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The spectroscopy and photophysics of three 9,10-diaryl phenanthrene derivatives

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Abstract

The spectroscopic and photophysical properties of three 9,10-diaryl phenanthrene derivatives (fluorophenyl, methoxyphenyl and hydroxyphenyl phenanthrenes) have been studied in cyclohexane and in methanol. The UV absorption, fluorescence excitation and emission spectra have been recorded for these three compounds. From these experiments, molar extinction coefficients, Stokes shifts and quantum yields have been calculated or measured. Fluorescence lifetimes have also been measured by using a time-correlated single-photon counting technique. The radiative decay rate constants based on the quantum yields and lifetimes have finally been obtained. Solvent polarity and the nature of the substituent have an influence on the spectroscopic characteristics.

Keywords: Spectroscopy; Photophysics; 9,10-Diaryl phenanthrene derivatives

1. Introduction

In this manuscript we describe the spectroscopic properties of three derivatives of phenanthrene, each with two 4-substituted phenyl rings in the 9- and 10-positions. The UV absorption and fluorescence properties we describe are very similar to those of 9-alkyl phenanthrene. There are no dramatic features which make their behaviour unusual. The reason for our interest in these compounds is not only that they are easy to prepare; the 9,10-di(4'-hydroxyphenyl)-phenanthrene is potentially a useful label for incorporating into condensation polymers, and the corresponding dimethoxyphenyl compound serves as a model for its dialkyl ethers. Other phenanthrene derivatives which serve this function are either difficult to prepare or expensive. Thus it is useful to report on the behaviour of these dyes in order to make others aware of their potential applications.

Phenanthrene and its derivatives are a family of aromatic compounds whose photophysical properties have been widely studied [1–3]. The essential spectroscopic features of phenanthrene and many of its derivatives are the absence of excimer formation and their insensitivity to solvent polarity and to self-quenching [4–6], all of which make these phenanthrenes ideal fluorescent probes for studying complex media.

Phenanthrene itself in cyclohexane has four vibronic bands in its fluorescence spectrum, a 0.13 quantum yield and a 55 ns fluorescence lifetime [7]. Generally speaking, phenanthrene derivatives have shorter fluorescence lifetimes (from 20 ns to 45 ns) and higher quantum yields (from 0.14 to 0.3) than phenanthrene itself. The substituents break the symmetry of the phenanthrene, increasing the radiative decay rate constant k_f, and they also affect the non-radiative deactivation pathways. For phenanthrene and most of its derivatives, little or no red shift is observed in their fluorescence emission upon increasing solvent polarity. For some phenanthrene derivatives, in very polar solvents, red shifts have been observed. Here production of solvated electrons may be involved in the radiationless decay process [1,4–6].

Recently, one of us reported the synthesis and characterization of three new phenanthrene derivatives (1, 2, 3) with pairs of substituents (fluorophenyl, methoxyphenyl and hydroxyphenyl) at the 9-, 10-positions [8] (synthetic procedures for compounds 2 and 3 are available on request). 3, in particular, lends itself to potential incorporation into polymers as a fluorescent label. We were interested in examining the photophysical properties of these molecules to see how the different substituents affect their spectroscopy. In this paper, the UV absorption, fluorescence excitation and emission

spectra are reported for these three compounds. In addition, the fluorescence quantum yields and lifetimes have been measured. Finally, the radiative decay rate constants were calculated from the quantum yields and fluorescence lifetimes.
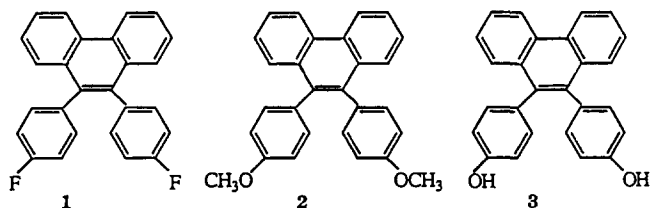
2. Experimental details

The synthesis and characterization of 1, 2 and 3 have been reported [8]. The solvents, cyclohexane and methanol (spectral grade, Caledon Laboratories), were used without further purification. Samples were prepared at 10^{-3} M and later diluted with spectral grade cyclohexane or methanol. All samples were degassed by nitrogen bubbling prior to the measurements.

Absorption spectra were recorded on a Perkin–Elmer UV–visible Lambda 19 or a Lambda 6 spectrophotometer with solution concentration less than 2×10^{-4} M, using 1 nm (full width at half-maximum (FWHM)) bandwidth. Fluorescence emission spectra were recorded with a Spex Fluorolog 2 spectrofluorometer and corrected by means of a rhodamine B quantum counter and an MgO reflecting surface [9]. A 1 cm optical path length sample cell was used in the normal 90° configuration at room temperature.

Quantum yields were determined by using the secondary standard method, with recrystallized phenanthrene in cyclohexane ($\Phi_f = 0.13$) as the reference [7]. Concentrations were adjusted to be below 10^{-5} M in the specified solvent with similar absorbance below 0.1 at λ_{ex}. Because of the substituent effect on the absorption spectrum, there is no excitation wavelength λ_{ex} that corresponds to a maximum for both the molecules of interest and the phenanthrene standard. We therefore repeat the measurement using $\lambda_{ex} = 289$ nm which corresponds to a minimum of phenanthrene and 292 nm which corresponds to a maximum. The following equation was applied for calculating the quantum yields:

$$\Phi_2 = \Phi_1 \frac{A_1(\lambda)}{A_2(\lambda)} \left(\frac{n_2}{n_1}\right)^2 \frac{\displaystyle\int_0^\infty F_2(\lambda\, d\lambda}{\displaystyle\int_0^\infty F_1(\lambda)\, d\lambda} \tag{1}$$

$A(\lambda)$ is the absorption of the solution at λ_{ex} (289 nm or 292 nm), n is the refractive index of the solvent (1.426 for cyclohexane and 1.329 for methanol), and the integral $\int F(\lambda)\, d\lambda$ is the area under the fluorescence spectrum. The index 1 refers to phenanthrene in cyclohexane (standard) and the index 2 refers to the phenanthrene derivatives in cyclohexane or methanol.

Fluorescence decay curves were measured with a time-correlated single-photon counting system equipped with an Nd:YAG laser (Coherent Antares 76-s) synchronously pumping a cavity-dumped dye laser (Coherent, model 700). A microchannel plate photomultiplier (Hammamatsu R15640-1) was used as the detector. The output from the dye laser was frequency doubled to produce pulses at 292 nm. The fluorescence emission was observed at 377 nm. A Glan–Taylor prism polarizer was placed on the emission side at the magic angle (54.75°) to the polarized plane of excitation light so as to remove the effect of photoselection. A Ludox dispersion was used to obtain the excitation profile of the system, indicating an instrumental response time (FWHM) of 100 ps. All fluorescence decays were collected to 17×10^3 counts in the peak channel (CPC) and over 512 channels. All profiles were exponential over three to four decades of the intensity decay.

3. Results and discussion

3.1. Absorption spectra

The UV–visible absorption spectra of the phenanthrene derivatives were recorded for their solutions in cyclohexane and in methanol. It was found that peak positions are somewhat sensitive to the presence of different substituents, but not to the change in solvent polarity. The increase in solvent polarity only caused slight broadening of the vibrational structure.

In Table 1 we collect peak positions and the corresponding molar extinction coefficients for these compounds in methanol. The spectra resemble those of phenanthrene and 9,10-diphenylphenanthrene in cyclohexane and in methanol [5,10,11], and by analogy, the peaks around 300 nm are assigned to be band K

Table 1

Absorption maxima and the molar extinction coefficients of phenanthrene derivatives in methanol

1		2		3	
λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ
352	3.454×10^2	353	4.572×10^2	354	5.690×10^2
343	2.487×10^2	346	2.971×10^2	349	3.455×10^2
336	3.892×10^2				
305	9.667×10^3	305	1.097×10^4	301	1.228×10^4

Table 2
The emission peak positions for phenanthrene derivatives in cyclohexane and in methanol

Derivatives	Cyclohexane				Methanol			
	a	b	c	d	a	b	c	d
1	354 [a]	371	392	416	354 [a]	371	392	415 [b]
2	359 [a]	377	398	423	360 [a]	377	396	
3	357 [a]	375	397	421	363 [a]	380	396 [b]	

[a] The (0, 0) band.
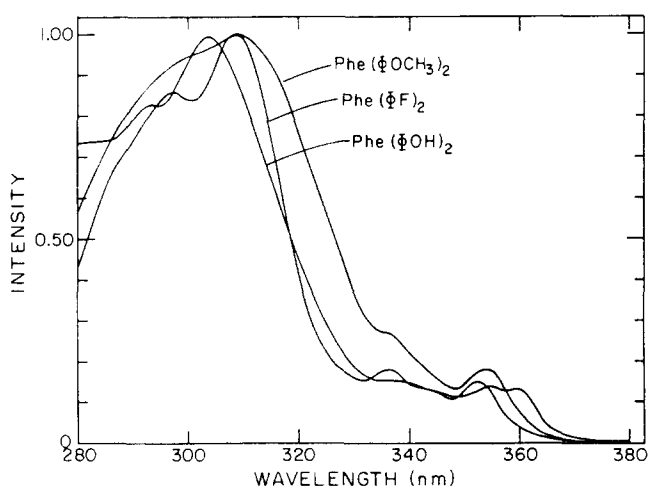[b] 396 nm, weak peak; 415 nm, peak is barely evident.

Fig. 1. Normalized excitation spectra of phenanthrene derivatives in methanol solvent. λ_{em} is at 377 nm.
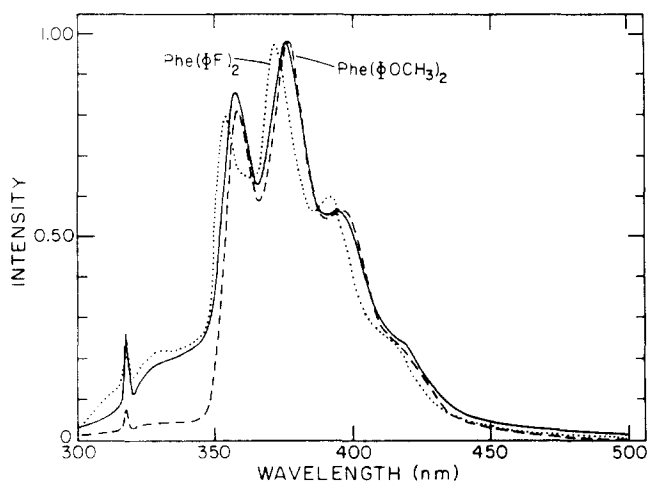

Fig. 2. Normalized fluorescence emission spectra of phenanthrene derivatives in cyclohexane. λ_{ex} is at 292 nm. The peaks at 320 nm are the Raman band of the solvent.
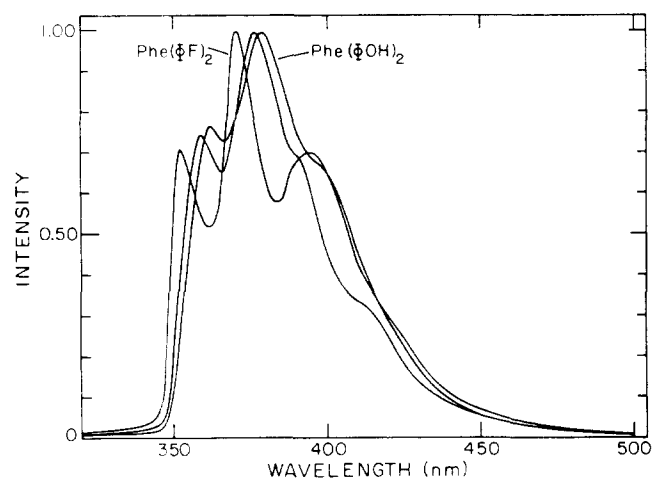

Fig. 3. Normalized fluorescence emission spectra of phenanthrene derivatives in methanol. λ_{ex} is at 292 nm.

Table 3
The Stokes shifts of phenanthrene derivatives as a function of Debye solvent polarizability function

Solvent	$\dfrac{\epsilon - 1}{\epsilon + 2}$	Stokes shifts (cm^{-1}) for the following compounds		
		1	**2**	**3**
Cyclohexane	0.25	160	474	238
Methanol	0.91	160	551	230

(^1L_a) while band B (^1L_b) extends from 325 nm to 360 nm, and contains vibrational fine structure.

3.2. Excitation and fluorescence emission spectra

Excitation spectra of **1**, **2** and **3** in methanol are shown in Fig. 1. It was observed that the shape and

the excitation maxima of ^1L_a bands are different for the three compounds. For compound **3** the ^1L_a band presents a blue shift of 5 nm in comparison with compounds **1** and **2**. The (0, 0) bands of compounds **1, 2** and **3** are at 353 nm, 354 nm and 360 nm respectively, a 5 nm red shift for compound **3**.

The fluorescence spectra of these compounds (emission from ^1L_b band) were obtained in cyclohexane (Fig. 2) and in methanol (Fig. 3). It is observed that the emission maxima do not shift for compounds **1** and **2** with increasing solvent polarity but, for compound **3**, the emission maximum exhibits a 5 nm red shift (Table 2).

Comparison of the excitation and the emission spectra of these compounds in methanol (Fig. 1 and Fig. 3)

Table 4
Quantum yields, lifetimes and radiative rate constants of phenanthrene derivatives in cyclohexane and methanol

Derivative	Cyclohexane			Methanol		
	Φ_f	τ (ns)	k_f ($\times 10^6$ s^{-1})	Φ_f	τ (ns)	k_f ($\times 10^6$ s^{-1})
1	0.14 ± 0.02	38.4	3.6	0.17 ± 0.02	36.8	4.6
2	0.19 ± 0.02	29.3	6.5	0.25 ± 0.03	26.6	9.4
3	0.27 ± 0.03	29.5	9.1	0.24 ± 0.03	23.1	10.4

shows that in both cases the compound 3 is the most red shifted. This indicates that the compound 3 is the most solvated in the excited state.

In comparison with pure phenanthrene emission, the substituents decrease the energy of the excited state. According to the nature of the substituents, the sequence of increasing red shift is F < OH < OCH$_3$ in cyclohexane and F < OCH$_3$ < OH in methanol. An explanation could be that, in cyclohexane, methoxy groups have a stronger electron donating effect than OH or F groups which would lower the energy of the excited state relative to the ground state; in methanol, OH groups are involved in hydrogen bonding interactions with the solvent molecules, which contributes to an increased red shift.

In the fluorescence spectra, the first emission peak of ^1L_b band (in wavenumber units) can be correlated with the Debye solvent polarizability function $(\epsilon - 1)/(\epsilon + 2)$. Careful examination of the excitation and emission spectra reveals that the magnitudes of the Stokes shifts for the three compounds are sensitive to the nature of the substituent and sometimes to the solvent (Table 3). One sees that the sequence of Stokes shifts is 1 < 3 < 2 in both polar and non-polar solvents.

### 3.3. Quantum yield and fluorescence lifetime measurement

Quantum yields of these phenanthrene derivatives in both cyclohexane and methanol have been determined from the UV and fluorescence emission measurements. It can be observed that the magnitude of the quantum yields for compounds 1 and 2 increases with increasing solvent polarity. In contrast, for compound 3, it decreases with increasing solvent polarity. For all these compounds, the change is small. The sequence of the fluorescence quantum yields for the different molecules is 1 < 2 < 3 for both the polar and the non-polar solvent.

Fluorescence decay measurements have also been performed for these three compounds. For each derivative, with increasing solvent polarity, the lifetime decreases. In both polar and non-polar solvents, compound 1 has longer lifetimes than compounds 2 and 3.

The radiative decay rate constants are calculated from fluorescence quantum yields and lifetimes, by

using the equation $\phi = k_f \tau$. In Table 4 the fluorescence quantum yields, lifetimes and radiative decay rate constants of these compounds in different solvents are given. The radiative decay rate constants for compounds 1 and 2 increase more than 27% with increasing solvent polarity. The radiative decay rate constant for compound 3 also increases with increasing solvent polarity, but the change is about 14%. In both polar and non-polar solvents, the sequence of radiative decay rate constants is 1 < 2 < 3.

These results show that the luminescence behaviour of these compounds depends not only on the surrounding solvent but also on the molecular structures. For solvent effects, one tentative explanation is that there are specific dipole–dipole and/or hydrogen bonding interactions between the probes and the solvents. The following molecular structure demonstrates that the phenyl rings are nearly perpendicular to the plane of the phenanthrene:
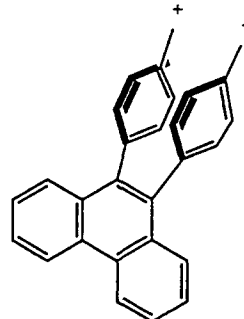
4. Conclusions

The spectroscopic properties of molecules 1, 2 and 3 are quite similar to those of 9-alkyl phenanthrene and 9,10-diphenyl phenanthrene. The UV absorption, fluorescence excitation and emission spectra show that 1 and 2 are not sensitive to the increase in solvent polarity but that 3 exhibits a small red shift. In both polar and non-polar solvents the sequence of the Stokes shifts is 1 < 3 < 2. The magnitude of the fluorescence quantum yields for compounds 1 and 2 increases when switching the solvent from cyclohexane to methanol,

whereas **3** has a smaller quantum yield in methanol. These changes are relatively small. When the solvent polarity is increased, the fluorescence lifetime decreases for each derivative.

Acknowledgments

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