

T. WEIDNER^{1,3}
J. VOR DER BRÜGGEN^{2,3}
U. SIEMELING^{2,3}
F. TRÄGER^{1,3}✉

Self-assembled nanostructures of redox-functionalized terpyridines monitored by optical second-harmonic generation

¹ Institut für Physik,
² Institut für Chemie,
and
³ Center for Interdisciplinary Nanostructure Science and Technology – CINSaT,
Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Received: 15 May 2003

Published online: 12 August 2003 • © Springer-Verlag 2003

ABSTRACT Adsorption and self-organization of ferrocenyl-functionalized terpyridines on gold substrates were investigated in situ by optical second-harmonic generation (SHG). Film growth of these organometallic compounds could be detected in the submonolayer regime. The SHG data have been compared to the results of ellipsometric measurements and show that *monolayer* films are formed. Film growth is followed by *self-assembly of ordered* redox-active ferrocenyl nanostructures.

PACS 81.07.Nb; 81.16.Dn; 42.65.Ky; 68.43.Mn; 81.70.Fy

1 Introduction

Preparation of highly ordered nanostructured surfaces has recently been of growing interest. In contrast to classical lithographic methods a particularly simple and promising approach is self-assembly of molecules deposited on a solid surface either from the gas phase or a liquid environment. Self-assembly can then proceed by intermolecular and molecular–substrate interactions. Most compounds used for this purpose contain head groups that accomplish chemisorption on the surface, spacer units and, finally, functional groups with desired properties. Many films formed of such compounds, for example thiols, are quite soft because of flexible spacer units that limit the overall film ordering and rigidity. For many purposes, however, rigid structures are highly desirable, for example if ordered films are needed to serve as templates for superstructures of atoms or other molecules. As a contribution to resolving this problem the experiments reported here focus on 2, 2′ : 6′, 2′′-terpyridine bearing a redox-active ferrocenyl as a functional group [1] attached to the 4′-position by means of very rigid π -spacers [2, 3] (see Fig. 1). Investigation of self-assembly of these molecules on gold substrates is part of a research project with the objective of understanding the role of all relevant parameters that play a part in the formation of highly ordered ultra-thin molecular structures and in developing the optimum molecular design for effective growth of rigid, well-ordered organometallic architectures for further nanostructure growth or electrochemical

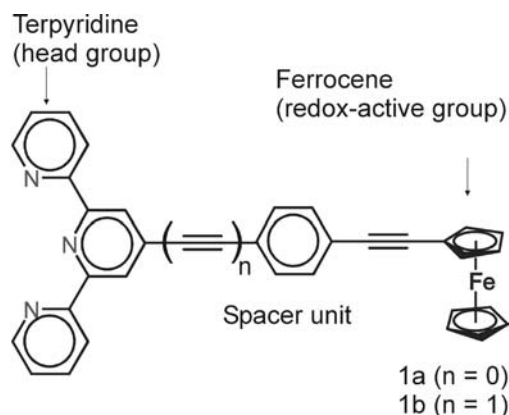


FIGURE 1 Ferrocenyl-functionalized terpyridines used for the adsorption experiments on polycrystalline gold

experiments. The present paper describes studies of the adsorption kinetics and of the ordering of the films.

In our experiments a particularly powerful and versatile technique was applied to study adsorption as well as ordering of the molecules, i.e. we have used in situ optical second-harmonic generation (SHG) and exploited the striking advantages of this method [4, 5]. Since a signal is generated only where inversion symmetry is broken, SHG is highly sensitive to the electronic properties of the interface between the substrate and the deposited molecules, i.e. the method allows one to follow formation of the surface molecular bond. Furthermore, SHG is sensitive to the orientation of the molecules with respect to the surface and can therefore be used to follow ordering within the film [6–8]. In many cases the sensitivity is large enough to make possible experiments even in the submonolayer regime. Since the SHG data are often more easily interpreted by comparison with the results of other surface analytical tools, we have also studied the adsorption of ferrocenyl-functionalized terpyridine as a function of time with ellipsometry.

2 Experimental

Details of SHG experiments for the investigation of interfaces and thin-film formation have been published elsewhere; see for example [9, 10]. We therefore describe the experimental arrangement (Fig. 2) only briefly here. The

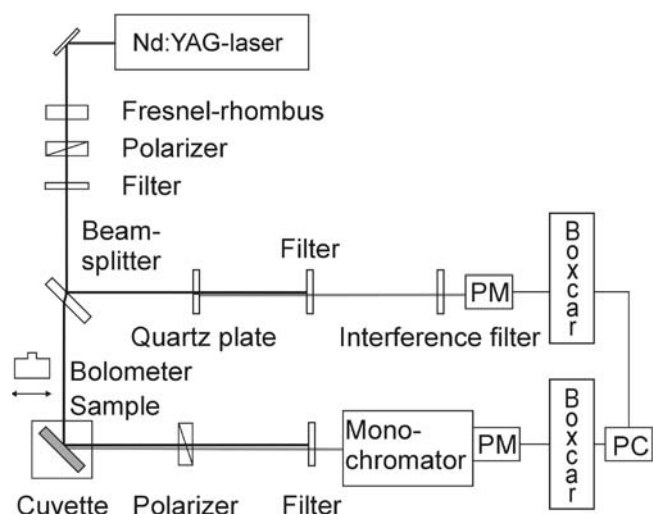


FIGURE 2 Experimental arrangement used for SHG measurements of the adsorption and self-assembly of redox-functionalized terpyridines on Au. Laser light with a wavelength of 1064 nm and a pulse duration of 7 ns was applied. The cuvette was filled with terpyridine compounds dissolved in acetonitrile. The SHG intensity was monitored as a function of immersion time

measurements were performed with a pulsed Nd:YAG laser operating at a repetition rate of 10 Hz and a wavelength of $\lambda = 1064$ nm. The pulse duration was 7 ns and the laser beam was incident on the sample surface under an angle of 45° . Gold films with a thickness of 100 nm on a Si (100) wafer served as substrates for adsorption of the terpyridine molecules. The generated second-harmonic light was separated from the fundamental beam using several color glasses (BG 39, OG 590, Schott) and filters in combination with a monochromator and finally detected by a photomultiplier operating in single photon counting mode. Its signal was processed by a boxcar averager and stored in a computer.

A small fraction of the light emitted by the laser was branched off by a dielectric beam splitter and directed onto a y-cut quartz plate in order to generate a SH reference signal. It was detected and processed as explained above and served to normalize the second harmonic light intensity of the sample to minimize the influence of intensity fluctuations of the laser light.

In order to study adsorption of the ferrocenyl-functionalized terpyridine molecules, pieces with a size of 1×1 cm² were cut from the gold-covered silicon wafer and placed in a cuvette filled with pure acetonitrile (photospectrometric grade, Merck). After adjustment of the optical arrangement the SHG signal of the clean substrate was recorded. As the next step the acetonitrile was exchanged for a solution of the terpyridine molecules in acetonitrile. These compounds (1a or 1b, see Fig. 1) were prepared according to published procedures [2, 3] and were analytically pure. The concentration typically was 10 μ mol/l. Immediately after exchange of the solution adsorption of molecules on the gold film commences and the SH signal was monitored in situ as a function of time. In addition to the SH intensity, we have also determined the phase of the nonlinear susceptibility for several stages during film formation [12].

In order to determine the coverage of the molecules on the gold film independently by ellipsometry, the substrate was im-

mersed in the solution for several periods of time and subsequently dried in a stream of pure nitrogen. The film thickness was then measured ex situ with a Woolam type M44 ellipsometer as a function of immersion time and compared to the data obtained by SHG.

3 Results and discussion

As an example of the experimental results, Fig. 3a displays the time-dependent second-harmonic signal recorded during immersion of the substrate in the solution of the ferrocenyl-functionalized terpyridine 1a. The SH intensity of the clean surface has been set to unity. As can be seen from Fig. 3a, the SH signal first rises to a value of 2.8. After about 600 s the signal saturates. Subsequently, the SH intensity drops off slowly, i.e. on a time scale of hours.

The ellipsometric measurements show that the film thickness increases as a function of immersion time until monolayer coverage is reached after about 1000 s, Fig. 3b. For longer immersion times no further film growth is observed within the experimental error.

Before we discuss the experimental results we first note that the intensity of the SHG signal I_{SHG} is proportional to the square of the total second-order nonlinear susceptibility [11–13]:

$$I_{\text{SHG}} \propto |\chi_{\text{tot}}^{(2)}|^2.$$

In general, $\chi_{\text{tot}}^{(2)}$ consists of three contributions, $\chi_{\text{sub}}^{(2)}$, $\chi_{\text{int}}^{(2)}$ and $\chi_{\text{ads}}^{(2)}$, which denote the second-order susceptibilities of the

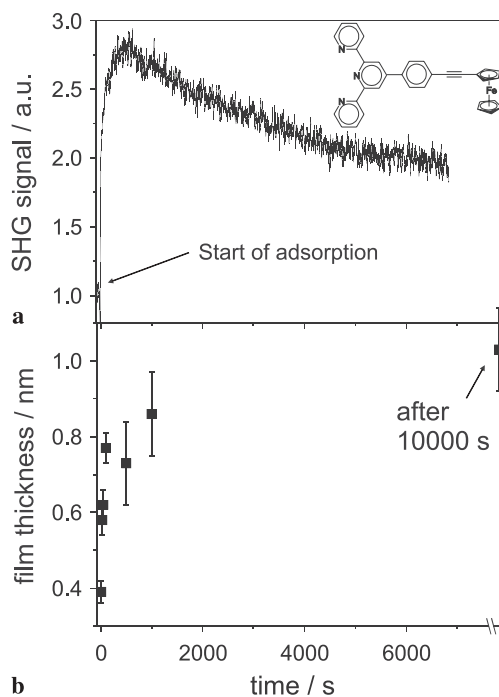


FIGURE 3 **a** SHG data recorded in real time during adsorption of ferrocenyl-functionalized terpyridine 1a onto gold from a 10 μ molar acetonitrile solution. **b** Ellipsometric measurement of the film thickness of the adsorbed molecules of the same compound and with the same concentration as a function of immersion time in an acetonitrile solution

clean substrate, of the chemical interaction between the adsorbate and the gold surface and of the molecules if the film lacks inversion symmetry, respectively. The nonlinear susceptibilities are complex numbers. Therefore, the total susceptibility $\chi_{\text{tot}}^{(2)}$ strongly depends on the phase of the individual contributions [11–13]:

$$|\chi_{\text{tot}}^{(2)}| e^{i\varphi_{\text{tot}}} = |\chi_{\text{sub}}^{(2)}| + |\chi_{\text{int}}^{(2)}| e^{i\varphi_{\text{int}}} + |\chi_{\text{ads}}^{(2)}(\langle\varrho\rangle)| e^{i\varphi_{\text{ads}}},$$

here $\langle\varrho\rangle$ is the mean distribution of angles of molecular orientation. $\chi_{\text{int}}^{(2)}$ changes during adsorption of molecules on the surface, while $\chi_{\text{ads}}^{(2)}$ reflects a variation of molecular orientation. φ_{tot} , φ_{int} and φ_{ads} denote the relative phase of the nonlinear susceptibilities denoted by the subscripts. The phase of the substrate susceptibility is set to 0° .

Comparison of the SHG with the ellipsometric data clearly shows that the SH signal rises due to adsorption of molecules, i.e. because of the increase of the surface coverage. Furthermore, the coverage saturates as soon as a single molecular layer has been formed. Obviously, the terpyridine molecules chemisorb on the surface forming an inert layer that does not permit further film growth. During adsorption the phase of the signal changes by less than 8° .

Since the coverage remains constant after the maximum of the SH intensity has been reached, the subsequent decay of the signal on a time scale of hours cannot be explained by a change of film thickness. Rather, it must be attributed to a change of the film structure. In other words, self-assembly and ordering of the molecules in the film give rise to the slow decrease of the SHG signal during which the phase varies by only about 10° .

As can be seen from Fig. 3, adsorption and conformational changes within the film take place on very different time scales. This makes it possible to study both processes independently. In the following we will analyze the adsorption kinetics of this compound by considering three different models.

1. First-order Langmuir kinetics, i.e. direct chemisorption from solution [14], described by

$$\Theta(t) = 1 - e^{-k_{\text{FO}}ct} \quad (1)$$

Here $\Theta \leq 1$ denotes the coverage, k is the rate constant and c stands for the concentration of the solution.

2. Second-order Langmuir kinetics involving a physisorbed precursor state prior to chemisorption [15]:

$$\Theta(t) = 1 - (1 + k_{\text{SO}}ct)^{-1}. \quad (2)$$

3. Diffusion-limited first-order Langmuir kinetics, i.e. diffusion of the molecules from the solution to the surface is taken into account [16]:

$$\Theta(t) = 1 - e^{-k_{\text{DL}}c\sqrt{t}}. \quad (3)$$

Figure 4 displays the experimental data together with theoretical fits according to (1), (2) and (3). The plotted quantities are chosen such that straight lines are obtained for each model of the adsorption kinetics. Since the surface coverage Θ is proportional to $\sqrt{I_{\text{SHG}}}$ the square root of the SH signal is

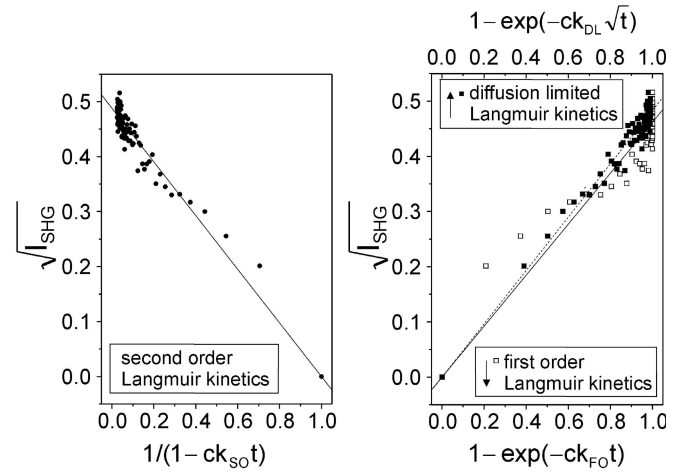


FIGURE 4 Time dependence of the coverage fitted by different adsorption models. The abscissae are chosen such that a straight line is obtained if the model holds. The SHG signal is plotted as a function of immersion time for the first 300 s

plotted instead of Θ [9]. For first-order kinetics the line has a slope of $+1$ and intersects the origin of the diagram. For second-order kinetics the slope is -1 and the straight line intersects the y-axis at 1. The rate constants k are obtained from the fits. Obviously, first-order Langmuir kinetics fails to describe the experimental data. Second-order and diffusion-limited kinetics show much smaller deviations from the data. Even though second-order kinetics cannot be excluded, the diffusion-limited first-order model is most consistent with the measurements. Therefore, the rate-limiting step for adsorption appears to be diffusion of terpyridine molecules from the solution to the surface.

Figure 5 shows a fit of the sum of the three contributions to the total SHG intensity as a function of time to the SH intensity recorded during adsorption of the ferrocenyl-functionalized terpyridine from acetonitrile at a concentration of $2 \mu\text{mol/l}$. Diffusion-limited adsorption has been used (see above) while the ordering of the ferrocenyl units on the surface was assumed to be a first-order process. Obviously,

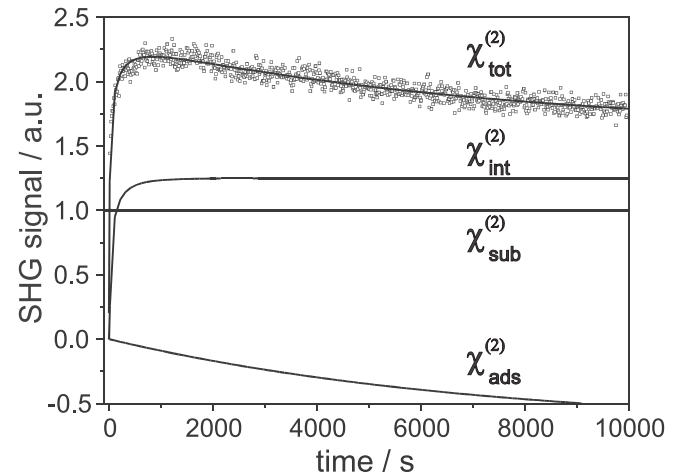


FIGURE 5 The sum of the three contributions to the total nonlinear susceptibility as a function of time describe the experimental data very well. For the adsorption process diffusion-limited Langmuir kinetics was used and the orientation of the molecules has been assumed to follow first-order kinetics

this description is in good agreement with the experimental data.

We have also carried out SH measurements during adsorption and orientation of molecules that are identical to the ones studied above with the exception of a modified spacer length, Fig. 6. The figure displays the data of the ferrocenyl-functionalized terpyridine 1b with one additional acetylene group in the spacer unit from an acetonitrile solution with a concentration of 10 $\mu\text{mol/l}$ onto a gold substrate. As above, the signal of the clean substrate is set to unity. The SH intensity first rises to a value of 1.5. It then drops off very quickly to a value of 0.3. The total intensity even decreases below the signal originally recorded for the clean substrate. This demonstrates again that the decrease of the SH signal after saturation is generated by destructive interference, i.e. an additional contribution $\chi_{\text{ads}}^{(2)}$ that is out of phase with the signal of the clean surface.

A very interesting further observation is that the spacer length turns out to be of major importance for the time scale on which molecular orientation in the film develops, Fig. 6. The longer spacer unit of the molecules accelerates the formation of orientation quite dramatically as compared to Fig. 3. In fact, it proceeds almost on the same time scale as adsorption.

The molecular orientation due to self-assembly was investigated by measurements with two polarization combinations of the incident and detected SH light [9]. *p*- and *s*-polarization refer to parallel and perpendicular orientation of the electric field vector with respect to the plane of incidence, respectively. Figure 7 displays SHG data recorded with (*p*, *p*) and (*s*, *p*) polarization during adsorption of the ferrocenyl-functionalized terpyridine. The signal for (*p*, *p*) polarization is identical to the measurements discussed above with the slow decrease of the signal at long immersion times. In contrast, there is no change of the signal as a function of coverage for (*s*, *p*) polarization. This shows that $\chi_{\text{int}}^{(2)}$ and $\chi_{\text{ads}}^{(2)}$ vanish in the direction parallel to the surface, and it appears that the second harmonic active part of the molecules must be oriented perpendicular with respect to the surface

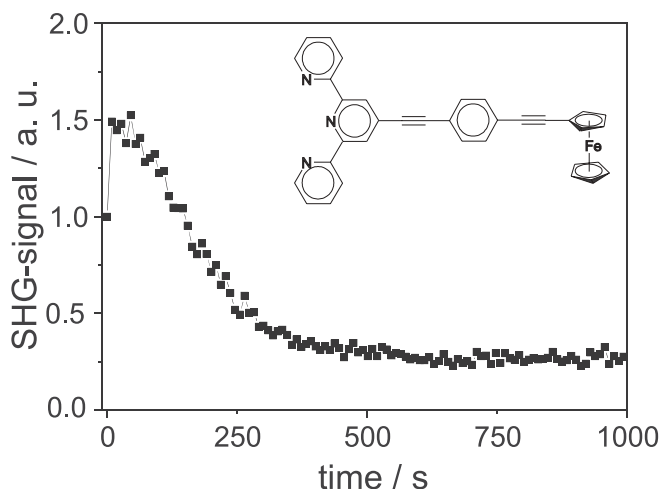


FIGURE 6 Adsorption and film ordering of compound 1b (ferrocenyl-functionalized terpyridine with an additional acetylene group in the spacer unit) monitored by SHG

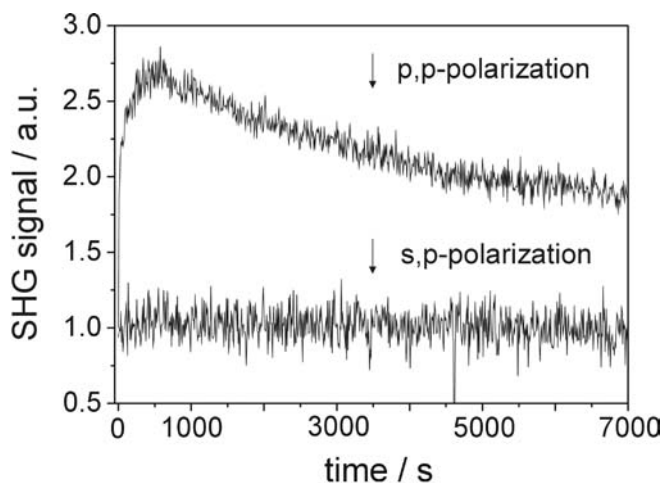


FIGURE 7 Comparison of the SHG signal as a function of surface coverage obtained by *s*- and *p*-polarized fundamental light. The analyzed SH light was *p*-polarized in both cases

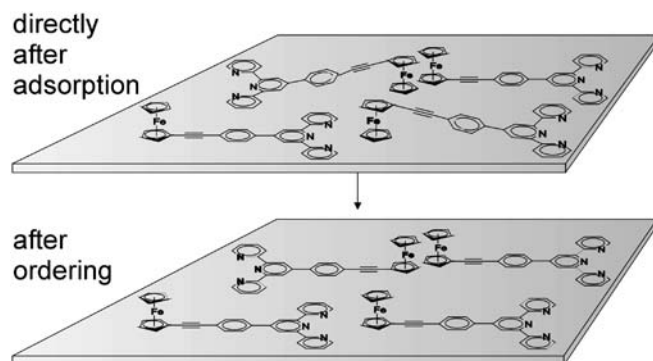


FIGURE 8 Model of ferrocene film orientation on gold surfaces. After “flat” adsorption of the extended π -system the orientation of the ferrocene units is perpendicular to the surface. Following adsorption, self-assembly leads to a nanostructure of parallel ferrocene units

normal. Recent studies of a variety of oligopyridines at gold interfaces report “flat” adsorption of these compounds for zero surface potential [17]. This orientation of the terpyridine and spacer unit of the molecules should lead to perpendicularly oriented ferrocenes on the surface. Based on this argument we conclude that the ferrocene unit is the second harmonic active component of adsorbed ferrocenyl-functionalized terpyridine.

Finally, all experimental data are in accord with, but do not prove, the model shown in Fig. 8. Following random orientation of the ferrocenyl unit directly after adsorption the ferrocenes are ordered by interaction of the π -system with the gold substrate. This process leads to a narrowing of the distribution of ferrocenyl orientation and gives rise to an increasing $\chi_{\text{ads}}^{(2)}$.

4 Conclusion

In conclusion, we have investigated adsorption and self-assembly of ferrocenyl-functionalized terpyridines on polycrystalline gold substrates in situ and in real time by optical second-harmonic generation. Coverages in the submonolayer regime could be detected. The SHG data have been compared to ellipsometric measurements. The

data clearly show that adsorption leads to formation of monolayer films at the interface on a time scale of typically several minutes. The adsorption process can be described by diffusion-limited Langmuir kinetics. Most importantly, we found that film growth is followed by self-assembly of ordered redox-active ferrocenyl nanostructures on a much longer time scale. This process of self-assembly is strongly influenced by the molecular architecture (spacer length).

Future experiments will focus on AFM/STM studies to investigate the lateral organization of the assembled films. Furthermore, the dependence of the film configuration on the surface potential will be monitored by second-harmonic generation. Moreover, the ferrocene surface structures will be used as a substrate for further film growth.

ACKNOWLEDGEMENTS We thank Dr. W. Schrepp, BASF AG Ludwigshafen, and Prof. Dr. H. Hillmer, Institut für Mikrostrukturtechnologie und Analytik (IMA) der Universität Kassel for providing the substrates. The ellipsometric measurements were performed in the laboratory of Prof. Dr. M. Grunze, Institut für Angewandte Physikalische Chemie der Universität Heidelberg, which we also gratefully acknowledge. This work was funded in part by the Fonds der Chemischen Industrie.

REFERENCES

- 1 A. Togni, T. Hayashi (Eds.): *Ferrocenes* (VCH, Weinheim 1995)
- 2 U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammer, P. Zanello, F. Fabrizi de Biani: *Eur. J. Inorg. Chem.*, 1 (1999)
- 3 U. Siemeling, J. Vor der Brügggen, U. Vorfeld, B. Neumann, A. Stammer, H.-G. Stammer, A. Brockhinke, R. Plessow, P. Zanello, F. Laschi, F. Fabrizi de Biani, M. Fontani, S. Steenken, M. Stapper, G. Gurzadyan: *Chem. Eur. J.* **9**, 2819 (2003)
- 4 Y.R. Shen: *Annu. Rev. Phys. Chem.* **40**, 327 (1989)
- 5 R.W. Boyd: *Nonlinear Optics* (Academic, London 1992)
- 6 T.F. Heinz, H.W.K. Tom, Y.R. Shen: *Phys. Rev. A* **28**, 1883 (1983)
- 7 M. Buck, C. Dressler, M. Grunze, F. Träger: *J. Adhes.* **58**, 227 (1996)
- 8 F. Eisert, O. Dannenberger, M. Buck: *Phys. Rev. B* **58**, 10860 (1998)
- 9 O. Dannenberger, M. Buck, M. Grunze: *J. Phys. Chem. B* **103**, 2202 (1999)
- 10 M. Buck, F. Eisert, J. Fischer, M. Grunze, F. Träger: *Appl. Phys. A* **53**, 552 (1991)
- 11 R.M. Corn, D.A. Higgins: *Chem. Rev.* **94**, 107 (1994)
- 12 M. Buck, F. Eisert, M. Grunze, F. Träger: *Appl. Phys. A* **60**, 1 (1995)
- 13 K.B. Eisenthal: *Chem. Rev.* **96**, 1343 (1996)
- 14 J.D. Andrade: *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 2: *Protein Adsorption* (Plenum, New York, London 1985)
- 15 K.A. Peterlinz, R. Georgiadis: *Langmuir* **12**, 4731 (1996)
- 16 J.T. Davies, E.K. Rideal: *Interfacial Phenomena* (Academic, New York, London 1963)
- 17 Th. Dretschkow, Th. Wandlowski: *J. Electroanal. Chem.* **467**, 207 (1998)