Polycyclic Aromatic Hydrocarbon Solute Probes. Part VII: Evaluation of Additional Coronene Derivatives as Possible Solvent Polarity Probe Molecules

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Fluorescence emission spectra are reported for dinaphtho[8,1,2abc; 2′,1′,8′klm]coronene, naphtho[8,1,2abc]coronene, naphth[2′,1′,8′,7′: 4,10,5]anthra[1,9,8abcd]coronene, dibenzo[bc,ef]coronene, benzo[1,2,3bc;4,5,6b′c′]dicoronene, anthra[2,3a]coronene, dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene, and tetrabenzo[de,hi,mn,qr]naphthacene dissolved in *n*-hexadecane, butyl acetate, dichloromethane, and acetonitrile. Results of these measurements are used to screen PAHs for potential solvent polarity probe behavior. Of the eight PAHs studied, only naphtho[8,1,2abc]coronene, dinaphtho[8,1,2abc;2′,1′,8′klm]coronene, and anthra[2,3a]coronene were classified as probe molecules. The fluorescence spectra of the first two PAHs show selective enhancement of the I band emission intensity in polar solvents. For anthra[2,3a]coronene, the measured ratio of emission intensities of bands I and II decreased systematically with increasing solvent polarity.

Index Headings: Fluorescence; Spectroscopic techniques.

INTRODUCTION

Fluorescence probe techniques are becoming increasingly popular for studying the surface micro-environment of chromatographic materials, surfactant micellization/absorption, polymer/surfactant interactions, microemulsions, and other organized solvent media. The method involves the use of a probe molecule (e.g., pyrene) which exhibits different fluorescence characteristics, depending upon the properties of the solubilizing media. The probe molecule selectively binds to a specific surface site or preferentially partitions into a molecularly organized structure. Appearance of new spectral bands, shifts in the emission wavelengths, or changes in the fluorescence emission intensities provide an indication of the environment immediately surrounding the probe. As typical examples, Street and Acree[1] estimated the effective dielectric constant of cyclodextrin cavities on the basis of the measured fluorescence properties of pyrene-3-carboxaldehyde. Hartner and co-workers[2] detected pyrene adsorbed from solution onto an octadecylsilica-derivatized fused-silica plate using a total internal reflection method. From the measured ratio of emission intensities for the I and III vibronic bands, the authors concluded that the interfacial environment of C_{18} alkyl layers on optically flat fused silica was more ordered than that of similar layers bound to porous, particulate silica supports. Ramis Ramos *et al.*[3] and Malliaris[4] reviewed probe methods used to characterize physicochemical structures of binary and ternary alcohol/surfactant/water systems, microemulsions, and micelles. Fluorescence measurements in organized solvent media yield valuable information regarding critical micelle concentrations (cmc), aggregation size, and interphase properties.

Polycyclic aromatic hydrocarbons (PAHs), particularly pyrene and its derivatives, have served as fluorescence solute probes in a number of different applications. Several solvent polarity scales have been developed on the basis of the photophysical properties of dissolved PAH molecules in fluid solution. Emission spectra of the PAH monomers consist of several major vibronic bands labeled I, II, etc., in progressive order. Earlier papers in this series[5–10] have reported that the intensities of the various bands show a strong dependence on the solvent environment. Significant enhancement was observed in the I vibronic band emission intensity for pyrene (Py), ovalene (Ov), benzo[ghi]perylene (BPe), coronene (Co), benzo[a]coronene (BCo), dibenzo[a,j]coronene (DCo), naphtho[2,3a]coronene (NCo), dibenzo[fg,ij]phenanthro[2,1,10,9,8,7pqrstuv]pentaphene (DBPP), and benzo[e]pyrene (BePy) in the presence of polar solvents. Ratios of bands I and III (or bands I and IV in the case of BePy = I/IV and DCo = I/IV, or bands I and II in the case of DBPP = I/II) serve as a quantitative measure of solvent polarity and structure. Depending upon the spectral characteristics of the organic solvent and/or molecular shape/size constraints imposed by the organized solvent media, one PAH probe may be preferred from an experimental standpoint.

As new PAH probes are identified, it is important to try to understand the enhancement phenomena at the molecular level. Interestingly, not all PAH solutes exhibit similar fluorescence behavior, and only a few of the molecules studied to date exhibit solvent-dependent intensity ratios. Ratios for perylene, naphtho[1,2,3,4 ghi]perylene, benzo[pqr]naphtho[8,1,2bcd]perylene, benzo[a]pyrene, dibenzo[a,e]pyrene, and tribenzo[de,kl,rst]pentaphene were nearly constant, irrespective of solvent polarity. For two additional pentaphene derivatives studied—dinaphtho[2,1,8,7defg; 2′,1′,8′,7′ijkl]pentaphene and benzo[rst]anthra[9,1,2cde]pentaphene—the number of clearly resolvable emission bands varied with solvent, and it was impossible to assign a common set of bands in the 25 nonelectrolyte solvents used. Published papers[11–16] attribute the enhancement effect to the

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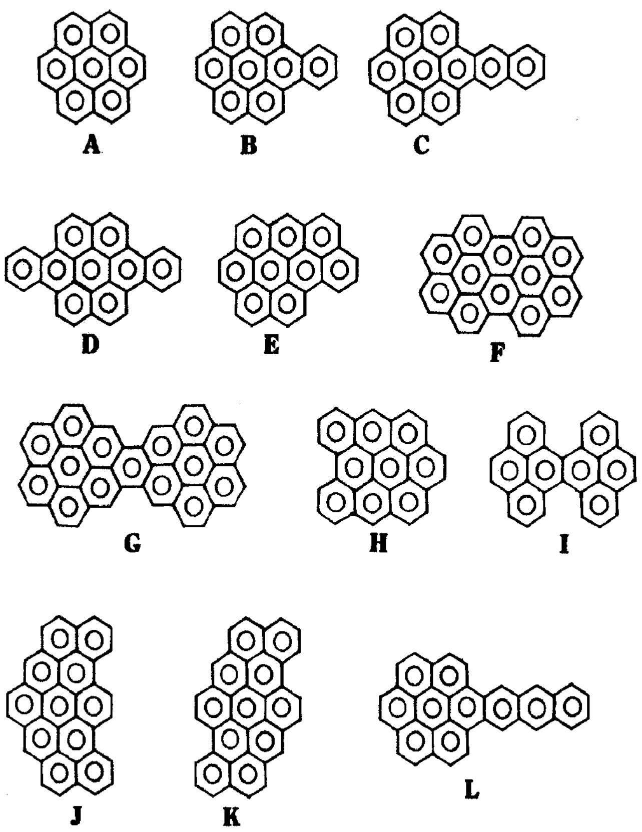

FIG. 1. Molecular structures of PAH compounds: (A) coronene; (B) benzo[a]coronene; (C) naphtho[2,3a]coronene; (D) dibenzo-[a,j]coronene; (E) naphtho[8,1,2abc]-coronene; (F) naphth[2′,1′,8′,7′:4,10,5]anthra[1,9,8abcd]coronene; (G) benzo[1,2,3bc;4,5,6b′c′]dicoronene; (H) dibenzo[bc,ef]coronene; (I) tetrabenzo[de,hi,mn,qr]naphthacene; (J) dinaphtho[8,1,2abc;2′,1′,8′klm]coronene; (K) dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene; and (L) anthra[2,3a]coronene.

reduction of symmetry of the PAH solute caused by complexation with surrounding solvent molecules. The strength of solute/solvent interactions and the molecular symmetry of the PAH molecule are expected to play major roles in determining to what extent the mixed allowed and forbidden transitions occur. The overall molecular symmetry, while important, is not the sole criterion for predicting which PAH molecules will have solvent-dependent emission intensity ratios. For example, coronene (D_{6h} point group) has a center of symmetry, a major 6-fold axis of rotation, and several vertical mirror planes. In comparison, benzo[ghi]perylene is a six-ring polycyclic aromatic hydrocarbon whose symmetry elements (C_{2v}) include only a single 2-fold rotation axis and the mirror plane that is common to all planar PAH molecules. The fluorescence emission intensity I/III band ratio of both molecules does vary with solvent polarity. Furthermore, coronene, benzo[a]coronene, naphtho-[2,3a]coronene, and dibenzo[a,j]coronene show probe character, irrespective of the position of the added naphtho- and benzo-aromatic rings (see Fig. 1 for molecular structures). This contrasts with the fluorescence behavior of perylene, which has a 2-fold major rotation axis and belongs to the D_{2h} point group. Like coronene and dibenzo[a,j]coronene, perylene also has a center of symmetry. The fluorescence spectra of perylene do not show, however, the selective enhancement of the I band emission intensity in polar solvents.

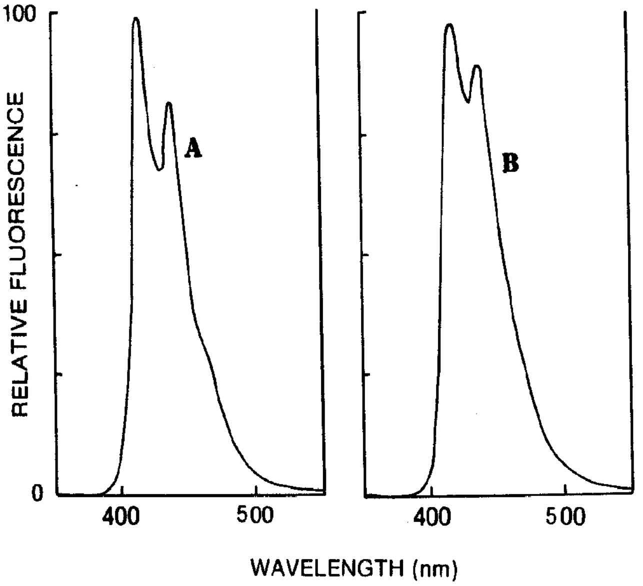

FIG. 2. Fluorescence emission spectra of tetrabenzo[de,hi,mn,qr]naphthacene dissolved in (A) *n*-hexadecane and (B) acetonitrile. The two major emission bands occur at about 420 and 439 nm in acetonitrile.

On the basis of our past experimental observations, we now believe that the "level" of detail in the fluorescence emission fine structure and the "structural distance" measuring how far away a molecule is from a known PAH probe structure both might be useful in predicting which polycyclic aromatic hydrocarbons will behave as solvent polarity probe molecules. To date, the most likely probe candidates have had dissimilar excitation and emission spectra, and the emission spectra have contained at least four (and very often five) "closely spaced" emission bands. To pursue these ideas further, we have measured the fluorescence spectra of dinaphtho[8,1,2abc;2′,1′,8′klm]coronene, naphtho[8,1,2abc]coronene, naphth-[2′,1′,8′,7′:4,10,5]anthra[1,9,8abcd]coronene, dibenzo-[bc,ef]coronene, benzo[1,2,3bc;4,5,6b′c′]dicoronene, anthra[2,3a]coronene, dinaphtho[8,1,2abc;2′,1′,8′jkl]-

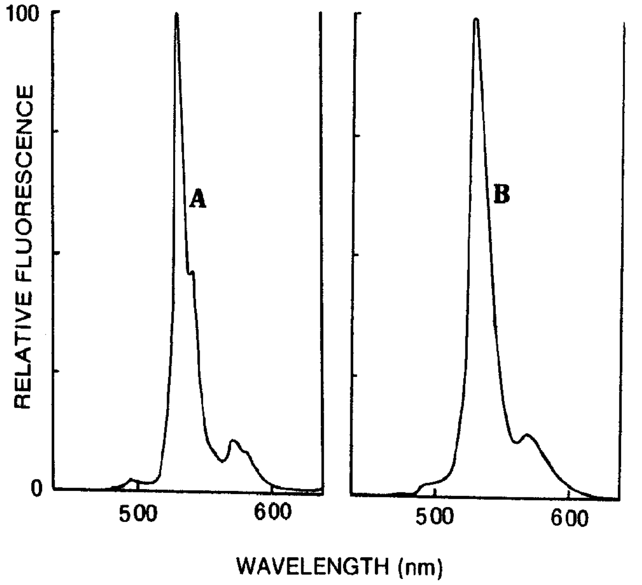

FIG. 3. Fluorescence emission spectra of dibenzo[bc,ef]coronene dissolved in (A) *n*-hexadecane and (B) acetonitrile. Emission bands occur at 532 nm (strong) and 571 nm (weak) in acetonitrile.

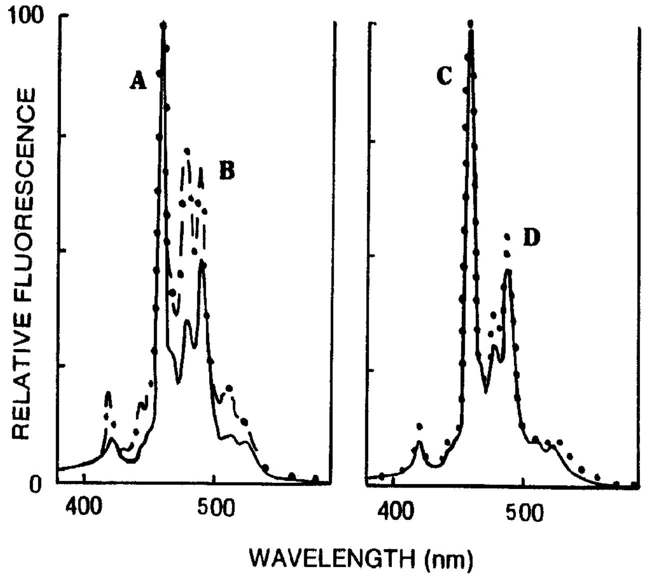

FIG. 4. Fluorescence emission spectra of naphtho[8,1,2abc]coronene dissolved in [A (——)] dichloromethane; [B (–·–·–)] *n*-hexadecane; [C (——)] acetonitrile; and [D (·····)] butyl acetate. In dichloromethane, the three major emission bands occur at about 460, 480, and 490 nm.

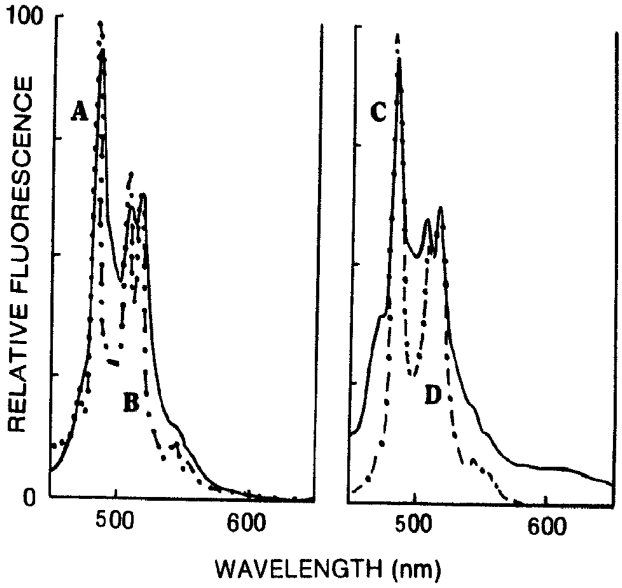

FIG. 6. Fluorescence emission spectra of naphth[2′,1′,8′,7′:4,10,5]anthra[1,9,8abcd]coronene dissolved in [A (——)] butyl acetate; [B (–·–·–)] *n*-hexadecane; [C (——)] acetonitrile; and [D (–·–·–] dichloromethane. In butyl acetate, the three major emission bands occur at about 486, 510, and 519 nm.

coronene, and tetrabenzo[de,hi,mn,qr]naphthacene. Results of these measurements are explained in terms of molecular symmetry and fluorescence emission fine structure of the various PAH molecules.

EXPERIMENTAL

The five coronene derivatives were prepared and purified by procedures described in the literature.[17,18] Tetrabenzo[de,hi,mn,qr]naphthacene was obtained by heating the twin $[0^{9,24}]$[2.1.2.1]metacyclophane-9-ene with palladium/charcoal and was purified by HPLC in accordance with the method of Grutzmacher and Husemann.[19] Stock solutions of each solute were prepared by dissolving the PAH in dichloromethane and were stored in the dark to retard any photochemical reactions between the PAH solutes and dichloromethane solvent. Carbon tetrachloride and chloroform (to a much lesser extent) are reported to react with polycyclic aromatic hydrocarbons via a hypothesized concerted transannular addition with free radical formation.[20–24] Small aliquots of the stock solution were transferred into test tubes, allowed to evaporate, and diluted with the organic solvent of interest. Limited solubility of the larger PAH solutes did present a problem in many of the solvents studied. The resulting solutions had to be vigorously vortexed and warmed to about 40–50°C in order to redissolve the PAH molecule back into solution from the test tube walls. Final solute

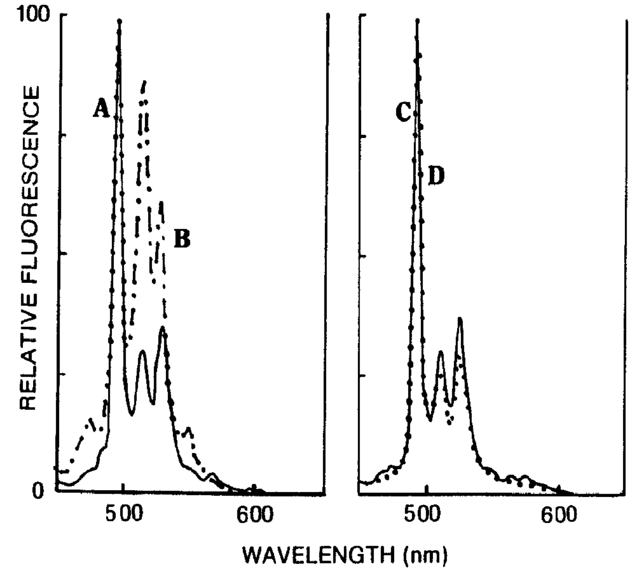

FIG. 5. Fluorescence emission spectra of dinaphtho[8,1,2abc; 2′,1′,8′klm]coronene dissolved in [A (——)] dichloromethane; [B (–·–·–)] *n*-hexadecane; [C (——)] butyl acetate; and [D (·····)] acetonitrile. Emission intensities are normalized to band I, which occurs at 490–495 nm. In dichloromethane, the three major emission bands occur at about 494, 514, and 528 nm.

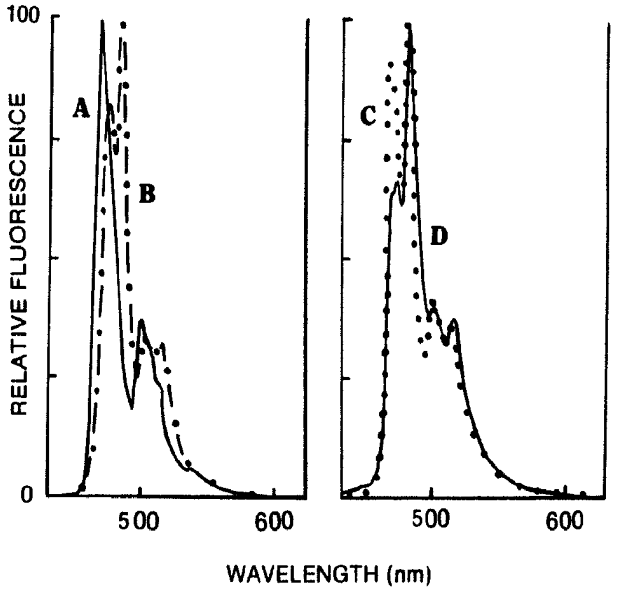

FIG. 7. Fluorescence emission spectra of dinaphtho[8,1,2abc; 2′,1′,8′jkl]coronene dissolved in [A (——)] *n*-hexadecane; [B (–·–·–)] dichloromethane; [C (·····)] butyl acetate; and [D (——)] acetonitrile. In butyl acetate, the four major emission bands occur at about 472, 481, 500, and 514 nm.

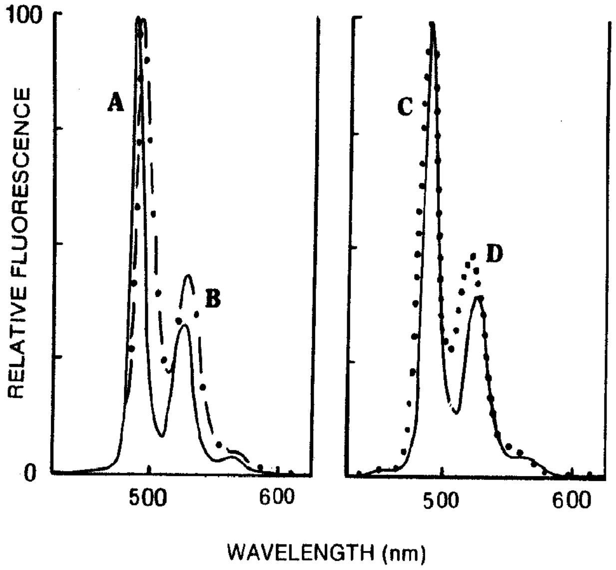

FIG. 8. Fluorescence emission spectra of anthra[2,3a]coronene dissolved in [A (——)] *n*-hexadecane; [B (-·-·-)] dichloromethane; [C (——)] butyl acetate; and [D (·····)] acetonitrile. In butyl acetate, the major emission bands occur at about 488, 525, and 562 nm (very weak).

TABLE I. Ratios of fluorescence emission intensities for pyrene, naphtho[8,1,2abc]coronene, dinaphtho[8,1,2abc;2′,1′,8′klm]coronene, and anthra[2,3a]coronene dissolved in select solvents.

Solvent	Py[a]	NaCo[b]	DNCo[c]	ACo[d]
Cyclohexane	0.58	1.33	1.60	2.93
Isooctane	0.59	1.32	1.69	2.90
n-Hexadecane	0.60	1.35	1.63	3.00
Benzene	1.05	2.05	2.61	2.73
2-Propanol	1.09	2.25	2.64	2.37
Butyl acetate	1.35	2.65	2.64	2.44
Methanol	1.35	2.60	2.80	2.22
Dichloromethane	1.35	2.84	2.82	2.29
Acetonitrile	1.79	3.19	2.88	2.03

[a] Values are taken from measurements of Dong and Winnik.[25]

[b] Defined as the ratio of band I at 458–462 nm to band II at 480–484 nm.

[c] Defined as the ratio of band I at 491–494 nm to band III at 524–528 nm.

[d] Defined as the ratio of band I at 484–492 nm to band II at 521–530 nm.

concentrations were set at 10^{-6} M or less to minimize solute inner filtering artifacts. Solvents were of HPLC, spectroquality, or AR grade, purchased commercially from Aldrich or Fisher Scientific, and the resulting solutions were optically dilute (absorbances $\text{cm}^{-1} < 0.05$) at all wavelengths investigated.

Absorption spectra were recorded on a Hewlett-Packard 8450A photodiode array spectrophotometer in the usual manner with the use of 1-cm-square quartz cells. The fluorescence spectra were run on a Shimadzu RF-5000U spectrofluorimeter with the detector set at high sensitivity. Solutions were excited at 322 nm (naphtho[8,1,2abc]coronene), 425 nm (dinaphtho[8,1,2abc;2′,1′,8′klm]coronene), 336 nm (dibenzo[bc,ef]coronene), 425 nm (naphth[2′,1′,8′,7′:4,10,5]anthra[1,9,8abcd]-coronene), 357 nm (anthra[2,3a]coronene), 370 nm (dinaphtho[2,1,8abc;2′,1′,8′jkl]coronene), and 318 nm (tetrabenzo[de,hi,mn,qr]naphthacene) in 1-cm² quartz cuvettes. Benzo[1,2,3bc;4,5,6b′c′]dicoronene solutions were excited at both 250 nm and 440 nm. Limited solubility of benzodicoronene was a major problem in many of the solvents examined, and by employing two different excitation wavelengths we could cover the entire 275–850 nm emission region. All fluorescence data were accumulated at 19°C, ambient room temperature, with excitation and emission slit width settings of 15 nm and 3 nm, respectively. The PAH fluorescence spectra, depicted in Figs. 2–8, represent a single scan which was then solvent blank corrected and verified by repetitive measurements.

RESULTS AND DISCUSSION

Representative fluorescence spectra of the five PAH solutes dissolved in *n*-hexadecane, butyl acetate, dichloromethane, and acetonitrile are given in Figs. 2–8. The four nonelectrolyte solvents were selected so as to encompass the entire range of solvent polarity, from the nonpolar *n*-hexadecane hydrocarbon to the moderately polar butyl acetate and dichloromethane solvents to the very polar acetonitrile molecule. The selection of this solvent set does differ somewhat from our past recommendations of using cyclohexane, carbon tetrachloride, methanol, and dimethyl sulfoxide to screen PAHs for possible probe behavior. Unfortunately, benzo[1,2,3bc;4,5,6b′c′]dicoronene, naphth[2′,1′,8′,7′:4,10,5]anthra[1,9-,8abc]coronene, and dinaphtho[8,1,2abc;2′,1′,8′k-lm]coronene did not readily redissolve in cyclohexane and methanol from the test tube walls, and it was difficult to measure accurately the fluorescence emission intensities of many of the weaker bands, even at the higher sensitivity setting on the detector. To overcome this problem, we decided to replace cyclohexane (Py = 0.58)[25] and methanol (Py = 1.35)[25] with solvents of comparable pyrene scale polarity, namely *n*-hexadecane (Py = 0.60)[25] and butyl acetate (Py = 1.35)[25], in hopes of facilitating redissolution through increased solute solubility. On a mole fraction basis, smaller PAH solutes such as anthracene, pyrene, and naphthalene are considerably more soluble in *n*-hexadecane than in cyclohexane.[26–29] Hexadecane does have the added advantage of being more viscous than cyclohexane, and one would expect an increase in the PAH emission intensity on this basis as well. Dichloromethane replaces carbon tetrachloride as the recommended chlorinated hydrocarbon because many PAH molecules are known to undergo rapid photochemical reactions with carbon tetrachloride.[10,20–24] Reactions between PAH molecules and dichloromethane appear to be much slower and, on the basis of our past studies, are not expected to significantly affect the emission intensity ratios measured in a 1-cm² quartz cuvette.[10]

Examination of the eight figures reveals that the PAH solutes can be divided into two categories, probe or nonprobe molecules, depending upon whether the ratio of emission intensities systematically changes with solvent polarity. For naphtho[8,1,2abc]coronene (NaCo) and dinaphtho[8,1,2abc;2′,1′,8′klm]coronene (DNCo), significant enhancement of the I band emission intensity relative to II and/or III band is observed in the more polar solvents. Values of NaCo and DNCo range from NaCo = 1.35 (I/II) and DNCo = 1.63 (I/III) for *n*-hexadecane to NaCo = 3.19 and DNCo = 2.88 for acetonitrile, which is the most polar solvent considered in the present study. Table I summarizes numerical values for nine different nonelectrolyte solvents, along with previously published Py values,[25] for comparison. Estimated uncertainties in the measured intensity ratio are believed to be on the order of ±0.05 (or less), on the basis of replicate measurements for select solvents over a three-day period of time. For the most part, the rank ordering of solvents by polarity is identical, at least to within the combined experimental uncertainties in the PAH values. Dibenzo[bc,ef]coronene initially appeared to show "probe-like" character. Upon closer examination of the fluorescence emission spectra, however, it was decided that the nonsystematic variation in the I/II band emission intensity ratio was a result of slight changes in the very weak signal at 571 nm. Small changes or uncertainties in the emission intensity of a weak signal can lead to a relatively large change in the calculated ratio.

Interestingly, not all of the coronene derivatives showed a selective enhancement of the I band emission intensity. For example, the calculated I/II band ratio in the anthra[2,3a]coronene (ACo) emission spectra decreased systematically with increasing solvent polarity, as shown in Table I. Of the twelve PAH solvent polarity probes that we have encountered thus far, only anthra[2,3a]coronene behaves in this manner. We further note that in benzene, dichloromethane, and carbon tetrachloride all three major emission peaks were shifted by 5–7 nm to longer wavelengths. The ACo value for carbon tetrachloride is not reported because we believe that a photochemical reaction may be occurring during the time it takes to accumulate the fluorescence data, in which case the calculated ratio will be in error. Abnormal fluorescence behavior prevents dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene from serving as a solvent polarity probe molecule. For dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene, the number of resolvable emission peaks increased with the "apparent" splitting of the 470-nm band into two identifiable peaks in several of the solvents studied (see Fig. 7).

Naphth[2′,1′,8′,7′:4,10,5]anthra[1,9,8abcd]coronene, benzo[1,2,3bc;4,5,6b′c′]dicoronene, and tetrabenzo[de,hi,mn,qr]naphthacene showed little enhancement of band I, and the calculated intensity ratios did not vary systematically with solvent polarity. The fluorescence behavior of tetrabenzonaphthacene was surprising since we expected to see considerable fine structure in the emission spectra. The molecular structure of tetrabenzonaphthacene contains two pyrene moieties fused together side by side. The emission spectra of pyrene contains five measurable vibronic bands located in the 370–470 nm spectral region. As shown in Fig. 2, the "pyrene-like" fine structure is completely lost upon addition of the second pyrene group. In retrospect, the nonprobe behavior and loss of fine structure might have been predicted on the basis of our previously reported measurements[6] on benzo[pqr]naphtho[8,1,2bcd]perylene. Like tetrabenzonaphthacene, benzonaphthoperylene contains two pyrene moieties (fused in a staggered configuration) and does not show selective enhancement of its I band emission intensity. Similarly, the characteristic coronene fine structure is absent in the emission spectra of benzodicoronene. Figure 9 shows only one major emission band centered around 510 nm and a shoulder at 545–560 nm. The published emission spectrum of benzodicoronene dissolved in trichlorobenzene has emission band maxima at 510, 549 and 593 nm.[30] Benzodicoronene is considerably more soluble in trichlorobenzene, and at the 10^{-6} molar (or less) concentrations that we were using, the 593-nm emission band was not observed.

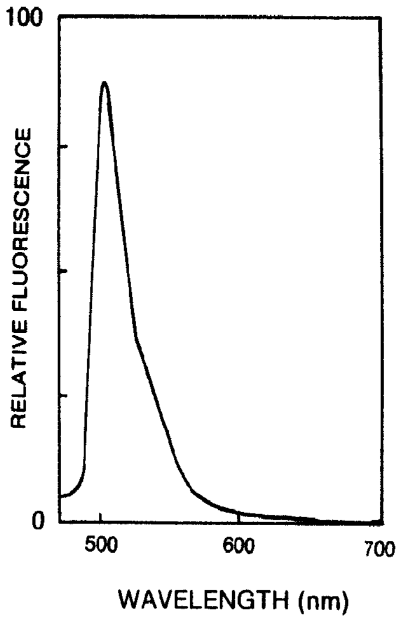

FIG. 9. Fluorescence emission spectra of benzo[1,2,3bc;4,5,6b′c′]dicoronene in dichloromethane.

As additional fluorescence data become available, it could be very informative to re-examine the entire spectral file to see whether any correlations exist between molecular structure and probe behavior. One simple method of grouping the various PAH molecular structures is by point groups and symmetry elements. A second possible classification scheme would be to divide the PAH molecules into the so-called "aromatic" ($4n + 2$) and "anti-aromatic" ($4n$) molecules on the basis of number of π-electrons. As shown in Table II, there is no apparent correlation between probe character and either of these properties. What does appear to be important is the level of detail in the fluorescence emission fine structure. Most of the probe molecules encountered to date had at least four (and very often five) fairly closely spaced emission bands. It is interesting to note that the only coronene derivatives to exhibit probe behavior were those molecules which had four to six benzene rings in the center chain. Furthermore, the length of the center chain always exceeds the remaining two chain lengths. Readers are reminded that dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene possesses these two structural features as well, but unfortunately the appearance of an intense spectral band in several solvents kept us from classifying this particular molecule as a fluorescent probe. Two 9-ring PAH compounds—dibenzo[a,j]coronene and dibenzo[bc,ef]coronene—behaved quite differently, depending upon where the substituent aromatic rings were placed. In dibenzo[a,j]coronene, the two added benzo-groups extended the center chain to five benzene rings, whereas in dibenzo[bc,ef]coronene, a benzo-group was located on both the top and bottom chain. Only dibenzo[a,j]coronene showed selective enhancement of the I band emission intensity in polar solvents. Both of the na-

TABLE II. Summary of the fluorescence behavior of select polycyclic aromatic hydrocarbons.

PAH molecule	Probe	π-Electrons	Point[a] group
Current study			
Dinaphtho[8,1,2abc;2′,1′,8′klm]-coronene	Yes	4*n*	C_{2v}
Naphtho[8,1,2abc]coronene	Yes	4*n* + 2	C_s
Naphth[2′,1′,8′,7′:4,10,5]-anthra[1,9,8abc]coronene	No	4*n* + 2	D_{2h}
Dibenzo[bc,ef]coronene	No	4*n* + 2	C_{2v}
Benzo[1,2,3bc;4,5,6b′c′]dicoronene	No	4*n*	D_{2h}
Tetrabenzo[de,hi,mn,qr]naphthacene	No	4*n* + 2	D_{2h}
Anthra[2,3a]coronene	Yes	4*n*	C_{2v}
Dinaphtho[8,1,2abc;2′,1′,8′jkl]coronene	NA[b]	4*n*	C_{2h}
Past studies[c]			
Coronene	Yes	4*n*	D_{6h}
Benzo[a]coronene	Yes	4*n*	C_{2v}
Naphtho[2,3a]coronene	Yes	4*n*	C_{2v}
Dibenzo[a,j]coronene	Yes	4*n*	D_{2h}
Pyrene	Yes	4*n*	D_{2h}
Benzo[ghi]perylene	Yes	4*n* + 2	C_{2v}
Benzo[pqr]naphtho[8,1,2bcd]perylene	No	4*n*	C_{2h}
Ovalene	Yes	4*n*	D_{2h}
Perylene	No	4*n*	D_{2h}
Naphtho[1,2,3,4ghi]perylene	No	4*n* + 2	C_{2v}
Benzo[a]pyrene	No	4*n*	C_s
Dibenzo[a,e]pyrene	No	4*n*	C_s
Tribenzo[de,kl,rst]pentaphene	No	4*n* + 2	D_{2h}
Benzo[e]pyrene	Yes	4*n*	C_{2v}
Dibenzo[fg,ij]phenanthro-[2,1,10,9,8,7qrstuv]pentaphene	Yes	4*n* + 2	C_{2v}
Dinaphtho[2,1,8,7defg;2′,1′,8′,7′ijkl]-pentaphene	NA[b]	4*n*	C_{2v}
Benzo[rst]anthra[9,1,2cde]pentaphene	NA[b]	4*n*	C_{2v}

[a] Point group assignments assume a planar molecule.

[b] NA indicates that the molecule is unacceptable as a probe because a common set of bands could not be assigned in all solvents studied. The molecule may exhibit selective enhancement of band I.

[c] Past studies are from Refs. 5–10.

phthocoronene isomers studied show probe behavior, and by careful examination of their molecular structures (see Fig. 1) one notes that either all (naphtho[2,3a]coronene) or part (naphtho[8,1,2abc]coronene) of the added naphtho-group is used to extend the center ring chain. The molecule's length-to-width ratio may provide a clue to its fluorescence behavior. On the basis of the very limited amount of fluorescence data, we can only speculate on the reason for the observed enhancement effect. We plan to continue measuring the fluorescence properties of additional PAHs in the hope that we can build up a sufficient spectral data base to allow us to examine possible correlations between probe behavior and various topological indices derived from molecular graph theory. Our preliminary observations concerning what structural and spectral features are common in the known PAH solute probes can only suggest possible PAH molecules for future studies. At the present time, the only definitive method for determining whether a given PAH behaves as a polarity solute probe is to actually measure its fluorescence properties in various solvents.

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