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Photoinduced intramolecular electron transfer and exciplex formation in anthracene and pyrene binary compounds

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Abstract

Two series of six donor–acceptor binary compounds, pyrene–dicyanovinylbenzene (Py-*n*-DCVB) and anthracene–dicyanovinylbenzene (An-*n*-DCVB), with different chain lengths were designed and synthesized. Using steady state spectroscopy and time resolved spectroscopy, the effects of solvent polarity, viscosity, temperature and salt content were studied. The photoinduced electron transfer and exciplex formation processes, as a function of the dynamics of chain conformation and the size of electron donor unit, are discussed and compared respectively for all six binary compounds.

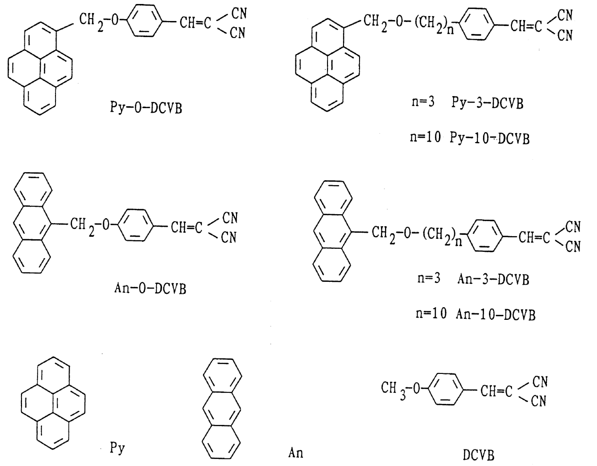
Keywords: Intramolecular electron transfer; Exciplex formation; Electron donor size effect

1. Introduction

Photoinduced electron transfer has received much attention in the areas of photophysics, organic synthesis, photobiology and many technological applications. The linkage of two chromophores by a non-absorbing and flexible chain is of great value in the study of the interaction between two chromophores in dilute solution [1,2]. Photoinduced intramolecular charge transfer, exciplex formation and charge separation are dependent on the driving force and the extent of the electronic interaction between the donor and acceptor, which is strongly influenced by the molecular structure, nature and length of the chain of the molecule, and the solvent polarity, viscosity and temperature [2–5].

The multipolar salt effect on exciplex dissociation and charge separation has been studied by several groups [6,7]. The salt could act to increase the efficiency of formation of free radical ions and to increase the lifetime of the reactive radical ions, which can be easily confirmed by spectroscopy and laser techniques.

In this study two series of electron donor–acceptor binary molecules linked covalently, pyrene–dicyanovinylbenzene (Py-*n*-DCVB) and anthracene–dicyanovinylbenzene (An-*n*-DCVB), with different chain lengths (Scheme 1), were synthesized and the intramolecular electron transfer reaction, exciplex formation and the salt effect on accelerating charge separation were investigated using steady-state spectroscopy and time-resolved spectroscopy.



Scheme 1. Structures of molecules investigated and the model compounds.

2. Experimental section

2.1. Materials

Hexane, toluene, chloroform, ethyl acetate, 2-methyl THF, THF, dichloromethane, acetonitrile were reagent grade and were purified [8] before use. Anthracene and pyrene were recrystallized from ether/hexane. $Bu_4N^+BF4^-$ and other reagents were reagent grade and were used as received.

2.2. Instrumentation

^1H nuclear magnetic resonance (NMR) spectra were measured on a Varian-FT80 spectrometer. IR spectra were

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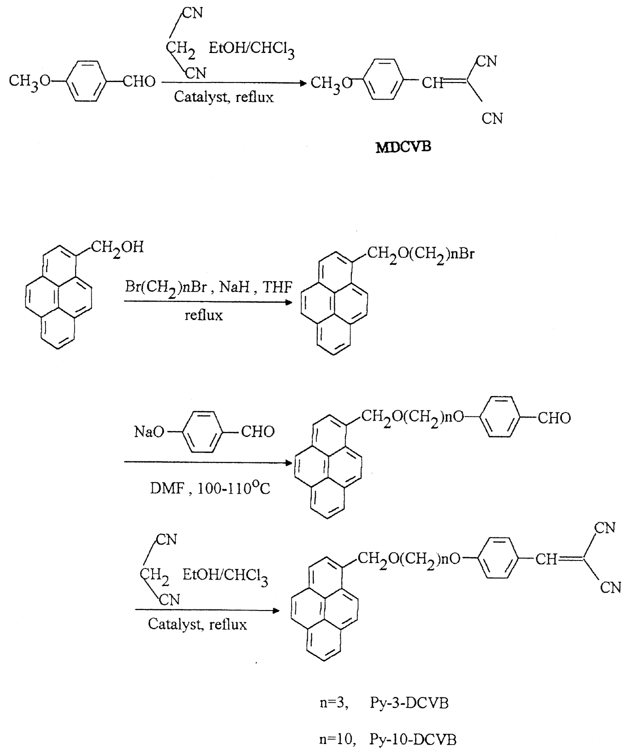


Scheme 2. Synthetic route for compounds Py-*n*-DCVB and MDCVB.

recorded on a Perkin-Elmer 983 G spectrometer. Elemental analyses were performed on a model 1104 (Carlo Erba) elemental analyzer. Absorption and fluorescence spectra were measured on a Hewlett-Packard 8451 spectrophotometer and a Hitachi model MPF-4 spectrophotometer respectively. Laser photolysis was performed using a Lambda Physik FL-3002 dye laser and a B.M. Industries 502D YAG laser.

2.3. Synthesis

The synthesis of the binary molecule Py-*n*-DCVB and a model compound, *p*-methoxydicyanovinylbenzene (MDCVB), was carried out as shown in Scheme 2. The other binary compounds were synthesized in a similar way to that shown in Scheme 2. All the products involved were characterized by elemental analysis, IR and ^{1}H NMR spectroscopies.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of all the binary compounds (Py-*n*-DCVB and An-*n*-DCVB) with different chain lengths are similar to those observed for the mixture (1:1 mol/mol) of model compounds anthracene (An) with MDCVB and pyrene (Py) with MDCVB respectively. No significant changes in position and shape of absorption were observed in a series of solvents with different polarity, which implies that there is no significant charge transfer interaction at the ground state in the two series of binary compounds.

3.2. ^{1}H NMR spectra

Fig. 1 shows part of the ^{1}H NMR (in $CDCl_3$) spectra for the model compound MDCVB compared with binary compounds Py-3-DCVB, An-3-DCVB, Py-0-DCVB and An-0-DCVB. The signals of MDCVB at δ (ppm) 6.97 (d, 2H), 7.60 (s, 1H) and 7.88 (d, 2H) are assigned to protons of groups (a), (c) and (b) respectively. In the two binary compounds Py-3-DCVB and An-3-DCVB, the signals for protons of groups (b) and (c) are merged with those of pyrene and anthracene moieties at lower field, while the signals for the protons of group (a) are at a higher field of 6.25 ppm with good resolution, which implies that protons of group (a) in the dicyanovinylbenzene moiety for compounds Py-3-DCVB and An-3-DCVB are located in the shielding region of pyrene and anthracene rings. That is reasonable, because the spacer between the donor and acceptor, i.e. pyrene (or anthracene) and dicyanovinylbenzene, with $–CH_2–O–(CH_2)_3–O–$, allows the two moieties to take a parallel or nearly parallel conformation, and the protons of group (a) in the dicyanovinylbenzene moiety are therefore in the shielding region (see Fig. 5). For the two binary compounds Py-0-DCVB and An-0-DCVB, the signals for group (a) protons are at a lower field of 7.1–7.2 ppm, which implies that protons of group (a) in the dicyanovinylbenzene moiety for these two compounds are located in the deshielding region of pyrene and anthracene rings. For the Py-10-DCVB and An-10-DCVB compounds, the signals for group (a) protons at 6.9–7.0 ppm are almost the same as that in the model compound MDCVB, which reveals that there is no intramolecular interaction between two moieties in the two binary compounds Py-10-DCVB and An-10-DCVB.

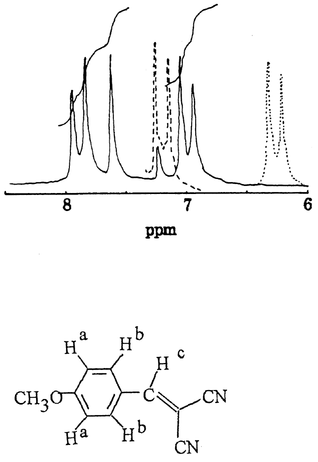


Fig. 1. Part of ^{1}H NHR spectra of model compound MDCVB (———), the compounds Py-3-DCVB (· · ·) and An-3-DCVB (· · ·), and the compounds Py-0-DCVB (- - -) and An-0-DCVB (- - -).

3.3. Thermodynamic discussion of electron transfer

The electron transfer rate constant k_{et} is given by [9]

$$k_{et}=\frac{2\pi}{h}\frac{H_{ps}^2}{(4\pi\lambda kT)^{1/2}}\exp\left[-\frac{(\lambda+\Delta G^{\neq})^2}{4\lambda kT}\right] \quad (1)$$

where H_{ps} is the electronic coupling between the precursor (D^*A) and successor (D^+A^-) states and $\Delta G^{\neq}$ is the Gibbs energy change for the electron transfer. The reorganization energy λ is the energy required to distort the precursor from its equilibrium state along its Gibbs energy surface to the equilibrium coordinates of the successor without transferring the electron [10]. λ has two components: an inner term λ_i arising from internal reorganization (primarily bond length changes) within the reacting molecules, and an outer term λ_o arising from changes in the surrounding medium, i.e.

$$\lambda=\lambda_i+\lambda_o \quad (2)$$

The relationship among $\Delta G^{\neq}$, λ and the free energy changes ΔG involved in an electron transfer process can be presented by

$$\Delta G^{\neq}=(\Delta G+\lambda)^2/4\lambda$$

Therefore, the intramolecular electron transfer reaction and exciplex formation are dependent on not only the driving force ΔG, but also the reorganization energy λ including the energy for conformation adjustment between D with A and for the corresponding changes in the surrounding medium.

ΔG can be calculated simply using Eq. (3) [11] in non-polar solvents and Eq. (4) [12], in polar solvents:

$$\Delta G=E_D^{ox}-E_A^{red}-E_s+0.38 \quad (3)$$

$$\Delta G=E_D^{ox}-E_A^{red}-E_s \quad (4)$$

where E_D^{ox} is the oxidation potential of the electron donor, E_A^{red} is the reduction potential of the acceptor and E_s is the electronic excitation energy of the fluorescer. The results are listed in Table 1.

The ΔG values shown in Table 1 are negative, which means that the electron transfer reactions are exothermic in both polar and non-polar solvents for both series of binary compounds, while the reorganization energy λ is different for every binary compound and in varying media.

Table 1
Redox potential, excitation energy and ΔG values

Compound	E_D^{ox} (V)	E_A^{red} (V)	E_s (eV)	ΔG (eV)
Model compounds				
Anthracene	1.16 [13]		3.28 [13]	
Pyrene	1.27 [13]		3.28 [13]	
MDCVB		−1.20 [14]		
Binary compounds				
An-*n*-DCVB				−0.92 [a] (−0.54) [b]
Py-*n*-DCVB				−0.88 [a] (−0.50) [b]

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

3.4. Fluorescence spectra

3.4.1. Chain length effect

The dual fluorescence emissions for both series of binary compounds (Py-*n*-DCVB and An-*n*-DCVB, $n=0$, 3, 10) with different chain lengths in $CHCl_3$ were observed (Fig. 2). The peak at shorter wavelength is the fluorescence of the locally excited state of the pyrene or anthracene moiety, and the peak at longer wavelength is the fluorescence of the intramolecular charge transfer exciplex of donor (Py or An) and acceptor (DCVB) moieties. The fluorescence intensity of exciplex for An-*n*-DCVB is An-0-DCVB > An-3-DCVB > An-10-DCVB. This reveals that in the anthracene series, the chain length is the main factor for exciplex formation—the longer the chain length between the donor (An) and acceptor (DCVB), the more difficult will it be to form the exciplex. The fluorescence intensity of exciplex for compounds Py-*n*-DCVB is Py-3-DCVB > Py-0-DCVB > Py-10-DCVB. The ^{1}H NMR spectral results indicate that for Py-3-DCVB and An-3-DCVB, the DCVB moiety is in the shielding region of the pyrene ring (or anthracene ring), i.e. the two moieties, electron donor and electron acceptor, are in parallel. In contrast to compounds of the anthracene series, perhaps owing to the large π-system of pyrene, the electron coupling between the donor and acceptor becomes the main factor for exciplex formation in the pyrene series, although the chain length effect exists also. Therefore the most appropriate compound for intramolecular charge transfer and

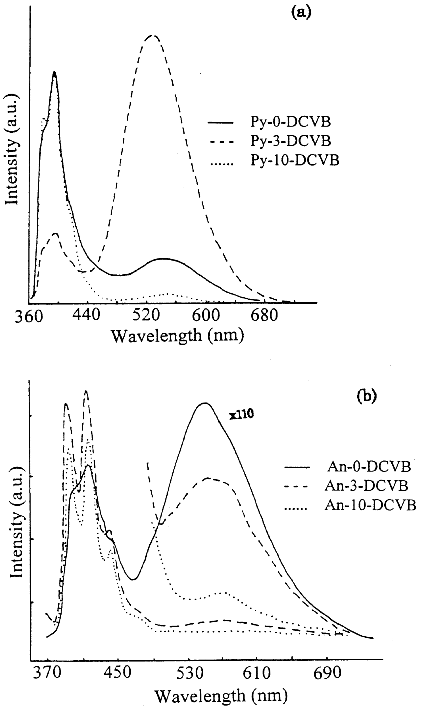


Fig. 2. Fluorescence spectra of binary compounds in $CHCl_8$: (a) Py-*n*-DCVB, (b) An-*n*-DCVB.

exciplex formation is Py-3-DCVB, not An-3-DCVB (see Section 3.4.3).

3.4.2. Solvent polarity effect

The fluorescence spectra of binary compounds Py-3-DCVB and An-3-DCVB in a variety of solvents with different polarity were investigated (Fig. 3).

Fig. 3 shows that as the polarity of the solvent increases, the fluorescence emission maximum shifts to longer wavelength with decreasing fluorescence intensity and exciplex emission on the tail of residual anthracene and pyrene fluorescence for compounds Py-3-DCVB and An-3-DCVB respectively. The dependence on solvent of the position of the exciplex emission is given by [15–17]:

$$\nu_{\max} = \nu_0 - \frac{2\mu^2}{hca^3}\left[\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2(2n^2+1)}\right]$$

$$= \nu_0 - \left[\frac{2\mu^2}{hca^3}\right]\left[f - \frac{1}{2f'}\right] \qquad (5)$$

where $\nu_{\max}$ is the wave number of the emission maximum, ν_0 is the hypothetical gas-phase emission frequency, μ is the exciplex dipole moment, h is Planck's constant, c is the velocity of light, a is the charge separation in the exciplex, ϵ is the solvent dielectric constant, and n is the solvent refractive index.

Plots of $\nu_{\max}$ vs. $f - 1/2f'$ gave reasonably straight lines (Fig. 4), from which the dipole moment of the intramolecular exciplexes could be estimated, assuming a charge separation of 5 Å (Table 2): compound An-3-DCVB, 9.8D; compound Py-3-DCVB, 11.3D. Using the same method, the dipole moments of the intramolecular exciplexes for the other binary compounds were also estimated and all these data are in good agreement with dipole moments reported for exciplexes [18].

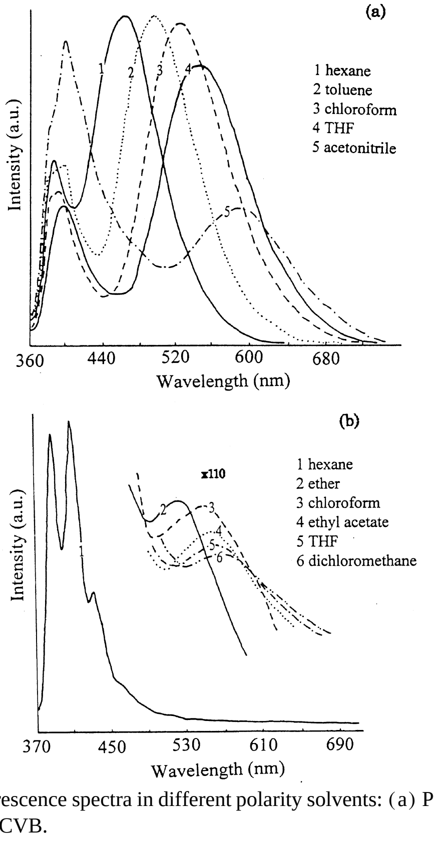


Fig. 3. Fluorescence spectra in different polarity solvents: (a) Py-3-DCVB; (b) An-3-DCVB.

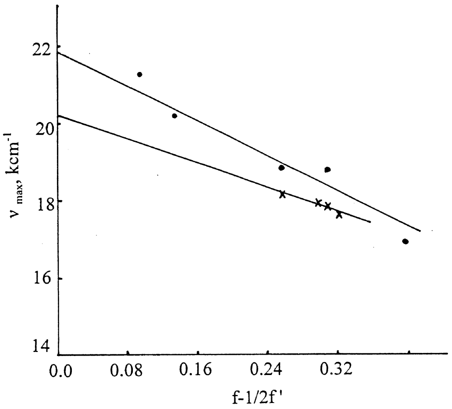


Fig. 4. Plot of $\nu_{\max}$ vs. $f - 1/2f'$ (Eq. (5) and Table 2) for Py-3-DCVB (●) and An-3-DCVB (×).

Table 2
Exciplex emission data

Solvent ($f - 1/2f'$)	Exciplex $\nu_{\max}$ (10^3 cm^{-1})	
	An-3-DCVB	Py-3-DCVB
Hexane (0.092)		21.42
Toluene (0.127)		20.28
Chloroform (0.254)	18.18	18.94
Ethyl acetate (0.292)	18.00	
THF (0.308)	17.86	18.98
Dichloromethane (0.319)	17.70	
Acetonitrile (0.393)		16.95
ν_0 (extrapolated) [a]	20.2	21.9
$2\mu^2/hca^3$ (cm^{-1}) [a]	7.73	0.36
μ (a=5 Å) (D) [a]	9.8	11.3

[a] From Eq. (5) and Fig. 4.

3.4.3. Chain conformation and electron donor size effects

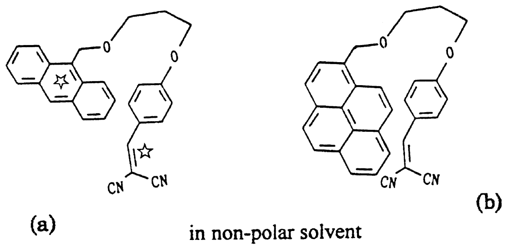
The driving force ΔG (Table 1) is a little stronger for compounds An-n-DCVB than for Py-n-DCVB and the exciplex formation therefore should be easier in compounds An-n-DCVB than in Py-n-DCVB. In fact (Fig. 2(a), (b) and Fig. 3(a), (b)), the intramolecular electron transfer and exciplex formation processes occur much more easily in compounds Py-n-DCVB than in An-n-DCVB. This could only be because the electron donor size effect of pyrene is larger than that of anthracene.

Taking compounds An-3-DCVB and Py-3-DCVB as examples, further discussion and illustration of the influence of molecular conformation and electron donor size effects on photoinduced intramolecular electron transfer and exciplex formation are as follows.

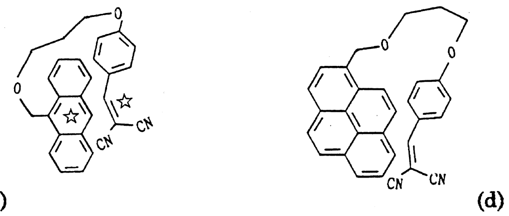
For An-3-DCVB, local fluorescence of the anthracene moiety with very high quantum yield occurs in a variety of solvents with different polarity (Fig. 3(b)). The fluorescence relative quantum yields Φ_r are 0.91 and 0.93 (relative to the model compound) in non-polar solvents and strongly polar solvents respectively, and the dual fluorescence emission, anthracene moiety local fluorescence and weak intramolecular exciplex fluorescence are exhibited in moderately polar solvents. This is presumably because of the complex dynamics of chain motions. In non-polar solvents, donor and acceptor connected with a polar chain $-CH_2-O-(CH_2)_3-O-$ would gather together owing to lipophobic force, which makes the conformation of An-3-DCVB like that in Fig. 5(a). In this case, the anthracene unit can hardly approach the dicyanovinylbenzene unit owing to the limitation of the dynamics of the chain conformation, which causes the center (★) of the electron donor to be apart from the center of the electron acceptor and poor overlap between the terminal groups in non-polar solvent. The electronic coupling (Eq. (1)) between the two units might not be efficient for electron transfer, and the fluorescence intensity of the anthracene unit is therefore very strong. The chain is stretched in polar solvents, because of the hydrophilic effect, and an end-to-end interaction of the linked donor and acceptor is inhibited (Fig. 5(e)). Consequently, the electron transfer interaction between the two moieties would not occur, and the fluorescence intensity of anthracene is very strong. In moderately polar solvents, the lipophobic effect is less strong than that in non-polar solvents. Hence, on the one hand the centers of donor and acceptor units are perhaps close (see ^{1}H NMR spectra in Section 3.2) and on the other hand the chain is not very rigid like that in non-polar solvents. This allows the conformational changes of the chain (Fig. 5(c)) and results in electron transfer interaction of the donor and acceptor and therefore exciplex formation.

From Fig. 3(a) and (b), we can obtain a general idea. The intramolecular exciplex formation is much easier in Py-3-DCVB than in An-3-DCVB. For Py-3-DCVB, dual fluorescence emission, pyrene moiety local fluorescence and intramolecular exciplex fluorescence are exhibited in a variety of solvents with different polarity (Fig. 3(a)). In non-polar solvent, hexane, a weak pyrene moiety emission ($\Phi_r = 0.02$, relative to the model compound pyrene) with a very strong intramolecular exciplex emission at longer wavelength are displayed. Similar to the case of An-3-DCVB, the lipophobic effect forces the intramolecular donor or acceptor to approach close to each other (see Fig. 5(b)). In addition, pyrene has a larger π system than anthracene, therefore the electronic coupling between donor and acceptor is very efficient in Py-3-DCVB, not in An-3-DCVB; the electron transfer interaction is much stronger in Py-3-DCVB than in An-3-DCVB. For the same reason mentioned above, a weak pyrene moiety emission ($\Phi_r = 0.05$–0.08) with a strong intramolecular exciplex emission are exhibited in moderately polar solvents. Even in polar solvent, acetonitrile, the donor and acceptor being separated (Fig. 5(f)), a fairly strong intramolecular exciplex emission still appears with a relatively strong pyrene moiety emission ($\Phi_r = 0.13$).

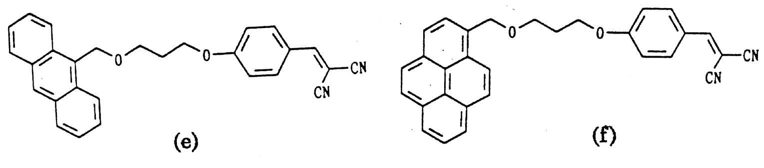
From the above discussion, it can be seen that molecular conformation and electron donor size effects could have a great influence on photoinduced electron transfer and exci-



in non-polar solvent



in moderately polar solvent



in polar solvent

Fig. 5. Conformation of compounds An-3-DCVB and Py-3-DCVB in solvents with different polarity.

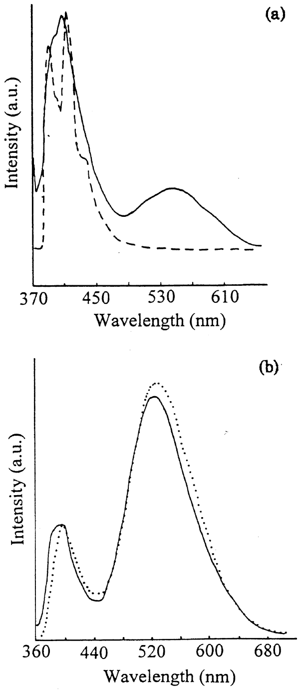


Fig. 6. Fluorescence spectra in 2-methyl THF (———) and 2-methyl THF–PMMA (7% w/w) (· · ·): (a) An-3-DCVB; (b) Py-3-DCVB.

plex formation and, therefore, the spectroscopic behaviors of Py-3-DCVB and An-3-DCVB are quite different.

3.4.4. *Viscosity and temperature effects*

2-Methyl THF, a moderately polar solvent, and PMMA were chosen for experiments on the viscosity effect (Fig. 6). The exciplex emission for An-3-DCVB nearly disappeared with increasing viscosity, but there was little influence for Py-3-DCVB. Fig. 7 reveals that the effect of temperature is the same as that of viscosity. The exciplex emission for An-3-DCVB disappeared at 77 K, but without any change for Py-3-DCVB. These results indicate that the electron transfer and exciplex formation processes depend to a great extent on the dynamics of chain conformation and the size of the electron donor of An-3-DCVB and Py-3-DCVB. In other words, the processes depend on the dynamics of chain conformation for An-3-DCVB, but not for Py-3-DCVB, owing to the electron donor size effect.

3.5. *Salt effect*

The reaction of exciplex with higher aggregates of R_4NBF_4 leads to dissociation of the exciplex to radical ions [6,7]. The addition of tetrabutylammonium tetrafluoroborate, $Bu_4^+BF_4^-$ (TBTF), 2×10^{-2}–8×10^{-2} mol dm^{-3}, effectively quenched the emission of the intramolecular exciplex of Py-3-DCVB in dichloromethane (Fig. 8).

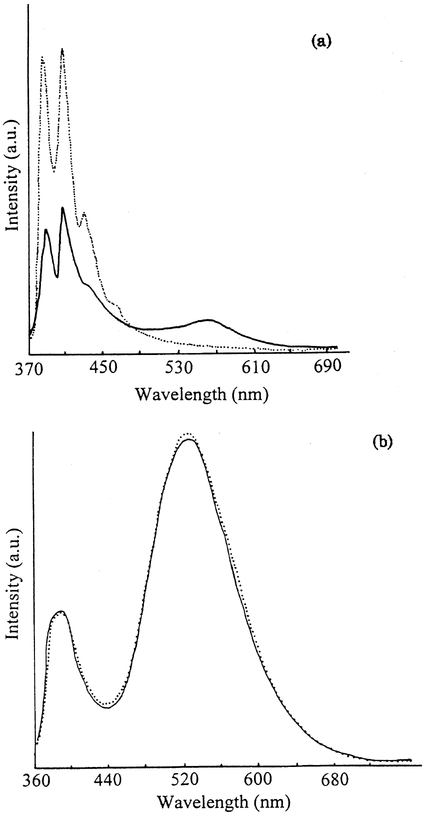


Fig. 7. Fluorescence spectra in 2-methyl THF at room temperature (———) and at 77 K (· · ·): (a) An-3-DCVB; (b) Py-3-DCVB.

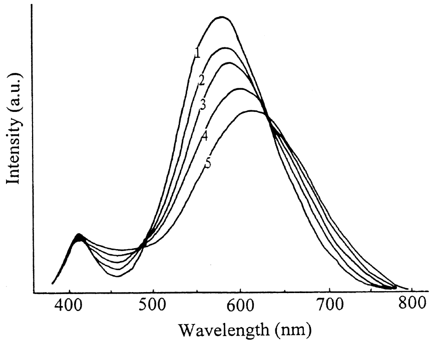


Fig. 8. Quenching of the exciplex for compound Py-3-DCVB in CH_2Cl_2 by [TBTF]: curve 1, 0; curve 2, 2×10^{-2}; curve 3, 4×10^{-2}; curve 4, 6×10^{-2}; curve 5, 2×10^{-2} mol dm^{-3}.

Laser (425 nm) excitation of compounds Py-0-DCVB, Py-3-DCVB and Py-10-DCVB respectively in dichloromethane under argon was carried out. The transient absorption spectra of ^{3}pyrene* ($^3D^\star$) for all three compounds are depicted in Fig. 9 (curve 1). After 500 ns laser excitation of the three systems in the presence of TBTF (1×10^{-1} mol dm^{-3}) the optical density (OD) of $^3D^\star$ absorption was decreased with a relatively strong increase in OD of pyrene$^{+\cdot}$ ($D^{+\cdot}$) absorption at 465 nm (Fig. 9, curve 2). The addition of the salt results in increased yield of $D^{+\cdot}$ with dicyanovinylbenzene$^{-\cdot}$ ($A^{-\cdot}$). ΔOD of $D^{+\cdot}$ observed after 500 ns laser excitation against the concentrations of TBTF is shown in Fig. 10.

In dichloromethane, these intramolecular exciplexes either deactivate by way of fluorescence emission, internal conversion and intersystem crossing as observed by formation of ^{3}pyrene*, or dissociate, though not efficiently, into $D^{+\cdot}$ and $A^{-\cdot}$. The addition of salt leads to quenching of the exciplex

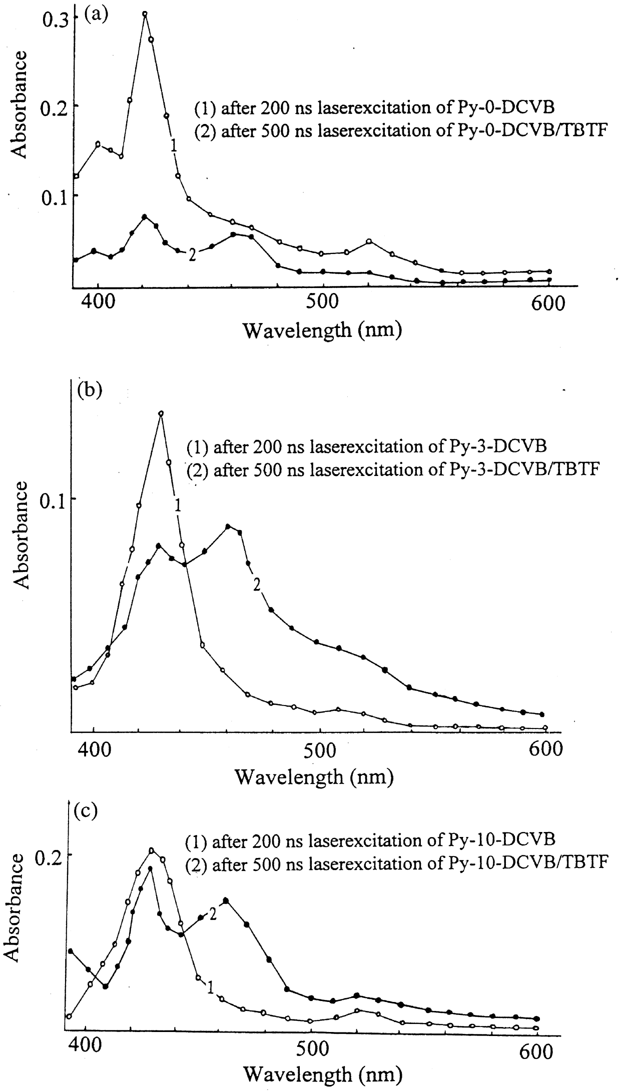


Fig. 9. Transient absorption spectra observed in dichloromethane: (a) Py-0-DCVB; (b) Py-3-DCVB; (c) Py-10-DCVB.

and its dissociation to $D^{+\cdot}$ with $A^{-\cdot}$. These results reveal that $D^{+\cdot}$ and $A^{-\cdot}$ are stabilized by Coulombic interaction with BF_4^- and Bu_4^+ respectively.

4. Conclusions

The solvent polarity, viscosity and temperature-dependent spectroscopic behaviors and salt effect were investigated for two series of pyrene and anthracene binary compounds. The electron transfer and exciplex formation processes depending on the dynamics of chain conformations and the size of the electron donor units were discussed. Among the two series of donor–acceptor binary compounds, compounds Py-*n*-DCVB are better than An-*n*-DCVB, and Py-3-DCVB is the most appropriate compound for intramolecular electron transfer and exciplex formation processes owing to the chain conformation and electron donor size effects.

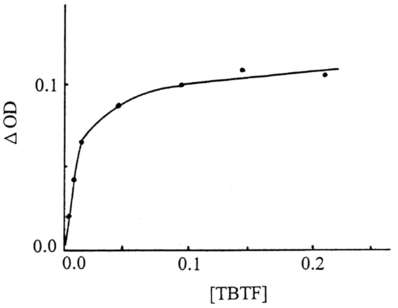


Fig. 10. The observed Δ OD of the resulting pyrene$^{+\cdot}$ against TBTF concentration after 500 ns laser excitation of compound Py-3-DCVB/TBTF.

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