Photocycloaddition of Anthracene-Functionalized Monolayers on Silicon(100) Surface

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Here we present detailed investigations of UV-photoinduced dimerization of anthracene substructures without solvent environment at the level of molecular monolayers prepared on a surface. Monolayers prepared on silicon(100) substrates were analyzed by means of X-ray photoelectron spectroscopy (XPS) in the valence band region revealing significant changes in the carbon C 2s region (11−20 eV). SVWN DFT calculations were performed to understand the influence of the structural changes by dimerization. The geometric structure of the functionality was retrieved through B3LYP DFT calculations, which were performed ahead of the SVWN DFT ones, and the result of these calculations matches with the measured vibration signature. FTIR investigations of polybutadiene (PBD) volume backboned functionality were performed before and after irradiation.

Introduction

The well-known anthracene [4 + 4] cycloaddition[1,2] combined with its immobilization on a surface represents an active photochemical and biochemical topic of interest of present years.[3] The chemical reactivity of anthracene units itself, based on the photocycloaddition, has been extensively studied in the past 60 years. A review of photophysical and photochemical aspects of this reaction was published by Cowan in 1976.[4] Different investigations of molecular structures containing anthracene functionalities were performed in subsequent years,[5,6] whereas the dependence of the photocyoladdition on explicit chemical solvent conditions or electronic conditions is still of current scientific interest.[7] The influence of anthracene functionalities on the formation of calixarene monolayers forming photoswitchable guest−host complexes on surface is also of current interest in this regard. Furthermore, the ability of the anthracene functionalities to achieve photocycloaddition on surface without any polar solvent environment is of relevance for UV photoswitching surface applications. In this article, we have studied the UV-induced photocycloaddition of anthracene functionalities **3** (see Figure 1) linked to a silicon surface by wet chemical monolayer preparation.

The film quality was determined by XPS core-level measurements, and the mentioned solvent-free photoreaction forming dimers of the anthracene monolayers functionality was studied by valence band XPS measurements of the monolayer samples. Valence band XPS spectroscopy was applied several years ago by Beamson[8] to reveal cross-linking or branching changes in polymeric chain structures. It was possible to compare the spectra of different kinds of plasma-modified polyethylene with each other, and thus identify a "polypropylene-like" feature (14.5 eV) in the C 2s region (11−17 eV) as a characteristic indication of C−(C−C) branches. DFT calculations, modeling the C 2s
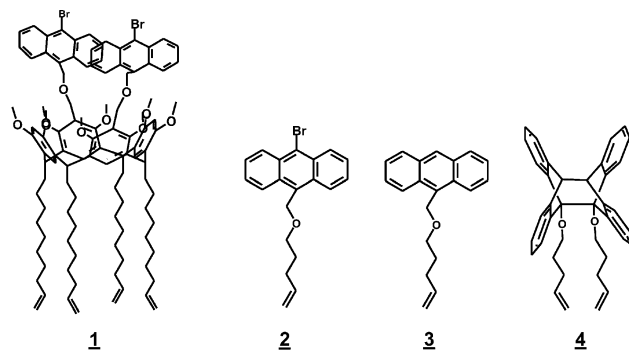
Figure 1. Investigated different anthracene-functionalized molecular systems. **1**−**3** were prepared as monolayers on etched silicon surface while **4** shows the system **3** after dimerization of the anthracene units.

fingerprint of different oligomers, were performed by S. Mähl,[9,10] so that the simulated spectroscopic signatures turned out to be associatable with the respective carbon chemical structures. A VWN (Vosko, Wilk, Nusiar) functional description of exchange energy correlation and a double numerical polarized (DNP) basis set was used in these calculations to achieve an agreement with measured VB XPS spectra.

The changes observed in measured valence band spectra of molecular monolayer and polymeric adlayers induced by UV irradiation, described in this article, have been interpreted by assumption of a **3** to **4** structural change (Figure 1) of functionality. The detailed geometric structure of the dimerized functionality **4** was retrieved from DFT modeling[11] matching measured FTIR vibration signature.

Experimental Section

Preparation. *Materials and Synthesis.* A detailed synthesis of compounds **1**−**3** is given in the Supporting Information, and the general synthesis procedure is as follows. The synthesis of the resorcinarenes is presented in Figure 2. Starting from the octamethylated, 4-fold brominated resorcinarene **5**, which was

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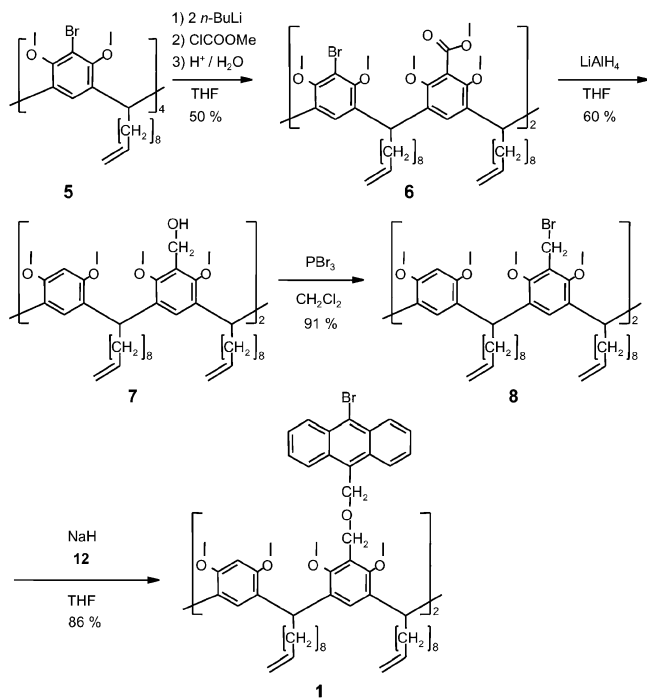§ Department of Chemistry, Bielefeld University.

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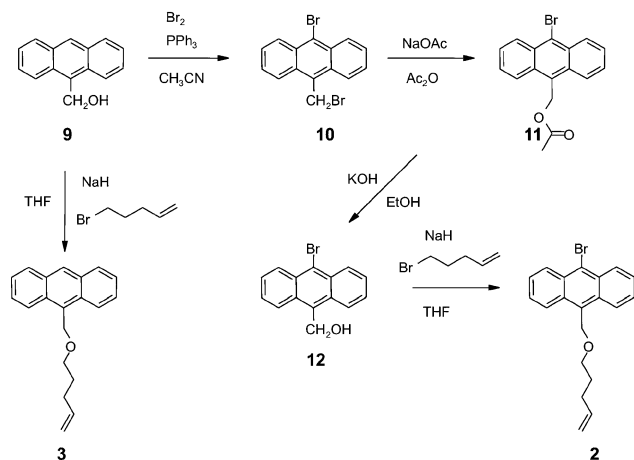**Figure 2.** Synthesis scheme of compound **1**.

Figure 3. Synthesis scheme of compounds **2** and **3**.

first synthesized by Reinhoudt et al.,[12] we used the same procedure as mentioned in our previous work[13] to introduce the corresponding anthracene alcohols. Therefore, we used 2 equiv of *n*-butyllithium on **5** and quenched with methyl chloroformate. After column chromatography on silica gel, we got compound **6** in 50% yield. The 2-fold ester **6** was reduced with lithium aluminum hydride to yield **7** in 60%. The two hydroxy groups of **7** were then substituted for bromine using phosphorus tribromide. The 2-fold benzylic bromide **8** was isolated in 91% yield and was further used for introduction of the anthracene derivative **12** (see Figure 3). The anthracene alcohol **12** was deprotonated with sodium hydride and mixed with **8** to get compound **1** after column chromatography in 86% yield. All compounds were characterized by NMR and HRMS techniques. The anthracene compounds **2** and **3** for the coating of silicon through hydrosilylation were synthesized according to Figure 3. The reactant, anthracene-9-methanol (**9**), was brominated with bromine in acetonitrile to yield compound **10** in 56%.[14] The benzylic bromide was substituted by an acetate group to yield compound **11** (80%).[15] In the next step, the ester was saponified to **12** with potassium hydroxide in ethanol (99%).[15] To get the

unsaturated anthracene compounds, both alcohols (**9** and **12**) were deprotonated with sodium hydride and the corresponding alcoholate reacted with 5-bromo-pent-1-ene to yield the target compounds **2** and **3** (41 and 42%, respectively). Both substances were isolated by column chromatography and tested for purity by GC/MS and NMR methods.

Preparation of Molecular Layers. *Monolayer Samples.* All monolayers were linked to the silicon substrate surface by a wet chemical hydrosilylation reaction of the allyl-ending molecules to the Si–H surfaces termination, which resulted from etching in a hydrogen fluoride/ammonium fluoride solution.[16,17]

Pieces of silicon wafers (100) were precleaned by a few washing cycles with acetone (p.a.) followed by a 10 min treatment in a supersonic bath in toluene and an UV cleaning process (173 nm; excimer lamp) for 15 min. The samples were etched for 20 min in a mixture of hydrogen fluoride (8 wt %, water) and ammonium fluoride (8 wt %, water) with a ratio of 1:5. After rinsing with Ultrapure water (Millipore) and methyl alcohol the samples were added to a 30 mM degassed immersion solution of the bromo-marked and the nonmarked molecular materials (a bromo-marked anthracene-functionalized resor-cinarene **1**, a bromo-marked anthracene derivative **2**, and a nonmarked anthracene derivative **3**) in toluene under dry nitrogen atmosphere at 100 °C for 18 h. The monolayer preparations were finished by further washing and a supersonic cleaning in toluene (p.a.). All samples were transferred to to the XPS apparatus in dry nitrogen environment (grade of purity 5.0).

Polymeric Sample Preparation. An amount of 7.8 mg of polybutadiene (PBD, Bayer Buna C24)[18] was dissolved in 6 mL of toluene and was mixed with a 50 mM solution of compound **3** in toluene in a ratio of 4:1. Polymerization by free radical addition was performed at a temperature of 100 °C, under continuous stirring (300 rpm), in a dry nitrogen environment for 3 days. The surface adlayers were prepared on precleaned (toluene bath) barium fluoride substrates (BaF$_2$ polished window W220, Medway Optics) by immersion at ambient temperature conditions in closed vials. This was followed by a further heating of the degassed and evacuated layers for 2 h. The surface quality of the BaF$_2$ substrates was classed as "optical polished" grade (finish 80–50 scratch/dig). A layer of the Buna C24 polymer material was prepared out of stirred and heated solution to be used as a spectroscopic reference. The regarding preparation steps were executed parallel to those of the functionalized adlayers.

Irradiation. The UV photoinduced anthracene dimerization of molecular monolayers and polymeric layers was performed using a nitrogen gas discharge (CO free) emission. The process gas was adjusted to 0.075 mbar. The gas flow was controlled to 8 sccm after evacuation to a base pressure of 3×10^{-6} mbar. The irradiation time was 20 s. The rf forward power was adjusted to 15 W. During processing, the layers were protected against ions by 0.7 mm thin glass sheets (AF37; PGO Praezi-sionsglas). These provided a strongly reduced optical transmission in the spectral region below 300 nm, in order to avoid a photoreaction back to the single anthracene units state.

X-ray Photoelectron Spectroscopy (XPS) Setup. X-ray photoelectron spectroscopy measurements were recorded using a PHI 5600ci multitechnique spectrometer with monochromatic Al Kα ($h\nu$ = 1486.6 eV) radiation of 0.3 eV fwhm bandwidth. The sample was kept at room temperature. The resolution of the analyzer was 1.5% of the pass energy, which is 0.35 eV. All spectra were obtained using a 400 μm diameter analysis area. During the measurements, the pressure in the main

TABLE 1: Fits of Core-Level Spectra of Br-Marked Structure 1 Prepared on Etched Silicon Substrate

peak	species	position (eV)	fwhm (eV)	area/RSF	measd (at %)[a]	stoich (at %)[a]
adsorbate						
C 1s	C			13050.9	97.06	90.00
	C(arm), C—C			10627.2	79.03	81.66
	C (arom.)	284.72	1.635	4966.0		
	C—C	285		5661.2		
	C—O—C, C—OH	286.56		2423.7	18.03	8.33
Br 3d	Br—C				2.21	1.67
Br 3d$_{5/2}$		70.64	1.19	294.7	2.19	
Br 3d$_{3/2}$		71.71		298.7	2.22	
Br 3d	(Br)				0.73	0
Br 3d$_{5/2}$		67.98	1.25	97.8	0.73	
Br 3d$_{3/2}$		68.99		99.2	0.74	
substrate						
Si 2p$_{3/2}$	Si	99.45	0.66	3012.1		
Si 2p$_{1/2}$		100.09		2884.9		
Si 2p$_{3/2}$	Si—O	102.93	1.46	636.9		
Si 2p$_{1/2}$		103.57		624.2		

[a] at %: atomic percents neglecting hydrogens.

Figure 4. Measured valence band XPS spectra of irradiated monolayer (a) of **3** and of nonirradiated monolayer (b) of **3** on etched silicon. The measured spectrum of an etched silicon reference substrate (c) is shown to estimate the spectroscopic background by the substrate. Dashed (bottom curve): simulated spectrum for a single molecule dimer of structure **3** based on SVWN DFT modeling.

chamber was kept in the range of 10^{-9} mbar. The samples were oriented at a surface normal angle of 45° to the X-ray source and −45° to the analyzer for all core-level and valence band XPS measurements. The energy scale of the spectra was calibrated as discussed below.

Fourier Transform Infrared (FTIR) Setup. The FTIR spectra were acquired with a Nicolet Nexus (Thermo Scientific) FTIR spectrometer used in transmission through the polymeric adlayer-coated BaF$_2$ substrates. An uncoated BaF$_2$ substrate has been used as spectroscopic reference in this measurements.

Results and Discussion

A monolayer of anthracene-functionalized resorcin[4]arene (**1**) was prepared on silicon surfaces from solution by immersion in order to quantify the layer quality by analyzing the C 1s, Br 3d, and Si 2p X-ray photoelectron spectra. The relative species amounts of structure **1** retrieved by fitting of the XPS spectra are listed in Table 1. The quantity area/RSF (RSF = relative sensitivity factor) is equal to the fitted areas normalized by the different relative cross sections of photoionization from the C 1s, the B 3d, and the Si 2p core levels. The relative sensitivity factors (RSF) quantifying these relative cross sections were published by Scofield.[19]

Analyzing the C 1s spectrum leads to a value of 13 050.9 for the area/RSF ratio. Taking a stoichiometric number of carbon atoms of **1** of 108 into account, the relative amounts of (C: Br—C:(Br)) were calculated as being (97.1: 2.2: 0.7). Considering an observed surplus of C—O bonded carbon of nearly 9.9 atom % (see Table 1), the amount of the Br—C bonded bromine can be quantified to nearly 2.4 atom % by this. Corresponding to this the amount of the noncarbon bonded species, identified by a shift of −2.7 eV in relation to the Br—C one and denoted as (Br) in Table 1, was found to be nearly 0.8 atom %. This species has to be interpreted as nonstoichiometric surplus taken the stoichiometric composition of **1** of (90.0:1.7:0) into account. In addition to this, a surplus of Br—C bonded bromine in the same quantitative region (0.7 atom %) has to be considered in comparison to the stoichiometric composition.

To get an idea of the influence of molecular geometric effects on the realized surface packing of the prepared monolayer of **1**, the mentioned Br—C (Br 3d 70.64, 71.71 eV) amount, which quantifies the molecular attachment to the substrate, was further analyzed in relation to the Si—O (Si 2p 102.93, 103.57 eV) amount, representing the oxidation of free substrate space
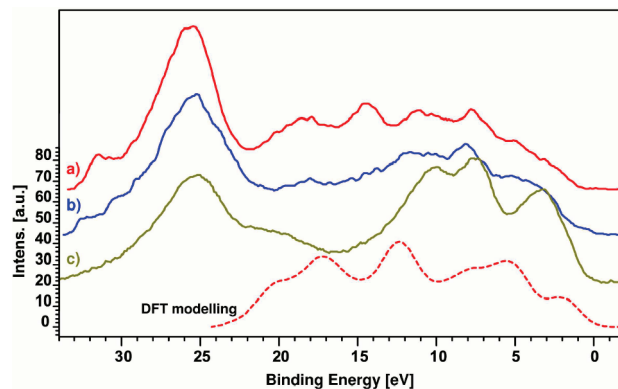
without linking of the molecular monolayer to it. For the monolayer of **1**, this revealed a packing density of 0.53. A monolayer of a bromo-marked pure carbon-chain system (bromoundecene) prepared in the same handling steps, executed parallel to the preparation of monolayer of **1**, results in a packing of 0.61, giving a reference for the quality of the applied preparation technique. This is in good agreement with the geometric model of a unit cell of the 11-bromo-undec-1-ene monolayer on Si(100) substrate calculated by Linford et al.[20] as being sized 0.67 × 0.38 nm. The reduced surface packing for the more complex structure **1** is consistent with the larger space required by the resorcin[4]arene. The distance of positions of monolayer-forming carbon chains at the resorcin[4]arene frame of **1** was calculated to be 1.3−1.4 nm referring to this. [The resorcin[4]arene calyx geometry was modeled by Ralf Brodbeck (Department of Theoretical Chemistry, Bielefeld University) performing PM3 methods.]. It can be supposed that a bromation of the highly reactive substrate occurs by halogen−anthracene dissociative chemistry in the liquid phase during the immersion (16 h at 100 °C). This leads to a Si−Br termination of the etched substrate (Si−H)[21] of the monolayer structure **1**, which requires large space. The occurrence of the bromine amount observed on surface denoted as (Br) in Table 1, which was not associatable to a carbon-binding environment, gives adequate proof of this.

Similar core-level measurements were performed for monolayers of nonmarked anthracene-functionalized resorcin[4]arene (**1** with hydrogens instead of the Br markers) and for a reduced system **2**. All carbon and silicon features found and quantified for the bromo-marked references were identified in these spectra as well. All monolayers were prepared in the same way as mentioned above. A nonstoichiometric surplus of marker species, as mentioned above, was only observed for the resorcin[4]arene system **1**, which was not suitable for the C 2s investigations because of the complex aromatic spectroscopic background[22] of the resorcin[4]arene. Core-level XPS measurements of **3** and **4** were performed in the same setup before valence band data were acquired. The oxidation of the unoccupied substrate space of the monolayer of reduced functionality **3** (used for the valence band XPS measurements) was quantified to 15% by a fit of the Si−O amount of Si 2p. Both valence band spectra, including the O 2s peak (25 eV), are shown in Figure 4. The spectrum of the irradiated monolayer sample (a) is shown in comparison with the spectrum of the nonirradiated

sample (b). For comparative reasons, the valence band spectrum of an etched silicon substrate (c), without any adlayer, was also measured. In addition to this, the DFT modeling result of a single molecule dimer of structure **3** was compared to the monolayer spectra in this figure. To minimize the influence of charging shifts toward the acquired valence band spectra, data sets of short acquisition times were summarized, once every single data set was aligned to the C 1s core-level spectrum, measured simultaneously for each single data set. By comparison of the valence band spectra shown in Figure 4, only the part of the C 2s monolayer signature at 11.1 eV is affected by a spectroscopic background of the etched silicon substrate at 10.4 eV.[23,24] For the region with higher binding energy than this, no specific signature of the substrate is present, and the C 2s spectra of both monolayer samples clearly differ from the substrate background. For both monolayers' spectra, a typical C 2s double-peak signature was observed at 11.1 and 18.5 eV. A direct comparison of the spectra of the irradiated (a) and the nonirradiated (b) monolayer reveals a significant signature change in the C 2s region between 11 and 20 eV. An additional feature at 14.5 eV (between the 11.1 and 18.5 eV features) was identified as an indication of molecular structural changes in the C−(C−C) bond system induced by the UV irradiation. In addition to the measured spectra the simulated spectrum for a single molecule dimer of **3**, retrieved from a SVWN DFT calculation, performed to gain a more detailed understanding of the C 2s spectroscopic signature of the dimerized functionality **3**, is shown in 4. The measured C 2s features, the dimer specific one at 14.5 eV and the one at 18.5 eV, correspond with the simulated features at 12.3 and 17.1 eV. The slightly asymmetric flank of the feature measured at 18.5 eV may be identified in the weak 20.5 eV feature in the simulated spectrum, which is not resolved in the measurement. An O 2s feature, caused by substrate oxidation, was observed for the measured samples. The highly reactive etched silicon substrate was partially oxidized during sample handling. The monolayer-coated substrate offers " free space " for oxidation at positions without a covalent bond to the molecular material. This oxidation is determined by the required space of the anthracene functionality of compound **3**. The observed oxidation amount of the monolayer samples resulting from a comparison of molecular C−O oxygen (C 1s core-level spectra) and the shown O 2s (25 eV) area amount in relation to the C 2s one are consistent with a nonstoichiometric oxygen surplus of only 14%. The substrate oxidation was also quantified by a fit of the Si−O amount in the Si 2p core level spectra of the monolayer samples. This led to an oxidized area amount of 15% (compared to 21% for the calyx-frame system **1**, which requires larger size on the surface).

To gain information about how the C 2s spectroscopic signature is affected by the photocycloaddition **3** to **4**, valence band XPS measurements of the functionality **3** linked to a polybutadiene (PBD) backbone and of this backbone reference material were performed. The polymeric adlayers were characterized by FTIR (Figure 6) before and after irradiation to verify the structural change of anthracene substructures. Figure 5 shows the result of the valence band XPS measurements of functionality **3** linked to polybutadiene (PBD) and UV irradiated (b) after correction of polymeric spectroscopic background (separate measurement of irradiated PBD reference), in comparison to the nonirradiated "pure" functionality (a). The backbone correction was done by use of normalized, intensity scaled, and Shirley background[25] subtracted spectra of functional and backbone reference samples from 0 to 22 eV. The irradiated functionality (curve b) shows a significant spectroscopic amount
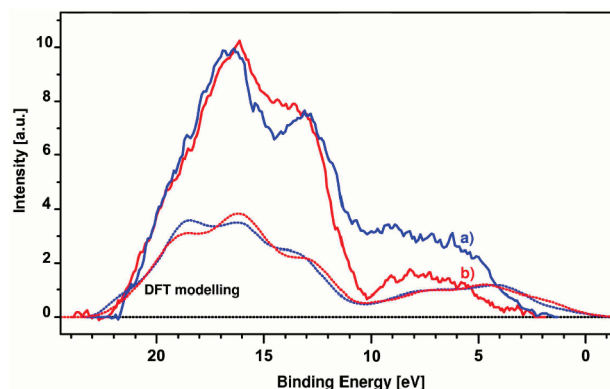
Figure 5. Valence band XPS spectra of nonirradiated pure functionality **3** (a) and of functionality **3** irradiated after linking to a polybutadiene (PBD) polymeric backbone (b). Bottom curves: simulated spectra of monomer (blue) and dimer (red) status of an oligomer (*n* = 4) of structure **3** based on SVWN DFT modeling.

of 18% of C 2s signature between the typical C−C features at 12.8 and 17.0 eV of the "pure" nonirradiated functionality **3** (curve a). This is comparable to the occurrence of the additional C 2s feature at 14.5 eV between the 11.1 and 18.5 eV features observed for the irradiated monolayer. The result of the DFT modeling for disordered oligomeric structures of **3** and the dimerized status **4** are also shown in Figure 5. Both simulated spectra were retrieved from a SVWN DFT calculation similar to the one used for the single molecule simulation (Figure 4). The calculated curves show different relative spectroscopic weights of the C 2s features for dimerized functionalities (Figure 5, dashed red curve) and monomers (dashed blue curve). The modeling related to the monomers shows significant C 2s features at 13.4, 16.1, and 18.7 eV with relative weights of 27:32:41, while the modeling for the dimerized status of disordered functionalities **3** shows C 2s features at 12.9, 16.0, and 19.0 eV with relative weights of 21:41:38. This proposes a relative increase of the spectroscopic C 2s amount between the typical C−C C 2s double peak signature of 28% for the irradiated functionality in comparison to the nonirradiated one. In the measurement (Figure 5, curve b) an increase of 18% was observed. This acts as a significant but nonspecific "filling". A discrete peak structure between the C−C double peak signature was not resolved by the measurement. This may be caused by the influence of the functionality to polymeric branching processes of the polybutadiene backbone structure by the UV irradiation, proceeding in addition to the dimerization of the anthracene substructures. A functionality-dependent branching is not considered in the backbone correction. Also the degree of disorder of the fairly branched polybutadiene (PBD) material[18] will not be taken into full account by the simple oligomer calculations performed. Both measured spectra shown in Figure 5 are affected by disorder of these molecular systems (functional polymer and pure functionality material without layer preparation). A spectroscopic effect due to structural disorder is also supported by the asymmetric C 2s high energetic flank of the 17 eV C 2s feature up to 22.5 eV found for both disordered molecular systems. As mentioned above, the functionalized PBD adlayer and the backbone reference adlayer, used for the valence band investigations, were characterized by FTIR measurements (Figure 6) before and after irradiation to verify the UV-induced photocycloaddition independent from the valence band XPS observation. The FTIR spectra shown in Figures 6 and 7 were normalized by areas across the displayed range in each case. In Figure 7, (left side) the FTIR spectra of irradiated (red) and nonirradiated layers (blue) are presented in the spectroscopic
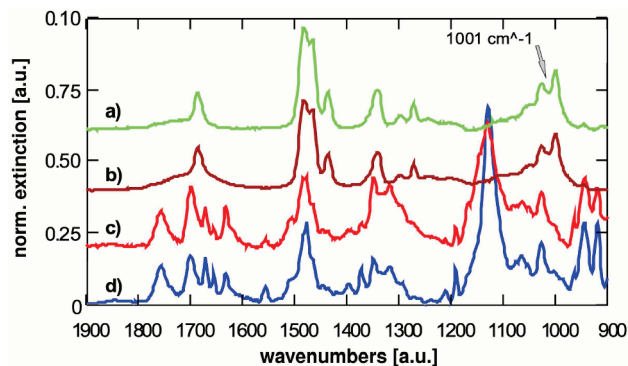
Figure 6. FTIR spectra of polymeric backbone after irradiation (a), polymeric backbone before irradiation (b), functionalized adlayer after irradiation (c), and functionalized adlayer before irradiation (d).

region from 1200 to 1800 cm^{-1}. In Figure 6 these spectra are shown together with the PBD reference measurements before (b) and after irradiation (a) in a spectroscopic range, which includes the marked vibrations at 1001 and 1026 cm^{-1} used to align spectra by PBD reference.[18] The observed vibrations were identified with regard to DFT structure calculations of the dimerized functionality **4** and of the PBD volume backbone material, calculated as an $n = 12$ oligomer. All measured vibrations associated with the polymeric backbone were well separated from those caused by the functionality substructure. Furthermore, comparing the spectra of the backbone before irradiation (Figure 6, curve b) to the one after irradiation (curve a) no UV-induced changes of PBD vibration signature were found. In spite of this, significant changes of the vibration signature were observed when comparing the spectra of the functionalized polymeric layer (Figure 7) before and after irradiation.

As a result of irradiation, the anthracene-specific triple peak C−C fingerprint (1635, 1658, 1674 cm^{-1}) is reduced to nearly a double-peak signature (1635, 1674 cm^{-1}). The 1658 cm^{-1} vibration is strongly suppressed. A similar effect was observed for the peak between 1351 and 1398 cm^{-1}. Both suppressed vibrations were identified by visualization of the B3LYP/DFT GAUSSIAN 03[26] calculation result using JMol[27] software. The vibration fingerprint result of the calculation itself is shown in Figure 7 together with the spectra of the functionalized polymer before and after irradiation. The simulated spectrum matches the measured FTIR spectra with miss-shifts from 11 to 15 cm^{-1}. Resulting from modeling visualization, the suppressed anthracene-specific modes at 1366 and 1643 cm^{-1} were affected by a reinforcement of geometrical trihedrons' (ABC) substruc-

ture near linking positions C and D as illustrated in the molecule sketch (Figure 7, right side). In the spectroscopic region of the observed triple to double-peak signature change, between and 1398 cm^{-1}, a similar suppression was found by Bratschkov.[28] This was seen to be induced by an anthracene dimerization of 9-anthryloxyhexyl methacrylate functionalities linked to *n*-butyl methacrylate.

Details of Calculations

The modelings performed to simulate the valence band spectra of monomeric and dimeric functionalities as single molecule or in oligomer structures were done by DFT calculations using an SVWN functional and a 6-31G** basis set. The geometric structure was optimized beforehand by DFT calculations using a B3LYP functional with the same basis set. To gain an impression of valence band spectroscopic features, the discrete energies were weighted by use of Gross populations[10,29,30] and atomic cross sections[19] associated with the different amounts of C 2s, C 2p related to molecular orbitals. The continuous simulated curves shown in comparison to the valence band spectra (Figures 4 and 5) were achieved by a spline and Gaussian convolution over 0.7 eV. The ionization potentials resulting from the pure SVWN calculations were scaled by a factor of 1.17 in order to consider an empirical correction of the correlation description. The correction factor was retrieved from cross comparison of analogous electronic SVWN calculations for the spectroscopically well-known systems polypropylene (PE), polyphenol (PPH), and the related spectra.[22] In addition to this, the spectroscopic weight in the region of atomic C 2p signature up to 9.3 eV was scaled down by the same cross comparison. The same 6-31G** basis set and B3LYP and SVWN funcionals were used for these modelings, performed for $n = 15$ oligomeric structures of PE and PPH. All DFT calculations were performed using GAUSSIAN 03 software.[26]

Conclusions

Anthracene-functionalized adsorbates were prepared as molecular monolayers and as polymeric PBD volume backboned layers. The surface packing qualities of the monolayers of the bromo-marked systems were quantified by XPS core-level measurements. In the case of the monolayer of **1**, a packing of 0.53 in comparison to a value of 0.61 for the bromoundecene reference monolayer was found. The nonmarked anthracene-functionalized monolayer of **3** as well as the polymeric layer was modified by UV irradiation. The solvent-free on-surface photocycloaddition of anthracene functionality **3** was investigated by valence band XPS and FTIR measurements of
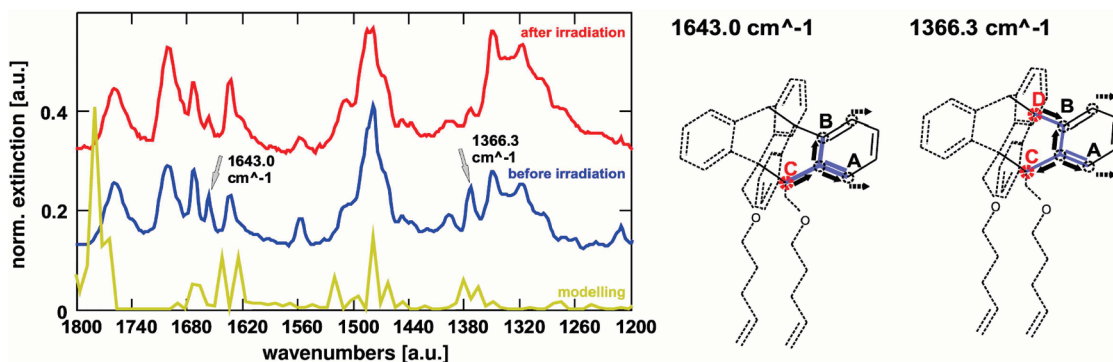
Figure 7. Zoom-in FTIR spectra of polymeric adlayer structure **3** linked to polybutadiene backbone before and after irradiation in comparison to a B3LYP DFT simulated IR spectrum of dimer **4** (left side), and visualization of vibrations (1643.0, 1366.3 cm^{-1}) affected by dimerization (right side).

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irradiated and nonirradiated samples. The significant changes in the C 2s region of the valence band spectrum observed for the monolayer and the polymeric backboned system were associated with a **3** to **4** structural change (Figure 1) based on DFT modeling for both systems. In addition to this, the DFT modeling of the dimerized pure functionality **4** is consistent with the observed suppression of vibrations in the FTIR spectrum at 1374, 1658 cm^{-1} (Figure 7), caused by reinforcement of the linking units.

Supporting Information Available: A detailed description of aspects of synthesis of compounds (**10**, **11**, **12 2**, **3**, **6 7**, **8**, and **1**) including NMR, GC/MS, and HRMS spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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