Functionalization of Amorphous SiO$_2$ and 6H-SiC(0001) Surfaces with Benzo[ghi]perylene-1,2-dicarboxylic Anhydride via an APTES Linker

Deb Kumar Bhowmick,* Steffen Linden, André Devaux, Luisa De Cola, and Helmut Zacharias*

The successful covalent functionalization of quartz and n-type 6H-SiC with organosilanes and benzo[ghi]perylene-1,2-dicarboxylic dye is demonstrated. In particular, wet-chemically processed self-assembled layers of aminopropyltriethoxysilane (APTES) and benzo[ghi]perylene-1,2-dicarboxylic anhydride are investigated. The structural and chemical properties of these layers are studied by contact angle measurements, attenuated total reflection infrared (ATR-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The optical properties are measured by confocal microscopy. The wetting angles observed for the organic layers are $\alpha = 68^\circ$ for the APTES-functionalized surface, while angles of $\alpha = 85^\circ$ and $78^\circ$ are determined for dye-functionalized quartz and 6H-SiC surfaces, respectively. However, not all amino groups of the APTES-functionalized surfaces react to bind dye molecules. Further dye functionalization is not uniform throughout the surface, showing different island sizes of the dye and including different chemical environments. The quartz surface exhibits a higher packing density of dyes than the 6H-SiC surface. The fluorescence lifetimes of the surface-attached dye show double exponential decays of about 1.4 and 4.2 ns, largely independent of the substrates.

1. Introduction

The attachment of functional self-assembled monolayers (SAMs) onto amorphous silicon dioxide (quartz)\cite{1-3} or carbon-based\cite{6} substrates constitutes an attractive approach for building novel interfaces for molecular electronics devices with applications ranging from solar energy conversion to chemical and biological sensing. Semiconducting surfaces such as doped Si and SiC are particularly relevant for the development of novel electrically addressable and switchable functional devices\cite{4,5} as their electronic properties are tunable by changing the concentration of dopants, or by generating electron–hole pairs under illumination. The development of methods to tune the surface properties of wide-bandgap silicon carbide would significantly increase the possible use of this material as well. Among others, SiC has found applications as waveguide material in refractometric or fluorescence detection, and as coating material for sensors based on electrical impedance or vibrating microcantilevers.\cite{7-12} Since SiC is completely bio-inactive, other developments envision the coating of biocompatible microdevices, such as SiC-based medical prosthesis and microelectrodes.\cite{13-18} For such sensing and biomedical applications, SiC would benefit from specific surface modifications. In this regard, Zuilhof and co-workers...
reported recently on the thermal and UV modification of flat Si₃N₄, [19,20,22] 6H-SiC, and polycrystalline 3C-SiC [21,22] using thermal and UV conditions close to those used for the surface modification of silicon.

Different procedures have been investigated to functionalize solid surfaces by organic molecules. Chemical functionalization using anchoring groups is one of the most convenient ways because it provides an efficient means to covalently attach organic molecules onto solid surfaces, and therefore maintaining the chemical composition during the measurements. The functionalization of surfaces via covalently bound SAMs occurs in two steps. The first step is the growth of SAMs with a chemically reactive terminal functionality. This is followed by the reaction of the functional group with the moiety of interest so that covalently bound functionalized SAMs are obtained. Organosilane reagents are commonly used to produce functionalized thin films under mild conditions on silicon oxide and other oxide substrates, 3-aminopropytriethoxysilane (APTES) for instance leads to amino-functionalized organic thin films. The amino functionality can be easily coupled with proteins and oligomeric nucleic acids resulting in their covalently immobilization on amino derivatives or on amino-terminated silicon surfaces during the fabrication of a variety of biosensing devices [23–27].

The optical and electronic properties of polyaromatic hydrocarbons (PAHs) attached to solid surfaces have proven to be a remarkably useful and sensitive tool for the characterization of interface organization and polarity. [28,29] PAHs are in fact outstanding molecules for their characteristic high fluorescence quantum yields, their sensitivity with respect to the local environment, the high chemical stability under ambient conditions, and the possibility to chemically tune a wide range of photophysical and electrochemical properties. [30] PAH-functionalized films are thus capable of functioning as chemical and/or biochemical sensors, optical display materials, and nanoelectronic devices. [31,32]

Recently, several PAH-functionalized SAMs have been reported, e.g., the epoxide-terminated SAMs with attached PAHs (pyrene and anthracene) or more polar chromophores (dansyl) on silica surfaces [33–36] amine- or adipoyl-chloride-terminated SAMs [37,38] that were used to immobilize various PAHs on either gold, indium-doped tin oxide (ITO); and oxidized silicon substrates. The photophysical properties of these chromophore-functionalized films and their use as chemical sensing elements were examined carefully in these studies. Some reports were more focused on the spectroscopic and electrochemical properties of covalently bound PAHs on SAMs to gain insight into the local organization that characterizes these systems and how that organization depends on the interface chemical identity. Reinholdt and co-workers have pioneered amine-terminated SAMs to attach chromophores including dansyl [39,40] coumarin [39] pyrene [41,42] and fluorescein [43] on selected substrates, in order to study host-guest interactions at surfaces [40,41] and design chemosensors for cationic and anionic species. [43,44]

The functionalization of interfaces with chemically or physically responsive compounds holds great promise for a wide range of sensing applications. Understanding the factors in details that give rise to the sensitivity of a particular

2. Results and Discussion

Figure 1 shows schematically the functionalization steps of amorphous SiO₂ and single-crystal 6H-SiC(0001) surfaces. The first step involves the hydroxylation of both surfaces. Then APTES molecules are attached as linker molecules via a silanization reaction. Finally, benzo[ghi]perylene-1,2-dicarboxylic anhydride reacts with the amine group of the APTES molecules and forms an imide bond with the linker molecule (Figure 1a). It may occur that this reaction is not complete and only an acid amide bond is formed with the linker molecule (Figure 1c). Since this reaction step is presently carried out under ambient conditions, carbon dioxide from air may react with the amine group of the APTES molecules yielding also an acid amide bond (Figure 1b). The schematic functionalization scheme is verified by various analytical methods, as indicated in the details in the following paragraphs. Immediately after the piranha acid treatment for 2 H, the quartz surfaces are hydrophilic and exhibit a static water contact angle of \( \alpha < 10^\circ \). For SiC, immediately after oxidation and etching with an aqueous solution of 48\%HF for 2 min the surfaces are even more hydrophilic and exhibit a water contact angle of \( \alpha < 10^\circ \). The attachment of APTES molecules on quartz and SiC surfaces was first monitored with static water contact angle measurements. APTES-functionalized quartz and 6H-SiC surfaces exhibit static water contact angles of about \( \alpha = 68^\circ \) and \( \alpha = 64^\circ \), respectively. After functionalization by benzo[ghi]perylene-1,2-dicarboxylic anhydride, the static contact angles increase for quartz (denoted Benzo/Qz) and SiC (denoted Benzo/SiC) surfaces to about \( \alpha = 85^\circ \) and 78\°, respectively. APTES-functionalized quartz and SiC surfaces have a free amine terminal group, but not all amine groups are pointing outwards from the surface. Some of them are facing towards the substrates; hence, the surfaces exhibit hydrophilic character but not as much as OH-terminated surfaces. From Figure 1, it is clear that the dye-functionalized surfaces should have a much more hydrophobic character than the APTES functionalized surfaces. This is also supported by the values of the contact angle measurements, but
not to the extent we would expect from Figure 1a. This indicates that not all amine groups react with dyes.

Attenuated total reflectance infrared (ATR-IR) spectra in the range of 4000–350 cm\(^{-1}\) were collected for APTES-modified substrates before and after a series of chemical reactions, including dye immobilization, as shown in Figure 1. All ATR-IR spectra contain similar spectral features between 2700 and 3100 cm\(^{-1}\) (see Figure 2) that originate from several aliphatic CH stretching modes of the intact (or modified) APTES backbone. Around 3250 cm\(^{-1}\) the symmetric NH stretching mode from amino groups is observable. The existence of a broad peak centered at 3400 cm\(^{-1}\) is due to adsorbed water and unreacted OH. The CH and the NH stretching modes confirm the presence of the organic layer on quartz and 6H-SiC substrates.

The chemical composition of each surface was analyzed by X-ray photoelectron spectroscopy (XPS) and the spectra obtained are shown in Figure 3 and 4 for the quartz and SiC substrates, respectively. The overview XPS spectra of piranha-acid-treated quartz (Figure 3a, lower black line) shows, as expected, the presence of a Si 2p peak at 105.3 eV, a Si 2s peak at 155.3 eV, and a O 1s peak at 532.7 eV. APTES-functionalized quartz surfaces (APTES/Qz) and quartz functionalized with benzo[ghi]perylene-1,2-dicarboxylic anhydride (Benzo/Qz) show additional spectral signatures: C 1s at an energy of \(E_b = 284.8 \text{ eV}\) and N 1s at \(E_b = 401 \text{ eV}\), which are associated with the presence of carbon and nitrogen atoms. As expected the C 1s signal is largest for the Benzo/Qz functionalized surface.

High-resolution X-ray photoelectron spectra are measured for the C 1s and N 1s peaks. They provide valuable information on the chemical binding states of the surface elements. After subtracting a Shirley background, five different chemical binding states can be identified in the C 1s region of Benzo/Qz surface (see Figure 3b). The peak at \(E_b = 285 \text{ eV}\) binding energy arises from the C-Si-O structural feature responsible for binding the APTES molecules to the substrate. The second peak at \(E_b = 285.7 \text{ eV}\) corresponds to aliphatic C–C bonds. The third peak at 286.4 eV corresponds to the aromatic C=C structural elements of benzo[ghi]perylene-1,2-dicarboxylic anhydride. The fourth peak at 287.6 eV is due
to the C–N bonds present in the APTES molecules while the fifth peak at 289.1 eV corresponds the carboxylic amide and imide (N–C=O) groups. This last spectral signature confirms the binding of the benzo[ghi]perylene to the aliphatic APTES chain. The high-resolution XP spectrum of N 1s provides four different chemical binding states (see Figure 3c). The peaks at 401 and at 403.1 eV are due to unreacted and protonated amine groups, respectively, of the APTES functionalization. The signal at 402 eV is due to acid amide groups in binding benzo[ghi]perylene-1,2-dicarboxylic anhydride as shown in the scheme of Figure 1c, and CO$_2$ absorbed by amine groups, as shown in the Figure 1b, since the surface is prepared under ambient condition. The peak at 402.5 eV corresponds to acid imide groups of the benzo[ghi]perylene-1,2-dicarboxylic anhydride bound to the APTES linker. The N 1s XP spectrum of functionalized quartz shows that not all amine groups of the linker molecules on the surface do react with the benzo[ghi]perylene-1,2-dicarboxylic anhydride dye. This is also corroborated by the comparatively strong CN signal in the C 1s spectrum. Further, those amine groups which react with the acid anhydride group of the dye do not all form imide bonds.

HF-treated SiC surfaces show as expected the presence of Si, C, and of O due to the formation of OH groups on the surfaces. SiC surfaces functionalized with APTES (APTES/SiC), and further modified SiC with benzo[ghi]perylene-1,2-dicarboxylic anhydride (Benzo/SiC) show the presence of N atoms, in a similar way as for the quartz substrates (see Figure 4a). Also the C 1s and O 1s peak intensities increase compared to the signals of the bare surface, witnessing the presence of organic molecules on the surface. As expected, the C 1s region of benzo[ghi]perylene on SiC is more complex. Here six different chemical binding states can be identified (see Figure 4b). The peak at 283.5 eV is due to the Si–C–Si structural bonds of the substrate. The second peak at 285.0 eV corresponds to a Si–C–O due to the siloxane bond of APTES to the surface. The third peak at 285.6 eV originates from the aliphatic C–C bonds in the benzo[ghi]perylene-1,2-dicarboxylic anhydride. The contribution at 287.7 eV is due to C–N bonds of APTES while the peak at 289.1 eV, with the highest binding energy, corresponds to the carboxylic amide (Figure 1b,c) and imide

**Figure 3.** a) X-ray photoelectron spectra of piranha-treated quartz (black), APTES-functionalized quartz (APTES/Qz) (blue) and (benzo[ghi]perylene-1,2-dicarboxylic anhydride)-functionalized quartz (Benzo/Qz) (red). b) High-resolution C 1s XPS data of Benzo/Qz surface and c) high-resolution N 1s XPS data of Benzo/Qz surface.
(N–C=O) groups. The high-resolution XP spectrum of N 1s, which is very much similar to the N 1s signal of Benzo/Qz, provides again four different chemical binding states (Figure 4c). The signals at 400.8 and 403.7 eV are due to unreacted and protonated amine groups, respectively, of the APTES molecules. The second peak at 401.8 eV is due to acid amide groups (Figure 1c) and reacted CO₂ (Figure 1b). The third peak (402.3 eV) corresponds to acid imide groups of the benzo[ghi]perylene-1,2-dicarboxylic anhydride bound to the linker molecule. Again, the C 1s spectrum shows the expected chemical bonds. The N 1s spectrum shows, besides unreacted amine groups of the linker molecules, the dominant contribution originating by the imide (–N(C=O)₂) groups of benzo[ghi]perylene-1,2-dicarboxylic anhydride bound to the linker molecules. The ordered substrate of the single-crystal SiC(0001) surface provides therefore a more homogeneous environment to attach the dye molecules to the linker than the amorphous SiO₂ surface.

The electronic spectrum of benzo[ghi]perylene-1,2-dicarboxylic anhydride gives insight into the local environment of the molecules. Absorption spectra of benzo[ghi]perylene-1,2-dicarboxylic anhydride were measured at different concentrations in pyridine solution. In the 300 to 800 nm spectral region, five absorption maxima of benzo[ghi]-perylene-1,2-dicarboxylic anhydride at λ = 340, 397, 453, 484, and 679 nm are observed (Figure 5). With respect to the other absorption maxima, the absorptions at 453, 484, and 679 nm increase as the concentration increases (Figure 5 upper trace). Perylene is a polyaromatic hydrocarbon and has a high tendency to form π-stacking complexes. By increasing the concentration of benzo[ghi]perylene-1,2-dicarboxylic anhydride, the tendency to form aggregates through π-stacking is higher. Thus the absorbance maxima at 453, 484, and 679 nm increase as the concentration increases (Figure 5 upper trace). Perylene is a polyaromatic hydrocarbon and has a high tendency to form π-stacking complexes. By increasing the concentration of benzo[ghi]perylene-1,2-dicarboxylic anhydride, the tendency to form aggregates through π-stacking is higher. Thus the absorbance maxima at 453, 484, and 679 nm increase as the concentration increases (Figure 5 upper trace).
around 476 nm is also a signature of aggregates formed with the benzo[ghi]perylen-1,2-dicarboxylic anhydride molecules bound to the surface. We suggest that also for these surface-bound molecules H–H aggregates are formed as in solution.\[46\]

For the fluorescence lifetime measurements we selected different surface regions with an area of 26 µm x 26 µm, yielding a very good signal/noise ratio. The fluorescence decay curves are shown in Figure 7. The data could be fitted with three exponential decay functions of the form \( f(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \). Since the shortest decay constant of \( \tau_1 = 0.5 \) ns reflects the response function of the detection system, it is discarded. Because the decay of the excited state population is a first-order process, the different lifetime components reflect the presence of multiple local environments for this chromophore. The observed fluorescence lifetimes of the Benzo/Qz and Benzo/SiC surfaces excited at 375 and 440 nm are shown in the Table 1. Two components showed lifetime values between \( \tau_2 \approx 1.2 \) to 1.8 ns and \( \tau_3 = 3.6 \) to 4.7 ns in all the four cases. In a semi-logarithmic plot, two well-developed straight lines associated with \( \tau_2 \) and \( \tau_3 \) are observed. On the well-ordered SiC substrates the lifetimes are generally slightly longer than on amorphous SiO\(_2\). Further, for both substrates, excitation at 440 nm increases slightly the weight of the longest component compared to that with 375 nm excitation. The shortest lifetime around 0.4 ns is at the limit of our instrument response. Because this signal shows intensity comparable or even higher than the other two components, we indeed believe that an ultrafast decay occurs in these systems. From the excited state lifetime results, it is clear that fluorescence lifetimes of benzo[ghi]perylen-1,2-dicarboxylic anhydride are largely independent on the substrate. Indeed the aliphatic APTES linker isolates the perylene dye electronically very well from the substrates.

Figure 8 shows the fluorescence decay of the functionalized substrates. Intensity and average lifetime images of the Benzo/Qz substrate are shown in the Figure 8a and Figure 8b.
Table 1. Excited state lifetime components of the fluorescence decay for Benzo/Qz and Benzo/SiC surfaces.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Excitation wavelength [nm]</th>
<th>Component</th>
<th>Rel. signal [%]</th>
<th>Lifetime $\tau$ [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo/Qz</td>
<td>375</td>
<td>2</td>
<td>42</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>10</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>Benzo/Qz</td>
<td>440</td>
<td>2</td>
<td>46</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>13</td>
<td>4.2 ± 0.1</td>
</tr>
<tr>
<td>Benzo/SiC</td>
<td>375</td>
<td>2</td>
<td>47</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>17</td>
<td>4.3 ± 0.1</td>
</tr>
<tr>
<td>Benzo/SiC</td>
<td>440</td>
<td>2</td>
<td>54</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>19</td>
<td>4.7 ± 0.1</td>
</tr>
</tbody>
</table>

3. Conclusion

We have prepared amino-terminated siloxane adlayers on amorphous quartz and single-crystal 6H-SiC(0001) that can bind covalently with benzo[ghi]perylene-1,2-dicarboxylic anhydride through an imide bond. The successful two-step functionalization of quartz and in particular silicon carbide by APTES and benzo[ghi]perylene-1,2-dicarboxylic anhydride is proven with ATR-IR and XPS measurements. ATR-IR spectra confirm the alkyl backbone of the functionalized surfaces. The XPS results show that at 6H-SiC surfaces a dominant contribution from the imide bond between

excited at 375 and 440 nm, respectively. Similar results are shown in Figure 8c and d for Benzo/SiC substrate excited at 375 and 440 nm, respectively. These images show that the surfaces are not uniformly covered by the dye. The quartz surface has higher dye coverage than the 6H-SiC surface. The lifetimes reported in Figure 7 are averages over the whole areas, and therefore, averages over different local concentrations. The detailed 2D images show further that the lifetime variation is larger on the quartz substrates than on the SiC surfaces. The single-crystal SiC surface thus provides a more homogeneous environment than the amorphous quartz surface.

Figure 7. Decay curves of a) Benzo/Qz excited at 375 nm using a long-pass filter at $\lambda = 420$ nm, b) Benzo/Qz excited at 440 nm using a long-pass filter at $\lambda = 470$ nm, c) Benzo/SiC excited at 375 nm using a long-pass filter at $\lambda = 420$ nm, and d) Benzo/SiC excited at 440 nm using a long-pass filter at $\lambda = 470$ nm.
benzo[ghi]perylene-1,2-dicarboxylic anhydride and APTES is present, which is quite different from the quartz surfaces. The average lifetime and intensity images of the confocal microscope measurements show a higher density of surface-bound benzo[ghi]perylene-1,2-dicarboxylic anhydride dye on quartz compared to silicon carbide. Fluorescence lifetime measurements indicate the presence of more than one local environment for surface-bound benzo[ghi]perylene-1,2-dicarboxylic anhydride independent of the substrates. The single-crystal SiC surface provides a more homogeneous environment than the quartz surface.

4. Experimental Section

**Chemicals:** Benzo[ghi]perylene-1,2-dicarboxylic anhydride (Sigma Aldrich), aminopropyl triethoxysilane APTES (Acros), triethyl amine (VWR), toluene (ABCR), imidazole (Sigma Aldrich), dimethyl formamide (Acros), zinc acetate anhydride (Zn(OAc)$_2$) (Sigma Aldrich), H$_2$SO$_4$ (VWR), and H$_2$O$_2$ (Acros) were purchased and used without further purification. Acetone and dichloroethylene were obtained from Rath. The 6H-SiC (0001) wafer (the Si face is CMP polished and the C face is standard polished) was obtained from Cree. Quartz and 6H-SiC slides of (0.05 cm × 0.8 cm × 1.2 cm) were used for spectroscopic measurements and XPS studies.

**Surface Characterization Methods:** XPS measurements were carried out at pressures between $10^{-9}$ and $10^{-8}$ mbar using an Al K$_\alpha$ (hv = 1486 eV) source and a hemispherical photoelectron analyzer (Specs, Phoibos 150) at a take-off angle of 47°. All peaks are referenced to the signature of the C 1s peak for carbon at $E_b = 284.6$ eV. Another effective surface characterization method is contact angle measurement which was performed on all of the different organic functionalized surfaces. Data from this technique can provide information on the hydrophobicity and morphology of the surface. The wetting properties of modified surfaces were characterized by automated static water contact angle measurements performed using an Erma Contact Angle Meter G-1.

**ATR-IR Spectroscopy:** The spectra were measured with a Bruker IFS 66v/S spectrometer. Absorbance spectra were collected using a spectral resolution of $\Delta \tilde{v} = 4 \text{ cm}^{-1}$, accumulating 1024 scans for each measurement.

**UV–Vis Absorbance Spectroscopy:** UV absorption spectroscopy were recorded using a Cary 500 (Varian/Agilent) spectrometer in a spectral range from 200 to 800 nm. The sample solutions and solute pyridine were filled in different quartz cuvettes and the measurements were performed using pyridine as a reference.

**Fluorescence Spectroscopy:** Fluorescence microscopy images were recorded on an Olympus IX71 microscope equipped with a XC10 color charge coupled device (CCD) camera and a xenon lamp as excitation source. Time-, space-, and spectrally resolved confocal microscopy was carried out with a PicoQuant MicroTime 200 featuring two single-photon avalanche diode detectors (from MPD and Perkin-Elmer). Pulsed diode lasers operating at 375 and 440 nm were used as excitation sources. Fluorescence excited at 375 nm is observed through a long-pass filter with $\lambda_c = 420$ nm, that excited with 440 nm radiation through a filter with $\lambda_c = 470$ nm. Time-correlated photon counting data were acquired through a PicoHarp 300 and the data analysis carried out with the SymPhoTime software package from PicoQuant (version 5.0). Single-crystal spectra were measured with a Peltier-cooled Andor
Newton back-illuminated electron multiplying CCD connected to a Shamrock SR-163 (Andor) spectrophotograph. Time-, space-, and spectrally resolved confocal fluorescence measurements were carried out to study the lifetime of surface-bound benzog[h] perylene-1,2-dicarboxylic anhydride-1,2-dicarboxylic anhydride derivatives on quartz substrates and on the Si face of 6H-SiC(0001) substrates.

**Substrate and Organic Layer Preparation:** The quartz and 6H-SiC(0001) samples were cleaned by sonication first with ethanol, followed by dichloroethylene and then with acetone. The clean quartz (Q) slides were hydroxylated by treating in piranha solution (H2O2 (30%)/concentrated H2SO4) 3/7, v/v) at 60 °C for 2 h. The substrates were then rinsed thoroughly with high-purity (Milli-Q) water and dried under a stream of Ar. The stability of both anhydrate (5 mg, 0.027 mmol) and imidazole (2.4 g, 35.2 mmol) remained intact after this treatment, as was checked by additional experiments.

**Substrate and Organic Layer Preparation:** The quartz and 6H-SiC(0001) samples were cleaned by sonication first with ethanol, followed by dichloroethylene and then with acetone. The clean quartz (Q) slides were hydroxylated by treating in piranha solution (H2O2 (30%)/concentrated H2SO4) 3/7, v/v) at 60 °C for 2 h. The substrates were then rinsed thoroughly with high-purity (Milli-Q) water and dried under a stream of Ar. The stability of both anhydrate (5 mg, 0.027 mmol) and imidazole (2.4 g, 35.2 mmol) remained intact after this treatment, as was checked by additional experiments.

**Immobilization of Benzog[h] perylene-1,2-dicarboxylic Anhydride on Quartz and 6H-SiC(0001) Wafers:** The APTES surface-modified substrates, were immersed into a solution of benzog[h] perylene-1,2-dicarboxylic anhydride (10 mg, 0.03 mmol), Zn(OAc)2 anhydrate (5 mg, 0.027 mmol) and imidazole (2.4 g, 35.2 mmol) in N,N-dimethylformamide (DMF, 20 ml) for 5 h at 140 °C. Finally the substrates were sonicated twice in toluene and then twice with methanol and acetone and were dried under a stream of Ar [11]. Then both samples were cured at 100 °C for 24 h. After this initial treatment the surfaces were characterized as well as used in further functionalization experiments.

**Immobilization of Benzog[h] perylene-1,2-dicarboxylic Anhydride on Quartz and 6H-SiC(0001) Wafers:** The APTES surface-modified substrates, were immersed into a solution of benzog[h] perylene-1,2-dicarboxylic anhydride (10 mg, 0.03 mmol), Zn(OAc)2 anhydrate (5 mg, 0.027 mmol) and imidazole (2.4 g, 35.2 mmol) in N,N-dimethylformamide (DMF, 20 ml) for 5 h at 140 °C. Finally the substrates were sonicated twice in toluene and then twice with methanol and acetone and were dried under a stream of Ar [11]. Then both samples were cured at 100 °C for 24 h. After this initial treatment the surfaces were characterized as well as used in further functionalization experiments.

**Acknowledgements**

The authors thank A. Studer (Organic Chemistry, WWU Münster) for providing laboratory space for the chemical synthesis and helpful discussions and P. Bieker (Physical Chemistry, WWU Münster) for the use of the ATR-IR instrumentation. D.K.B. acknowledges support from the NRW International Graduate School of Chemistry, Münster. The project is financially supported by the Deutsche Forschungsgemeinschaft via project B9 of the Transregional Research Center TRR 61 “Multilevel Molecular Assemblies: Structure, Dynamics and Function”.

This Full Paper is part of the Special Issue on Multilevel Molecular Assemblies: Structure, Dynamics, and Functions, featuring contributions from the Transregional Collaborative Research Center (TRR 61).

Received: September 16, 2011
Published online: January 19, 2012