Ultraviolet–Visible Fluorescence Spectroscopy of Selected Polyaromatic Hydrocarbons and Organometallics on Hexagonal Graphite and Boron Nitride

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Several organic and organometallic compounds including polynuclear aromatic hydrocarbons (PAHs), anthracene, pyrene, and coronene and the organometallics zinc etioporphyrin and zinc phthalocyanine, adsorbed on the basal planes of highly ordered pyrolytic graphite (HOPG), a semimetal, and highly ordered pyrolytic boron nitride (HOPBN), an insulator, were studied using ultraviolet–visible fluorescence spectroscopy to examine surface interactions. The organometallics showed definite substrate effects with fluorescence quenching on HOPG but not HOPBN, which is consistent with the different electronic properties of these two substrates, but which seems not to have been previously reported for these molecules. Zinc etioporphyrin also showed a red shift and spectral distortion on HOPG. The PAHs, as expected from the literature, showed no substrate-specific effects.

Introduction

In this paper the ultraviolet–visible fluorescence of several organic and organometallic compounds adsorbed onto the basal planes of inorganic substrates, highly oriented pyrolytic graphite (HOPG), and boron nitride (HOPBN) was studied to serve as a probe of these surface–adsorbate interactions.

Boron nitride and graphite are quite similar structurally, exhibiting a tightly-bound hexagonal arrangement of atoms to form layers which are weakly coupled by van der Waals bonds which facilitate cleaving of the substrates to produce fresh basal plane surfaces for study. The C–C and B–N bond lengths in the hexagonal units are 1.42 and 1.45 Å, respectively. From an electronic point of view the graphite and the boron nitride are considerably different. Graphite exhibits a semimetallic conductivity in the basal plane and is less conductive by a factor of approximately 10^4 in the c direction, perpendicular to the basal plane. The boron nitride on the other hand is a wide-gap insulator ($E_g = 5.4$ eV). Optical studies of HOPBN have reported strong intergap absorption which was identified as impurities and/or defects associated with vacant B or N atom sites.[1-4]

The organics studied were polynuclear aromatic hydrocarbons (PAHs, anthracene, pyrene, coronene) and the organometallics were zinc etioporphyrin (ZnEtio) and zinc phthalocyanine (tetraazotetrabenzporphyrin) (ZnPc). These compounds all have relatively rigid and flat structures, delocalized π-bonded ring structures of different sizes, and

relatively high fluorescence yields so that submonolayer coverages may be studied.

Fluorescence spectroscopy is an especially useful technique for the study of classes of compounds with relatively high fluorescence yields. For such compounds, the sensitivity is high enough so that trace concentrations corresponding to low surface area coverage can give measurable signals (from well under a monolayer to several monolayers). As is well documented in the fluorescence literature for organic molecules in solution or on solid surfaces, one measures transitions from the lowest vibrational level, $\nu = 0$, of the first electronic excited singlet state to various vibrational levels of the electronic ground state.[5,6] For polyaromatic compounds this is a π–π^* transition and for organometallic compounds it is still essentially a π–π^* transition but modified by the interaction with the orbitals of the metal ion.[7-11] The theory of the electronic spectra of polyaromatic molecules has been extensively studied and discussed in refs 5 and 6, while the theory of the electronic and vibrational spectra of porphyrins and phthalocyanines has been discussed in refs 9 and 12–15.

Fluorescence has been used in the past as a probe for microenvironments[16,17] and for examining surface in-

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teractions.[18-24] Other advanced surface analysis techniques such as scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and X-ray diffracrtion (XRD) have also been used to examine PAHs on substrates such as graphite.[25,26] Strong surface interactions may indicate a potential for the formation of intercalation compounds or at least for the use of graphite surfaces doped with organometallics for chemical sensor coatings.

Experimental Section

Chemicals and Substrates. The chemicals used were all commercially available. The chemical compounds included anthracene (98%) pyrene (99%), coronene (94%) (Chem Services, Inc.), zinc etioporphyrin (98+%) (Porphyrin Products), and zinc phthalocyanine (98%) (Kodak). The solvents (cyclohexane and methanol) were of spectroquality grade and were acquired from Burdick and Jackson. The substrate materials HOPG and HOPBN were provided by A. W. Moore, Union Carbide. The properties of the HOPG and HOPBN surfaces are described in the literature.[1-4,27-29]

Known amounts of the fluorescent probes were applied in solution to freshly cleaved basal planes of HOPG and HOPBN surfaces by casting a film using a Hamilton series 7105 5-μL syringe and applying a known volume ((1-20) $\pm$ 0.05 μL) of a known concentration (2 $\times$ 10^{-5}-1 $\times$ 10^{-7} M) and measuring the spot size (typically 3-6 $\pm$ 0.5 mm diameter). Therefore, the values for the surface coverages of the fluorescent probes on the HOPG and HOPBN are only approximate but satisfactory for the comparison of the relative surface interactions of the two substrates in the present study. The approximate surface coverage, θ, was calculated for each case, with $\theta = 1$ representing 100% coverage or one monolayer. The assumption was made that the molecules were flat on the basal planes of the substrates. This is consistent with STM and LEED measurements of copper phthalocyanine on silver[30] and PAHs on graphite previously reported.[25,26] The error in coverage calculations was approximately 20-30%. The spectra were then measured by front surface luminescence with surface coverages ranging from submonolayers to several monolayers. All experiments were performed under ambient atmospheric conditions. For a check on reproducibility, the solutions were reapplied to freshly prepared surfaces before measuring the spectra and the measurements repeated 3-4 times.

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Instrumentation. Ultraviolet–visible (UV–vis) emission spectra were measured at fixed excitation wavelengths corresponding to ultraviolet or visible peaks of the absorption spectra of the compounds. A Spex Fluorolog-2 spectrofluorometer was used to collect all fluorescence spectra. The system included a double-excitation monochromator and a double-emission monochromator. The monochromator gratings were ruled at 1200 grooves/nm and blazed at 300 (excitation) and 500 nm (emission). The excitation source consisted of a 450-W ozone-generating xenon lamp. The photomultipler tubes used were a Hamamatsu R928 for the emission detector and a Hamamatsu R508 for the reference detector (rhodamine B reference quantum counter). The spectrofluorometer was interfaced to a Spex DM3000 MS-DOS-based personal computer.

All spectra were collected in the S/R mode ratioing the emission signal to the reference signal which corrects for variations in the lamp intensity. The spectra of the anthracene, pyrene, and coronene were collected using a radiometric correction (calibration by comparison with scatter from an NIST standard lamp) which corrects for the spectral response of the emission monochromator and the emission detector. The spectra of the zinc phthalocyanine and zinc etioporphyrin were collected without using the radiometric correction because of the uncertainty in the correction factor beyond 650-700 nm. The spectrofluorometer was regularly wavelength calibrated using a mercury pen lamp with daily wavelength calibration done using a standard consisting of ovalene dissolved in poly(methyl methacrylate) which was obtained from Starna Cells, Inc.

The excitation wavelengths (Ex) used in the various spectra are listed in the figure captions, as are the bandpasses (BP) of the slits for the excitation and emission monochromators. Excitation by a 450-W xenon arc lamp was normal to the surface of the sample and the front surface fluorescence was collected at an angle of 22.5° to the excitation. The sample was continuously exposed to exciting light during the spectral scan. In some cases as expected by the photochemical literature,[31,32] appreciable photodegradation of the signal was observed after the illumination (e.g., within 30 min for anthracene on graphite). The spectral scans normally required 5 min.

Results

Fluorescence measurements were made for both hydrocarbons and organometallics on HOPG surfaces and HOPBN surfaces for comparison. Fluorescence spectra of anthracene, pyrene, coronene, ZnEtio, and ZnPc were measured in solution and at high surface coverages ((θ = 1.0–2.0) greater than a monolayers) and low coverages ((θ = 0.1–1.0) less than one monolayer) on fresh cleavage planes of HOPG exposed briefly (less then 3 min before sample application) to air. Anthracene, ZnEtio and ZnPc were also measured on HOPBN at high and low surface coverages.

There was no appreciable fluorescence background observed with the HOPG. A broad fluorescence band in the ultraviolet and visible regions was observed in the HOPBN fluorescence spectra[29] which occurred in the same region as the fluorescence of the PAHs but did not interfere seriously with the fluorescence measurements on the organometallics. Because of the high fluorescence background for the HOPBN, in the emission region of pyrene and coronene, it was only possible to observe anthracene (riding on a high fluorescence background) on the HOPBN surface.

The fluorescence spectra for the hydrocarbons on HOPG and anthracene also on HOPBN, generally showed little spectral change due to the presence and nature of the substrates, except for red shifts compared to cyclohexane solutions, but the organometallics showed relatively large changes. For anthracene no evidence of interaction clearly specific to the HOPG surface was observed, contrary to
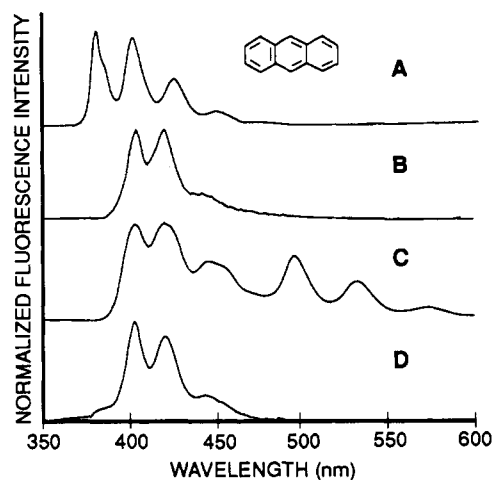
Figure 1. Anthracene UV–vis fluorescence spectra, excitation λ = 338 nm, bandpasses 8 nm for excitation monochromator, 2 nm for emission monochromator. (A) 2×10^{-5} M in cyclohexane; (B) on HOPG, θ = 0.2; (C) on HOPG, θ = 2.3; (D) on HOPBN, θ = 0.2.

Figure 2. Pyrene UV–vis fluorescence spectra, excitation λ = 320 nm, bandpasses 8 nm for excitation monochromator, 2 nm for emission monochromator. (A) 2×10^{-5} M in cyclohexane; (B) on HOPG, θ = 0.1; (C) on HOPG, θ = 0.4.

what will be reported later for the organometallics, where quenching of the fluorescence spectra was observed at less than a monolayer coverage.

The results for the PAHs on HOPG are discussed first. Although various scientists have reported UV–vis fluorescence spectra for PAHS on other inorganic substrates such as clay,[33] silica,[34,35] and other inorganic substrates,[36] the present UV–vis fluorescence data for PAHs on HOPG graphite are of interest for comparison to the organometallics since they were analyzed under exactly the same experimental conditions (other surface studies for PAHs on graphite have not usually included fluorescence measurements).

The two dominant peaks in the spectrum for anthracene on HOPG are shifted by approximately 20 nm to the red compared with the solution spectrum of anthracene in reagent-grade cyclohexane (Figure 1A). The dominant difference between the spectra at relatively high (θ = 2.3) and low (Ω = 0.2) levels of anthracene coverage on graphite is the presence of additional peaks at longer wavelengths for the higher levels of anthracene coverage, presumably due to the formation of aggregates such as dimers or polymers (Figure 1B,C). Some reduction in signal intensity and some broadening of the two dominant spectral features is also observed upon increasing the coverage, though peak wavelengths remain unchanged.

Since a similar red shift for anthracene was observed on the HOPBN surface relative to the solution spectrum (Figure 1D), there is no evidence of an interaction specific to the graphite surface. On the fresh HOPG cleavage surface, apparent photodegradation of anthracene was observed on excitation at 254 nm and to a lesser extent at 338 nm. This degradation behavior was not observed in anthracene solution in cyclohexane or for anthracene on filter paper measured under the same ambient atmospheric conditions. The photochemistry of the PAHs is well-known for other substrates.[20,21,31,32] Here it is not a major factor since the fluorescent spectrum for the most photoreactive compound, anthracene, only decays slowly
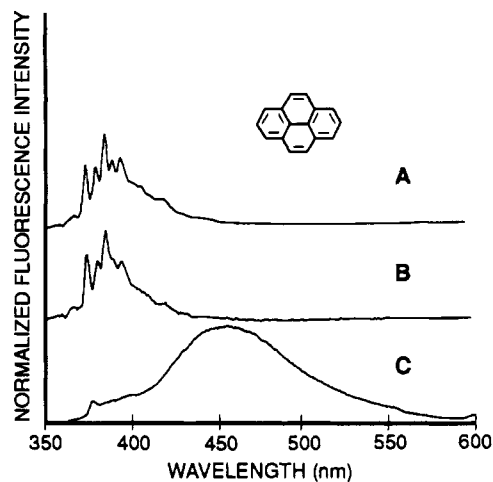
with slight band broadening under continuous UV illumination, over 20 min.

For pyrene (Figure 2), only minor changes in the vibrational structure of the fluorescence peak and essentially no red shifts were observed on comparing the solution spectrum at 300 ng/mL (ppb) and the pyrene spectrum on HOPG at a coverage of θ = 0.1. At a pyrene coverage of θ = 0.4 on HOPG, a broad peak at approximately 455 nm, presumably due to the excimer, dominates the spectrum. This may indicate greater than expected multilayer layer or island formation at surface defects possibly due to surface diffusion as was observed for monolayer films of FePc on graphite as studied by penning ionization electron spectroscopy (PIES)[30] or that estimating the errors in surface coverage were greater then expected. The experiment was repeated several times with the onset of broadening occurring at similar θ values.

Coronene has a circular structure of seven fused benzene rings and would therefore come close to fitting the graphite lattice. Coronene in cyclohexane solution is known to have very sharp spectra with considerable vibrational structure, showing an onset in the emission spectrum at approximately 400 nm, and the strongest peak at 445 nm (Figure 3A). At a coverage of θ = 0.1 on HOPG, the coronene showed fairly sharp structure, with an onset at about 380 nm (Figure 3B). At high coverages (θ = 3.4) of coronene on HOPG, the peak onset is shifted to about 430 nm, with the first strong peak at 474 nm and the strongest peak at 500 nm (Figure 3C). This corresponds to a red shift of 30–55 nm depending on which peak in the film is identified with the strongest peak in solution.

The organometallics studied (zinc etioporphyrin (ZnEtio) and zinc phthalocyanine (ZnPc)) showed more evidence for interaction specific to the HOPG basal plane than did the polynuclear aromatic hydrocarbons (especially anthracene) studied. Both organometallics showed evidence of a decrease in spectral intensity at low coverages (θ < 1) on HOPG as compared to HOPBN. In addition, at moderate coverages, ZnEtio showed a distorted spectrum on HOPG as compared to HOPBN at the same coverages, which indicates a difference in interactions for these substrates. Details are described below.

The solution spectrum (on excitation at 529 nm) of ZnEtio in cyclohexane at 1×10^{-7} M has a (0,0) peak at

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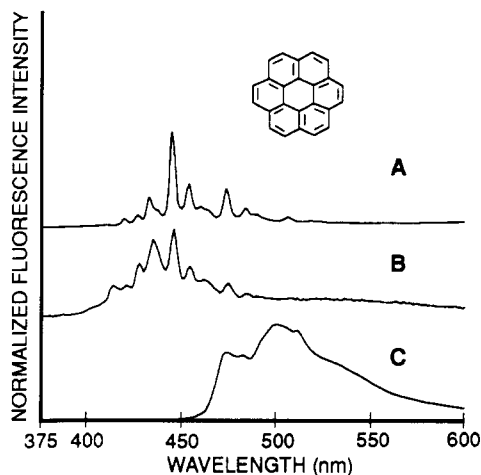(36) Thomas, J. K. *J. Phys. Chem.* **1987**, *91*, 267.

Figure 3. Coronene UV–vis fluorescence spectra, excitation λ = 338 nm, bandpasses 8 nm for excitation monochromator, 2 nm for emission monochromator. (A) 1×10^{-6} in cyclohexane; (B) on HOPG, θ = 0.1; (C) on HOPG, θ = 3.4.
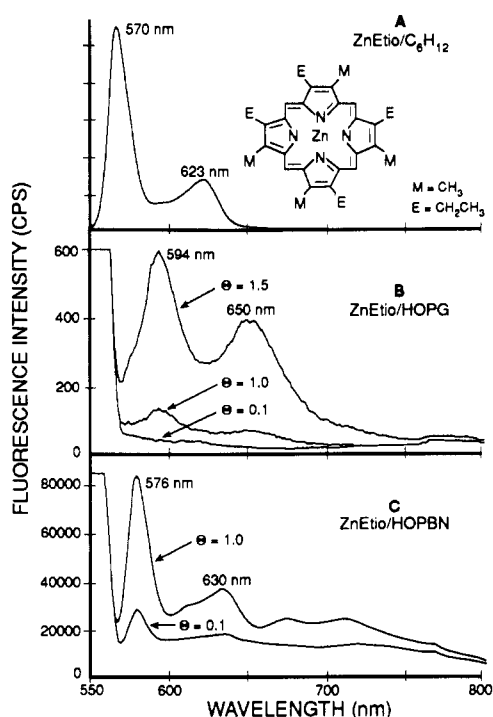

Figure 4. Zinc etioporphyrin UV–vis fluorescence spectra, excitation λ = 529 nm, bandpasses 8 nm for excitation monochromator, 8 nm for emission monochromator. (A) 1×10^{-7} M in cyclohexane, (B) on HOPG, θ = 0.1, 1.0 and 1.5; (C) on HOPBN, θ = 0.1 and 1.0.

570 nm and a (0,1) vibrational peak at 623 nm (Figure 4A). When spotted on HOPG at a coverage of θ = 1.5, ZnEtio yielded a spectrum (Figure 4B) showing a greatly weakened peak (0,0) at 594 nm (a red shift of 24 nm from the spectrum in cyclohexane) and a presumable (0,1) vibrational peak at 650 nm (a red shift of 27 nm). This indicates apparent partial suppression of the (0,0) peak and a red shift between 24 and 27 nm, which might indicate a moderately strong interaction between the ZnEtio and the HOPG. Despite the delocalized π-bonding, a close fit of the ZnEtio to the graphite lattice would be prevented by the difference in shape between the five-membered pyrrole rings in the ZnEtio[10,11] and the six-membered rings in graphite.

In comparison ZnEtio on HOPBN (Figure 4C) has a strong (0,0) peak at 576 nm (a red shift of only 6 nm from
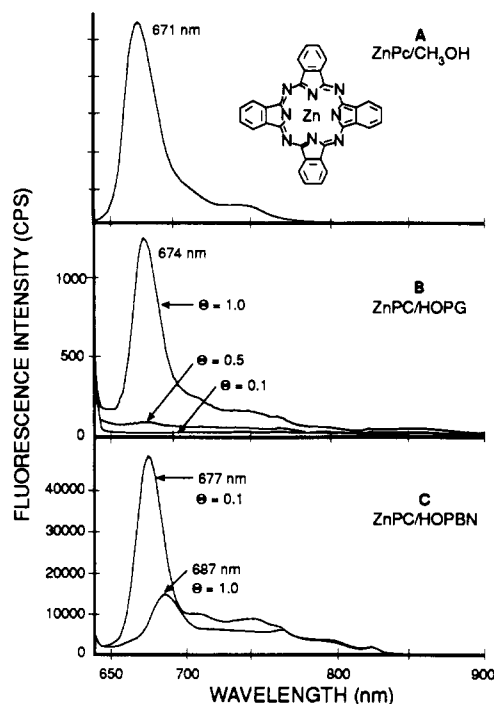

Figure 5. Zinc phthalocyanine UV–vis fluorescence spectra, excitation λ = 608 nm, bandpasses 8 nm for excitation monochromator, 8 nm for emission monochromator. (A) 1×10^{-7} in methanol; (B) spotted on HOPG, θ = 0.1, 0.5, 1.0; (C) spotted on HOPBN, θ = 0.1 and 1.0.

the spectrum in cyclohexane) and a weaker (0,1) peak at 630 nm. Thus, the interaction between ZnEtio and a HOPG (semimetal) basal plane is much greater than for a HOPBN (insulator) basal plane.

ZnPc in spectroquality methanol shows a strong peak at 671 nm with shoulders at approximately 705 and 745 nm (Figure 5A). ZnPc on HOPG at higher coverages (θ = 1.0; Figure 5B) showed a peak at 674 nm, a red shift of only 3 nm, but on this substrate only very weak signals could be observed at lower coverages (θ < 0.5).

For contrast, ZnPc on HOPBN shows a strong signal with a peak maximum at 677 nm for a coverage of θ = 0.1 (Figure 5C), and the signal could still be observed with coverages as low as θ = 0.02 (not shown).

Discussion

Fluorescence emission spectra for two classes of compounds, (1) polynuclear aromatic hydrocarbons (PAHs; anthracene, pyrene, and coronene) and (2) organometallics (zinc etioporphyrin and zinc phthalocyanine), were used as molecular probes to explore surface interactions with two inorganic substrates: (1) graphite, a semimetal (HOPG) and (2) boron nitride, HOPBN, an insulator. The PAHs showed spectra on HOPG and for anthracene also on HOPBN at low surface coverages (θ < 1) which were only slightly different from solution spectra, except for red shifting, indicating only relatively weak interactions with the surfaces. At higher surface coverages (θ nearer to or greater than 1) spectral distortions as expected from aggregation effects were observed, not specific to the substrate. For PAHs, especially for anthracene, there was also some evidence of photochemical degradation on freshly cleaved HOPG surfaces as was expected from the literature, but this was slow enough not to affect spectral reproducibility.

The organometallics, however, showed a high degree of fluorescence quenching for ZnPc and ZnEtio at low coverages ($\theta < 1$) on HOPG as compared to the behavior of the same molecules under the same conditions on HOPBN. At higher coverages there is at least partial shielding of the substrate by the molecules already present, so that fluorescence can be observed from molecules presumably not directly in contact with the surfaces. At higher coverages ($\theta = 1.0$ and 1.5) and ZnEtio on HOPG the spectra were distorted with respect to the solution spectrum (both a large red shift (24–27 nm)) and a different peak ratio and broadening). The spectra for ZnPc on HOPG could not be observed at all at lower coverages and was only weakly observable at a coverage of $\theta = 0.5$, and then the spectra were only slightly shifted from solution.

In contrast, both ZnEtio and ZnPc could be observed at low surface coverage ($\theta = 0.1$) on HOPBN and the spectra appeared only slightly shifted from the solution spectra. This evidence is indicative of at least a moderately strong interaction of these organometallics with the HOPG semimetal as opposed to the HOPBN insulator.

The fluorescence quenching of large delocalized π-bonded ring molecules such as ZnEtio and an even larger more delocalized π-bonded molecule such as ZnPc on a semimetal such as HOPG (as opposed to HOPBN, an insulator) can be qualitatively understood in contrast to the smaller, less delocalized π-bonded structures for the PAHs on the same substrates. The additional large red shift and spectral distortion for the ZnEtio on HOPG are harder to explain in the absence of a similar effect for the ZnPc. Perhaps the fact that ZnEtio is smaller and less inert and has side groups (methyl and ethyl which are more available for H bonding) may indicate its greater availability for chemical bonding. For both ZnEtio and ZnPc the five-membered pyrrole rings do not closely correspond to the graphite structure so that a strong epitaxy effect is not the likely explanation.

The importance of the organometallic compounds on HOPG for sensor applications is that organometallic-graphite systems, showing at least partial fluorescence quenching (for ZnPc and ZnEtio) or large spectral shifts, as was the case for ZnEtio, are more sensitive to changes in the microenvironment caused by perturbations by ternary interactions from small amounts of pollutant molecules. Such systems may show spectral, conductivity, or electrochemical changes due to relatively minor perturbations with increased sensitivity to small changes in pollutant concentrations. Phthalocyanines or porphyrins as thin films on carbon or other substrates have been used as conductivity, mass, and electrochemical sensors for the detection of some gaseous pollutants.[37-44]

The spectral results for the organometallic compounds (ZnEtio and ZnPc) were interesting and somewhat un-

expected. For both ZnEtio and ZnPc on HOPG (semi-metal) fluorescence quenching was observed. This perhaps could be expected for large delocalized π-bonded electron cloud structures on a semimetal. Possible explanations include a mechanism such as electron injection as discussed by Ponte Goncalves and references listed therein,[22] or a subtler energy-transfer mechanism due to overlap of the largely delocalized π-electrons with the electron cloud of the graphite. The signal reappearing at higher coverages probably was due to partial shielding of the substrate due to coverage by the organometallic compounds. Since these molecules have a tendency to form dimers and congregate around step defects, some molecules may be shielded even at coverages of less than one monolayer. These phenomena were not observed for the smaller, somewhat less delocalized π-bonded PAHs which suggests that a large delocalized π-system is required. The substrate specificity of these phenomena for the organometallics but not for the PAHs indicates that the π-electrons of the organometallics are freer to interact with the substrate and that the semimetal perturbs the organometallic molecules enough to cause quenching. Any decrease of signal for organometallics on HOPBN at higher concentrations can be explained by formation of the less fluorescent, more red-shifted dimer and perhaps also by radiationless energy transfer between closely packed molecules. The large red shift and spectral distortion for ZnEtio on HOPG and not for the ZnPc on HOPG are harder to explain but are probably an indication of greater interaction and perhaps stronger hybridization of orbitals for ZnEtio (ZnPc is more inert and lacks methyl and ethyl side groups). The results presented here in addition to those found in a similar report[45] of a stoichiometric intercalation compound for the layered material tantalum disulfide intercalated with phthalocyanine suggest that further studies of graphite surfaces with large organometallic chemicals will be of interest.

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