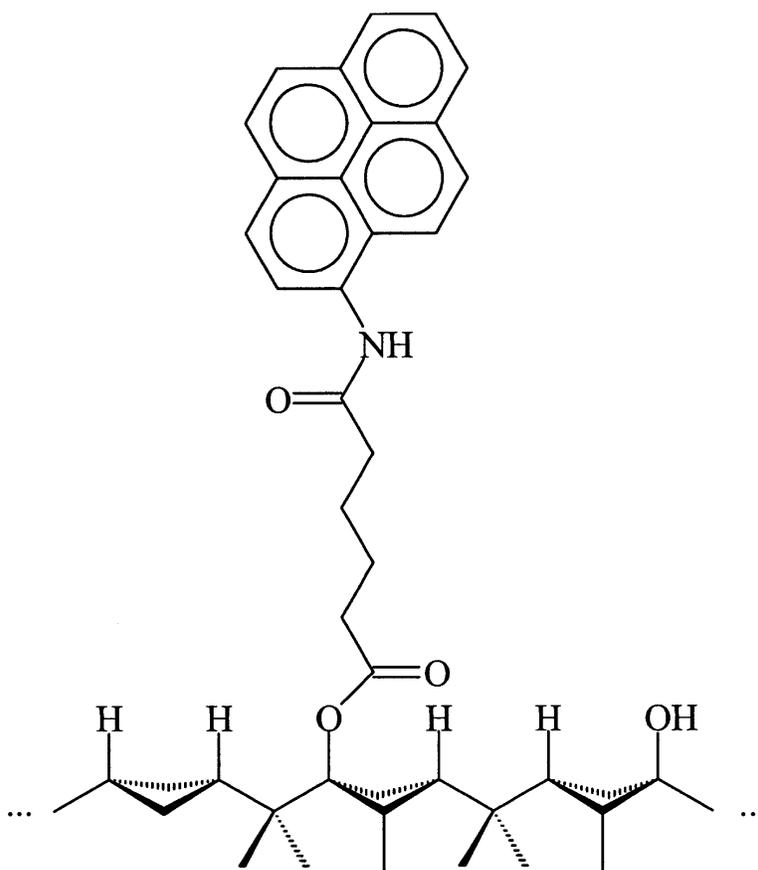


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Covalent Adlayer Growth on a Diamond Thin Film Surface

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Diamond thin films have emerged as important materials, not only because of their high mechanical strength, but also because these films can be doped with boron to become conductive while retaining their favorable optical properties. Recent work by the Swain group has demonstrated that boron-doped diamond (BDD) thin film electrodes afford a substantial enhancement in long-term stability and a wider potential window than other more commonly used electrode materials, such as glassy carbon.^{1,2} One reason for the high stability of diamond thin films is their relatively unreactive nature. While this inertness is beneficial in terms of electrode stability, it may ultimately limit the utility of diamond thin films in sensing applications, where adlayer attachment will be required to impart selectivity. The electrochemical modification of BDD films with diazonium salts³ and of diamond films with alkenes^{4,5} has been reported before, so it is clear that these surfaces can be modified under the appropriate conditions. We report here on the spontaneous covalent growth of monomolecular adlayers on boron-doped diamond thin films. This advance opens the door to using a wide array of surface modification reactions previously limited to metallic and oxide substrates, on diamond thin films.

Our recent work on the covalent attachment of monomolecular adlayers to a variety of surfaces has shown that simple displacement reactions can be used on essentially any surface where a hydrous oxide is present. We have attached adlayers covalently to silica, oxidized silicon, indium-doped tin oxide (ITO), and electrochemically generated gold oxide surfaces by reacting the surface functional group (–OH) with an acid chloride.^{6,7} This chemistry has proven to be equally well suited to adlayer growth on amine-terminated surfaces, and the resulting interface is stable to washing or immersion in organic solvents, as measured spectroscopically and electrochemically. The covalently bound adlayer is not as ordered as alkanethiol-gold SAMs,⁸ but they exhibit more organization than amorphous physisorbed adlayers.

We have covalently attached a monomolecular adlayer to a boron-doped diamond surface and have characterized the resulting monolayer. The typical case for a diamond thin film is that the surface is terminated by hydrogen, rendering it hydrophobic. Surface hydroxyl and carbonyl groups have been formed on diamond thin films exposed to strong oxidizing agents, with submonolayer coverage of the diamond surface being the usual result.^{9,10} We have treated microcrystalline BDD thin films with piranha solution (10 min, 40 °C) to produce a hydrophilic surface. While this treatment yields reproducible results, our data show that the resulting surface is covered with only a small fraction of a monolayer of hydroxyl functionalities (vide infra). We reacted this surface with adipoyl chloride to produce an acid chloride-terminated surface, as described in refs 6 and 7. Briefly, the BDD substrates were reacted with adipoyl chloride in dry acetonitrile, using 4-methylmorpholine as a Lewis base (1:50:1, v/v/v) under nitrogen for ca. 12 h. The reacted

substrates were removed from the reaction vessel, rinsed with ethyl acetate, and dried under nitrogen. Next, the resulting terminal acid chloride functionalities were reacted with 1-aminopyrene by exposing substrates covered with an adipoyl chloride adlayer to 10 mL of 0.5 mM 1-aminopyrene in dry acetonitrile with 0.1 mL of 4-methylmorpholine under nitrogen overnight. The initial adlayer deposition reaction is sufficiently fast and favorable that close to a complete reaction is achieved during the first step, limited by any steric constraints imposed by the substrate structure or possibility of bridging two surface sites of the substrate by the two COCl terminal groups of the same adipoyl chloride molecule. Given the modest density of surface functionality on a normally unreactive BDD surface, the maximum coverage will be significantly less than a monolayer, and we can place a lower limit on this coverage electrochemically. The efficiency of pyrene coupling is not as high as that of the initial acid chloride layer, as seen by the IR spectra of these films. The density of the chromophores was sufficiently low that we did not observe excimer formation, in agreement with reports on the fractional coverage of BDD surfaces with hydroxyl termini. The resulting chromophore coverage of the adipoyl chloride-modified BDD substrate was evaluated by means of cyclic voltammetry, based on its known electrochemistry^{11,12} and using the so-called “electrochemical” area of a BDD electrode. The electrochemical area was determined with use of a standard ferric/ferrous hexacyanide redox couple, as reported in our earlier work on ITO and Au substrates.^{6,7}

The pyrene-modified BDD surface was measured to have a coverage of 4.25×10^{-12} mol cm⁻², a result consistent with the spectroscopic data, corresponding to ca. 0.5% of a full monolayer. This finding demonstrates the level of coverage achievable on this substantially inert BDD substrate (the accepted value for surface density of a thiol/gold SAM is 7.7×10^{-10} mol cm⁻²).⁸ It is useful to compare this result to our previous work using the same covalent attachment chemistry to bind substituted pyrene to ITO^{6,7} (1.7×10^{-11} mol cm⁻²) or ferrocenemethanol to oxidized Au (1.5×10^{-10} mol cm⁻²).¹³

Infrared spectroscopic data on these interfaces were acquired in reflection mode at 4 cm⁻¹ resolution using a Nicolet Magna 750 FTIR spectrometer, with the spectrum of a piranha-cleaned BDD substrate used as the background spectrum. These data show the covalent growth of the adlayers and the presence of substantial unreacted and non-hydrogen bonded –OH functionality (Figure 1). The band(s) centered at 1676 cm⁻¹ are indicative of amide linkage formation, and the two bands at 1745 and 1763 cm⁻¹ are C=O ester resonances. The spectral region between 2800 and 3000 cm⁻¹ is characteristic for the –CH₂– stretching vibrations of the adipoyl chloride adlayer, with the positions of the bands (2922 and 2961 cm⁻¹) indicating the absence of interchain organization, a result consistent with submonolayer loading density. The pyrene aromatic CH stretches at ~3100 cm⁻¹ lie beneath our detection limit. The most prominent bands, in the 3700 cm⁻¹ region, suggest the

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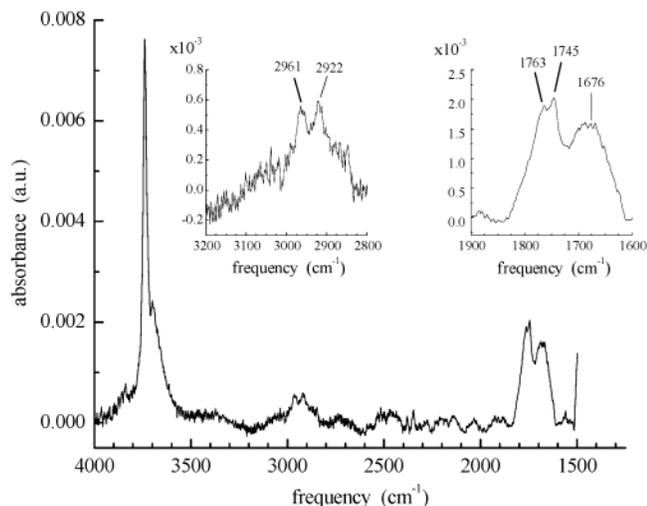


Figure 1. IR reflection–absorption spectrum of 1-amidopyrene hexanoate bound covalently to a microcrystalline boron-doped diamond (BDD) substrate. Center inset shows CH stretching region, and right inset shows C=O and amide stretching region.

presence of unreacted surface-bound functionalities on the oxidized surface of BDD. The absence of a broad absorption centered near 3300 cm^{-1} indicates that there is neither bulk water nor significant hydrogen bonding between —OH groups at the BDD interface.

We have used the fluorescence lifetime and motional dynamics of tethered pyrene to characterize the properties of several interfaces⁶ using a time-correlated single photon counting spectrometer that has been described elsewhere.¹⁴ Time-domain fluorescence is a useful spectroscopic tool because it provides information on the motional freedom available to the bound chromophores and about the (dipolar) coupling between the chromophore and the substrate. Such information is difficult to obtain by other methods. In certain circumstances, time-domain data can provide insight into the substrate morphology.^{15–17} We have studied the time-domain fluorescence response of 1-amidopyrene hexanoate bound covalently to the BDD substrate in an effort to understand the behavior of this material relative to other materials, such as ITO. Our experimental time-resolved fluorescence data ($\lambda_{\text{ex}} = 290\text{ nm}$) show that the BDD substrate is characterized by an emission transient at $\sim 400\text{ nm}$ (Figure 2a, bottom trace), and this response is believed to be associated with the boron doping sites. We recover a two-component exponential population decay for this transient, with time constants of 425 ps (57%) and 3.09 ns (43%). Further studies are underway to characterize the dopant-density dependence of this response. The time-domain response of tethered pyrene is clearly resolvable from that of the substrate (Figure 2a, top trace). The background-subtracted population decay of surface-bound pyrene exhibits a two-component exponential population decay with time constants of 60 ps (74%) and 472 ps (26%). The BDD interface quenches the pyrene fluorescence substantially, given the dominant 60 ps decay time, indicating strong chromophore–substrate coupling. This result shows the chromophore to be in close proximity to the dopant sites present on the BDD substrate surface, further indicating these sites as the chemically reactive locations. The second decay component, with a time constant $\sim 50\text{ ps}$ longer than the fast BDD response, likely results from excitation transport between the BDD dopant centers and the tethered pyrene. Both of the pyrene lifetime components indicate that the chromophore is in close proximity to the BDD substrate.

The time-resolved anisotropy data for the tethered pyrene bound to the BDD do not correspond to those seen for the same chromophore on other substrates (e.g., SiO_2 , ITO, Au). Earlier work

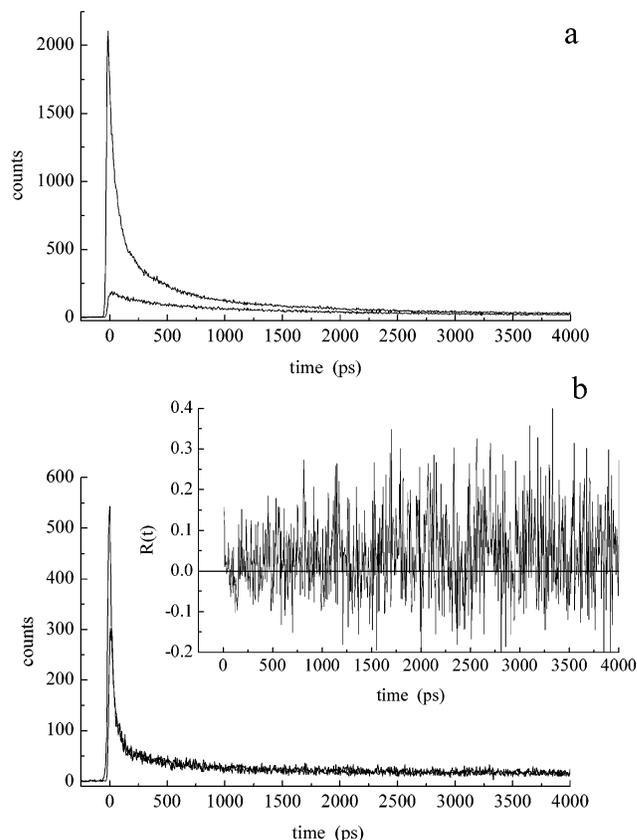


Figure 2. (a) Top trace: Time-resolved intensity data for a monolayer of 1-amidopyrene hexanoate bound covalently to microcrystalline diamond. Bottom trace: Same data for a BDD substrate. (b) Time-resolved emission polarized parallel and perpendicular to vertical excitation polarization. Inset: $R(t)$ function for these data, indicating no dynamics and no steady-state anisotropy.

has shown that tethered pyrene exhibits no early-time motional dynamics and that the time-independent anisotropy is determined by substrate–chromophore coupling.⁶ The anisotropy data we recover for tethered pyrene on BDD show neither any motional dynamics nor steady-state anisotropy (Figure 2b). There are two possible explanations for this remarkable result. In either case, the absence of any time-dependence to the anisotropy signal points to the chromophores residing in a relatively rigid environment over the $\sim 5\text{ ns}$ time scale of the measurement. The first explanation for the observation of $R(0) = R(\infty) = 0$ is that the angle between the excited and emitting transition moments is 54.7° . If this is the case, the data reveal nothing about the orientational distribution of the bound chromophores. The second explanation is that the chromophore orientational distribution is sufficiently broad to approximate a random distribution. We assert on plausibility grounds that the latter situation is more likely, especially when viewed in light of the morphology of microcrystalline BDD films (Figure 3, left). The anisotropy measurements we reported previously⁶ were made on relatively smooth substrates (e.g., ITO, Figure 3, right), and for such systems the angle between the excited and emitting chromophore transition dipole moments can be evaluated. The microcrystalline BDD substrates we use here are characterized by a highly featured surface morphology (Figure 3, left), and our anisotropy data, of the form $R(0) = R(\infty) = 0$, are consistent with the observed morphology of the BDD substrate. The absence of fast pyrene motion suggests its existence in a relatively confining environment, and the absence of any steady-state anisotropy is reflective of the large orientational distribution of the substrate

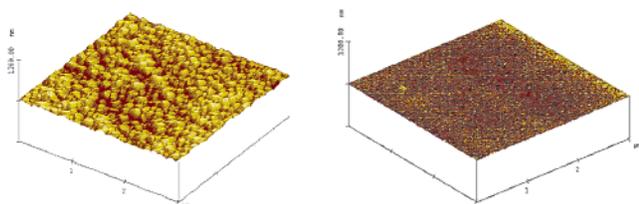


Figure 3. (left) AFM image of a $3\ \mu\text{m} \times 3\ \mu\text{m}$ area of a microcrystalline BDD substrate; RMS roughness for this surface is 14.4 nm. (right) AFM image of a $3\ \mu\text{m} \times 3\ \mu\text{m}$ area of an ITO-coated substrate; RMS roughness for this surface is 3.3 nm.

surface. It is fair to consider that the incident light in this experiment is vertically polarized so, at least at early time, one may expect a nonzero anisotropy on geometric grounds. Because of the morphological and optical properties of the microcrystalline BDD interface, substantial polarization scrambling of the incident UV beam will occur, and we believe this to be the reason for the absence of a measurable early-time nonzero anisotropy value.

The FTIR and time-resolved emission data are fully consistent with covalent binding of a monomolecular adlayer to BDD using simple acid chloride chemistry. The vibrational spectroscopic data point to the formation of the expected ester and amide linkages, and the time-resolved data show that the chromophore is in close proximity to the BDD interface. Our data show there to be a large orientational distribution of chromophores on the BDD surface, consistent with the mesoscopic morphology of this system. Our work points the way to a general scheme for growing robust adlayers on this important material.

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