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Intramolecular exciplex and cation-mediated charge-transfer fluorescence in a podand carrying terminal electron donor and acceptor groups

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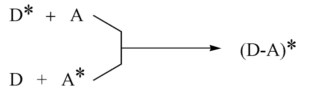
A podand carrying terminal electron donor and acceptor groups (DPA) has been synthesized. There is no intramolecular interaction between the two chromophores in the ground state. Selective excitation of the acceptor moiety, and a very weak and structureless exciplex emission was observed in benzene. In acetonitrile, only quenching of the monomer fluorescence occurred. In the presence of calcium ions conformational modification through complexation with the non-cyclic poly(oxyethylene) chain resulted in the formation of a charge-transfer (CT) complex in the ground state. Selective excitation of the acceptor moiety (380 nm) or at the CT band (340 nm) gave rise to intramolecular excited CT complex emission. The similarity in the fluorescence maxima exhibited by the exciplex and the excited CT complex implies that the electronic structures of their fluorescent states are very similar. The slight difference in the fluorescence quantum yields and decay rate constants between the exciplex and excited CT complex suggests that they have different geometries. Exciplex fluorescence was also observed in γ-CD, depending on the γ-CD concentration.

Introduction

Intramolecular charge transfer (CT) or electron transfer processes, as an important mechanism for the quenching of fluorescence, have been studied extensively using bichromophoric molecules of donor (D) and acceptor (A) systems.[1–4] The quenching of fluorescence is often accompanied by the appearance of a new and broad structureless emission attributed to excited-state complex (DA)* formation in non-polar or weakly polar media, while in strongly polar media only quenching of the fluorescence occurs.

The excited-state complex could be formed by two distinctly different processes. In reaction (1) the photoexcited donor D*



$$\left.\begin{array}{l} D^* + A \\ D + A^* \end{array}\right\} \longrightarrow (D\text{-}A)^* \qquad (1)$$

(or acceptor A*) reacts with a ground-state acceptor A (or donor D) in a specific orientation yielding an exciplex.

In reaction (2) the donor D forms a complex with acceptor A in the ground state, then an excited complex is produced by selective excitation of the ground-state complex. Whether the exciplex produced in reaction (1) is the "same" species as the excited complex form in reaction (2) is still a matter of debate.

$$(D–A)_{CT} + h\nu \rightarrow (D–A)_{CT}^* \qquad (2)$$

Itoh and Mimura[5] reported that the electronic structures of the fluorescent state of the exciplex and charge transfer complex are the same in a non-polar solution of 9,10-dicyanoanthracene and 2-methylnaphthalene. However, Itoh *et al.*[6] also reported the observation of both an intramolecular exciplex and an excited charge transfer complex fluorescence in the (9,10-dicyanoanthracene)–$(CH_2)_3$–(naphthalene) system which are spectroscopically distinguishable. The electronic interactions leading to the differences in the excited fluorescent states of the exciplex and the CT complex can be explained by the assumption that the internal or geometrical conversions from their respective Franck–Condon excited states to the identical fluorescent states, which may be allowed in the intermolecular interaction, is inhibited by a steric factor concerned with the methylene chain linked compounds. Recently, Pal *et al.*[7] observed red-shifted charge transfer complex emissions that were different from that of the exciplex emission spectrum of fullerene-aromatic amine systems using steady-state fluorescent measurements. Support for the exciplex and CT emission has also been obtained from fluorescence lifetime measurements. Both the exciplex and the CT complex are supposed to interconvert depending on the amine concentration.

In order to elucidate the geometric effect and orientational specificity in intramolecular excited-state complex formation, we have synthesized a donor–spacer–acceptor system DPA, in which *N*,*N*-dimethylaniline group, as electron donor, is linked to an anthracene moiety as electron acceptor *via* a flexible poly(oxyethylene) (POE) chain. Conformational modification through cation complexation with the non-cyclic poly(oxyethylene) chain may lead to the formation of a charge-transfer complex between D and A in the ground state. Thus, studies of the fluorescence from excited complexes in the absence and presence of metal ions enable us to understand the properties of the exciplex and the excited charge-transfer complex.

Results and discussion

Electronic absorption spectra

The absorption spectra of DPA were recorded in benzene and acetonitrile (Fig. 1). We can see that the absorption spectra of DPA are identical and correspond to the sum of the reference compounds ethyl anthracene-2-carboxylate and ethyl 4-(dimethylamino)benzoate. This indicates that there is no

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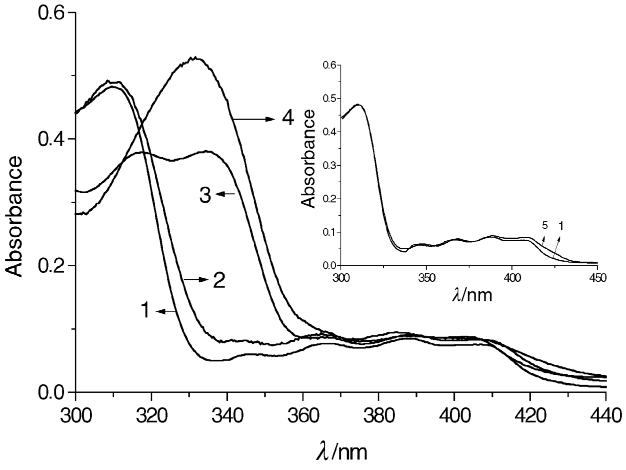


Fig. 1 Absorption spectra of DPA (*ca.* 2.5 × 10^{-5} M) and its calium ion complex ($c_{\mathrm{MAX}} = 2.5 \times 10^{-4}$ M) in benzene and acetonitrile. 1) Free DPA in benzene, 2) free DPA in acetonitrile, 3) DPA + Ca^{2+} in benzene, 4) DPA + Ca^{2+} in acetonitrile, 5) (insert) a mixture of ethyl anthracene-2-carboxylate and ethyl 4-(dimethylamino)benzoate (*ca.* 2.5 × 10^{-5} M) in benzene.

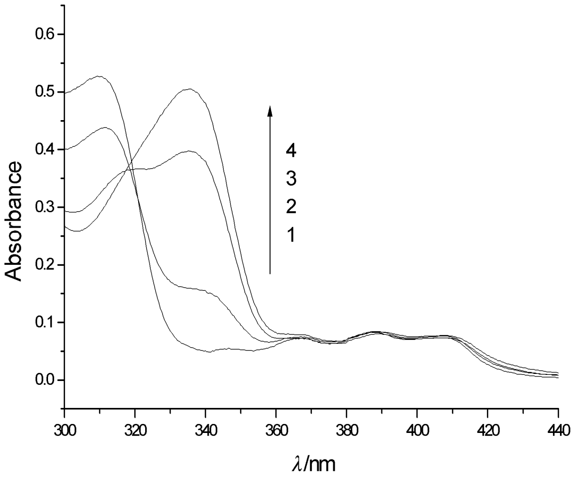


Fig. 2 Absorption of DPA (2.5 × 10^{-5} M) with different concentrations of Ca^{2+} in benzene. 1) 0 M, 2) 2.5 × 10^{-5} M, 3) 1.25 × 10^{-4} M, 4) 2.5 × 10^{-4} M.

interaction between the donor and acceptor moieties in the ground state. A small bathochromic shift in the absorption spectra in acetonitrile is observed in comparison with that in benzene. In the presence of calcium ions, the absorption spectra undergo significant changes with the appearance of a new absorption peak at 340 nm attributed to the formation of a charge-transfer (CT) type ground-state complex. In benzene solution, by increasing the calcium ion concentration, the absorbance at 340 nm increased until the absorbance reached a maximum at $c_{\mathrm{MAX}} = 2.5 \times 10^{-4}$ M, where it remained constant as the concentration was further increased, indicating that equilibrium had been attained. The representative spectra in benzene are shown in Fig. 2. No spectroscopic changes were observed when alkali metal ions such as sodium or potassium ion were added. These findings show that calcium ions can induce an optimum conformation of the system in which the two chromophores (D and A) may interact in the ground state.

The stability constant for the ground-state CT complex formation in the present system can be estimated following the Benesi–Hildebrand relation[8] for 1 : 1 complex formation (see Experimental section). The stability constants are 3.5 × 10^3 M^{-1} and 1.2 × 10^4 M^{-1} with correlation coefficients of 0.999 in benzene and acetonitrile, respectively. Generally, the complex formation involving cyclic crown ethers such as 18-crown-6 is more stable in non-polar solvents.[9] It has been reported that the conformation about the central C–C bond of the OCH_2CH_2O unit in a poly(oxoethylene) chain[10–12] is predominantly *anti* in less polar media, but predominantly *gauche* in highly-polar media. Accordingly it has been suggested that the poly(oxoethylene) chain forms a pseudo lipophilic hydrocarbon core in low polar media, and in contrast, a pseudo hydrophilic electron-rich cavity is formed in highly polar media, in which cations can be coordinated Scheme 1. As a result, the same complex will be more stable in acetonitrile than it will be in benzene. Although the POE chain is flexible, the number of oxygen atoms is not enough to fully surround the central metal ion and it can only form a hollow space while coordinating the metal ion. The stability constants of non-cyclic crown ethers are two or three orders of magnitude smaller than those of the cyclic crown ethers like 18-crown-6.

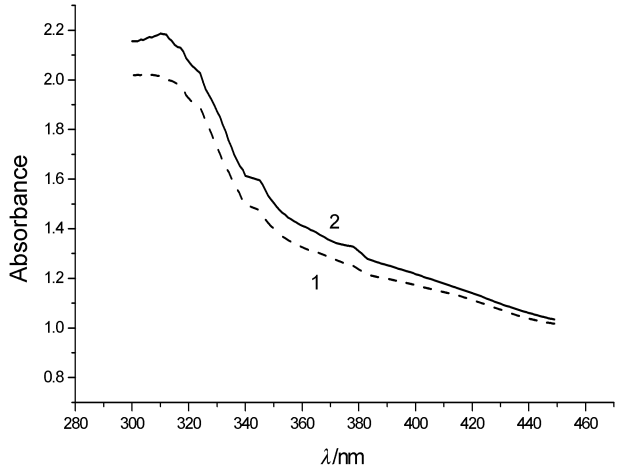
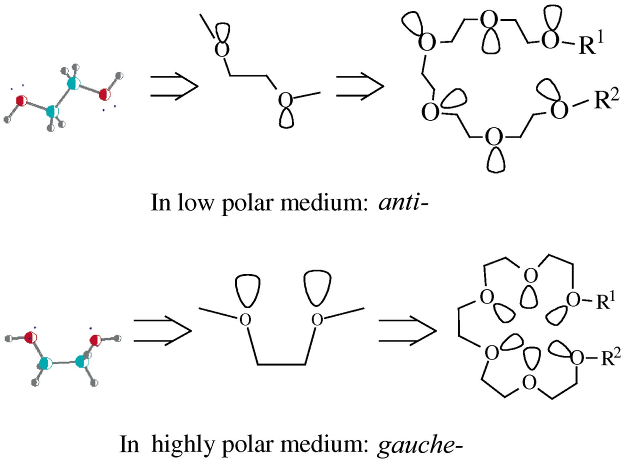


Fig. 3 Absorption spectra of DPA (2.5 × 10^{-5} M) and the mixture of ethyl anthracene-2-carboxylate and ethyl 4-(dimethylamino)benzoate (*ca.* 2.5 × 10^{-5} M) in an aqueous solution of γ-CD (5 × 10^{-3} M). 1) A mixture of ethyl anthracene-2-carboxylate and ethyl 4-(dimethylamino)benzoate, 2) free DPA.



Scheme 1 Conformational model of DPA derived from the PCMODEL of OCH_2CH_2O unit in the poly(oxoethylene) chain.

The absorption spectra of DPA and the mixture of ethyl anthracene-2-carboxylate and ethyl 4-(dimethylamino)benzoate are compared in γ-CD as shown in Fig. 3. The results indicate that there is no ground-state interaction between A and D moieties in γ-CD.

Fluorescence spectra

The fluorescence of the reference compound and DPA in the absence and presence of calcium ions in benzene and acetonitrile are shown in Fig. 4 and 5, respectively.

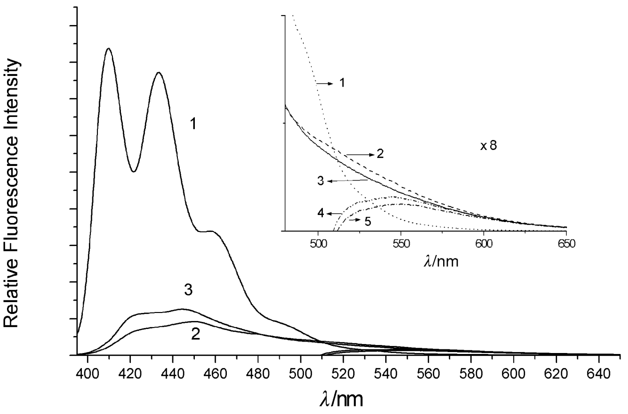


Fig. 4 Fluorescence spectra of free DPA (2.5×10^{-5} M) and its metal ion complex in benzene ($c_{MAX} = 2.5 \times 10^{-4}$ M). ($\lambda_{Ex} = 380$ nm). 1) Reference compound, 2) DPA + calcium ions, 3) free DPA, 4) excited CT emission, 5) exciplex.

Fluorescence spectra of DPA in benzene. Selective excitation of the anthracene (A) moiety at 380 nm, gave fluorescence in the range of 400 to 480 nm in DPA that was strongly quenched compared with the reference compound ethyl anthracene-2-carboxylate. A weak and broad structureless emission, which was obtained by means of spectra subtraction (Inset of Fig. 4), appeared at a higher wavelength of λ_{max} at 535 nm and was attributed to the fluorescence from the exciplex formed between the anthracene S_1 excited state and the ground state 4-(dimethylamino)benzoate moiety. The ratio of the relative intensity of the exciplex fluorescence I_E (at 535 nm) to the monomer fluorescence I_M (at 425 nm) $F = I_E/I_M$ equals 0.17. In the linked DPA system described here, two chromophores are separated by a flexible POE chain, such that they cannot interact with each other in the ground state. Upon selective excitation of A (or D), conformational changes to the POE chain may occur so that the two chromophores approach each other even in very dilute solution. The excited A* (or D*) then reacts with D (or A) in the ground state leading to the formation of an exciplex characterized by a broad, structureless red-shifted emission relative to the monomer fluorescence as indicated in Fig. 4. The flexible nature of the POE chain permits a number of conformations to be adopted in the excited state. It is the Brownian chain dynamics that is responsible for the weak exciplex emission. In the presence of calcium ions, selective excitation of DPA at the CT band or at 380 nm, gives fluorescence in the range of 400 to 480 nm, the intensity of which decreases more than in the absence of calcium ions and is accompanied by the emission of excited complex (Inset of Fig. 4). The ratio of the relative fluorescence intensity of the excited CT complex emission I_E to the monomer emission I_M ($F = I_E/I_M$) is 0.65 showing a greater contribution of the excited CT complex to the fluorescence in the presence of calcium ions. The similar wavelength of fluorescence in benzene (*ca.* λ_{max} at 535 nm indicates that in this particular system, the exciplex and the excited CT complex relax to a very similar and perhaps identical emitting state. That is, the exciplex and excited CT complex are spectroscopically very similar. Determination of the fluorescence quantum yields and the non-radiative as well as radiative rate constants for the exciplex and the excited CT complex enables us to elucidate the properties of these excited states. Fluorescence quantum yields of DPA in benzene are given in Table 1. Alkali metal ions were found to exert no significant effect on the fluorescence spectra of DPA.

Fluorescence spectra of DPA in acetonitrile. Fig. 5 shows the fluorescence spectra of DPA in the absence and presence of calcium ions in acetonitrile. There is no detectable exciplex fluorescence in acetonitrile owing to the formation of solvated ion pairs which are non-fluorescent. In contrast, addition of calcium ions to the DPA in acetonitrile lead to a broad and red-shifted emission at around 540 nm which was obtained by means of spectra subtraction (Inset of Fig. 5). This suggests that the the distance between the D and A moieties in the metal ion–DPA complex is controlled in such a way that the radical ions ($D^{+\bullet}$ P $A^{+\bullet}$) formed from excitation of DPA are not allowed to diffuse apart and be solvated.

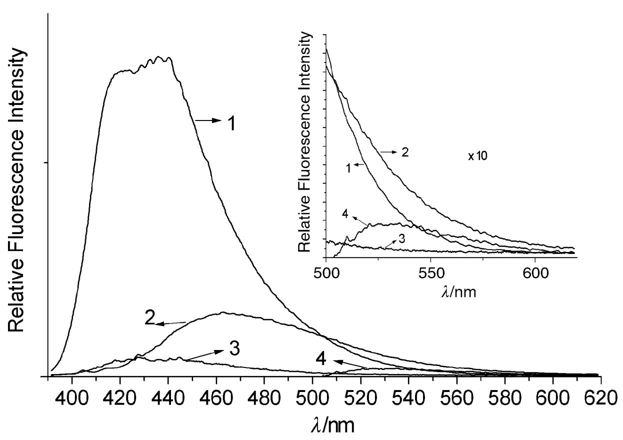


Fig. 5 Fluorescence spectra of DPA (2.5×10^{-5} M) and its metal ion complex in acetonitrile ($c_{MAX} = 2.5 \times 10^{-4}$ M), ($\lambda_{Ex} = 380$ nm). 1) Reference compound, 2) DPA + calcium ions, 3) free DPA, 4) excited CT complex emission.

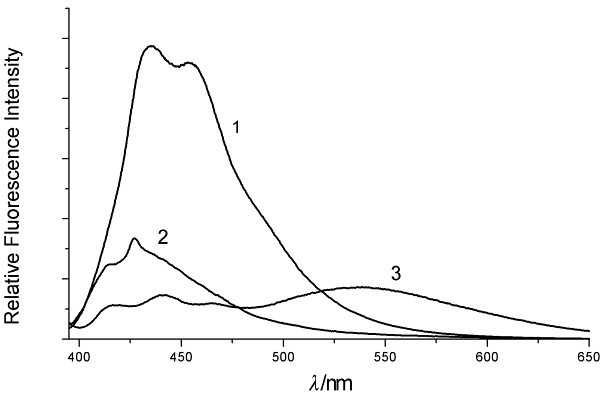


Fig. 6 Fluorescence spectra of DPA (2.5×10^{-5} M) in H_2O, β-CD and γ-CD ($\lambda_{Ex} = 380$ nm). 1) β-CD (5×10^{-3} M), 2) H_2O, 3) γ-CD (5×10^{-3} M).

Fluorescence spectra of DPA in CD. Cyclodextrins (CDs) have the ability to complex hydrophobic organic species into their central cavity to form inclusion complexes. It has been reported[13] that β-CD can hold one benzene and/or naphthalene molecule while γ-CD can hold two naphthalene and/or one anthracene molecule in their hydrophobic pockets. Enhancement of the fluorescence intensity such inclusion complexes has often been observed. Turro and co-workers[14] have observed the enhancement of the intramolecular exciplex emission of 1-(1-naphthyl)-3-(dimethylamino)propane in β-CD. Here, we describe the spectroscopic behavior of the DPA system with different CDs. Fig. 6 shows the fluorescence spectra of DPA in aqueous β- and γ-CD solution and compares these with the spectrum of DPA in water. The fluorescence peaks at about 420 nm which is attributed to the emission of the monomer of the anthracene unit. In β-CD, enhancement of the fluorescence intensity of anthracene is observed. This indicates that the anthracene moiety binds strongly in the CD cavity with the dimethylaminobenzoate unit extending outside. Thus, interaction between the moieties is prohibited. In γ-CDs of sufficient concentration, quenching of the anthracene monomer emission occurs accompanied by the appearance of a red-shifted exciplex

Table 1 Fluorescence quantum yields and wavelengths for maximum exciplex fluorescence of DPA and its Ca^{2+} complex in benzene

		Quantum yield		
	λ_{max}/nm	Anthracene moiety (φ')	Exciplex (φ_e)	CT complex (φ_e)
DPA	535	6.2×10^{-2}	6.6×10^{-3}	
DPA + Ca^{2+}	535	4.8×10^{-2}		8.2×10^{-3}

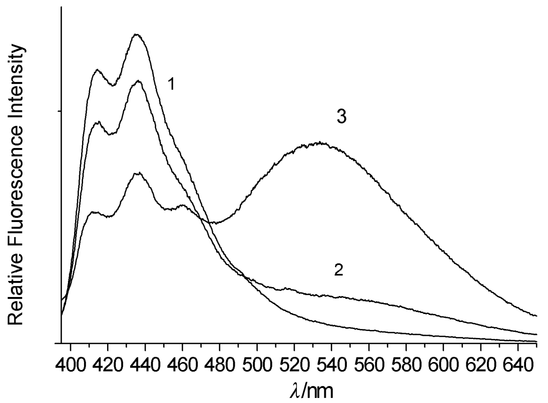
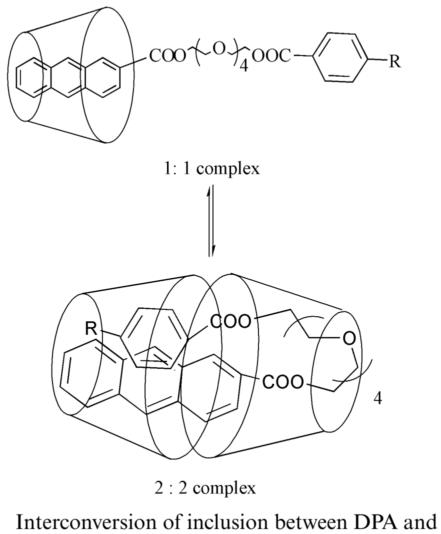


Fig. 7 Fluorescence spectra of DPA (2.5×10^{-5} M) in various concentrations of γ-CD in aqueous solution (λ_{Ex} = 380 nm). 1) 5×10^{-4} M, 2) 1×10^{-3} M, 3) 5×10^{-3} M.

emission at around 540 nm. It is interesting to see the effect of γ-CD concentration on the fluorescence spectra of DPA as shown in Fig. 7. The anthracene monomer fluorescence intensity increases as the CD concentration is increased to 5×10^{-4} M. At higher concentrations, quenching of the anthracene monomer emission occurs accompanied by the appearance of a strong exciplex emission at 540 nm. This finding suggests that at low CD concentrations, owing to the steric constraints imposed by the POE chain, the DPA molecule is orientated longitudinally in the γ-CD cavity with the dimethylaminobenzoate group extending outside. As the CD concentration is increased further, the strong exciplex fluorescence that is observed can be attributed to the formation of an inclusion complex in which one molecule of DPA is held within the hydrophobic pockets of two molecules of γ-CD (Scheme 2). Thus, with selective excitation of the acceptor moiety, DPA will adopt a favorable conformation such that intramolecular exciplex formation can occur.



Scheme 2 Interconversion of inclusion between DPA and γ-CD.

Table 2 The fluorescence decay parameters for DPA in benzene

	$\lambda_{Em}/\lambda_{Ex}$ [a]	τ_i/ns (Q_i(%)) [b]		
DPA	425 / 380	1.6 (72.2)	14.9 (27.8)	
	535 / 380	1.3 (9.2)	18.7 (50.3)	63.6 (40.5)
	535 / 320	2.4 (15.6)	16.5 (38.3)	59.8 (46.2)
DPA + K^+	425 / 380	1.6 (85.2)	15.0 (14.8)	
	535 / 380	1.2 (9.1)	18.7 (51)	58.9 (39.9)
DPA + Ca^{2+}	425 / 380	1.5 (30.3)	16.1 (69.7)	
	535 / 380	3.7 (6.0)	14.9 (34.3)	38.1 (59.7)
	535 / 340	5.0 (21.4)	15.3 (19.6)	40.7 (59)

[a] λ_{Em} and λ_{Ex} (in nm) are the monitored and excitation wavelengths, respectively. [b] Q corresponds to the mole fraction of the monomer being quenched, the unquenched monomer and the complex, respectively.

Table 3 The fluorescence decay parameters for DPA in acetonitrile and γ-CD

	$\lambda_{Em}/\lambda_{Ex}$ [a]	τ_i/ns (Q_i (%)) [b]	
DPA in acetonitrile	425/380	0.9 (47.3)	16.5 (52.7)
DPA + Ca^{2+}	425/380	1.4 (21.9)	15.2 (78.1)
In acetonitrile	535/380	3.7 (19.9)	11.3 (80.1)
	535/340	2.3 (11.0)	9.4 (89.0)
DPA in γ-CD	425/380	0.2 (85.3)	9.8 (14.7)
	535/380	10.3 (31.5)	30.0 (68.5)

[a] λ_{Em} and λ_{Ex} (in nm) are the monitored and excitation wavelengths, respectively. [b] Q corresponds to the mole fraction of the monomer being quenched, the unquenched monomer and the complex, respectively.

Fluorescence Decay

Time-dependent fluorescence was recorded at 425 and 535 nm; these wavelengths correspond to the locally excited monomer and the exciplex species emissions, respectively. The results are listed in Tables 2 and 3. For the free DPA at 425 nm, the fluorescence decay is fitted well by the sum of two exponentials both in benzene and acetonitrile. The short-lived components correspond to the lifetime of the monomer (A) being quenched by D, while the longer lived components correspond to the lifetime of the unquenched monomer.

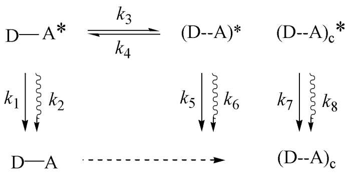
The fluorescence decay of the excited complex in benzene is satisfactorily fitted by the sum of three exponentials which correspond to the lifetime of the excited monomer being quenched and the fluorescence of the monomer and the exciplex (τ = 60 ns), respectively. In the presence of calcium ions, with selective excitation at the CT band or at 380 nm, for emission monitored at 425 and 535 nm, fluorescence decays biexponentially and triexponentially respectively in benzene. The component with the longest lifetime is assigned to the excited CT complex (τ_{CT} = 40 ns). It is interesting to note that in the presence of calcium ions the decay of the excited CT complex can be fitted to the sum of two exponentials and the lifetime of the excited CT complex is shorter (τ_{CT} = 10 ns) in acetonitrile (Table 2) compared with that in benzene (τ_{CT} = 40 ns) indicating that the decay time of the excited CT complex fluorescence decreases with increasing solvent polarity.

In γ-CD, the fluorescence decay at both 425 and 535 nm are fitted to the sum of two exponential functions; the lifetime of the exciplex emission is 30 ns which is shorter than that in benzene. This demonstrates that the γ-CD environment is more polar than benzene and less polar than acetonitrile.

The mechanism for the exciplex and CT complex formation and decay processes are shown in Scheme 3, where D and A are the electron donor and acceptor, respectively. (D–A)* and

Table 4 Radiative and non-radiative rate constants (s^{-1}) of DPA and its Ca^{2+} complex in benzene

	Anthracene-moiety		Exciplex			CT complex		
	k_1	$k_2 + k_3$	φ'_f	k_5	k_6	φ'_f	k_7	k_8
DPA	3.9×10^7	5.9×10^8	7×10^{-3}	1×10^5	1.5×10^7			
DPA + Ca^{2+}	3.2×10^7	6.4×10^8				8.5×10^{-3}	2.2×10^5	2.6×10^7



Scheme 3

$(D–A)_c$* are the exciplex and excited state of the CT complex, respectively. The CT complex in the ground state is expressed by $(D–A)_c$.

From the fluorescence quantum yields and lifetime determinations the decay rate constants can be calculated. In DPA, the fluorescence quantum yield and lifetime of the anthracene moiety are expressed by eqns. (3) and (4). In non-polar solvent, k_2 may be negligible compared with k_1 and k_3, which can be calculated.

$$\varphi' = k_1(k_1 + k_2 + k_3)^{-1} \quad (3)$$

$$\tau' = (k_1 + k_2 + k_3)^{-1} \quad (4)$$

The apparent fluorescence quantum yield of the exciplex φ_e can be expressed by eqn. (5),[6]

$$\phi_e = \phi_e' \frac{k_3\tau}{1+k_4\tau_e'}\left(1+\frac{k_3\tau}{1+k_4\tau_e'}\right)^{-} \quad (5)$$

where $\tau = (k_1 + k_2)^{-1}$, $\tau'_e = (k_5 + k_6)^{-1}$ and $\varphi'_e = k_5\tau'_e$. Since k_4 can be neglected in the intramolecular exciplex formation and decay processes,[6] k_5 and k_6 can be estimated from the values of τ, τ'_e, k_3 and φ_e obtained in the benzene solution of DPA (Tables 1 and 2). These results are listed in Table 4 and show that the rate constants for fluorescence in the exciplex and excited complex are of a similar order of magnitude. In both cases, the non-radiative decay processes are as much as 100 times faster than that of the radiative decay processes. These results present further evidence that in this particular system, the exciplex and excited CT complex are similar fluorescence species. The slightly different decay rate constants illustrate that the conformational effects upon complexation control the dynamic excited complex decay processes.

Computational studies based on PCMODEL provide detailed pictures of the geometry of DPA and its complex (Fig. 8). In the free podand, the value of the dihedral angle between the two chromophores is about 60°, but when Ca^{2+} is nestled within the pseudo crown ether cavity upon complexation, the planes of the two chromophores are almost parallel. However a potassium ion, which has a larger diameter than that of calcium ion, sits above the pseudo crown ether and no significant conformational change could be detected. Hence the conformation of the K^+ complex is very similar to that of the free podand, such that the potassium ion does not effect the photophysics.

Experimental

Materials

Acetonitrile was purified using the procedure reported in a previous paper.[15] The other solvents were dried and distilled before use according to standard methods. Anthracene-2-carboxylic acid and ethyl anthracene-2-carboxylate were prepared in our laboratory. Alkali metal and alkaline-earth metal perchlorates were purchased from Acros.

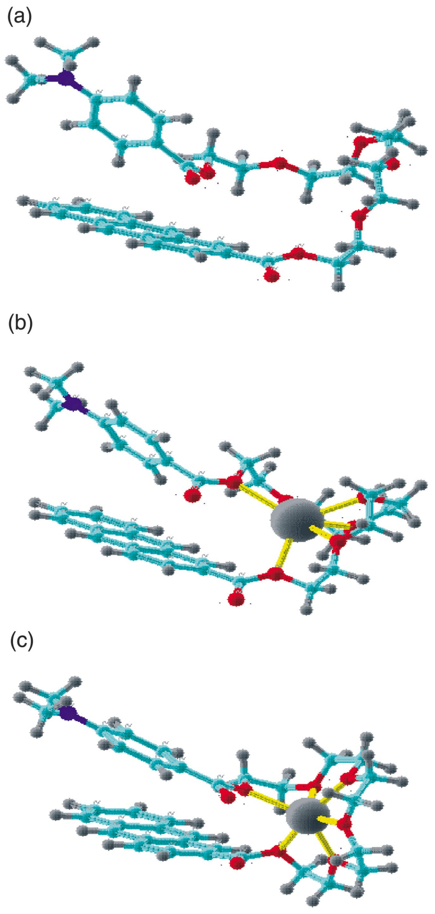


Fig. 8 Minimizing structures of DPA and its ion complex derived from a PCMODEL calculation. (a) Free DAP top, (b) potassium ion complex and (c) calcium ion complex.

Preparation of reaction solutions

Calcium perchlorate $Ca(ClO_4)_2 \cdot 4H_2O$ was dissolved in methanol to obtain a 0.1 M solution. Small portions (2.5–25 μL) of the methanol solution of calcium perchlorate and 1 mL DPA–benzene solutions (2.5×10^{-4} M) were added by means of micropipettes to 10 mL measuring flasks, then the solutions were diluted to 10 mL with benzene. The preparation of the acetonitrile solutions was similar to that of the benzene solutions. The concentration of all free podands was *ca.* 2.5×10^{-5}M. The concentration of metal ion was 10 times that of the free podand if not specified.

Apparatus

^{1}H NMR spectra were obtained on a Varian Gemini 200 spectrometer. IR spectra were recorded on aBIO-RAD FTS 165. Mass spectra were recorded on a Trio 2000 spectrometer. Absorption spectra were recorded on a U-2001 spectrophotometer. The fluorescence spectra were obtained on a Hitachi Fluorescence spectrophotometer F-4500. Except for definitive elucidation, the wavelength of excitation was selected at 380 nm with slit bandwidths of 5 and 2.5 nm for emission and excitation, respectively. Fluorescence quantum yields were determined using anthracene as standard ($\varphi_f = 0.27$ in benzene, $\lambda_{Ex} = 365$ nm).[16] Fluorescence decay measurements were performed on a Horiba Time-resolved Spectrofluorometer NAES-1100 single-photon-counting apparatus. The fluorescence lifetime was determined from data on the fluorescence transient waveform of the material to be tested and the lamp waveform data using the least squares iterative deconvolution method. The error in the lifetime is under 10%. The range of χ^2 (chi-squares) is from 1.0 to 1.5.

Determination of the stability constant

The formation of the ground-state complex in 1 : 1 stoichiometry in the present system ($M + L \rightleftharpoons ML$) can be expressed by eqn. (6). The stability constant can be estimated from eqn. (7), where a and b are constants, A_0 and A are the

$$K_s = [ML]/([M][L]) \qquad (6)$$

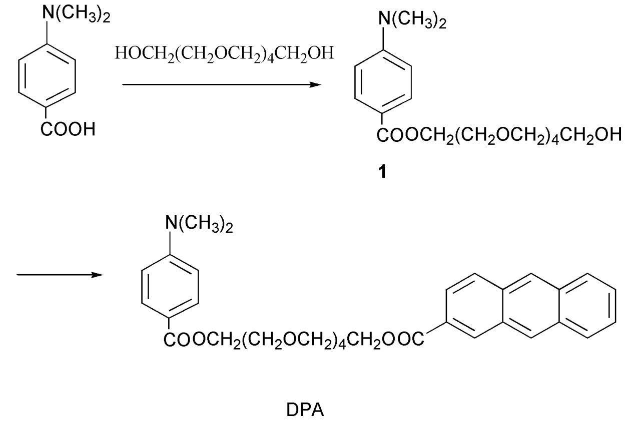
$$\frac{A_0}{A_0 - A} = \frac{a}{a-b}\left(\frac{1}{K_S[M]} + 1\right) \qquad (7)$$

absorbances of the podand in the absence and presence of calcium ions, respectively. From a plot of $A_0/(A_0 - A)$ *vs.* $[M]^{-1}$, the stability constant can then be obtained frm the value of the intercept/slope.

Synthesis (Scheme 4)

1-Hydroxy-14-(*p*-dimethylaminobenzoyloxy)-3,6,9,12-tetraoxatetradecane (1). 4-Dimethylaminobenzoic acid (1.65 g, 10 mmol) was added to excess 3,6,9,12-tetraoxatetradecane-1,14-diol (10 mL). The mixture was stirred at room temperature followed by gradual addition of 0.2 mL 98% H_2SO4. The solution was heated to 80 °C. After 18 h the mixture was cooled to 30 °C, then neutralized to pH = 7 with ammonia. The excess glycol was removed under reduced pressure. The residue was purified by chromatography on silica gel (eluant: ethyl acetate) to give an oil (2 g, 52%). IR (KBr, ν_{max}/cm^{-1}): 3435 (OH), 2871 (CH_3), 1700 (C=O), 1445 (CH_3N), 1279, 1185, 1108 (C–O). ^1H NMR (δ, ppm): 6.60–7.93 (m, 4H, Ar-H), 4.42 (t, 2H, OCH_2), 3.70–3.92 (m, 18H, OCH_2), 3.04 (s, 6H, NCH_3). MS (*m*/*z*): 385 (M^+).

1-(*p*-Dimethylaminobenzoyloxy)-14-(2-anthrylcarbonyloxy)-3,6,9,12-tetraoxatetradecane (DPA). Anthracene-2-carboxylic acid 2.22 g, 10 mmol) and thionyl chloride (10 mL) were refluxed for 6 h. After removal of excess thionyl chloride, anhydrous benzene (20 ml), compound **1** (2 g, 5.2 mmol) and DMAP (80 mg) were added. The mixture was stirred for 2 h, and then cooled and filtered. The solvent was removed. The crude product was purified by chromatography on silica gel (eluant: ethyl acetate–petroleum ether 3 : 2) to give a yellow oil (0.9 g). IR (KBr, ν_{max}/cm^{-1}): 2872 (CH_3), 1702 (C=O), 1446, 1369 (CH_3N), 1277, 1183, 1100 (C–O). ^1H NMR (δ, ppm): 8.80–6.78 (m, 13H, Ar-H), 4.58 (t, 2H, OCH_2), 4.41 (t, 2H, OCH_2), 3.60–3.92 (m, 16H, OCH_2), 3.03 (s, 6H, NCH_3). MS (*m*/*z*): 589 (M^+).



Scheme 4

Conclusions

The excited complexes formed in the absence of calcium ions (exciplex) and in the presence of calcium ions (charge transfer complex) show similar fluorescence maxima. The results indicate that the electronic structures of their fluorescent states are very similar. The slight differences in the fluorescence quantum yields and the lifetimes of the excited complexes, hence the decay rate constants, have been attributed to the conformational differences between the exciplex and the excited CT complex. Exciplex emission was observed in solutions of γ-CD of sufficient concentration.

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