Polycyclic Aromatic Hydrocarbon Solute Probes

Part II.* Effect of Solvent Polarity on the Fluorescence Emission Fine Structures of Coronene Derivatives†

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The fluorescence properties of coronene (Co), benzo[*a*]coronene (BCo), naphtho[2,3-*a*]coronene (NCo), dibenzo[*a,j*]coronene (DCo), naphtho[1,2,3,4-*ghi*]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene and dibenzo[*cd,lm*]perylene dissolved in solvents of varying polarity are reported. Measurements indicated that the emission intensities of the four coronene derivatives depended on solvent polarity. The Co, BCo and NCo scales have been defined as the ratio of the fluorescence intensities of bands I and III of the vibronic spectra. Band III of dibenzo[*a,j*]coronene was not clearly identifiable in all the solvents studied, and the DCo scale was therefore defined as the intensity ratio of bands I and IV. Emission intensity ratios of the three perylene derivatives remained nearly constant, irrespective of solvent polarity.

Keywords: Fluorescence; polarity scales; coronene derivatives; perylene derivatives; solvent effects

Polycyclic aromatic hydrocarbon (PAH) solute probes and fluorescence probe techniques are becoming increasingly popular for studying the surface micro-environment of reversed-phase chromatographic materials,¹⁻³ surfactant micellisation/adsorption,⁴⁻¹⁰ polymer-surfactant interactions¹¹⁻¹³ and micro-emulsions.^{14,15} The method involves the use of a polycyclic aromatic hydrocarbon solute (*e.g.*, pyrene) which exhibits different fluorescence characteristics depending on the properties of the solubilising media. Variations in the emission intensity ratio as a function of surfactant concentration enable the critical micelle concentration to be estimated. Similarly, spectrofluorimetric methods have been proposed for measuring the cavity size and polarity of cyclodextrins,¹⁶ and for determining association constants for pyrene-cyclodextrin inclusion complexes¹⁷⁻²⁰ based on the fluorescence emission intensity ratio of two vibronic bands for the pyrene monomer.

Inclusion complexation is influenced strongly by both the micro-environment of the host cyclodextrin cavity and the molecular structure of the guest solute molecule. Solute size and shape determine, to a large extent, whether the solute can fit into the cyclodextrin cavity. The three most commonly studied members of the cyclodextrin (CDx) family, α -CDx, β -CDx and γ -CDx, have cavities of diameter 4.5–6.0, 6.0–8.0 and 8.0–10.0 Å, respectively. The depth of the three cyclodextrin cavities is approximately 8 Å. The cavities have been found to be hydrophobic and hence provide favourable interactions for appropriately sized apolar solutes.²¹

Spectrofluorimetric methods based on the photophysical properties of pyrene have been proposed for measuring the cavity size and polarity of β -CDx and γ -CDx.¹⁶ The emission spectrum of the pyrene (Py) monomer consists of five major vibronic bands labelled I–V in progressive order, *i.e.*, the 0–0 band being labelled I, etc. Intensities of the various bands show a strong dependence on the solvent environment. Significant enhancement is observed in the 0–0 vibronic band intensity in the presence of polar solvents. The ratio of the

emission intensities for bands I and III ($\text{Py} = \text{I/III}$) serves as a quantitative measure of solvent polarity and structure.^{22,23} Instrumental effects associated with the accurate determination of the fluorescence emission intensity ratio are discussed in greater detail elsewhere.^{24,25}

Pyrene is a suitable PAH solute probe for the smaller cyclic oligosaccharides. For γ -CDx, the cavity is larger and the spectrofluorimetric method is more complicated because of the possibility of concurrent effects due to cyclodextrin-pyrene dimer inclusion complexes. Experimental evidence has established the formation of additional inclusion complexes such as $\text{Py}_2 - \gamma\text{-CDx}$ and $\text{Py}_2 - \gamma\text{-CDx}_2$.¹⁸ Larger PAH solute probes would minimise this possibility. There are numerous PAH solutes and it would be beneficial to study systematically their photophysical properties to determine if better fluorescent PAH probes exist. In this paper, we report the results of fluorescence measurements on coronene, benzo[*a*]coronene, naphtho[2,3-*a*]coronene, dibenzo[*a,j*]coronene, naphtho[1,2,3,4-*ghi*]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene and dibenzo[*cd,lm*]perylene. Their molecular structures are given in Fig. 1. New solvent polarity scales are defined based on the properties of coronene (Co), benzo[*a*]coronene (BCo), dibenzo[*a,j*]coronene (DCo) and naphtho[2,3-*a*]coronene (NCo) dissolved in fluid solution. Numerical Co ($\text{Co} = \text{I/III}$), BCo ($\text{BCo} = \text{I/III}$), DCo ($\text{DCo} = \text{I/IV}$) and NCo ($\text{NCo} = \text{I/III}$) values are determined experimentally for 25 solvents of varying polarity, and are compared to previously reported Py values.²³

Experimental

The seven PAH solute probes were synthesised by procedures described in the literature^{26,27} and stock solutions were prepared by dissolving the purified solute in dichloromethane. Small aliquots of the stock solutions were transferred into test-tubes, allowed to evaporate and dissolved with the solvent of interest. Final solute concentrations were 10^{-6} M (or less) to minimise inner filtering artifacts. Solvents were of HPLC, spectroquality or analytical-reagent grade and were purchased from Aldrich, Burdick and Jackson or Fisher Scientific. The resulting solutions were optically dilute ($\leq 0.05 \text{ A cm}^{-1}$) at all wavelengths investigated. Solutions were not deoxygenated.

Absorption spectra were recorded on a Hewlett-Packard 8450A photodiode array spectrophotometer in the usual

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Fig. 1. Molecular structures of (A) coronene, (B) benzo[a]coronene, (C) dibenzo[a,j]coronene, (D) naphtho[2,3-a]coronene, (E) naphtho[1,2,3,4-ghi]perylene, (F) dibenzo[cd,lm]perylene, and (G) benzo[pqr]naphtho[8,1,2-bcd]perylene

Fig. 2. Fluorescence emission spectra for coronene in the Co scale calibration solvents: A, dimethyl sulfoxide; B, methanol; C, carbon tetrachloride; and D, cyclohexane. Co is defined as I (at 426-430 nm)/III (at 445-449 nm)

manner using 1-cm silica cells. The fluorescence spectra were run on a Perkin-Elmer Model LS-5 spectrofluorimeter equipped with a Model 3600 data station. Solutions were excited at 334 (coronene), 316 (benzo[a]coronene), 333 (naphtho[2,3-a]coronene), 324 (dibenzo[a,j]coronene), 316 (naphtho[1,2,3,4-ghi]perylene), 325 (benzo[pqr]naphtho[8,1,2-bcd]perylene) and 324 nm (dibenzo[cd,lm]perylene) in a silica 1-cm square cuvette. All fluorescence data were accumulated at 21°C, ambient room temperature. Spectra obtained represent the average of at least three scans which were blank corrected. For several of the alkane hydrocarbons the number of scans varied between 3 and 25, depending on the observed fluorescence intensity. Blank corrections were negligible for many of the more polar and viscous solvents that enhance PAH fluorescence; however, in a few instances the corrections proved to be greater than the experimental uncertainty. Subtraction of the solvent blank eliminated solvent contributions (*i.e.*, Raman bands, impurities) from the measured PAH spectrum. The solvent blank therefore served as the baseline from which the PAH emission intensities are measured. Spectra were not corrected for the quantum efficiency of the photomultiplier tube. Excitation and emission slit widths were 5 and 3 nm, respectively.

Results and Discussion

The weakly allowed vibronic transitions in coronene, benzo[a]coronene, dibenzo[a,j]coronene and naphtho[2,3-a]coronene are depicted in Figs. 2-5, respectively. Pronounced

Fig. 3. Fluorescence emission spectra for benzo[a]coronene in the BCo scale calibration solvents: A, dimethyl sulfoxide; B, methanol; C, carbon tetrachloride; and D, cyclohexane. BCo is defined as I (at 432-435 nm)/III (at 450-452 nm)

Fig. 4. Fluorescence emission spectra for dibenzo[a,j]coronene in the DCo scale calibration solvents: A, dimethyl sulfoxide; B, methanol; C, carbon tetrachloride; and D, cyclohexane. DCo is defined as I (at 432-436 nm)/IV (at 452-456 nm)

Fig. 5. Fluorescence emission spectra for naphtho[2,3-a]coronene in the NCo scale calibration solvents: A, dimethyl sulfoxide; B, methanol; C, carbon tetrachloride; and D, cyclohexane. NCo is defined as I (at 444-447 nm)/III (at 462-466 nm)

enhancement of the intensity of band I relative to band III is observed with increasing solvent polarity. Values of Co (I/III) range from 0.14 for the non-polar solvent cyclohexane to 0.98 for dimethyl sulfoxide. Similarly, BCo (I/III) and NCo (I/III) values range from BCo = 0.38 and NCo = 0.57 for cyclohexane to BCo = 1.25 and NCo = 1.86 for dimethyl sulfoxide, which is the most polar solvent studied. The fluorescence spectra of dibenzo[a,j]coronene show a similar enhancement effect. For dibenzo[a,j]coronene band III was not clearly identifiable in every solvent using our LS-5 spectrofluorimeter with a 3-nm emission slit width. The DCo scale is defined therefore as the ratio of band I (at 432-436 nm) to band IV (452-456 nm). Interestingly, dibenzo[cd,lm]perylene, naphtho[1,2,3,4-ghi]perylene and benzo[pqr]naphtho[8,1,2-bcd]perylene do not show an enhancement of band I (see Figs. 6-8 respectively). The ratio of emission intensities

Fig. 6. Fluorescence emission spectra for dibenzo[*cd,lm*]perylene dissolved in: A, dimethyl sulfoxide; B, carbon tetrachloride; and C, cyclohexane

Fig. 7. Fluorescence emission spectra for naphtho[1,2,3,4-*ghi*]perylene dissolved in: A, dimethyl sulfoxide; B, carbon tetrachloride; and C, cyclohexane

Fig. 8. Fluorescence emission spectra for benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene dissolved in: A, dimethyl sulfoxide; and B, cyclohexane. The spectra for benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene in carbon tetrachloride is almost identical to that in dimethyl sulfoxide

(I/III) for naphtho[1,2,3,4-*ghi*]perylene varied from 4.31 in cyclohexane to 4.48 in dimethyl sulfoxide. A nearly constant ratio of emission intensities makes the three perylene derivatives unsuitable as PAH solute probes of solvent polarity.

Numerical Co, BCo, NCo and DCo values, together with literature Py values, are summarised in Table 1 for 25 solvents of varying polarity. Estimated uncertainties in the measured intensity ratio are believed to be of the order of ± 0.02 (or less) based on replicate measurements for selected solvents. As an example, measured values for methanol over a 5 d period of BCo = 0.85, 0.86, 0.84, 0.85 and 0.85 indicate very good reproducibility. Close examination of Table 1 reveals that the dynamic range of Py is slightly larger than that of the NCo scale, which in turn is slightly larger than that of the BCo scale, etc. With the exception of the chloroalkanes, the ordering of solvents by polarity remains unchanged, at least to within experimental uncertainties in the five scales. Plots of the Co, BCo and NCo scales versus the Py scale are shown in Fig. 9. For a single substituent, the emission intensity ratios increase with the number of benzene rings added.

Table 1. Relative band intensities for pyrene (Py), coronene (Co), benzo[*a*]coronene (BCo), naphtho[2,3-*a*]coronene (NCo) and dibenzo[*a,j*]coronene (DCo) in various solvents

Solvent	Py*	Co†	BCo‡	NCo§	DCo¶
Hexane	0.58	0.12	0.38	0.57	1.23
Heptane	0.58	0.14	0.38	0.57	1.24
Cyclohexane	0.58	0.14	0.38	0.59	1.25
Methylcyclohexane	0.58	0.12	0.39	0.59	1.27
2,2,4-Trimethylpentane	0.59	0.14	0.39	0.57	1.25
Carbon tetrachloride	—	0.41	0.73	0.85	1.75
Dibutyl ether	0.84	0.33	0.56	0.92	1.34
<i>p</i> -Xylene	0.95	0.44	0.73	1.15	1.55
Toluene	1.04	0.49	0.77	1.18	1.59
Benzene	1.05	0.51	0.79	1.23	1.64
Propan-2-ol	1.09	0.52	0.77	1.31	1.46
Chloroform	1.25	0.59	0.96	1.44	1.90
Butyl acetate	1.35	0.61	0.85	1.35	1.59
Methanol	1.35	0.62	0.85	1.41	1.46
Tetrahydrofuran	1.35	0.64	0.87	1.45	1.51
Methylene chloride	1.35	0.63	0.99	1.58	1.89
Ethyl acetate	1.37	0.65	0.92	1.42	1.63
1,2-Dichloroethane	1.46	0.65	0.98	1.61	1.86
Cyclohexanone	1.47	0.72	0.96	1.61	—
Ethylene glycol	1.64	0.76	1.01	1.65	1.67
Acetone	1.64	0.76	0.97	1.66	—
Acetonitrile	1.79	0.79	1.12	1.77	1.81
<i>N,N</i> -Dimethylacetamide	1.79	0.90	1.14	1.82	1.75
<i>N,N</i> -Dimethylformamide	1.81	0.88	1.13	1.82	1.76
Dimethyl sulfoxide	1.95	0.98	1.25	1.86	2.00
Dynamic range	1.37	0.86	0.87	1.29	0.77

* Experimental Py values are from Dong and Winnik²³ except for heptane which was measured as part of this study.

† Defined as I (at 426–430 nm)/III (at 445–449 nm).

‡ Defined as I (at 432–435 nm)/III (at 450–452 nm).

§ Defined as I (at 444–447 nm)/III (at 462–466 nm).

¶ Defined as I (at 432–436 nm)/IV (at 452–456 nm).

|| Defined as the difference between the largest and smallest PAH value.

Fig. 9. Plot of PAH scale versus Py scale for coronene (Co), benzo[*a*]coronene (BCo) and naphtho[2,3-*a*]coronene (NCo). Halo-genated solvents are denoted with solid triangles

In addition, the coronene and substituted coronene scales are highly correlated with the $E_{T(30)}$ scale.²⁸ As examples, the correlation coefficients, r , for equations (1) and (2) are 0.935 and 0.939, respectively, for 19 non-hydrogen bonding solvents.

$$\text{Co} = 0.0464E_{T(30)} - 1.187 \quad \dots \quad (1)$$

$$\text{BCo} = 0.0481E_{T(30)} - 0.975 \quad \dots \quad (2)$$

The effect of a halogen substituent on the calculated intensity ratio is further documented in Table 2 for dibenzo[*a,j*]coronene dissolved in selected chloroalkane and bromoalkane solvents. The presence of chlorine and bromine atoms increases the emission intensity ratio beyond what would be

Table 2. Emission intensity ratio (I/IV) for dibenzo[*a,j*]coronene (DCo) dissolved in selected halogenated solvents

Solvent	DCo
1-Chlorohexadecane	1.40
1-Bromopentane	1.52
2-Bromo-2-chloro-1,1,1-trifluoroethane	1.98
1-Bromobutane	1.55
1-Chlorohexane	1.41
1-Chlorobutane	1.44
1-Chlorooctane	1.42
Chlorocyclohexane	1.52
Methylene chloride	1.89
1,2-Dichloroethane	1.86
Carbon tetrachloride	1.75
Chloroform	1.90

expected based on a consideration of molecular polarity. Larger chloroalkanes such as 1-chlorohexadecane should be similar in polarity to their alkane homomorph as the molecules consist primarily of methylene groups. The chlorine atom represents only a small fraction of the molecule. Experimentally, though, 1-chlorohexadecane appears to be more polar than hexadecane which has DCo = 1.29. The halogen solvent substituent becomes more pronounced in the bromoalkanes as shown by DCo = 1.44 for 1-chlorobutane *versus* DCo = 1.55 for 1-bromobutane.

At present, we are not able to explain fully the halogen solvent substituent effect. Bromine and chlorine are known to be "heavy atoms" which promote inner system crossing and depletion of the excited singlet state. We do not feel that inner system crossing is a viable explanation in this particular instance. This would serve only to deplete the excited state and should not affect emission intensity ratios. Most probably the halogen effect is a ground-state phenomenon caused by selective interaction involving one or more ground-state vibrational levels, hence altering the various vibronic transition probabilities.

The Py, Co, BCo, DCo and NCo scales provide a quantitative measure of solvent polarity. Depending on the application, inclusion host cavity size and/or spectral characteristics of the solvent, one scale may be preferred from an experimental standpoint. Inner filtering is a major problem associated with obtaining correct fluorescence data, which assumes that the sample is optically dilute ($\leq 0.05 \text{ A cm}^{-1}$) at all analytical wavelengths. In emission experiments (as in PAH scale determinations) small amounts of primary inner filtering often can be ignored as the excitation wavelength remains constant. Consequently, the absolute values obtained from the emission experiment are independent of small amounts of primary inner filtering. This assumption may not be true where large amounts of primary inner filtering are involved in conjunction with large cuvettes, high absorbances and in the recording of high-resolution spectra, as is required in the PAH solvent polarity scale determination.²⁹ Elimination of solvent inner filtering effects can be accomplished in principle by using a different solute probe. For example, ovalene and benzo[*ghi*]perylene were suggested as suitable PAH solute probes in Part I of this series.³⁰ Added to our earlier list of probe molecules is benzo[*a*]coronene, which has an excitation wavelength of 373 nm. Calculated emission intensity ratios for benzo[*a*]coronene are independent of excitation wavelength. The results of these measurements are summarised in Table 3 for excitation at 316 and 373 nm.

For secondary inner filtering the most prominent concern is preferential absorption of one emission wavelength by the sample. Reduced solute concentrations allow the minimisation of self inner filtering contributions from the PAH solute probe. The elimination of solvent inner filtering effects can be very tedious, if not impossible. Solvent inner filtering of the emission radiation is illustrated clearly in Fig. 10 which shows

Table 3. Effect of excitation wavelength on the emission intensity ratio for benzo[*a*]coronene

Solvent	Emission intensity ratio (I/III)	
	316 nm	373 nm
Hexane	0.38	0.41
Cyclohexane	0.38	0.41
Carbon tetrachloride	0.73	0.73
<i>p</i> -Xylene	0.73	0.76
Toluene	0.77	0.76
Benzene	0.79	0.78
Butyl acetate	0.85	0.83
Methylene chloride	0.99	0.97
Cyclohexanone	*	0.96
Acetone	*	0.97
<i>N,N</i> -Dimethylacetamide	1.14	1.12
<i>N,N</i> -Dimethylformamide	1.13	1.11

Average difference: ± 0.02

* Solvent inner filtering prevented determination.

Fig. 10. Absorbance spectra of (A) pyrene and (B) TBAN showing gross solvent inner filtering of the 338-nm excitation and the 370–385-nm emission radiation. Preferential absorption of the 373-nm pyrene emission radiation is observed, with TBAN absorbances of 0.57 and 0.38 at 373 and 383 nm, respectively

the emission region (370–385 nm) of pyrene with reference to the absorbance spectrum of tributylammonium nitrate (TBAN). The solvent absorbance is much larger at 373 nm (0.57 A cm^{-1}) than at 383 nm (0.38 A cm^{-1}). As Py is calculated as the intensity of band I (373 nm) divided by the intensity of band III (383 nm), the calculated Py value for TBAN would be erroneously low. Coronene, benzo[*a*]coronene and naphtho[2,3-*a*]coronene probe solutes would permit fluorescence measurements to be made at longer wavelengths where secondary inner filtering effects are virtually eliminated. For benzo[*a*]coronene, TBAN absorbances are almost identical, 0.13 and 0.11 A cm^{-1} , at bands I and III (see Fig. 11). These small absorbance values may be due to an offset resulting from the use of a water reference.

Conclusions

The results of this study, combined with earlier fluorescence measurements on pyrene, benzo[*ghi*]perylene and ovalene solute probes,³⁰ show that many PAHs exhibit similar fluorescence behaviour. Each of these molecules could serve as a probe for its own independent solvent polarity scale. In addition, a generalised PAH scale could be developed in the future, possibly by combining emission intensity data for the different PAH solute probes. Readers are reminded that the determination of accurate PAH values requires careful attention to experimental detail. A standard set of conditions should be adopted in the subsequent reporting of PAH values for interlaboratory comparison. The conditions, many of which are based on our prior observations,^{24,25} should include

Fig. 11. Absorbance spectra of (A) benzo[a]coronene and (B) TBAN showing modest primary and very slight secondary inner filtering. The TBAN absorbances are 0.13 and 0.11 at 428 and 450 nm, respectively

the following specifications. (1) A standard 10^{-6} M (or less) solute solution should be employed for all PAH determinations in order to eliminate solute inner filtering effects. (2) The narrowest of emission slit settings should be employed with 1.0 nm as the recommended minimum value. (3) As many instruments do not have such small spectral slit widths, several standard solvents spanning the entire PAH range should be employed as reference calibrants. Cyclohexane, carbon tetrachloride, methanol and dimethyl sulphoxide are recommended as these four solvents are available commercially in high purity and the PAHs appear to have sufficient solubility to permit accurate fluorescence measurements. Further, carbon tetrachloride or another chloroalkane solvent is essential to screen potential PAH solute probes for anomalous fluorescence behaviour. (4) The effect of temperature is not fully understood,^{24,31,32} and hence it is recommended that the temperature at which the data were taken be reported. Measurements are planned to study systematically the photophysical properties of additional polycyclic aromatic hydrocarbons hopefully to understand better solute - solvent interactions in solution, and the role that solute symmetry plays in determining which PAH molecules have selective band intensity enhancement.

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