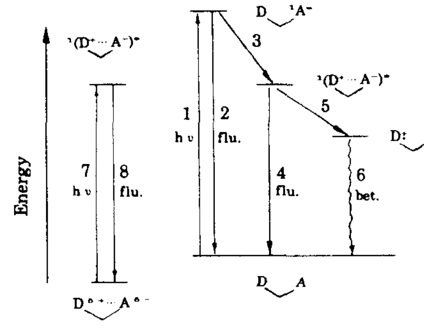


Fig. 2. (a) Fluorescence spectra of compound I in solvents of different polarity: cyclohexane (full line); $CHCl_3$ (broken line); CH_3CN (dotted line). [C] = 2×10^{-5} M; λ_{ex} = 350 nm. (b) Fluorescence spectra of compound II in solvents of different polarity: cyclohexane (full line); $CHCl_3$ (broken line); CH_3CN (dotted line). [C] = 2×10^{-5} M; λ_{ex} = 370 nm.



Scheme 1. Simplified energy diagram of intramolecular electron transfer and exciplex formation of compounds I and II: A, anthracene or 9-cyanoanthracene moiety; D, *N*,*N*-dimethylaniline moiety.

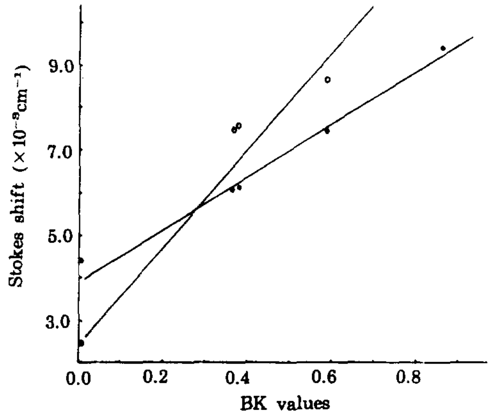


Fig. 3. Stokes shift of compounds I (●) and II (○) vs. BK values.

both compounds I and II form fluorescent exciplexes, and dual fluorescence (local and exciplex) emission is observed (Fig. 2). With an increase in the polarity of the solvent, the exciplex emission displays a large bathochromic shift and the emission intensity decreases dramatically (Fig. 2 and Table 1). In polar acetonitrile, a very weak exciplex emission was observed for compound I, while the intramolecular exciplex emission of compound II was hardly detected. The molecular structure of compound II was more extended and corresponded to that of a solvent-separated radical ion pair formed by intermolecular electron transfer [3], where energy dissipation occurs via back electron transfer (BET) without fluorescence emission (Scheme 1, step 6).

The quantitative correlation of the spectral shift of the fluorescence with the polarity of the solvent has been proposed in several theoretical treatments [10,11]. These treatments relate the 0–0 transition in the absorption and emission spectra (ν_a and ν_f) to the dipole moments of the ground and excited states (μ_g and μ_e), the dielectric constant (ϵ), the refractive index (n) of the solvent and the cavity radius (a) in Onsager's theory of the reaction field. The dipole moment difference between the excited and ground states ($\Delta\mu$) can be calculated if the other physical parameters are known (see Eq. (3)) [12]

$$\nu_a - \nu_f = \frac{2(\Delta\mu)^2}{hca^3} \times \mathrm{BK} + \text{constant} \qquad (3)$$

$$\mathrm{BK} = \frac{(\epsilon-1)/(2\epsilon+1) - (n^2-1)/(2n^2+1)}{[1-(n^2-1)/(2n^2+1)]^2} \times \left(1 - \frac{\epsilon-1}{2\epsilon+1}\right)$$

$$\Delta\mu = \mu_e - \mu_g$$

where h is Planck's constant and c is the velocity of light. The physical parameters related to Eq. (3) are listed in Table 1.

Plots of the Stokes shifts ($\nu_a - \nu_f$) vs. the BK values give two straight lines as shown in Fig. 3. From the slopes of the two lines, the $\Delta\mu$ values were obtained as 12.4 D for compound I and 21.5 D for compound II. The $\Delta\mu$ value of compound II is greater than 20 D, which suggests that complete charge separation may occur in polar media in the excited compound [13].

3.2.2. *Temperature effect*

Fig. 4 shows the fluorescence spectra of compounds I and II in diethyl ether at different temperatures. Diethyl ether was chosen as the solvent because its polarity increases with decreasing temperature and it possesses a fast relaxation time [14]. At room temperature, compounds I and II show dual fluorescence emission. The local emission is located at shorter wavelengths (Scheme 1, step 2) and the exciplex emission is located at longer wavelengths (Scheme 1, step 4). For compound I, the intensity of the local emission increases and that of the exciplex emission decreases with a red shift with decreasing temperature (Fig. 4(a)). For compound II, the exciplex emission decreases significantly with a red shift with decreasing temperature as shown in Fig. 4(b). This is due to an increase in the polarity of diethyl ether with decreasing temperature. However, for compound I, only a very strong local emission can be observed and the exciplex emission disappears when the temperature is lowered to 77 K. This phenomenon reveals that exciplex formation between the donor and acceptor in fluid media is a dynamic process and there is no appreciable population of the CT conformer in the ground state. Step 3 (Scheme 1) is a very important process in the formation of the exciplex, involving the stretching and twisting of molecular bonds and the reorganization of the medium to allow the two chromophoric faces to approach for exciplex formation. With a decrease in temperature, such motions decrease. Consequently, the intensity of the local emission increases and that of the exciplex emission decreases. In rigid glass (at 77 K), molecules are frozen and their motion is inhibited, which makes step 3 (Scheme 1) very difficult. Therefore the local emission increases strongly and the exciplex emission disappears.

However, a new, blue-shifted emission band (510 nm) appears in the region of the local emission band for compound II at 77 K (Fig. 4(b)). As indicated above, compound II possesses a stronger electron acceptor with a larger π conjugated system than compound I. Because of the strong CT interaction between the two chromophores in compound II, a significant population of the ground state CT conformer may exist. The excitation spectra of compound II are shown in Fig. 4(c). Compared with the spectrum obtained at 450 nm (broken line), the spectrum obtained at 550 nm (full line) is broadened and slightly red shifted, and the intensity around 410 nm increases strongly. Therefore it is concluded that a CT band is superimposed. At 77 K, the motion of molecule II is severely restricted and step 3 (Scheme 1) is blocked. Consequently, the relaxation of the molecule and the reorganization of the medium can be neglected. Thus the emission at 510 nm can be assumed to originate from the ground state CT conformer. In this case, the CT conformer

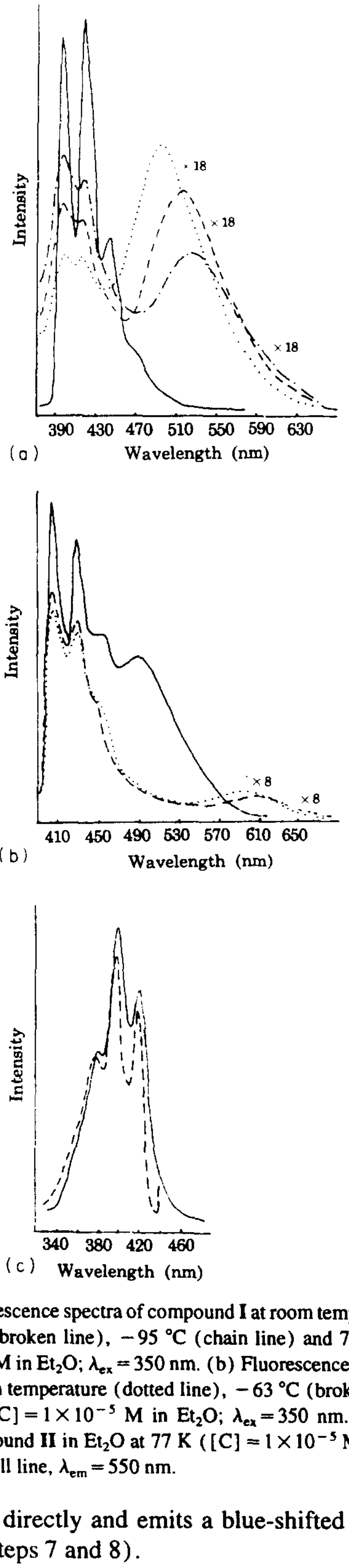


Fig. 4. (a) Fluorescence spectra of compound I at room temperature (dotted line), −63 °C (broken line), −95 °C (chain line) and 77 K (full line). [C] = 1×10^{-5} M in Et_2O; λ_{ex} = 350 nm. (b) Fluorescence spectra of compound II at room temperature (dotted line), −63 °C (broken line) and 77 K (full line). [C] = 1×10^{-5} M in Et_2O; λ_{ex} = 350 nm. (c) Excitation spectra of compound II in Et_2O at 77 K ([C] = 1×10^{-5} M): broken line, λ_{em} = 450 nm; full line, λ_{em} = 550 nm.

absorbs light directly and emits a blue-shifted fluorescence (Scheme 1, steps 7 and 8).

4. Conclusions

Photoinduced intramolecular charge transfer is a complex phenomenon. The roles of the spacer and structure are important in electron transfer and exciplex formation. For compounds **I** and **II**, the donor and acceptor are linked by one methylene group which prevents a parallel plane configuration. The exciplex formation of compounds **I** and **II** strongly depends on the dynamics of the chain. Motions of the chain adjust the faces of the donor and acceptor to yield strong coupling, which is the geometrical requirement for exciplex formation. For compound **II**, exciplex emission is observed in non-polar and moderately polar solvents, but not in polar solvents, due to its extended structure corresponding to a solvent separated radical ion pair in polar solvents. For compound **I**, exciplex emission is not detected in non-polar solvents. For compound **II**, but not compound **I**, a CT fluorescence emission appears when the temperature is lowered to 77 K. Therefore the experimental results on the effect of solvent and temperature indicate that charge transfer and exciplex formation are easier for compound **II** than for compound **I**, possibly due to the fact that the 9-cyanoanthracene moiety in compound **II** bears a stronger electron acceptor with a larger π conjugated system than that of the anthracene unit in compound **I**. The driving force is therefore relatively strong, and the coupling of the amine lone pair with the 9-cyanoanthracene π orbital is more efficient than that of compound **I**.

Acknowledgements

The authors wish to thank the NSFC and NAMCC for financial support.

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