Interactions of hydrophobic and hydrophilic self-assembled monolayers with water as probed by sum-frequency-generation spectroscopy

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ABSTRACT

Hydrophilic and hydrophobic self assembled monolayers of alkanethiols were examined in air and in water using sum frequency generation spectroscopy (SFG). Hydrophilic films showed significant changes in peak intensity and position upon exposure to water, indicating extensive interaction of water mole cules with the film. Spectra of hydrophobic films were similar in air and water, indicating only weak interactions of water with the film. Density Functional Theory (DFT) calculations were also performed to identify the vibrational modes contributing most significantly to the observed effects. These results demonstrate how SFG can be used to detect the interaction of water with molecules in thin films at interfaces.

1. Introduction

Spectroscopic analysis of solid/liquid interfaces and thin films in situ holds great potential for answering some of the most crucial questions in the fields of environmental, biomedical, and materials sciences [1 4]. The technique of sum frequency generation (SFG) spectroscopy in particular has emerged as a tool well suited to the investigation of liquid/solid interfaces, due to its surface sensi tivity, molecular level detection capabilities, and the ability to function under standard conditions [5 8]. Furthermore, this tech nique offers the potential for probing the same sample in air and in liquid [9 11], making it possible to bridge the gap between mea surements in situ and those that need to be performed under ultra high vacuum or other non standard conditions.

However, analyzing in situ SFG spectra of larger molecules or dynamic processes can be difficult, not only because of the inher ent complexity of the molecules and processes themselves, but also because the coupling of water molecules to polar groups in samples in situ can lead to conformational changes which alter the resulting spectra. Due to the relatively recent appearance of SFG as an in situ spectroscopic technique, however, there is cur rently comparably less literature available which examines these changes [12 17]. Furthermore, there is little information on these changes in basic contrasting systems simple hydrophobic and hydrophilic functionalized surfaces despite the fact that this information could be highly useful in interpreting in situ spectra of more complex samples such as biomolecules and polymers.

Self assembled monolayers (SAMs) of alkanethiols often serve as model systems due to their relative simplicity and ability to be used to easily create hydrophilic and hydrophobic surfaces [18,19]. To date, there have been many theoretical and experimen tal studies performed on SAMs with methyl terminated hydropho bic and hydroxyl terminated hydrophilic tail groups. The majority of these studies have focused on structural and dynamic properties of water at the interface, and have found a substantially reduced water density in the direct vicinity of methyl terminal groups for hydrophobic films and a partially solvated state for hydroxyl ter minal groups in hydrophilic films [20 22]. However, these studies did not examine the effect of water interaction on the internal structure of the film itself. Bain and coworkers investigated the relationship between macroscopic contact angles and molecular level details in methyl terminated SAMs in air and in increasingly polar liquids. In order to vary the water contact angle between 77° and 112°, they used alkanthiols with oxygen atoms at varying dis tances relative to the terminal methyl group [12,13]. Other studies have focused on structural changes within the SAMs, although using more complicated molecules [15,17,23]. Here we examine hydroxyl terminated alkanethiol SAMs in air and in water using broadband SFG spectroscopy. These molecules are often employed as a protective group in the manufacturing of a variety of thiolated biomolecules including DNA [9,24 26] and are also used as back filling molecules to increase order in films of biological molecules [27]. Furthermore, we compare these results to hydrophobic

methyl terminated SAMs and use Density Functional Theory (DFT) calculations to support peak assignments for both systems.

2. Materials and methods

2.1. Preparation of hydrophobic and hydrophilic SAMs

Silicon wafers sputter coated with 100 nm of gold were cleaned by a UV/ozone cleaner (42 220, Jelight) for 2.5 h, rinsed in ethanol, and placed in 3 mM solutions of 1 dodecanethiol (DDT) (Fig. 1) to form hydrophobic surfaces or 11 mercaptoundecanol (MCU) (Fig. 4) to form hydrophilic surfaces (Sigma Aldrich). After 36 h of incubation at room temperature samples were removed from the solutions, rinsed thoroughly in ethanol, and dried under flow ing N_2. Sample quality was verified via X ray photoelectron and infrared spectroscopy.

2.2. Sum frequency generation spectroscopy (SFG)

SFG Spectra were recorded using a femtosecond SFG spectrom eter overlapping a broadband infrared and a narrow band visible beam at 800 nm. All spectra were recorded in ppp polarization in the order of increasing wavelengths (SFG, visible and infrared). Each sample was first measured in air, then in H_2O using a liquid cell as previously described [9,11]. Briefly, samples were probed through a prism (half cylindrical CaF_2 crystal) and a thin layer of H_2O (1 2 μm) located above the sample. The repetition rate of the laser system was 1 kHz allowing for the recording of SFG spec tra with reasonable signal to noise ratio within 1 min. Each spec trum was then background corrected and normalized to the spectral profile of the broadband IR pulse. SFG spectra of films on gold substrates show an intensive non resonant SFG signal origi nating from the gold substrate together with a resonant signal emanating from the film of interest. The non resonant gold signal is constant over the displayed SFG frequency range and is assumed to have a 180° phase shift with respect to the resonant contribu tion of the SAM. It should be noted that only the absolute value of the resonant contributions are shown here.

2.3. DFT calculations

We employed DFT as implemented in the Turbomole simulation package [28] using a localized basis set and effective core poten tials to model the electron ion interaction. The Kohn Sham equa tion was solved for a given exchange correlation (XC) functional for the valence electrons. In the present work, we used the well established PBE functional [29]. To take into account van der Waals interactions between alkanethiols and water, we used the DFT + D approximation [30] incorporating the long range disper sion contribution to the XC functional. The vibrational frequencies were calculated in the framework of the frozen phonon method [31]. Calculations for molecules in H_2O were made using a single molecule of water. In order to permit direct comparison between experiments and theory we calibrated the calculated frequencies to match those observed for the symmetric and asymmetric CH_3 vibrations of the methyl terminal group in the DDT film. This yielded a redshift of the calculated spectra by 99.5 cm^{-1}.

Simulations were performed assuming a single molecule in a vacuum and neglecting the presence of a metallic substrate, there fore a deviation between calculated and experimental values of up to 20 cm^{-1} was considered acceptable.

3. Results and discussion

3.1. Hydrophobic films

Fig. 2 shows the SFG spectra of self assembled monolayers of methyl terminated DDT on gold in air (orange, upper trace) and in water (blue, lower trace) in the region between 2800 and 3000 cm^{-1}. The major bands present in these spectra are attributed to vibrations of the methyl terminal groups (located at 2880, 2940, and 2968 cm^{-1}) [32,33]. Vibrations from methylene groups within the alkane chain can not be observed in the SFG spectra, with the exception of minor contributions from the methylene groups adja cent to the sulfur atom (located at 2885 and 2928 cm^{-1}) (Table 1). This is due to the selection rules for second order nonlinear optical processes which dictate that only molecular arrangements with broken inversion symmetry can contribute to an SFG response. In air, the close packed DDT film is assumed to have a highly ordered structure with an all trans conformation of the alkane chains [34]. In this configuration a center of inversion is located in between the methylene groups in the alkane chain, leading to the suppression of the corresponding SFG signal. Indeed, the DFT calculation for the all trans conformation reveals that none of the collective al kane chain CH_2 vibrations in the observed spectral range are both Raman and IR active. Note, that according to group theory, (SFG ac tive) vibrations with broken inversion symmetry must be both Ra man and IR active. In addition, the absence of bands originating from gauche defects in the alkane chain (see Table 1) confirms the presence of an ordered SAM.

Furthermore, the CH_3 as vibration has both in plane (ip, 2965 cm^{-1}) and out of plane (op, 2955 cm^{-1}) contributions. In the polarization combination used in these experiments (ppp, in the order of increasing wavelength SFG, visible, and IR), IR tran sition dipole moments perpendicular to the interface are maxi mized, while those parallel to the surface are vanishing. The presence of the ip vibration and absence of the op vibration in these spectra indicate that the methyl groups are oriented perpen dicular to the substrate, as is expected for a highly ordered film of this type [34].

It was observed that placing the DDT films in water (Fig. 2, low er blue trace) did not significantly change the spectrum in either band position or relative intensity, in agreement with previous re sults [12,13]. This indicates that the water molecules have only weak interactions with terminal methyl groups of the film and that the orientation of the methyl groups of this film remains the same. As a high density or close proximity of water molecules near the methyl groups would cause a change in the vibrations and thus a change in the spectra, these findings support previous results ob tained by MD simulations [20], neutron [35], and X ray relfectivity [21,22], suggesting a reduced water density near the surface of this hydrophobic film [20 22].

To further investigate this result, we have computed the shift in frequency of the three major vibrations of the methyl group as it is approached by a water molecule (Fig. 3). The experimentally
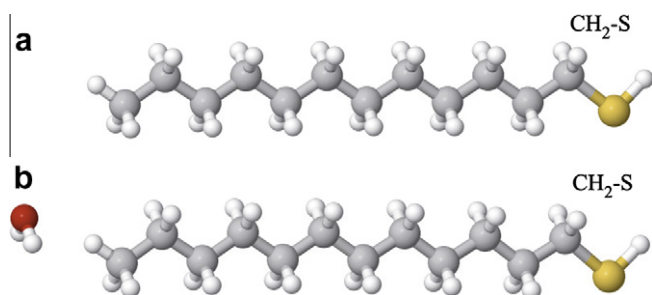

Fig. 1. Graphic of a single DDT molecule as used for DFT calculations. (a) molecule as used for calculations in air and (b) molecule as used for calculations in water.
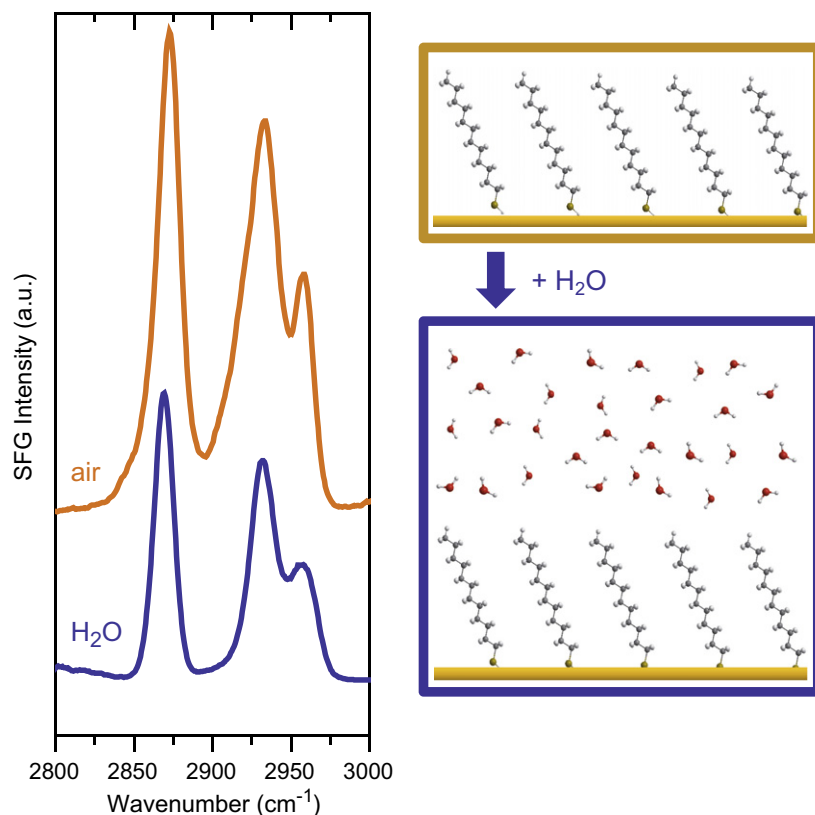
Fig. 2. SFG spectra of a self-assembled monolayer of hydrophopic, methyl-terminated 1-dodecanethiol on gold in air (above) and in water (below). No significant changes in relative peak intensities or positions were observed upon exposure to water, indicating that there is only a weak interaction (e.g. induced dipole, van-der-Waals) between water molecules and the film.

Table 1

Peak positions and assignments for DDT and MCU monolayers in air and in water. s: symmetric, as: asymmetric, FR: Fermi resonance. The $CH_2(2)$ group in MCU is located 2 carbon atoms away from the OH terminal group as depicted in Fig. 4.

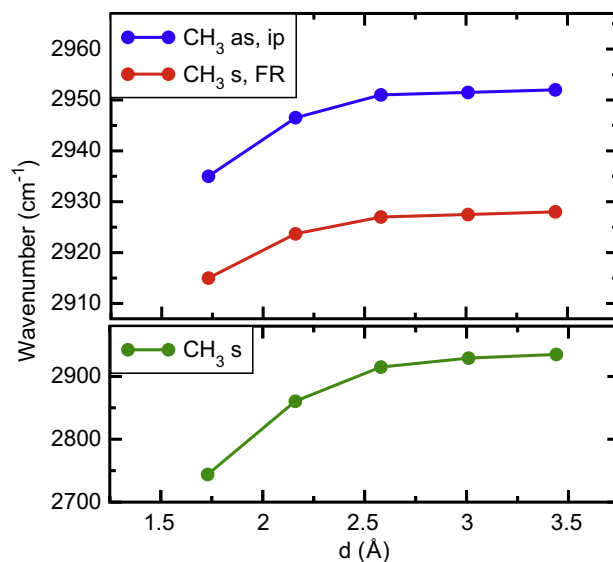| Assignment	DDT Positions				MCU Positions			
	Air		H_2O		Air		H_2O	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
CH_3 as, ip	2965	2957	2965	2952	–	–	–	–
CH_3 s, FR	2940	2946	2939	2929	–	–	–	–
CH_3 s	2880	2864	2876	2865	–	–	–	–
CH_2-S as	2928	2939	2928	2933	2928	2938	2929	2934
CH_2-S s	2885	2877	2885	2877	2885	2877	2882	2870
$CH_2(2)$ as	–	–	–	–	2911	2919	–	–
$CH_2(2)$ s	–	–	–	–	2865	2866	–	–
CH_2 gauche	–	–	–	–	–	–	2945	2955
CH_2 gauche	–	–	–	–	–	–	2909	2924

Fig. 3. Calculated peak position of the three major methyl vibrations upon hydration as a function of the distance between the oxygen in the water molecule and the carbon atom in the methyl group. These calculations show that a water molecule within a distance of $d = 2.2$ Å would cause a red shift in the observed spectra.

determined values of 2880, 2940 and 2968 cm^{-1} correspond to the equilibrium distance of 3.44 Å between the water molecule and the methyl group.

In order to estimate the distance between the methyl group and the water layer we have performed model calculations, where we place a single water molecule at a given distance from the methyl headgroup and compute the methyl vibrations as a function of distance. While such a model may seem naive, it gives an idea of the lower bound on the water methyl distance, due to the fact that the interactions between water and the methyl headgroup are very weak. The DFT calculations indicate that the frequency of these modes may shift to lower wavenumbers when the distance d between the oxygen in the water molecule and the carbon in the methyl group is less than 2.2 Å. In the vicinity of a hydrophobic surface, water mobility is reduced, thus inclusion of additional water molecules has little effect on this critical radius, which approximates the lower bound between water and the headgroup

of the film. We have performed calculations for MCU with up to three water molecules and found no significant effect on the critical headgroup water distance even for this more strongly interacting system. However, it should be noted that this model includes some ambiguities such as dependence on the potential used in the DFT calculations and possible changes in the dielectric constant induced by the presence of the bulk water further away from the surface.

3.2. Hydrophilic films

In Fig. 5, SFG spectra of the hydrophilic, OH terminated MCU SAMs are shown. According to our DFT calculations, the only Raman and IR active bands in this region are collective CH_2 vibrations mainly located at the second CH_2 group from the OH termination ($CH_2(2)$) and the CH_2 group adjacent to the sulphur atom (CH_2 S) (Table 1 and Fig. 4). A peak at 2964 cm^{-1} is also apparent in the MCU spectra in both air and water, but as this peak was not present in the DFT calculations we refrain from assigning it here. Collective vibrations located primarily at the first group from the OH termination ($CH_2(1)$) are found to be located in the region below 2800 cm^{-1}, which was not probed in these experiments. The high overall intensity of this spectrum and presence of peaks due only to terminal or near terminal groups indicate that this film also has a high degree of order, as the alkane chain methylene vibrations are suppressed (see discussion in the previous section on symmetry arguments in an all trans conformation).

When this film is exposed to water, however, drastic changes occur (Fig. 5, lower blue trace). First, the overall intensity of the peaks decreases significantly compared to the peaks in air (both spectra were normalized to the non resonant background). Second, the relative intensities of these peaks are substantially changed. Third, new peaks attributed to CH_2 vibrations from further down the alkyl chains appear at 2909 and 2945 cm^{-1}. These are now visible due to the appearance of gauche defects caused by the water molecules interacting with this film and causing a change in the orientation of the hydroxyl terminal groups. These assignments are supported by the DFT calculations showing that these vibrations are only present in CH_2 groups adjacent to a kink in the alkyl chain. It should be noted, however, that the positions of the peaks assigned to CH_2 S vibrations remain unchanged. This indicates that while the interaction with water is disrupting the upper part of the film, it is not disrupting lower part of the film, as would be expected for a well formed SAM.

4. Conclusions

We have examined hydrophobic methyl and hydrophilic hydroxyl terminated self assembled monolayers in air and in water using SFG spectroscopy. Hydrophobic SAMs with methyl terminal groups showed similar spectra both in air and in water, demonstrating that these films do not change in either conformation or orientation upon exposure to solution, in agreement with previous
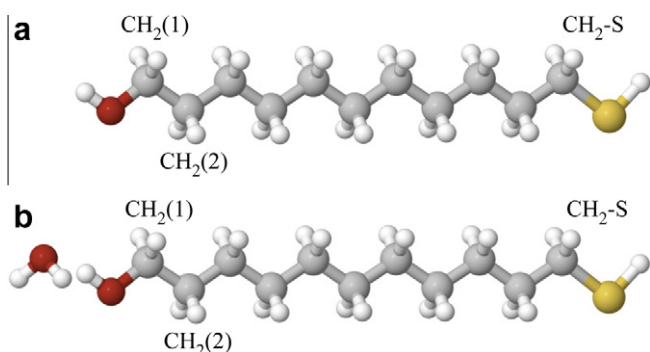

Fig. 4. Graphic of a single MCU molecule as used for DFT calculations. (a) molecule as used for calculations in air and (b) molecule as used for calculations in water.
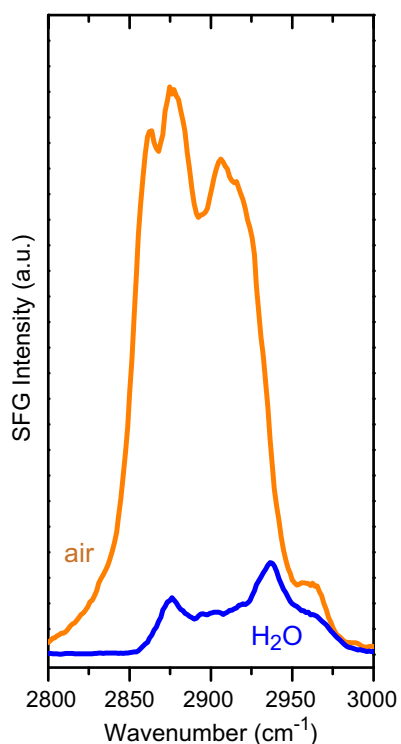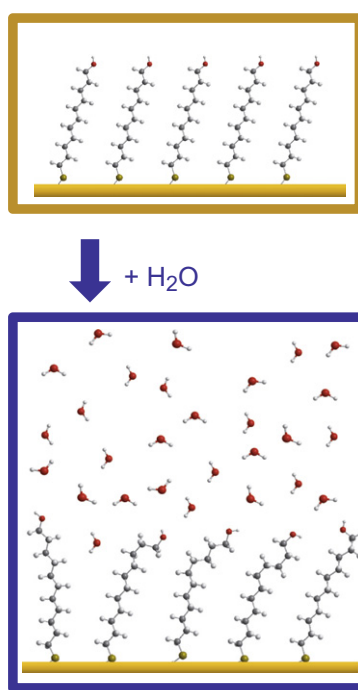

Fig. 5. SFG spectra of hydrophilic, hydroxyl-terminated 1-mercaptoundecanol in air (upper trace), and in water (lower trace). Peak positions changed drastically upon exposure to water, as did both relative and overall intensities, indicating significant interaction of the water molecules with the film.

results and supporting the concept of a reduced water density in close proximity to the hydrophobic interface suggested by other techniques.

Hydrophilic SAMs with hydroxyl terminal groups revealed substantially different SFG spectra in air and H_2O, attributed to a significant decrease in order and interaction of water molecules with the film. DFT calculations made for these molecules substantiate the peak assignment and the presence of gauche defects in the alkane chain when the film is exposed water.

These results demonstrate that SFG is a useful and comparably simple method for deducing the effect of *in situ* environments on model hydrophobic and hydrophilic films, and that in conjunction with DFT calculations can be used to analyze the effect of aqueous environments on a molecular level. The findings presented here may be applied to the interpretation of SFG spectra of more complex or mixed alkanethiol/biomolecule films.

Acknowledgments

References

[1] D.G. Castner, B.D. Ratner, Surface Sci. 500 (2002) 28.
[2] B. Kasemo, Surface Sci. 500 (2002) 656.
[3] G.L. Richmond, Chem. Rev. 102 (2002) 2693.
[4] F.M. Geiger, Annu. Rev. Phys. Chem. 60 (2009) 61.
[5] Y.R. Shen, V. Ostroverkhov, Chem. Rev. 106 (2006) 1140.
[6] Z. Chen, Y.R. Shen, G. Somorjai, Annu. Rev. Phys. Chem. 53 (2002) 437.
[7] S. Roke, ChemPhysChem 10 (2009) 1380.
[8] A.J. Hopkins, C.L. McFearin, G.L. Richmond, Curr. Opin. Solid State Mater. Sci. 9 (2005) 19.
[9] C. Howell, R. Schmidt, V. Kurz, P. Koelsch, Biointerphases 3 (2008) FC47.
[10] S.R. Walter, F.M. Geiger, J. Phys. Chem. Lett. 1 (2010) 9.
[11] V. Kurz, M. Grunze, P. Koelsch, Chem. Phys. Chem. 11 (2010) 1425.
[12] T.H. Ong, P.B. Davies, C.D. Bain, Langmuir 9 (1993) 1836.
[13] T.H. Ong, R.N. Ward, P.B. Davies, C.D. Bain, J. Am. Chem. Soc. 114 (1992) 6243.
[14] R.N. Ward, P.B. Davies, C.D. Bain, J. Phys. Chem. 97 (1993) 7141.
[15] M. Buck, Phys. Chem. Chem. Phys. 5 (2003) 18.
[16] A.J. Pertsin, M. Grunze, H.J. Kreuzer, R.L.C. Wang, Phys. Chem. Chem. Phys. 2 (2000) 1729.
[17] M. Zolk, F. Eisert, J. Pipper, S. Herrwerth, W. Eck, M. Buck, M. Grunze, Langmuir 16 (2000) 5849.
[18] K.L. Prime, G.M. Whitesides, Science 252 (1991) 1164.
[19] C. Vericat, M.E. Vela, G.A. Benitez, J.A.M. Gago, X. Torrelles, R.C. Salvarezza, J. Phys.: Condens. Matter 18 (2006) R867.
[20] M.J. Stevens, G.S. Grest, Biointerphases 3 (2008) FC13.
[21] A. Yang, C. Weng, J. Chem. Phys. 129 (2008) 154710.
[22] M. Mezger et al., Proc. Natl. Acad. Sci. USA 103 (2006) 18401.
[23] L. Dreesen, C. Humbert, P. Hollander, A.A. Mani, K. Ataka, P.A. Thiry, A. Peremans, Chem. Phys. Lett. 333 (2001) 327.
[24] N. Ballav, P. Koelsch, M. Zharnikov, J. Phys. Chem. C 113 (2009) 18312.
[25] Y. Sartenaer, G. Tourillon, L. Dreesen, D. Lis, A.A. Mani, P.A. Thiry, A. Peremans, Biosens. Bioelectron. 22 (2007) 2179.
[26] L. Baugh, T. Weidner, J.E. Baio, P.-C.T. Nguyen, L.J. Gamble, P.S. Stayton, D.G. Castner, Langmuir. doi:10.1021/la1007389.
[27] C.-Y. Lee, P. Gong, G.M. Harbers, D.W. Grainger, D.G. Castner, L.J. Gamble, Anal. Chem. 78 (2006) 3316.
[28] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölme, Chem. Phys. Lett. 162 (1989) 165.
[29] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[30] S. Grimme, J. Comput. Chem. 27 (2006) 1787.
[31] R. Maul, F. Ortmann, M. Preuss, K. Hannewald, F. Bechstedt, J. Comput. Chem. 28 (2007) 1817.
[32] M. Porter, T. Bright, D. Allara, C. Chidsey, J. Am. Chem. Soc. 109 (1987) 3559.
[33] R. Nuzzo, L. Dubois, D. Allara, J. Am. Chem. Soc. 112 (1990) 558.
[34] M. Himmelhaus, F. Eisert, M. Buck, M. Grunze, J. Phys. Chem. B 104 (2000) 576.
[35] M. Maccarini et al., Langmuir 23 (2007) 598.