

INTRAMOLECULAR FLUORESCENCE QUENCHING AND EXCIPLEX FORMATION IN ω -(1-PYRENYL)ALKYL PARA-SUBSTITUTED BENZOATES

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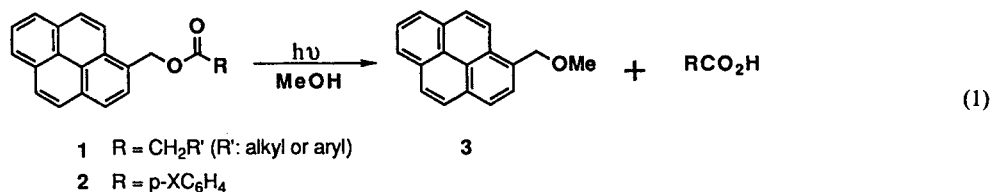
Measurements of absorption and emission spectra, fluorescence quantum yields (Φ_f) and lifetimes (τ_f) of ω -(1-pyrenyl)alkyl *para*-substituted benzoates PnX ($X = H, Cl, CF_3, CN, NO_2$, with $n = 1-4$) were carried out in solvents of various polarity. Intramolecular interaction in the ground state is not observed in any of these compounds. $PnCN$ ($n = 2-4$) shows an intramolecular exciplex emission in solvents of low to high polarity. The broad, structureless emission at longer wavelength observed in ethyl acetate solution of $P1CN$ is ascribed to an 'exciplex-type' emission which does not require actual overlapping of the two chromophores. $P2CF_3$ also shows an exciplex emission in solvents of medium to high polarity. The solvent dependence of both Φ_f and τ_f increases as the electron-withdrawing ability of the *para*-substituents increases. The relationship between fluorescence quenching by electron transfer and *para*-substituents of PnX is discussed by means of the free energy for electron transfer, ΔG_{ET} , obtained from the oxidation and reduction potentials of pyrene and methyl *para*-substituted benzoates in acetonitrile, respectively. PnH , with positive ΔG_{ET} , does not show a solvent dependence of Φ_f , except for $P1H$, in which ca 40% of the fluorescence is quenched in acetonitrile. $PnCl$, with slightly negative ΔG_{ET} , shows more efficient quenching, but does not show exciplex emission. $PnCN$, $PnCF_3$ and $PnNO_2$ have ΔG_{ET} values between -0.36 and -0.65 eV, and their fluorescence is fairly efficiently quenched. The fluorescence of $PnCN$ is concluded to be strongly quenched by intersystem crossing from the singlet exciplex to the locally excited pyrene, and by electron transfer from the pyrene part to the benzoate part. That the formation of a singlet exciplex is necessary for intersystem crossing in bichromophoric compounds containing pyrene is thus clearly illustrated.

INTRODUCTION

There have been extensive studies on intramolecular fluorescence quenching and exciplex formation in bichromophoric compounds of the general structure D-spacer-A, where chromophores D and A are connected by a non-conjugated spacer.¹ Studies on compounds with various kinds and combinations of donors, acceptors and spacers have revealed many factors necessary for intramolecular exciplex formation, such as the mutual distance and conformation and oxidation-reduction potential difference between donor and acceptor. In particular, mechanisms and structural

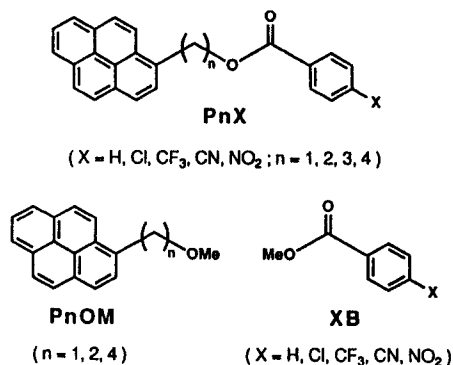
requirements for exciplex formation and fluorescence quenching in pyrene – $(CH_2)_n$ – amine systems have been well established.² Although the effects of intermolecular donor-acceptor interaction on quenching and exciplex formation have been well surveyed, there have been only a few studies in which the effects of intramolecular interaction were systematically treated by subtle structural changes of the components.³

In the course of a study on photolabile and fluorescent protecting groups, we found that the photolysis of 1-pyrenylmethyl carboxylates (**1** and **2**) in methanol 1-pyrenylmethyl ether (**3**) and carboxylic acids as shown in equation (1):⁴



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The absence of arylalkane, a radical coupling product derived from homolytic cleavage followed by decarboxylation, among the reaction products indicates that heterolytic cleavage is favoured in the photolysis of **1** and **2**. Although the aliphatic carboxylates **1** efficiently undergo this photolytic reaction, the benzoates **2** carrying strongly electron-withdrawing *para*-substituents such as cyano are not photolysed; they are entirely photostable.⁵ Instead, considerable fluorescence quenching and a decrease of the excited state lifetime even in non-polar solvents are observed for these photostable compounds. The relationship between photo-reactivity and fluorescence quenching in **1** and **2** has to be elucidated. Since electron transfer from a donor to an acceptor often results in fluorescence quenching, intramolecular electron transfer might be more or less responsible for the fluorescence quenching in **2** ($X = \text{CN}, \text{NO}_2$). On the other hand, for a molecule in which two chromophores are separated by more than three atoms, intramolecular exciplex formation is often observed as a result of strong electron transfer.⁶ Whereas the pyrene (**D**) and the benzoate (**A**) moieties of **2** are connected by three atoms ($\text{CH}_2\text{—O—CO}$),⁷ intramolecular exciplex formation is not observed. However, this might not necessarily mean that intramolecular electron transfer is insufficient to give rise to an exciplex formation, because the *s-trans* conformation around the ester O—CO bond is expected to be energetically more favourable than the *s-cis* conformer in the excited state and in the ground state, so that rotation around the O—CO bond for overlapping of the two chromophores is not possible.⁸ There is a possibility of exciplex formation in a system with more than one methylene chain between pyrene and the benzoate, where rotation around the $\text{CH}_2\text{—CH}_2$ bond makes overlapping of the two chromophores possible. Here we report the results of a detailed study on the influence of *para*-substituents of benzoates and of the length of the intervening methylene chains on fluorescence quenching and exciplex formation, and propose a mechanism for the fluorescence quenching in ω -(1-pyrenyl)alkyl *para*-substituted benzoates PnX ($n = 1\text{--}4$, $X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}, \text{NO}_2$).



RESULTS AND DISCUSSION

Absorption spectra

Electronic absorption data for P2X in isooctane and in acetonitrile are summarized in Table 1. The absorption spectra of PnX ($n = 1, 3, 4$) do not show any difference in shape and intensity from those of the corresponding P2X compounds. The UV absorption spectra of PnX are superimposable on the corresponding equimolar mixture of the reference compounds PnOM and BX ($X = \text{H}, \text{Cl}, \text{CF}_3, \text{CN}$). Figure 1 shows the spectra of P1CN and an equimolar mixture of P1OM and BCN as a typical example. The absorption spectrum of PnX above 300 nm is similar to that of pyrene, and no new absorption at longer wavelength is observed. From these observations, we conclude that strong interaction between the donor **D** (pyrene) and the acceptor **A** (*para*-substituted benzoate) is absent in the ground states of PnX .

Emission spectra

On excitation at 313 or 340 nm, the fluorescence spectra of PnH , PnCl , and PnNO_2 ($n = 1, 2, 4$) in isooctane, ethyl acetate and acetonitrile at room temperature are almost the same as that of pyrene, although they differ in intensities. The absence of intramolecular exciplex formation in these compounds is therefore concluded. Fluorescence quantum yields in solvents of various polarity were obtained relative to that of pyrene as shown in Table 2. Whereas the emission of PnH was as strong as that of pyrene, the emission of PnNO_2 was almost completely quenched unless the spectrum was taken with the sample degassed by careful freeze-pump-thaw cycles.

P1CN in ethyl acetate shows a slight broadening of the longer wavelength emission peak, but its excitation spectrum matches its absorption spectrum. The emission and absorption spectra of P1CN are shown in Figure 2. We assume that this broadening is caused by sufficient intramolecular electronic interaction to give rise to the weak 'exciplex-type' emission,⁹ which does not require direct overlap of the chromophores. Therefore, rotation around the ester O—CO bond of P1CN from the energetically more favourable *s-trans* to the less favourable *s-cis* conformation is not necessary. In isooctane and acetonitrile, the emission spectra of P1CN are the same as those of pyrene, indicating the absence or extreme weakness of the 'exciplex-type' emission. The emission from P1CF_3 was also very weak, but broadening of the emission peak was not observed in any solvent used.

For PnX with $n > 2$, the conformation suitable for an exciplex formation can be attained by rotation around the $\text{CH}_2\text{—CH}_2$ bond without changing the *s-trans* conformation of the ester O—CO bond.

Table 1. Electronic absorption data for P2X (X = H, Cl, CF₃, CN, NO₂) in isooctane and acetonitrile

λ_{max} (nm) [$\log \epsilon (\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})^a$]					
P2H		P2Cl		P2CF ₃	
Isooctane	Acetonitrile	Isooctane	Acetonitrile	Isooctane	Acetonitrile
233 (4.7)	233 (4.8)	234 (4.7)	234 (4.8)	234 (4.7)	233 (4.7)
243 (4.9)	242 (4.9)	243 (4.9)	242 (4.9)	243 (4.9)	242 (4.9)
255 (4.1)	255 (4.1)	264 (4.4)	265 (4.4)	255 (4.1)	255 (4.1)
265 (4.5)	265 (4.5)	275 (4.7)	275 (4.7)	265 (4.4)	265 (4.4)
275 (4.8)	275 (4.7)	311 (4.0)	312 (4.1)	275 (4.7)	276 (4.7)
311 (4.1)	312 (4.1)	325 (4.5)	325 (4.5)	311 (4.1)	312 (4.1)
325 (4.5)	325 (4.5)	341 (4.7)	341 (4.7)	325 (4.5)	325 (4.5)
341 (4.7)	341 (4.7)		375 (2.8)	341 (4.7)	341 (4.6)
375 (2.4)	375 (2.8)			375 (2.6)	375 (2.9)
		P2CN		P2NO ₂	
Isooctane	Acetonitrile	Isooctane	Acetonitrile	Isooctane	Acetonitrile
233 (4.6)	234 (4.9)	234 (4.6)	234 (4.9)	233 (4.6)	233 (4.6)
242 (4.8)	242 (5.0)	243 (4.8)	242 (5.0)	242 (4.8)	242 (4.8)
255 (4.3)	265 (4.5)	264 (4.3)	265 (4.5)	255 (4.3)	255 (4.4)
264 (4.5)	275 (4.8)	275 (4.6)	275 (4.8)	264 (4.5)	265 (4.5)
275 (4.7)	312 (4.2)	311 (4.0)	312 (4.2)	275 (4.6)	275 (4.7)
311 (4.0)	326 (4.6)	325 (4.3)	326 (4.6)	311 (4.0)	311 (4.1)
325 (4.4)	342 (4.7)	341 (4.5)	342 (4.7)	325 (4.4)	325 (4.4)
341 (4.5)	375 (3.1)	375 (2.6)	375 (3.1)	341 (4.5)	341 (4.6)
376 (3.2)				375 (2.8)	376 (3.2)

^a Values in parentheses.

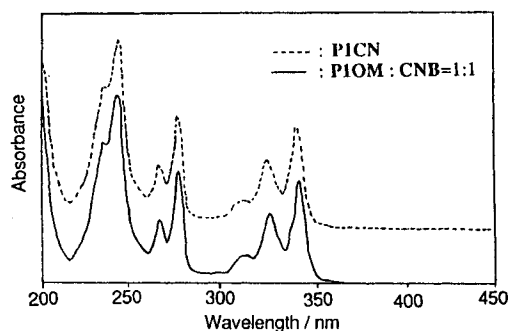


Figure 1. UV absorption spectra of **P1CN** and an equimolar mixture of **P1OM** and **CNB** in acetonitrile at room temperature

Whereas PnX ($X = H, Cl, NO_2$) do not show any change in the emission spectra, **P2CN**, **P3CN** and **P4CN** in isooctane show broadening of the emission peaks at the longest wavelength, which grow into new broad, red-shifted bands as the polarity of the solvent increases. The ratio of the new emission band vs pyrene emission (locally excited emission) reaches a maximum in dichloromethane, and then decreases as the polarity of the solvent increases. In acetonitrile, the new bands are very weak in **P2CN** and **P3CN** and invisible in **P4CN**. The excitation spectra of these compounds observed at 377 and 500 nm are identical with the absorption spectra, indicating that these new longer wavelength emissions are due to the excited state complex formation, i.e. intramolecular exciplex formation. The ratio of the exciplex emission band vs the locally excited emission (pyrene) band is largest in **P3CN** among these three. The fluorescence spectra of **P2CN** and **P4CN** in several solvents at room temperature are shown in Figures 3 and 4. **P2CF₃** shows an exciplex emission in solvents of medium to high polarity such as ethyl acetate and acetonitrile, but not in isooctane, as shown in Figure 5. This exciplex emission and its solvatochromic shift are much smaller than those of **P2CN**. **P4CF₃** does not show an exciplex emission in either ethyl acetate or acetonitrile.

The solvent dependence of the exciplex emission frequency (ν_f) and the dipole moment of the exciplex (μ_e) are generally expressed by equation (2):¹⁰

$$\nu_f = \nu_f(0) - (2\mu_e^2/hc\rho^3) \Delta f \quad (2)$$

where $\nu_f(0)$ denotes the wavenumber of the gas-phase exciplex emission maximum and ρ the radius of a spherical cavity in which the molecule fits (Onsager model¹¹); Δf represents a measure of solvent polarity defined by the dielectric constant ϵ and the optical refractive index n , as shown in the equation

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2) \quad (3)$$

The dipole moments of the exciplex (μ_e) can be obtained for the slope of a plot of ν_f versus Δf , using a properly estimated value of ρ , which is usually 40% of the longest axis for a flexible molecule.¹² For PnX , the ρ value is thus calculated to be between 3.6 and 5.2 Å from the molecular models for the extended conformations. However, based on the emission decay and precise ¹H NMR analyses, we previously reported that the exciplex of **P2CN** is formed only from its 'folded' conformer in the ground state.¹³ The molecular model for the folded conformation of **P2CN** gives $\rho = 4$ Å, which is approximately the same as above. We therefore use the values of ρ obtained from '40% of the longest axis' for the calculation of the dipole moments, on the assumption that ρ values for $PnCN$ ($n = 3, 4$) and **P2CF₃** might be approximately the same regardless of the ground-state conformation giving an exciplex.

Table 3 gives the fluorescence data in various solvents, the slopes ($2\mu_e^2/hc\rho^3$) obtained from the plots and the dipole moments calculated by using the estimated ρ values. From the slope, μ_e of **P2CF₃** is calculated to be about 80% of μ_e of **P2CN**, assuming that distance between the chromophores (ρ value) is the same. Although the dipole moment values obtained contain a certain degree of arbitrariness owing to the ambiguity of ρ values, the dipole moment of 10–14 D indicates that the degree of charge separation in $PnCN$ and **P2CF₃** is smaller than in other systems with large charge separations such as pyrene-(CH₂)_n-amine, which has μ_e between 17 and 19 D.²

Effects of solvent polarity on fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_f) relative to that of pyrene and lifetimes (τ_f) of PnX in isooctane, ethyl acetate and acetonitrile are given in Table 2. The lifetimes listed were monitored at 377 nm in the nano-second domain, so that τ_f of less than 1 ns could not be determined. When monitored at longer wavelength, lifetimes of the exciplex are obtained for $PnCN$ and **P2CF₃**. The decay curve of $PnCN$ ($n > 2$) in isooctane, monitored at 377 nm, consists of two components: fast (< 1 ns) and slow (> 10 ns) components. While the fast decay corresponds to the decay of the 'locally excited' pyrene, the slow component is assigned to the solvated ion pair derived from the 'extended' conformer.¹³

All **P1X** compounds studied have smaller values of fluorescence quantum yields (Φ_f) and lifetimes (τ_f) in acetonitrile than those in isooctane. These aryl carboxylates, **P1X**, differ strikingly in this respect from 1-pyrenylmethyl esters of aliphatic carboxylic acids (**1**), which do not show any solvent dependence of Φ_f and τ_f . These effects of solvents are therefore ascribed to a certain kind of intramolecular interaction between the pyrene part and the arylcarboxylate part, which is more effective in a strongly polar solvent. Taking into

Table 2. Fluorescence lifetimes and fluorescence quantum yields

Solvents	Parameter	X											
		H				CN				Cl			
		P1	P2	P4	P1	P2	P3	P4	P1	P2	P4	P1	P2
Isooctane	$\tau_f(\text{ns})^a$	238	243	251	<1	<1	<1	<1	237	275	235	64	283
	$\Phi_{f,\text{total}}$	0.57	0.56	0.53	0.018	0.068	0.080	0.26	0.51	0.51	0.52	0.036	0.53
	$\Phi_{f,\text{LE}}$	0.57	0.56	0.53	0.018	0.025	0.028	0.23	0.51	0.51	0.52	0.036	0.53
	$\Phi_{f,\text{EX}}$					0.043	0.052	0.03					
Ethyl acetate	$\Phi_{f,\text{total}}$	0.53	0.50	0.58	0.010	0.011	0.052	0.031	0.51	0.52	0.54	0.006	0.075
	$\Phi_{f,\text{LE}}$	0.53	0.50	0.58	0.005	0.001	0.004	0.003	0.51	0.52	0.54	0.006	0.050
	$\Phi_{f,\text{EX}}$				0.005	0.010	0.048	0.028					0.025
	$\tau_f(\text{ns})^a$	137	192	172	<1	<1	<1	<1	15	93	148	<1	<1
Acetonitrile	$\Phi_{f,\text{total}}$	0.31	0.56	0.56	0.0002	0.0004	0.017	0.006	0.034	0.23	0.38	0.002	0.003
	$\Phi_{f,\text{LE}}$	0.31	0.56	0.56	0.0002	0.0003	0.010	0.006	0.034	0.23	0.38	0.002	0.001
	$\Phi_{f,\text{EX}}$					0.0001	0.007						0.002

^a Monitored at 377 nm by nanosecond fluorescence lifetime measurement.^b Not detected.

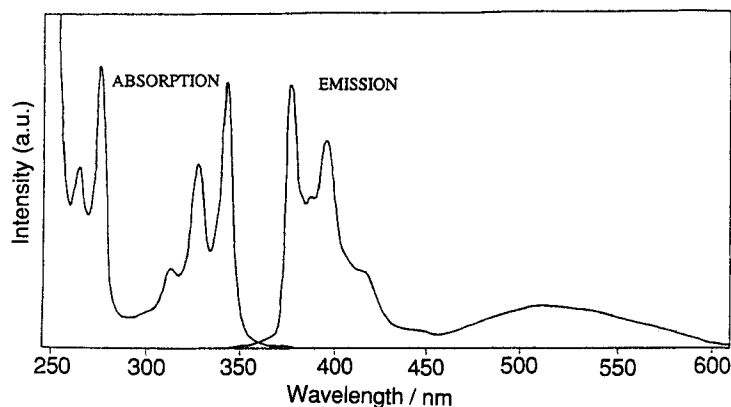


Figure 2. Emission and absorption spectra of **P1CN** in ethyl acetate at room temperature

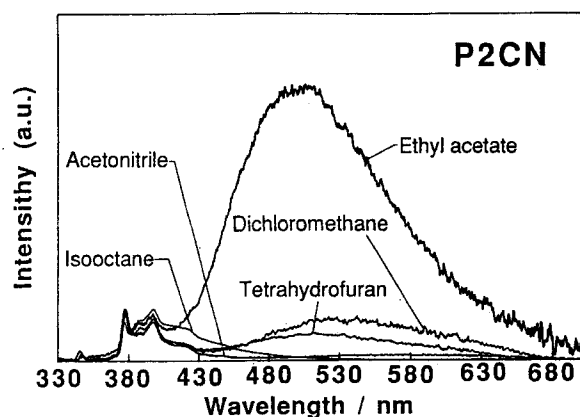


Figure 3. Emission spectra of **P2CN** excited at 313 nm in solvents of various polarity at room temperature

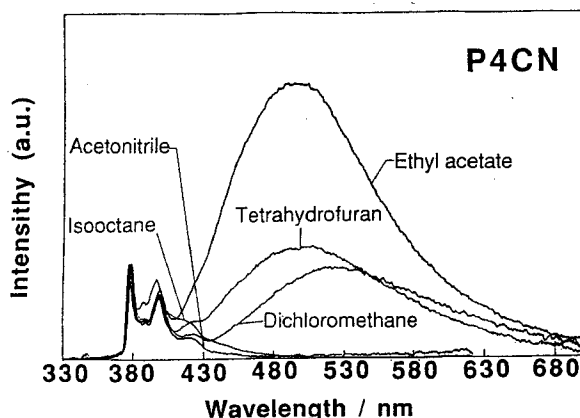


Figure 4. Emission spectra of **P4CN** excited at 313 nm in solvents of various polarity at room temperature

account that large decreases in Φ_f of **P1CF₃**, **P1NO₂** and **P1CN** are observed even in isooctane, intramolecular electron transfer may be one, but not the only, cause of this fluorescence quenching. It should be noted that **P1CF₃**, **P1NO₂** and **P1CN** are not photolysed in methanol.⁵ On the other hand, other **P1X** compounds are photolysed, although the photolysis proceeds more slowly as the electronegativity of the substituent increases. These results clearly show that the efficiency of fluorescence quenching and the decrease in fluorescence lifetimes compete with the photolytic cleavage of the ester CO—OCO bond of **P1X**.

An increase in methylene chain length decreases the effects of solvent polarity on both Φ_f and τ_f , although their correlation is not good. For instance, the difference between Φ_f in acetonitrile and that in isooctane is much larger in **P1Cl** (0.034 and 0.51) than in **P4Cl** (0.38 and 0.52). For the lifetimes, a similar tendency is observed in **P1Cl** (15 and 237 ns) and **P4Cl** (148 and 235 ns). The effects of the substituent X on Φ_f and τ_f are attenuated by the addition of methylene chains: the Φ_f values of **P1CF₃** and **P4CF₃** in isooctane are 0.036 and 0.51, respectively. Any other **P_nX** also shows similar effects of both solvent polarity and the length of the methylene chains, although they are more strongly dependent on the substituent X. The dependence of Φ_f on the length of methylene chains indicates that through-bond, rather than through-space, interactions such as electron transfer from the pyrene part to the arylcarboxylate part are operative in the series of **P_nX** ($n=1-4$). It is noted that an exciplex formation is observed only for those, except for **P_nNO₂**, which show substantial fluorescence quenching even in a non-polar solvent.

Mechanism of fluorescence quenching

It is known that electron transfer and exciplex for-

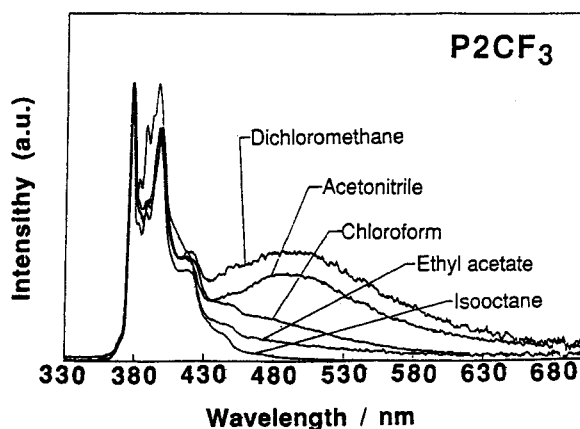


Figure 5. Emission spectra of **P2CF₃** excited at 313 nm in solvents of various polarity at room temperature

mation are possible for a system with a negative value of free enthalpy of electron transfer (ΔG_{ET}), given by the Rehm–Weller equation:¹⁴

$$\Delta G_{ET} = IP_D - EA_A - E_{00} - C + \Delta G_{solv} \quad (4)$$

where IP_D is the ionization potential of a donor, EA_A is the electron affinity of an acceptor, E_{00} is the excitation energy of the excited molecule, and C and ΔG_{solv} are a Coulombic energy and solvation of the ion pairs, respectively. A fairly accurate value of ΔG_{ET} can be calculated with the equation¹⁵

$$\Delta G_{ET} \text{ (eV)} = E_{(D/D^+)} - E_{(A^-/A)} - \Delta E_{00} - [e^2/\epsilon\rho] - [(e^2/r_{\pm})(1/36.2 - 1/\epsilon)] \quad (5)$$

using the oxidation and reduction potentials [$E_{(D/D^+)}$ and $E_{(A^-/A)}$] of a donor and an acceptor separated by ρ with average individual ionic radii $r_{\pm}$ in a solvent with dielectric constant ϵ when the redox potentials of the donor and the acceptor were determined in acetonitrile solution ($\epsilon = 36.2$ D). In order to evaluate the free energy of electron transfer in **PnX** series, cyclic voltammetric (CV) measurements of pyrene and methyl *para*-substituted benzoates were carried out in acetonitrile at room temperature. The oxidation potential of pyrene [$E_{(D/D^+)}$] was 0.91 V vs Ag/Ag^+ . The reduction potentials [$E_{(A^-/A)}$] of methyl benzoates carrying *p*-H, *p*-Cl, *p*-CN and *p*-NO₂ were -2.63, -2.47, -2.11 and -1.97 V vs Ag/Ag^+ , respectively. A Hammett plot of these reduction potentials shows a good linear correlation, from which $E_{(A^-/A)} = -2.19$ V for *p*-CF₃ benzoate is obtained. If we assume that the donor and acceptor parts of **PnX** in the extended conformation are separated by a distance between 9 Å ($n = 1$) and 13 Å ($n = 4$) obtained from the molecular model, ΔG_{ET} is calculated from equation (5) (individual ionic radii are

assumed to be 4.3 Å) using the excitation energy for pyrene $\Delta E_{00} = 3.43$ eV determined from the absorption and fluorescence spectra. ΔG_{ET} for the folded conformation is also calculated with 4 Å ($n = 2$) as the minimum value for distance between the donor and acceptor. As shown in Table 4, although the distance between 13 and 4 Å does not give a significant difference in the values of ΔG_{ET} in acetonitrile, in isoctane the effect of the distance on ΔG_{ET} is large. ΔG_{ET} decreases as the electronegativity of the *para*-substituents of the acceptor benzoates increases. Combination of pyrene (D) with *p*-CN-, *p*-Cl-, *p*-CF₃- or *p*-NO₂-benzoates (A) gives negative ΔG_{ET} , indicating that both exciplex formation and electron transfer are possible in acetonitrile for these systems.^{16,17} However, exciplex formation is rarely observed in acetonitrile, probably because the formation of a solvent-separated radical ion pair is more favourable. Hence it is noted that **P2CN**, **P3CN** and **P2CF₃** show exciplex emission in acetonitrile. Negative ΔG_{ET} values for $\rho = 4$ Å in isoctane indicate that exciplex formation is possible if a molecule is taking the folded conformation. However, exciplex formation in isoctane is observed only in **PnCN** ($n = 2-4$).

Although HB as a acceptor gives positive ΔG_{ET} (0.07 eV), Φ_f of **P1H** in acetonitrile decreases by as much as 50% of that in isoctane (Table 2). No fluorescence quenching is observed in **P2H** and **P4H**. Since other **P1X** compounds with electron-donating substituents such as *p*-methoxy or -methyl also show a decrease of Φ_f in polar solvents,⁵ the fluorescence quenching is assumed to be one of the characteristics of 1-pyrenylmethyl esters of benzoic acids. Whereas **C1B** has only a slightly negative ΔG_{ET} (-0.09 eV), more than 90% fluorescence quenching is observed in **P1Cl**, and the degree of the fluorescence quenching is decreased as methylene chain length increases. In **P1Cl**, the efficiency of quenching is attenuated for both electron transfer and the effect mentioned above.

Intersystem crossing to a triplet-state molecule is another possible route for dissipation of the singlet excited state. Hence nitroaromatic compounds are known to be mostly non-emissive, probably owing to efficient intersystem crossing,¹⁸ and the substantial fluorescence quenching of **PnNO₂** even in isoctane is reasonably understood. Although the heavy atom effect can accelerate intersystem crossing, this is not the case with **PnCl**. Whereas the efficiency of quenching via this process is assumed to be less dependent on solvent polarity than the electron transfer process, decreases in the fluorescence quantum yields of **PnCl** are only observed in polar solvents.

Very small Φ_f values of **PnCN** ($n = 1-3$), even in a non-polar solvent such as isoctane, cannot be explained by electron transfer alone, but might be properly explained by participation of a quenching mechanism via efficient intersystem crossing which

Table 3. Exciplex emission maxima, slopes of equation (2), estimated ρ values and excited-state dipole moments (μ_e)

Compound	$\lambda_{\max}$ (nm)						$2\mu_e^2/hc\rho^3$ (cgs) ^a	ρ (Å) ^b	μ_e (D)
	Isooctane	Chloroform	Ethyl acetate	Tetrahydrofuran	Dichloromethane	Acetonitrile			
P2CF ₃	— ^c	455	464	472	491	491	12 000	4.4	10
P2CN	430	505	505	515	530	565	18 000	4.4	12
P3CN	411	487	476	477	504	520	17 000	5.0	14
P4CN	445	492	497	504	530	— ^c	14 000	5.2	14

^a Slopes obtained from the plots of equation (2).^b ρ values were obtained for 40% of the longest axis of the molecular models of PnX in the extended conformation.^c Exciplex emission was not observed.

Table 4. Free enthalpy of electron transfer (ΔG_{ET})^a between pyrene and XB (X = H, Cl, CF₃, CN, NO₂) in acetonitrile and isoctane

D-A	σ_p^b	ΔG_{ET} (eV mol ⁻¹)					
		$\rho = 4 \text{ \AA}$		$\rho = 9 \text{ \AA}$		$\rho = 13 \text{ \AA}$	
		Acetonitrile	Isooctane	Acetonitrile	Isooctane	Acetonitrile	Isooctane
Py-HB	0.00	0.01	-0.11	0.07	0.89	0.08	1.2
Py-ClB	0.23	-0.15	-0.27	-0.09	0.73	-0.08	1.1
Py-CF ₃ B	0.54	-0.43	-0.55	-0.37	0.37	-0.36	0.77
Py-CNB	0.66	-0.51	-0.63	-0.45	0.37	-0.44	0.69
Py-NO ₂ B	0.78	-0.65	-0.77	-0.59	0.23	-0.58	0.55

^a Calculated from equation (5) using oxidation potential (vs Ag/Ag⁺) of +0.91 V for pyrene (Py) and reduction potential (vs Ag/Ag⁺) of -2.63, -2.47, -2.19, -2.11 and -1.97 V for HB, ClB, CF₃B, CNB and NO₂B, respectively.

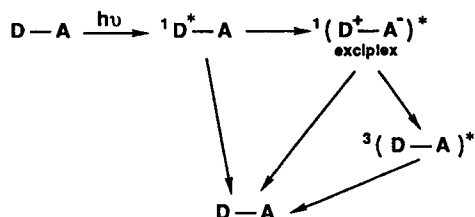
^b Hammett σ values for *para*-substituents.

dissipates most of the singlet excited state. Phosphorescence emission is not observed from any one of them, so that a non-emissive deactivation pathway has to be taken into consideration. There are some precedents in which existence of intersystem crossing was proved by detection of a triplet species. For example, triplet pyrene has been detected by its time-resolved absorption spectrum in the 1-pyrenyl-(CH₂)_n-amine system.¹⁹ There, the non-radiative decay of the exciplex proceeds through intersystem crossing to the locally excited state of pyrene and internal conversion to the ground state. Of particular interest for us is that the relative efficiency of this intersystem crossing process decreases compared with the efficiency of the internal conversion process to the singlet ground state as the solvent polarity increases.²⁰ Although we have not yet attempted the direct detection of a triplet species, it can be said that intersystem crossing from an exciplex singlet state takes place in PnX in the case when it forms an exciplex. Scheme 1 is a proposed overall mechanism for the fluorescence quenching in PnX. Since PnCN (*n* = 2 or 3) in isoctane shows exciplex emission and efficient fluorescence quenching, the extent of the intersystem crossing might be large. On the other hand, although P4CN shows an exciplex emission in isoctane, the fluorescence quenching is small. This may be due to the comparatively large distance

between the donor and acceptor which makes the orbital interaction required for intersystem crossing weaker. Since the fluorescence of P1CF₃ and P1CN in isoctane is strongly quenched, it is assumed that they form an exciplex-type species in the excited state which dissipates almost all of the energy by intersystem crossing to a triplet state. Hence this series of compounds, PnX, is one of a few examples that illustrate the intervention of exciplexes playing an important role in fluorescence decay by intersystem crossing. However, for the determination of the definite process of fluorescence decay, precise information on the non-radiative decay is needed.

CONCLUSION

Whereas intramolecular interaction in the ground state is not observed in any PnX, their spectroscopic feature in the excited state depends strongly on the *para*-substituents of the benzoates: fluorescence quenching becomes more efficient as the electron-withdrawing ability of the *para*-substituents increases. The relationship between fluorescence quenching by electron transfer and *para*-substituents of PnX is discussed by means of ΔG_{ET} values obtained from the oxidation and reduction potentials of pyrene and methyl *para*-substituted benzoates, respectively. PnCN, with the corresponding $\Delta G_{ET} = -0.45$ eV, shows an intramolecular exciplex or 'exciplex-type' (*n* = 1) emission in solvents of low to high polarity. P2CF₃, $\Delta G_{ET} = -0.37$ eV, also shows an exciplex emission in solvents of medium to high polarity. PnNO₂ is exceptional, since the fluorescence of nitroaromatic compounds is always strongly quenched by efficient intersystem crossing. The fluorescence of PnCN is assumed to be strongly quenched by intersystem crossing from the singlet exciplex to the locally excited pyrene, as well as by electron transfer from the pyrene



part to the benzoate part. That the formation of a singlet exciplex is necessary for intersystem crossing in bichromophoric compounds containing pyrene is thus clearly demonstrated.

EXPERIMENTAL

General methods. ^1H NMR spectra were recorded on a Jeol GSX 270 spectrometer with TMS as an internal standard. UV-visible absorption spectra were measured with a Hitachi Model 330 spectrometer. Fluorescence spectra were measured on a Hitachi Model 850 spectrofluorimeter and phosphorescence spectra were measured on the same instrument using a Dewar bottle with quartz windows. Fluorescence quantum yields were determined at room temperature relative to those of pyrene ($\Phi_f = 0.58$ in a non-polar solvent and 0.53 in a polar solvent)²¹ for solutions of matched absorbance (0.1) at the excitation wavelength (313 nm). Fluorescence lifetimes were measured with photon counting apparatus (Horiba NAES-1100) with a hydrogen arc lamp (Hamamatsu Photophysics, time resolution *ca* 1 ns). Cyclic voltammograms of pyrene and methyl *para*-substituted benzoates were obtained at a scan rate of 0.2 V s^{-1} by the use of a Huso Model 956B potentiostat, an HECS 317S function generator, WX 1100 recorder and a three-electrode cell composed of a glassy carbon working electrode, platinum wire counter electrodes and an Ag/AgNO_3 reference electrode. All the sample solutions were *ca.* 0.5 mM in substrates and 0.1 in tetra-*n*-butylammonium perchlorate as a supporting electrolyte in CH_3CN . The peak potentials were read and calibrated with reference to ferrocene added as an internal standard after each measurement.

Materials. Spectrograde solvents (Fluorosol, supplied by Cica-Merck) were used without further purification. For measurements of absorption and emission spectra and lifetimes, all the *PnX* compounds were purified by repeated column chromatography on silica gel and recrystallization. Their purity was confirmed by HPLC with UV absorption and fluorescence emission detection. In cases where impurities were detected even after several stages of recrystallization and chromatography, the sample solution was collected directly from HPLC. The concentrations of the solutions for spectroscopic studies were adjusted less than 10^{-5} M , where no intermolecular interaction was found and the absorbance at the excitation wavelength was less than 0.1 . The samples were degassed by freeze-pump-thaw cycles on a high-vacuum line and sealed under vacuum.

ω -(1-Pyrenyl)alkanols. ω -(1-Pyrenyl)alkanols were obtained by the reduction of ω -(1-pyrenyl)alkanoic acids. ^1H NMR spectra and melting points of these

compounds were identical with literature values. Pyrenylacetic acid was obtained by hydrolysis of pyrenylacetamide, which was synthesized by a Willgerodt reaction²² from acetylpyrene. A description of the synthesis of pyrenylpropanoic acid is given in Ref. 23. 4-(1-Pyrenyl)butanoic acid was purchased from Aldrich.

ω -(1-Pyrenylalkyl) *para*-substituted benzoates (*PnX*). The preparation of P2CN is typical for all *PnX* from the corresponding ω -(1-pyrenyl)alkanols and *para*-substituted benzoylchloride. A solution of 2-(1-pyrenyl)ethanol (190 mg , 0.77 mmol), *p*-cyanobenzoyl chloride (120 mg , 0.72 mmol), triethylamine (0.2 cm^3) and 4-dimethylaminopyridine (5 mg) in chloroform (10 cm^3) was refluxed for 5 h with stirring, and then cooled to room temperature. Extraction with dichloromethane, washing first with 5% hydrochloric acid and then with 5% sodium hydrogen-carbonate, drying over anhydrous magnesium sulphate and concentration under vacuum gave a crude product. Chromatography on silica gel with benzene as eluent yielded pure 2-(1-pyrenyl)ethyl *p*-cyanobenzoate (P2CN) (215 mg , 79%), m.p. $152\text{--}153^\circ\text{C}$ (found: C, 83.19 ; H, 4.66 ; N, 4.03 , $\text{C}_{26}\text{H}_{17}\text{O}_2\text{N}$ requires C, 83.18 ; H, 4.56 ; N, 3.73%); ν_{max} (KBr) (cm^{-1}) 2230 (CN), 1721 (C=O), 1270 (C—O); δ_{H} (270 MHz ; CDCl_3 ; Me_4Si) 3.83 (2H, t, $J = 7.0$, 2-H), 4.80 (2H, t, $J = 7.0$, 1-H), 7.69 (2H, d, $J = 8.5$, Ph), $7.92\text{--}8.41$ (11H, m, pyrene and Ph).

1-Pyrenylmethylbenzoate (P1H): m.p. $144(145^\circ\text{C})$ (found: C, 85.34 ; H, 4.82 , $\text{C}_{24}\text{H}_{16}\text{O}_2$ requires C, 85.69 ; H, 4.79%); ν_{max} (KBr) (cm^{-1}) 1719 (C=O), 1270 (C—O); δ_{H} (270 MHz ; CDCl_3 ; Me_4Si) 6.09 (2H, s, 1-H), $7.35\text{--}7.57$ (3H, m, Ph), $8.00\text{--}8.43$ (11H, m, pyrene and Ph).

1-Pyrenylmethyl *p*-chlorobenzoate (P1Cl): m.p. $136\text{--}137^\circ\text{C}$ (found: C, 77.62 ; H, 4.08 , $\text{C}_{24}\text{H}_{15}\text{O}_2\text{Cl}$ requires C, 77.73 ; H, 4.08%); ν_{max} (KBr) (cm^{-1}) 1727 (C=O), 1267 (C—O), 1091 (Cl); δ_{H} (270 MHz ; CDCl_3 ; Me_4Si) 6.02 (2H, s, 1-H), 7.36 (2H, d, $J = 9.0$, Ph), $7.96\text{--}8.40$ (11H, m, pyrene and Ph).

1-Pyrenylmethyl *p*-trifluoromethylbenzoate (P1CF₃): m.p. $132\text{--}134^\circ\text{C}$ (found: C, 74.36 ; H, 3.88 , $\text{C}_{25}\text{H}_{15}\text{O}_2\text{F}_3$ requires C, 74.25 ; H, 3.74%); ν_{max} (KBr) (cm^{-1}) 1731 (C=O), 1332 (CF₃), 1270 (C—O); δ_{H} (270 MHz ; CDCl_3 ; Me_4Si) 6.12 (2H, s, 1-H), 7.66 (2H, d, $J = 8.0$, Ph), $8.00\text{--}8.42$ (11H, m, pyrene and Ph).

1-Pyrenylmethyl *p*-cyanobenzoate (P1CN): m.p. 172°C (found: C, 83.05 ; H, 4.27 ; N, 3.88 , $\text{C}_{25}\text{H}_{15}\text{O}_2\text{N}$ requires C, 83.09 ; H, 4.18 ; N, 3.88%); ν_{max} (KBr) (cm^{-1}) 2230 (CN), 1719 (C=O), 1276 (C—O); δ_{H} (270 MHz ; CDCl_3 ; Me_4Si) 6.12 (2H, s, 1-H), 7.69 (2H, d, $J = 8.5$, Ph), $8.01\text{--}8.39$ (11H, m, pyrene and Ph).

1-Pyrenylmethyl *p*-nitrobenzoate (P1NO₂): m.p. $157\text{--}158^\circ\text{C}$ (found: C, 75.49 ; H, 4.02 ; N, 3.90 , $\text{C}_{24}\text{H}_{15}\text{O}_4\text{N}$ requires C, 75.58 ; H, 3.96 ; N, 3.67%);

$\nu_{\max}$ (KBr) (cm^{-1}) 1725 (C=O), 1531 (NO_2), 1346 (NO_2) 1270 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 6.19 (2H, s, 1-H), 8.00–8.40 (13H, m, pyrene and Ph).

2-(1-Pyrenyl)ethylbenzoate (P2H): m.p. 100–101 °C (found: C, 85.5; H, 5.38. $\text{C}_{25}\text{H}_{18}\text{O}_2$ requires C, 85.69; H, 5.18%); $\nu_{\max}$ (KBr) (cm^{-1}) 1727 (C=O), 1270 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.84 (2H, t, $J=7.5$, 2-H), 4.77 (2H, t, $J=7.5$, 1-H), 7.36–7.60 (3H, m, Ph), 7.96–8.46 (11H, m, pyrene and Ph).

2-(1-Pyrenyl)ethyl *p*-chlorobenzoate (P2Cl): m.p. 119–120 °C (found: C, 78.24; H, 4.56; Cl, 9.21. $\text{C}_{25}\text{H}_{17}\text{O}_2\text{Cl}$ requires C, 78.02; H, 4.45; Cl, 9.21%); $\nu_{\max}$ (KBr) (cm^{-1}) 1711 (C=O), 1272 (C—O), 1091 (Cl); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.82 (2H, t, $J=7.0$, 2-H), 4.76 (2H, t, $J=7.0$, 1-H), 7.38 (2H, d, $J=8.5$, Ph), 7.90–8.44 (11H, m, pyrene and Ph).

2-(1-Pyrenyl)ethyl *p*-trifluoromethylbenzoate (P2CF₃): m.p. 138 °C (found: C, 74.85; H, 4.21. $\text{C}_{26}\text{H}_{17}\text{O}_2\text{F}_3$ requires C, 74.64; H, 4.1%; $\nu_{\max}$ (KBr) (cm^{-1}) 1719 (C=O), 1334 (CF_3), 1272 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.84 (2H, t, $J=7.0$, 2-H), 4.80 (2H, t, $J=7.0$, 1-H), 7.67 (2H, d, $J=8.0$, Ph), 7.94–8.43 (11H, m, pyrene and Ph).

2-(1-Pyrenyl)ethyl *p*-nitrobenzoate (P2NO₂): m.p. 157–158 °C (found: C, 75.16; H, 4.49. $\text{C}_{25}\text{H}_{17}\text{O}_4\text{N}$ requires C, 75.94; H, 4.33%); $\nu_{\max}$ (KBr) (cm^{-1}) 1725 (C=O), 1520 (NO_2), 1348 (NO_2), 1267 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.85 (2H, t, $J=7.0$, 2-H), 4.81 (2H, t, $J=7.0$, 1-H), 7.94–8.43 (13H, m, pyrene and Ph).

3-(1-Pyrenyl)propyl *p*-cyanobenzoate (P3CN): m.p. 121–122 °C; $\nu_{\max}$ (KBr) (cm^{-1}) 2228 (CN), 1723 (C=O), 1278 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 2.24–2.37 (2H, m, 2-H), 3.46 (2H, t, $J=7.0$, 3-H), 4.40 (2H, t, $J=6.0$, 1-H), 7.42 (2H, d, $J=8.5$, Ph), 7.71–8.22 (11H, m, pyrene and Ph).

4-(1-Pyrenyl)butylbenzoate (P4H): m.p. 113 °C (found: C, 85.74; H, 5.89. $\text{C}_{27}\text{H}_{22}\text{O}_2$ requires C, 85.69; H, 5.86%); $\nu_{\max}$ (KBr) (cm^{-1}) 1713 (C=O), 1280 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.88–2.12 (4H, m, 2-H and 3-H), 3.44 (2H, t, $J=7.0$, 4H), 4.41 (2H, t, $J=6.0$, 1-H), 7.35–7.59 (3H, m, Ph), 7.84–8.32 (11H, m, pyrene and Ph).

4-(1-Pyrenyl)butyl *p*-chlorobenzoate (P4Cl): m.p. 121 °C (found: C, 78.77; H, 5.19; Cl, 8.51. $\text{C}_{27}\text{H}_{21}\text{O}_2\text{Cl}$ requires C, 78.54; H, 5.13; Cl, 8.59%); $\nu_{\max}$ (KBr) (cm^{-1}) 1715 (C=O), 1276 (C—O), 1091 (Cl); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.88–2.10 (4H, m, 2-H and 3-H), 3.43 (2H, t, $J=7.0$, 4-H), 4.39 (2H, t, $J=6.0$, 1-H), 7.35 (2H, d, $J=9.0$, Ph), 7.84–8.30 (11H, m, pyrene and Ph).

4-(1-Pyrenyl)butyl *p*-trifluoromethylbenzoate (P4CF₃): m.p. 84 °C (found: C, 75.33; H, 4.74. $\text{C}_{28}\text{H}_{21}\text{O}_2\text{F}_3$ requires C, 74.58; H, 4.74%); $\nu_{\max}$ (KBr) (cm^{-1}) 1719 (C=O), 1328 (CF_3), 1278 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.88–2.12 (4H, m, 2-H and 3-H), 3.44 (2H, t, $J=7.0$, 4-H), 4.41 (2H, t, $J=6.0$,

1-H), 7.63 (2H, d, $J=8.0$, Ph), 7.84–8.30 (11H, m, pyrene and Ph).

4-(1-Pyrenyl)butyl *p*-cyanobenzoate (P4CN): m.p. 147 °C (found: C, 83.41; H, 5.30; N, 3.54. $\text{C}_{28}\text{H}_{21}\text{O}_2\text{N}$ requires C, 83.35; H, 5.25; N, 3.47%); $\nu_{\max}$ (KBr) (cm^{-1}) 2228 (CN), 1721 (C=O), 1278 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.88–2.12 (4H, m, 2-H and 3-H), 3.34 (2H, t, $J=7.0$, 4-H), 4.40 (2H, t, $J=6.0$, 1-H), 7.63 (2H, d, $J=9.0$, Ph), 7.84–8.30 (11H, m, pyrene and Ph).

4-(1-Pyrenyl)butyl *p*-nitrobenzoate (P4NO₂): m.p. 163–164 °C (found: C, 75.72; H, 4.91; N, 3.31. $\text{C}_{27}\text{H}_{21}\text{O}_4\text{N}$ requires C, 76.58; H, 5.00; N, 3.31%); $\nu_{\max}$ (KBr) (cm^{-1}) 1721 (C=O), 1528 (NO_2), 1342 (NO_2), 1276 (C—O); δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.88–2.13 (4H, m, 2-H and 3-H), 3.43 (2H, t, $J=7.0$, 4-H), 4.41 (2H, t, $J=6.0$, 1-H), 7.84–8.30 (13H, m, pyrene and Ph).

ω -Methoxy-1-pyrenylalkane (PnOM). The preparation of P2OM is typical for all PnOM from the corresponding ω -(1-pyrenyl)alkanols and methyl iodide. A suspension of 2-(1-pyrenyl)ethanol (98 mg, 0.40 mmol) and sodium hydrides (10 mg, 0.42 mmol) in dimethylformamide (14 cm^3) was stirred for 30 min at room temperature. Methyl iodide (0.025 cm^3 , 40 mmol) was added to the reaction mixture. The stirring was continued for 30 min at room temperature, then the solution was poured into cold water and the precipitate was filtered with suction. Chromatography of the precipitate on silica gel with benzene as an eluent yielded 2-methoxypyrenylethane (53 mg, 51%), δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.41 (3H, s, Me), 3.64 (2H, t, $J=7.5$, 1-H), 3.83 (2H, t, $J=7.5$, 2-H), 7.86–8.57 (9H, m, pyrene).

1-Methoxy-1-pyrenylmethane (P1OM): m.p. 44–45 °C; δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 3.51 (3H, s, Me), 5.19 (2H, s, 1-H), 7.90–8.40 (9H, m, pyrene).

4-Methoxy-1-pyrenylbutane (P4OM): m.p. 44–45 °C; δ_{H} (270 MHz; CDCl_3 ; Me_4Si) 1.70–1.80 (2H, m, 2-H), 1.90–2.00 (2H, m, 3-H), 3.33 (3H, s, Me), 3.40 (2H, t, $J=7.5$, 1-H), 3.45 (2H, t, $J=7.5$, 4-H), 7.80–8.30 (9H, m, pyrene).

Methyl para-substituted benzoates XB ($X=\text{H}$, Cl, CF_3 , CN, NO_2). XB was prepared from the corresponding *para*-substituted benzoyl chloride and methanol by the same method of preparation as for PnX. ^1H NMR spectra and melting points of these compounds were identical with literature values.

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