## A spectroscopic study of self-assembled monolayer of porphyrin-functionalized oligo(phenyleneethynylene)s on gold: the influence of the anchor moiety

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Porphyrin-functionalized oligo(phenyleneethynylene)s (OPE) are promising molecules for molecular electronics applications. Three such molecules (1-3) with the common structure P-OPE-AG (P and AG are a porphyrin and anchor group, respectively) and different anchor groups, viz. an acetyl protected thiol,  $-S-COCH_3$  (1), an acetyl protected thiol with methylene linker,  $-CH_2-S-COCH_3$  (2), and a trimethylsilylethynyl group,  $-C \equiv C-Si(CH_3)_3$  (3) have been synthesized and the corresponding self-assembled monolayers (SAMs) on Au(111) substrates have been prepared. The integrity and structural properties of these films were studied by X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. The results suggest that the films formed from 1 have a high orientational order with an almost upright orientation and dense packing of the molecular constituents, *i.e.* represent a high quality SAM. In contrast, molecule 2 formed disordered molecular layers on Au, even though the molecule-surface bonding (thiolate) is the same as in the case of molecule 1. This suggests that the methylene linker in molecule  $\mathbf{2}$  has a strong impact on the quality of the resulting film, so that a well-ordered SAM cannot be formed. The silane system, 3, is also able to bind to the gold surface but the resulting SAM has a poor quality, being significantly disordered and/or comprised of strongly inclined molecules. The above results suggest that the nature of the anchor group along with a possible linker is an important parameter which, to a high extent, predetermines the entire quality of OPE-based molecular layers.

## 1. Introduction

The idea of molecular electronics has recently received much attention in connection with the ongoing feature size reduction of electronic devices. In order to operate such an electronic, the electron transport through the molecular devices is essential. Oligo(phenyleneethynylene) (OPE) derivatives have attracted special interest due to their largely delocalized  $\pi$ -conjugated systems, resulting in a relatively high electrical conductivity along the molecular backbone.<sup>1-9</sup> By introducing a porphyrin as the tail group onto the OPE molecules, a wirelike molecule with optical and redox properties can be created and be of potential interest for application in solar cells,<sup>10,11</sup> sensors<sup>12-14</sup> and other optoelectronic devices.<sup>15-18</sup> The immobilization of the molecules on the electrode, e.g. gold, can be achieved by self-assembly, by which molecules organize themselves on the surface<sup>19</sup> in so-called self-assembled monolayers (SAMs). In recent years, a variety of studies on SAMs with porphyrin tailgroups have been reported.<sup>20–29</sup> In many cases, thiolate (S-) was used as an anchor which chemically binds the molecule to the gold surface. This anchoring is frequently used for the fabrication of SAMs on coinage metal and semiconductor substrates.<sup>30</sup> However, thiolate is not the only head-group suitable for formation of SAMs on these substrates. Several other groups are available as well. In addition, the structural parameters of SAMs can be improved by introduction of a linker between the molecular spacer and the head-group. In particular, a short aliphatic chain of a proper length was found to be a suitable linker for oligophenyl SAMs with thiolate and selenolate headgroups.<sup>31–35</sup>

In this study, we prepared and characterized SAMs formed on Au(111) from newly synthesized free-base porphyrinfunctionalized OPE (1–3), Scheme 1, with the common structure P–OPE–AG (P and AG are porphyrin and anchor group, respectively) and three different AGs, *viz.* an acetyl protected thiol, –S–COCH<sub>3</sub> (1), an acetyl protected thiol with methylene linker, –CH<sub>2</sub>–S–COCH<sub>3</sub> (2), and a trimethylsilylethynyl group, –C $\equiv$ C–Si(CH<sub>3</sub>)<sub>3</sub> (3). For the first two anchor moieties, the acetyl protecting groups are used to avoid the problem associated with oxidation, disulfide formation and a multitude of possible side reactions during synthesis.<sup>36,37</sup> The acetyl groups are expected to be removed upon the adsorption, resulting in the formation of a thiolate–gold bond.<sup>36</sup> In the

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Scheme 1 (i) Pd<sub>2</sub>(dba)<sub>3</sub>, triphenylphosphine, diisopropylethylamine, THF, 40 °C, 12 h; (ii) Pd<sub>2</sub>(dba)<sub>3</sub>, triphenylarsine, TEA, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, 40 °C, 12 h.

case of **2**, by inserting a methylene linker in-between the sulfur and the OPE moiety, we intended to achieve an improvement of orientational order and increase of the packing density, as occurring in oligophenyl-substituted alkanethiol and alkaneselenol SAMs on gold.<sup>31–35,38,39</sup> The above adsorbates with the linker consisting of an odd number of the methylene groups were found to be densely packed and less inclined on Au than the respective oligophenylthiol SAMs themselves.<sup>33,38,39</sup> In the case of 3, we took into account that the high reactivity displayed by the acetyl group in thiophenolesters can complicate or even make the syntheses of complex molecules impossible. A less labile group, still suitable for the SAM formation, would therefore be of vital importance for the successful construction of functionalized molecules of the complexity necessary for future applications. One such group might be the trimethylsilyl (TMS) group, a well established protective group in organic synthesis with a desirable reactivity pattern, which has been shown to be suitable for the formation of SAMs when attached to alkynes. However, the interaction of the trimethylsilyl with the gold surface is still unknown. For that reason, we have chosen to explore the TMS-ethynyl group as the molecular anchor. Our recent experiments on a series of OPEs with the different TMS-based anchors showed that the TMS-ethynyl group supports the formation of SAMs on Au(111).<sup>37</sup>

The headgroup–substrate interface in the films of this study was characterized by high resolution X-ray photoelectron spectroscopy (HRXPS). This technique was also used to determine the composition and effective thickness of the films. The chemical and structural information on the systems under consideration was provided by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy; this technique provides an information which is complementary to HRXPS. The structure, packing density, and the orientation of the films comprised of porphyrin-functionalized OPEs were analyzed and compared with those for OPE SAMs without a porphyrin tailgroup.

## 2. Experimental

## 2.1 Synthesis

5-(3, 5-Di-*tert*-Butylphenyl)-2, 8, 12, 18-tetraethyl-3,7,13,17-tetramethyl-15-{4- [4- (4-acetylthiophenylethynyl) phenylethynyl]phenyl}porphyrin (1). To 1-Acetylthio-4(4'-ethynyl)phenylethynyl)benzene (9.0 mg, 33  $\mu$ mol), 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-*p*-iodophenylporphyrin (21 mg, 24  $\mu$ mol) and triphenylphosphine (15 mg, 55  $\mu$ mol) put under an argon atmosphere and dry toluene (10 ml) and diisopropylethylamine (2 ml) were added, followed by bubbling with argon for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (9.9 mg, 9.6 µmol) was added and the reaction mixture was stirred at 40 °C for 12 h and then concentrated to give a red solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and added to a short silica pad, washed with CH<sub>2</sub>Cl<sub>2</sub>, and eluted with diethylether. Evaporation of the solvent gave a red solid which was purified by column chromatography (pentane/diethylether, 10 : 1 followed by pentane/diethylether, 1 : 1) followed by SEC (toluene) to give **1** as a red solid (7 mg, 6.9 µmol, 29%); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  –2.44 (br s, 2H), 1.50 (s, 18H), 1.77 (m, 12H), 2.45 (m, 9H), 2.55 (s, 6H), 3.97–4.06 (m, 8H), 7.43 (d, 2H), 7.58–7.62 (m, 4H), 7.69 (d, 2H), 7.80 (m, 1H), 7.90 (d, 2H), 7.93 (d, 2H), 8.10 (d, 2H), 10.23 (s, 2H); HRMS (FAB) calculated for [C<sub>70</sub>H<sub>73</sub>N<sub>4</sub>OS] + 1017.5506, found 1017.5504.

**5-(3,5-Di**-*tert*-**Butylphenyl**)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[4-(4-acetylthiomethylphenylethynyl)phenylethynyl]phenyl}porphyrin (2). Using the same reaction conditions as for 1, with the exception that the quota toluene/diisopropylethylamine was 10:3, 5-(3,5-di-*tert*-butylphenyl)-2, 8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-para-iodophenylporphyrin (21 mg, 24 µmol) and 1-acetylthiomethyl(-4-(4-ethynyl)-phenylethynyl)benzene (10 mg, 33 µmol) was coupled. The crude product was purified to give 2 as a red solid (18 mg, 17 µmol, 61%); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ -2.43 (br s, 2H), 1.51 (s, 18H), 1.78 (m, 12H), 2.39 (s, 3H), 2.46 (s, 6H), 2.55 (s, 6H), 3.98–4.06 (m, 8H), 4.15 (s, 2H), 7.31 (d, 2H), 7.50 (d, 2H), 7.60 (d, 2H), 7.68 (d, 2H), 7.81 (m, 1H), 7.90–7.96 (m, 4H), 8.11 (d, 2H), 10.24 (s, 2H)); HRMS (FAB) calculated for [C<sub>71</sub>H<sub>75</sub>N<sub>4</sub>OS] + 1031.5662, found 1031.5675.

5-(3,5-Di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[4-(4-trimethylsilylethynylphenylethynyl)phenylethynyllphenyl porphyrin (3). 1-Iodo(-4(4'-trimethylsilylethynyl) phenylethynyl)benzene (3.5 mg, 8.7 µmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.74 mg, 0.71 µmol) and triphenylarsine (1.3 mg, 4.2 µmol) were put under an argon atmosphere. To the mixture, a solution of P2 (0.67 ml, 10 µmol) in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> (2.33 ml) was added, followed by addition of MeOH (3 ml) and TEA (80 µl). The reaction mixture was stirred at ambient temperature overnight and then concentrated affording a brownish solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and added to a silica pad, washed with CH<sub>2</sub>Cl<sub>2</sub>, and eluted with diethylether. Subsequent evaporation and SEC (toluene) gave 3 as a red solid (4.7 mg, 4.5  $\mu$ mol, 52%); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  -2.43 (br s, 2H), 0.26 (s, 9H), 1.50 (s, 18H), 1.78 (m, 12H), 2.46 (m, 6H), 2.56 (s, 6H), 3.97-4.07 (m, 8H), 7.46-7.53 (m, 4H), 7.60 (d, 2H), 7.69 (d, 2H), 7.81 (m, 1H), 7.91 (d, 2H), 7.94 (d, 2H), 8.11 (d, 2H), 10.24 (s, 2H) HRMS (FAB) calculated for  $[C_{73}H_{79}N_4Si]$  + 1039.6075, found 1039.6061.

**1-(S-Acetylthiomethyl)-4-[4-(4-phenylethynyl)phenylethynyl] benzene (5).** 1-Ethynyl-4-(phenylethynyl)benzene<sup>40,41</sup> (26 mg, 0.13 mmol), 1-acetylthiomethyl-4-iodobenzene<sup>42</sup> (48 mg, 0.17 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5.1 mg, 4.9 µmol), triphenylphosphine (7.9 mg, 30 µmol), and CuI (2.0 mg, 11 µmol) were dissolved in THF (5 ml) and diisopropylethylamine (5 ml) under argon. The solution was stirred for 20 h at ambient temperature, filtered, and concentrated to afford a brown solid. The solid was dissolved in boiling hexane/DCM (4:1), and after cooling, a dark brown precipitate was filtered off. The filtrate was concentrated to give the desired product as a yellowish solid. Flash chromatography (hexane/DCM, 2:3) yielded a solid which was recrystallized in hexane to afford **5** as a light red solid (12 mg, 33  $\mu$ mol, 25%); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.28 (s, 9H), 7.36 (m, 3H), 7.50–7.57 (m, 10H). Elemental analysis calcd (%) for C<sub>25</sub>H<sub>18</sub>OS C: 81.93 H: 4.95, found C: 81.75 H: 4.86.

**Materials.** Reagents and solvents were purchased from Acros and Aldrich and used without further purification. Tetramethylsilane was used as reference for the chemical shifts ( $\delta_{\rm H} = 0$  ppm) in NMR experiments. Solvents were dried by distillation under nitrogen, triethylamine (TEA) from calcium hydride and toluene and tetrahydrofurane (THF) from sodium/benzophenone. Inert argon atmosphere was applied by three repetitive vacuum-argon cycles that replaced the atmosphere above the reactants. Solvents were removed using a rotary evaporator at reduced pressure unless stated otherwise. Reference compounds **4**<sup>43</sup> and **6**<sup>44</sup> (Fig. 1) were prepared according to published procedures.

Gold substrates were purchased from Georg Albert PVD-Beschichtungen (Heidelberg Germany). They were prepared by thermal evaporation of 300 nm of gold onto mica. Then the gold films were flame-annealed with a butane torch in air until they reached the point where the orange glow was visible. After that the samples were immediately quenched and stored in argon.<sup>45-47</sup> This resulted in a polycrystalline film with (111) orientation of the individual crystallites.<sup>45,47</sup> The substrates were stored under argon before film preparation and used without further cleaning.

**Methods.** Column chromatography was performed on silica gel (Matrex, normal phase, LC60Å/35–70  $\mu$ m). The porphyrin systems were purified using size exclusion chromatography (SEC) (Bio-Rad, Bio-beads S-X3, 200–400 mesh). Proton (400 MHz) NMR spectroscopy was performed on a Varian UNITY-400 NMR spectrometer, while carbon (100.6 MHz) NMR was performed on a JEOL Eclipse 400 apparatus, both at ambient temperature in CDCl<sub>3</sub>.

## 2.2 SAM preparation

The target compounds **1–3** were dissolved in THF to give a 1 mM solution. The gold substrate was immersed into 1–2 ml of this solution for 20 h; the reaction vessels were kept in argon, at room temperature, and in the dark. In the case of compounds **1** and **2**, an excess (2–3 drops) of a 1% ammonium hydroxide solution in THF (prepared from ammonium hydro-xide, 25–30% NH<sub>3</sub>) was added to the reaction vessels to remove the acetyl protective group and form the free thiol. Later, the assembly formed the thiolate upon exposure to the gold surface. For the silane, **3**, no such additional activation was needed. After the immersion, the samples were thoroughly rinsed with THF (several times), dried with nitrogen and stored under argon in the absence of light to avoid oxidation



Fig. 1 Reference OPE-based systems.

and photoinduced degradation.<sup>48,49</sup> Additional cleaning of the samples using sonication was regretfully not possible due to flaking of the gold substrate. As discussed below, it is uncertain whether all three molecular layers can be regarded as true SAMs. However, for simplicity, we use the notation SAM 1, SAM 2 and SAM 3 for molecular layers formed from compound 1, 2, and 3, respectively.

## 2.3 High-resolution X-ray photoelectron spectroscopy (HRXPS)

The SAMs were characterized by synchrotron-based HRXPS. The measurements were carried out at the synchrotron storage ring MAX II at MAX-lab in Lund, Sweden, using the beamline D1011. The beamline is equipped with a Zeiss SX-700 plane-grating monochromator and a two-chamber ultrahigh vacuum experiment station with a SCIENTA type analyzer. The spectra were acquired in normal emission geometry. The Au 4f and C 1s spectra were collected at photon energies of 350 and 580 eV. The photon energies of 350 and 160 eV were used to probe the S 2p and Si 2p core level regions, respectively. The N 1s region was also monitored with photon energy 580 eV. The binding energy (BE) scale of every spectrum was calibrated using the Au  $4f_{7/2}$  emission line of a dodecanethiol SAM on an Au substrate at 83.95 eV.<sup>50</sup> The energy resolution of the spectrometer was better than 100 meV. The HRXPS spectra were fitted by a symmetric Voigt function with a variable Lorentz-Gauss ratio,<sup>51</sup> and a Shirley background.<sup>52</sup> The S  $2p_{3/2,1/2}$  doublets were fitted by using a 1.2 eV spin-orbit splitting and a branching ratio (S  $2p_{3/2}/S 2p_{1/2}$ ) of 2. The Si 2p<sub>3/2,1/2</sub> doublets were fitted by using a spin-orbit splitting of 0.6 eV. Both  $2p_{3/2,1/2}$  components were fitted with the same full width at half-maximum (fwhm). If there were several different species in a particular spectrum, the same fwhm was used for all individual emissions related to the same core level. The effective film thicknesses were estimated using the intensity ratio of the C 1s and Au 4f signals and standard attenuation lengths.53,54

# 2.4 Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy

This technique can give information about the electronic and structural properties of molecular films by probing electron transitions from core-levels to unoccupied molecular orbitals which are characteristic of specific bonds or functional groups.<sup>55</sup> Furthermore, the average molecular orientation can be determined by monitoring the intensity variation of the absorption resonances in the spectra when the X-ray incidence angle is varied. The NEXAFS measurements of SAM 1-3 were performed at the same beamline and experimental station as in the case of HRXPS. In addition, the NEXAFS spectra of the building blocks of molecules 1-3, viz. three reference OPE systems with corresponding anchor moieties but without the porphyrin tailgroup (Fig. 1), were measured at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin (Germany). Both the MAX-lab and BESSY II spectra were acquired at the C K-edge in the partial electron yield mode with a retarding voltage of -150 eV. The incidence angle of the light was varied from  $90^{\circ}$  (*E*-vector in the surface plane) to  $20^{\circ}$  (*E*-vector near surface normal) to monitor the molecular orientation. The NEXAFS spectra were normalized to the incident photon flux by dividing the raw spectrum by a spectrum of a clean, freshly sputtered gold substrate. The spectra were then reduced to the standard form by setting the pre-edge region to zero and normalization to the height of the absorption edge.

## 3. Results

## 3.1 Synthesis

Three free-base porphyrin systems were synthesized (Scheme 1). These systems are characterized by different groups responsible for the attachment of the SAM-constituent to the gold substrate, viz. an acetyl protected thiophenol, benzylic thiol, and a TMS-ethynyl group. The syntheses of the OPE building blocks 1B, 2B and 3B (see Scheme 1) and the porphyrins P1 and P2 have been reported elsewhere.<sup>56-58</sup> Terminal alkynes and aryl halides are normally cross-coupled by palladium catalysis in the presence of cuprous salts. However, since copper can be readily inserted into the porphyrin cavity, copper-free conditions had to be used for the preparation of compounds 1-3. Compound 3 was prepared in a satisfactory yield by a cross-coupling of the acetylene functionalized porphyrine P2 with the bridge-building block 3B using the conditions optimized for couplings of substrates of this kind.41,59 Due to the high reactivity of the acetyl protection group towards nucleophiles, other coupling conditions were necessary for the preparation of compounds 1 and 2.60 The sterically hindered and less nucleophilic diisopropylethylamine had to be used as the base instead of more favourable bases with higher nucleophilicity. Also triphenylarsine, a preferred ligand under copper-free conditions, interfered with the acetyl protective group and the less efficient triphenylphosphine had to be used.<sup>61</sup> The substantial difference in obtained yields of compounds 1 and 2 reflects the difference in stability of the two different acetyl-protected thiols towards nucleophiles. In contrast to the high lability of the acetyl-protected thiols, the TMS-ethynyl group is stable under a large variety of reaction conditions. This would make it an attractive anchor group if it supports the formation of high-quality SAMs.

### 3.2 HRXPS measurements

The S 2p, Si 2p, and Au 4f HRXPS spectra were examined to characterize the binding motif of the molecules 1–3 to the Au surface. The S 2p spectra of both thiol-derived porphyrin SAMs are shown in Fig. 2. Both spectra show a relatively poor signal-to-noise ratio, which mostly results from the attenuation of the initially weak S 2p signal (there is just 1 monolayer of S) by the thick hydrocarbon overlayer. The quality of the spectra further deteriorated due to a very intense inelastic background at the position of the S 2p emission; this background originates from the Au 4f emission of the gold substrate. Note that the spectra acquisition time was limited by possible X-ray induced damage, so that the spectra statistics could not be improved significantly.

In spite of the poor signal-to-noise ratio, one can clearly see that the S 2p spectrum of SAM 1 does not represent a single S  $\,$ 



Fig. 2 S 2p HRXPS spectra of SAMs 1 and 2 (the respective target molecules contain a sulfur headgroup). The spectrum of SAM 1 was decomposed into two components (thin solid line). The background is shown by dotted lines. The BE of the S  $2p_{3/2}$  peak in the thiolate-related doublet is indicated.

 $2p_{3/2,1/2}$  doublet with a characteristic branching ratio of 2:1. At the same time, this spectrum can be tentatively described as a superposition of two doublets (see the respective spectrum decomposition in Fig. 2). The BE position of the first doublet is ~162 eV (S  $2p_{3/2}$ ). This energy is characteristic of the thiolatetype sulfur bound to the metal surface  $^{62-66}$  indicating that a significant part of the molecules 1 bind to the gold substrate through the thiolate anchor. Another doublet at a BE of ~163.5 eV (S  $2p_{3/2}$ ) is usually associated with a disulfide or unbound sulfur.<sup>67</sup> This doublet can presumably indicate the occurrence of residual physisorbed molecules at the SAMambient interface, which could not be removed in spite of the extensive washing of the samples. Alternatively, this doublet could arise from an intercalation of the unbound molecules with the bound ones due to the  $\pi$ - $\pi$  interaction between the OPE moieties and the porphyrin groups. However, we consider this second scenario as less probable or, at least, occurring to a minor extent, since such an intercalation will presumably destroy the orientational order in the film, which is not the case (see below). The relative contributions of the chemi- and physisorbed species were estimated from the ratio between the intensity of the respective doublets and the total intensity of the S 2p signal. However, for the physisorbed species, the molecules were assumed to reside at the SAM-ambient interface, which is, in our opinion, the most probable scenario. Therefore, the intensity of the peak related to the physisorbed molecules has to be scaled down to correct for the lack of attenuation of the respective S 2p signal. For this correction, the film thicknesses obtained from the intensity ratio of the C 1s and Au 4f signals (see below) and the attenuation length given by Lamont et al.54 were used. As a result, the ratio between bound and unbound sulfur was estimated to be 98:2 for SAM 1. (If the lack of attenuation is not taken into account, the ratio between bound and unbound sulfur will be 62:38.) Although these values are not exact because of the poor signal-to-noise ratio of the S 2p spectra and the possible effect of a partial intercalation, they clearly indicate, nevertheless, that most of the molecules in the films are attached to the substrate by the thiolate–gold bond.

The intensity of the S 2p features for SAM 2 is lower than that for SAM 1, but the form of this spectrum is quite similar, so that it can also be tentatively described as a superposition of two components assigned to the bound (by thiolate anchor) and unbound molecules. Whereas a spectra decomposition is even less reliable than that for the case of SAM 1, it is clearly seen that the major spectra weight is at about 162.0 eV, which is characteristic of the thiolate–gold bond. Therefore, it can be assumed that the majority of the molecules in SAM 2 were bonded to the substrate by the respective anchor.

For SAM 3, the interaction of TMS-acetylene,  $\mathbf{R}$ -C  $\equiv$  C-Si(CH<sub>3</sub>)<sub>3</sub>, with the gold substrate being investigated by probing the Si 2p core levels. The respective spectrum is shown in Fig. 3. Note that at the same packing density in films 1-3, the total intensity of the Si 2p signal is expected to be higher than that of the S 2p signal by a factor of 3 due to the photoionization cross section difference for the given photon energies and core levels.<sup>68</sup>

Due to the small spin–orbit splitting of both components, the Si  $2p_{3/2,1/2}$  doublet looks like a single slightly asymmetric peak. There is only one such peak in the Si 2p spectrum of SAM 3. The BE of this peak is 101.9 eV, which is characteristic of the Si–C bond in the TMS group.<sup>69,70</sup> The fwhm of this peak is 1.2 eV. In recent studies of the alkylsilane ( $C_nH_{2n-1}$ SiH<sub>3</sub>) SAMs on Au, the Si  $2p_{3/2,1/2}$  peak was observed at a BE of 99.8 eV and with fwhm of 0.4 eV.<sup>71,72</sup> It was proposed that three Si–H bonds are cleaved during the SAM formation, and then Si atoms form three covalent bonds to the gold surface.<sup>71,72</sup> In the case of the TMS–ethynyl system of this study,



Fig. 3 Si 2p HRXPS spectrum of SAM 3. The Si  $2p_{3/2}$  and Si  $2p_{1/2}$  components are merged in an asymmetric peak. The BE and fwhm of this peak are indicated.





**Fig. 4** Au  $4f_{7/2}$  HRXPS spectra of a clean Au and SAMs 1–3. The BE and fwhm of the Au  $4f_{7/2}$  peaks and their components are indicated.

the observed BE position of the Si 2p peak (101.9 eV) is higher, which indicates that not all Si–CH<sub>3</sub> bonds are cleaved upon the film formation. This suggests that the binding of molecules **3** to the Au surface is different from the alkylsilane case. Importantly, the Si 2p signal for SAM **3** is quite intense which would not be the case if the respective molecule did not bind to the Au surface, since all (or almost all) physisorbed species should be removed when the samples were thoroughly rinsed with the solvent during the SAM preparation.

The Au  $4f_{7/2}$  spectra of clean gold substrate and SAM 1–3 acquired at a photon energy of 350 eV are presented in Fig. 4. The spectrum of the clean gold substrate shows two components at BEs of 83.95 and 83.62 eV (with fwhm of 0.40 eV). They are assigned to gold atoms in the bulk and in the topmost layer, respectively.<sup>73–76</sup> In contrast, the spectra of all SAMs of this study exhibit just a single peak. We interpret this peak as the result of the adsorbate-induced shift of the Au  $4f_{7/2}$  surface component.<sup>73,74,76</sup> Note that the relatively low Au 4f signal intensity for SAM 1 indicates a thicker film as compared to SAMs 2 and 3.

The C 1s spectra of SAMs 1–3 are shown in Fig. 5. The total C1s intensity for SAM 1 is significantly higher than that for SAM 2, which, in its turn, is much higher than that for SAM 3. The main emission peaks were observed at BEs of 284.7, 284.4, and 284.3 eV for SAMs 1, 2, and 3, respectively. These peaks are composed of the C 1s emissions originated from both OPE moiety and porphyrin group. However, these different contributions merge and cannot be unequivocally resolved by curve fitting, but are just reflected in a rather large fwhms ( $\sim$ 1.2–1.3 eV) of the joint peak as compared to porphyrin-free



**Fig. 5** C 1s HRXPS spectra of SAMs 1–3. The BE and fwhm of the individual peaks are indicated. The spectra were acquired at a photon energy of 350 eV.

systems (0.86 eV).<sup>77</sup> For SAMs **2** and **3**, the main C 1s peak is accompanied by a small shoulder at a higher BE of 285.6–286.0 eV. This shoulder is most probably related to contamination, although analogous features have previously been observed for different aromatic SAMs and were alternatively assigned to either the carbon atom bound to the sulfur headgroup or a shake-up process.<sup>78–81</sup>

In Fig. 6, N 1s HRXPS spectra of SAMs 1-3 are presented. For SAM 1, two N 1s emissions at BEs of 396.7 and 398.7 eV were observed (with a fwhm of 1.0 eV). They can be assigned to two chemically different nitrogen atoms present in the freebase porphyrin, i.e. N and NH, respectively. In this case, the intensity ratio of these two peaks (N: NH = 43: 57) is close to the expected stoichiometric value (1:1). Also, the BE difference between the peaks (2.0 eV) agrees well with the values typically observed in free-base porphyrins (2.1  $\pm$  0.1 eV).<sup>82–84</sup> At the same time, the absolute BE positions of these peaks are lower by  $\sim 1.0$  eV compared to those for free-base octaethylporphyrins.<sup>82,85</sup> This is presumably related to the difference in substitution patterns between topical porphyrin and octaethylporphyrin. The N 1s electrons in a macrocycle are very sensitive to perturbations.<sup>82,86</sup> Compared to octaethylporphyrin, which has hydrogen atoms in the 5 and 15 positions, the topical porphyrins are substituted with a phenyl ring and an OPE moiety on two opposite meso positions. Consequently, nitrogen atoms gain an additional electron density from the



Fig. 6 N 1s HRXPS spectra of SAMs 1–3. Peak positions are indicated. The spectra were acquired at a photon energy of 580 eV.

*meso* substituents, which results in a downward shift of the respective emissions.

In contrast to SAM 1, the N 1s spectra of SAMs 2 and 3 show only a single peak at 398.7 and 398.6 eV, respectively (with a similar fwhm of 1.0 eV). This result is unexpected for a free-base porphyrin, and the origin of this phenomenon is not completely clear (see below). Note that a single N 1s peak is commonly observed in metalloporphyrins, in which all four nitrogen atoms become equivalent.<sup>82,87</sup> In particular, Yasseri *et al.* have observed a single N 1s peak at BE of 398.2  $\pm$  0.1 eV in the SAM bearing the OPE bridge, zinc porphyrin as a tailgroup, and the same anchor moiety as 2.<sup>22</sup>

The effective thickness of films 1-3 was estimated on the basis of the Au 4f and the C 1s XPS spectra acquired at a photon energy of 580 eV and the standard attenuation lengths for the Au 4f and C 1s emission.<sup>53</sup>

$$\frac{I_{\rm C}}{I_{\rm Au}} = k \frac{1 - \exp\left[\frac{-(d_{\rm eff} - d_{\rm S(or Si)})}{\lambda_{\rm C}}\right]}{\exp\left[\frac{-d_{\rm eff}}{\lambda_{\rm Au}}\right]}$$
(1)

where  $I_{\rm C}$  and  $I_{\rm Au}$  are the total intensity of the C 1s and Au 4f signals, respectively, k is an instrument-specific constant for a given photon energy,  $\lambda_{\rm C}$  and  $\lambda_{\rm Au}$  are the attenuation lengths for the C 1s and Au 4f photoelectrons, respectively, at the given kinetic energy,  $d_{\rm s(or~Si)}$  is the S–Au or Si–Au distance, both assumed to be 1.8 Å and  $d_{\rm eff}$  is the effective thickness of

the film. The k value was determined using the reference system of hexadecanethiolate SAM on Au(111).  $\lambda_{\rm C}$  and  $\lambda_{\rm Au}$  were obtained using the expression  $\lambda = 0.3 E_{\rm kin}^{0.64}$  for alkanethiolate SAMs.<sup>54</sup> The resulting values of the effective thickness obtained for SAMs **1**, **2**, and **3** are 2.9, 1.2, and 1.1 nm, respectively.

#### 3.3 NEXAFS measurements

The C *K*-edge NEXAFS spectra of SAMs 1–3 acquired at an X-ray incidence angle of 55° are shown in Fig. 7 (top curves) along with the spectra of the reference OPE SAMs with corresponding anchor moieties but without the porphyrin group (bottom curves). The positions of the observed absorption resonances and those for the porphyrin endgroup<sup>88,89</sup> (as a reference) are indicated. Note that at this particular geometry (close to magic angle of X-ray incidence,  $\theta = 54.7^{\circ}$ , see eqn (2) below) the spectra are exclusively representative of the electronic structure of the target systems and are unaffected by molecular orientation.<sup>55</sup>

The spectra of all SAMs comprised of the non-substituted molecules in Fig. 7 (bottom curves) exhibit a dominant peak at ~285.0 eV assigned to the  $\pi_1^*$  resonance of the phenyl rings in OPE moiety. This peak is accompanied by a weaker  $\pi_2^*$  resonance at ~288.6 eV and broad  $\sigma^*$  resonances at higher photon energies of 293.5 and ~303 eV. The C *K*-edge NEX-AFS spectrum of porphyrin (from ref. 86 and 87) exhibits a  $\pi^*$  resonance at 285.2 eV, a  $\sigma^*$  resonance at 287.3 eV (assigned to the C–H moieties in the alkyl groups surrounding the porphyrin), a further  $\pi^*$  resonance at 288.3 eV, and broad  $\sigma^*$  resonances at about 294 and 303 eV.

The NEXAFS spectra of SAMs 1–3 (Fig. 7 top curve) can be fairly described as a superposition of the spectrum of the respective reference OPE SAM and the spectrum of porphyrin with a clear dominance of the contribution from the porphyrin moiety. At the same time, whereas the shapes of the spectra for SAMs 1 and 2 are quite similar, they differ to some extent from that for SAM 3. The latter spectrum exhibits a weak  $\pi_1^*$ resonance structure and a clear signature of contamination, *e.g.* a  $\pi^*$  resonance related to C=O moiety at 288.6 eV.

The average orientation of the molecules in the target SAMs can be estimated by monitoring the linear dichroism of the NEXAFS spectra, *i.e.* dependence of the absorption resonance intensity on the X-ray incidence angle. Generally, the intensity of a NEXAFS resonance depends on the orientation of the electric field vector (*E*-vector) of the incidence light with respect to the transition dipole moment (TDM) of the probed transition.<sup>55</sup> The intensity is maximal if the *E*-vector direction and the TDM are parallel to each other and is equal to zero if they are orthogonal. Furthermore, a pronouced linear dichroism in the NEXAFS spectra implies an orientational order in the film. These linear dichroism effects disappear when the molecules are randomly oriented or when the TDM of the molecules is oriented with a tilt angle  $\alpha = 54.7^{\circ}$  (magic angle) with respect to surface normal (see eqn (2) below).

The C K-edge NEXAFS spectra of SAMs 1–3 acquired at X-ray incidence angles of 20, 55, and 90° are shown in Fig. 8, along with the respective differences between the 90 and 20° spectra. For SAM 1, the  $\pi^*$  resonances are more intense



**Fig. 7** The C *K*-edge NEXAFS spectra of SAM **1** (a), **2** (b), and **3** (c) (top curves) in comparison with the spectra of the reference OPE SAMs on Au with corresponding anchor moieties but without the porphyrin tailgroup (bottom curves); the positions of the characteristic absorption resonances are indicated by dotted lines. All spectra were acquired at an X-ray incidence of  $55^{\circ}$ . The positions of the characteristic absorption resonances of the porphyrin tailgroup<sup>88,89</sup> are indicated by the solid lines.

at normal than at grazing incidence while the  $\sigma^*$  features exhibit the opposite behavior. Considering that the TDMs for the transition to the  $\pi^*$  and  $\sigma^*$  orbitals are oriented perpendicular to and along the molecular axis, respectively, the observed linear dichroism suggests that, on average, the constituents of SAM 1 have an almost upright orientation and the SAM is well-ordered. Since the orientational order results from intermolecular interaction, SAM 1 can be assumed to be densely packed as well. The film thickness derived from XPS data corresponds well with these results for SAM 1 (see below). In contrast, for SAM 2, the intensity of  $\pi^*$  resonances decreases with increasing X-ray incidence angle, which means that its constituents are significantly inclined. Also, XPS- derived thickness is very low for SAM 2, supporting a large inclination of the molecules with a low packing density in this film. Finally, the NEXAFS spectra of SAM 3 exhibit almost no linear dichroism. This can either indicate that the film has a low orientational order or the molecules are strongly inclined with the average tilt angle of the TDM close to the magic angle ( $\alpha = 54.7^{\circ}$ ). At this particular angle, the NEXAFS intensity does not depend on the angle of light incidence (see eqn (2)). It is principally not possible to distinguish between these two possibilities on the basis of the NEXAFS data alone. However, a comparison between the film thickness derived from NEXAFS and XPS data (see below) and a very weak  $\pi_1^*$  resonance, which is characteristic of both OPE moiety and



Fig. 8 The C K-edge NEXAFS spectra of SAMs 1–3 acquired at X-ray incidence angles of 90, 55, and  $20^{\circ}$ , along with the difference between the 90 and  $20^{\circ}$  spectra. The dashed line corresponds to zero.

porphyrin tailgroup, suggested that SAM 3 has a poorly defined orientational order.

We have previously found, in accordance with the literature data, that reference compound 4 (same as 1, but without the porphyrin tailgroup) forms a highly oriented and a densely packed SAM, with the SAM constituents being almost upright.<sup>77,90–92</sup> Along with the above results for SAM 1, this suggests that the anchor group 1 (R-S-) is suitable for the SAM formation. In contrast, the NEXAFS spectra of the film formed from the reference compound 5 (same as 2, but without the porphyrin tailgroup), in Fig. 9 show a similar "negative" dichroism as the spectra of SAM 2, suggesting that it is not the porphyrin tailgroup but the CH<sub>2</sub> linker that is responsible for the low quality of the film.

Apart from the above qualitative considerations, the average tilt angle of the SAM constituents can be determined from numerical analysis of the NEXAFS data.<sup>55</sup> The average tilt angle  $\alpha$  of the respective TDM with respect to the surface normal is given by

$$I(\theta,\alpha) \propto 1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\alpha - 1)$$
(2)

OPE with CH<sub>2</sub> linker

90°

55°

20°

**NEXAFS: C1s** 



difference spectrum 90°-20°

where  $I(\theta, \alpha)$  is the intensity of the selected absorption resonance and  $\theta$  is the X-ray incidence angle. The TDM tilt angle  $\alpha$  is related to the average tilt angle of the molecular axis  $\varphi$  and the twist angle  $\gamma$  of the molecule with respect to the plane spanned by the surface normal and molecular axis by

$$\cos \alpha = \cos \gamma \sin \varphi \tag{3}$$

For the evaluation, the  $\pi_1^*$  resonance at photon energy ~285.0 eV has been selected as the most pronouced absorption feature in the spectra, and the intensity ratios  $I(\theta)/I(20^\circ)$  were used instead of the absolute intensities to avoid normalization problems. The average tilt angles  $\alpha$  of the  $\pi_1^*$  TDM for SAMs 1, 2 and 3 were determined to be 61, 49, and 55°, respectively. Assuming the twist angle to be 32°, as found from the prior experimental results of thioaromatic SAMs (*e.g.* oligo(phenyleneethynylene)),<sup>32,90,93</sup> the average tilt angles of the molecular axis  $\varphi$  were estimated to be ~ 35, 50 and 42° for SAMs 1, 2 and 3, respectively. However, it is likely that the OPE moiety and porphyrin tailgroup are not in-plane, but are rotated with respect to each other by 90° around the molecular axis.<sup>94</sup> This makes the estimated values of the average tilt angles somewhat uncertain.

NEXAFS data can be used to estimate the effective thickness on the basis of the derived average tilt angles. Taking a theoretical length of the molecule  $d_{\text{theo}}$ , spacing  $d_{\text{S} \text{ (or Si)}} = 1.8 \text{ Å for S-Au or Si-Au distances and the NEXAFS-derived average tilt angle <math>\varphi$ , the effective thickness  $d_{\text{eff}}$  of the film can be calculated by

$$d_{\rm eff} = d_{\rm theo} \cos \varphi + d_{\rm s} \tag{4}$$

Assuming SAMs 1, 2, and 3 are well ordered with the respective average molecular tilt angle derived by NEXAFS, the NEXAFS-estimated thicknesses will be 2.9 nm for SAM 1, 2.3 nm for SAM 2 and 2.8 nm for SAM 3. The NEXAFS-derived thickness for SAM 1 is in good agreement with the thickness obtained by XPS. This supports an ordered layer with a molecular tilt angle of  $35^{\circ}$  for SAM 1, as shown by the angular dependence in the NEXAFS spectra. In contrast, the NEXAFS-derived thicknesses for SAM 2 and 3 give a much higher value compared to the XPS results. This discrepancy suggests a low orientational order in those two SAMs.

#### 4. Discussion

Monomolecular layers were prepared from the porphyrin decorated oligo(phenyleneethynylene) molecules with three different anchor moieties. The HRXPS and NEXAFS data for all three films under study correlate well with each other. Both techniques consistently reveal that all the molecules form SAM-like layers on the Au substrate, but with different molecular orientation, structural order, and packing density. The C *K*-edge NEXAFS spectra of all molecular layers show the absorption resonance features which are characteristic of both OPE moiety and porphyrin tailgroup.

Both molecules 1 and 2 are bound to the substrate *via* a gold-thiolate bond as evidenced by the characteristic doublet in the S 2p XPS spectra. The molecule without the methylene

ntensity (arb. units)

linker between the OPE moiety and the sulfur (molecule 1) was found to form SAMs of significantly higher quality than the one with the linker (molecule 2). This conclusion can be drawn on the basis of both HRXPS and NEXAFS data, which suggest severe differences in the packing density and molecular inclination between SAMs 1 and 2: whereas SAM 1 has a high packing density and is comprised of almost upright standing molecules, SAM 2 exhibits a low packing density, a poor orientational order, and strongly inclined molecules. Along with the qualitative results, this conclusion is supported by clear numerical parameters such as the effective film thickness and average tilt angle of the SAM constituents. In addition, there is a subtle observation: a lower BE of the major C1s emission for SAM 2 as compared to SAM 1, implying a difference in the packing density and molecular orientation.

Furthermore, the N 1s HRXPS spectrum of SAM 1 exhibits two emission peaks, as expected for the two different nitrogen species (N and NH) in the free-base porphyrin tailgroup, while the N 1s spectrum of SAMs 2 and 3 shows a single emission peak, indicating a significant disturbance or decomposition of the porphyrin units. Since both the chemical structure of the target molecules 1-3 and preparation conditions of the respective SAMs were quite similar, we do not believe in the decomposition scenario. This belief is further supported by the observation of the characteristic absorption resonances of porphyrin in the NEXAFS spectra of SAMs 2 and 3. So, we are only left with the disturbance hypothesis. Whatever the reason for such a disturbance, it presumably resulted in the equivalency of all N atoms in the porphyrin unit as it occurs in metalloporphyrins.<sup>86,87</sup> In the present case, one may speculate that the interaction of the strongly inclined molecules with the Au substrate could lead to metal-coordinated porphyrins and be thereby responsible for the single N 1s peak. An Au coordination of the porphyrin has previously been proposed by Katsonis et al., who performed STM and XPS studies on SAM of meso-tetradodecylporphyrin on Au(111).95 However, the respective N 1s XPS spectra were quite complex and contained several peaks, even though one of them was clearly dominating.95

Another possibility of the porphyrin disturbance is the intermolecular interaction between these moieties and phenyl rings in the OPE moiety. Due to the strong molecular inclination in SAMs 2 and 3, porphyrin moieties can move sufficiently close to the phenyl rings in the OPE chains of the neighbor molecules and build complexes, kept together by the  $\pi$ - $\pi$  interaction, as observed for porphyrin and phenyl rings before.<sup>83,96–98</sup> This interaction can affect the charge distribution at the nitrogen atoms, even though it is not clear whether it can result in their equivalency. In particular, Sarno *et al.* reported that free-base porphyrins exhibit two N 1s XPS peaks regardless of any intermolecular interaction.<sup>83</sup>

In the case of molecule 2, a methylene group was inserted inbetween the sulfur and OPE moiety with the purpose of enabling the molecule to orient more upright on the surface and thereby improve the packing density in the molecular layer. Surprisingly, SAM 2 exhibits the opposite features such as strongly inclined molecules and low packing density, which correspond to a poor quality layer. Furthermore, we found that even the non-substituted OPE molecule with methylene linker (the reference compound **5**) does not form a wellordered and densely packed SAMs. This result for the OPE molecules with the methylene spacer is remarkably different from the reported behavior of oligo(phenylene)-substitued alkanethiolate and -selenolate SAMs on Au, in which wellordered and upright standing SAM constituents were observed in the films formed from the molecules with the methylene linked systems.<sup>31–35,38,79,99</sup> Also, it has been reported that methylthioacetate terminated tolane, an analogous compound to our reference **5**, formed well-ordered SAMs after incubation in vacuum at room temperature for 10 days.<sup>100</sup>

In the case of SAM 3, the respective molecules are likely to adsorb on the Au surface as indicated by an intense Si 2p doublet and the shift of the surface component of the Au 4f emission (compared to the clean Au substrate) in the HRXPS spectra. The BE position of the Si 2p emission (101.9 eV) suggests that not all the Si-CH<sub>3</sub> bonds are broken upon the adsorption. The above results are in accordance with recently reported studies which show that molecules with the same binding group,  $\mathbf{R}$ -C=C-Si(CH<sub>3</sub>)<sub>3</sub>, form SAMs on Au surfaces.<sup>101,102</sup> The reported STM images showed a densely packed arrangement with an intermolecular distance equal to the diameter of the trimethylsilyl group,  $Si-(CH_3)_3$ , which is about 5.0 Å.<sup>101,102</sup> However, the nature of the bonding between the trimethylsilyl group and Au surface is still not well understood. It has been proposed that Si becomes pentavalent and binds to the Au surface in an axial position.<sup>101-103</sup> The bound Si should have a higher binding energy compared to a clean Si sample (99.3 eV).<sup>71</sup> The observed Si 2p peak at 101.9 eV in our HRXPS spectra is consistent with this model. A very small, negative linear dichroism observed in the NEXAFS spectra of SAM 3 suggests either a large molecular inclination or/and a poorly defined monolayer consisting of randomly oriented molecules (we favor the latter model). It is reasonable to assume that the interaction between the trimethylsilyl and Au substrate is not strong enough to enable the self-assembly of such large molecules, as our OPEporphyrin moieties, which makes them strongly inclined and oriented randomly on the surface, resulting in a loosely packed film

### Conclusions

Porphyrin-functionalized OPEs with the same molecular structure but three different binding moieties. viz. acetylprotected sulfur with and without methylene linker and trimethylsilylethynyl were synthesized and used for the preparation of monomolecular films on polycrystalline Au(111) substrate. The resulting films were characterized by synchrotron-based HRXPS and NEXAFS spectroscopy. We demonstrated that molecule 1, containing the thiophenolate structure (without the methylene linker between the sulfur and the OPE moiety) forms the best quality SAMs of all three precursor molecules. According to the HRXPS and NEXAFS data, SAM 1 has a high packing density and high orientational order with a small inclination angle  $(35^{\circ})$  of the molecular adsorbates. In contrast, molecule 2, containing the methylene linker between the sulfur and the OPE moiety, which was expected to form a highly ordered and densely packed SAMs on Au, with an upright orientation of the individual constituents, shows the opposite result. Although it binds to the gold surface through the thiolate anchor similarly to SAM 1, it forms a low packing density film with poor orientational order and large inclination of the molecular adsorbates. Also, even if Si seems to bind to the gold surface, the trimethylsilyl-ethynyl group gives a low-quality molecular layer comprised of inclined and randomly oriented species. Thus, among the three porphyrin-functionalized OPEs with different anchor moieties, only the anchor group 1 is suitable for the SAM formation, even in the case of such a large tailgroup as porphyrin used in this study, while anchor moieties 2 and 3 are less suitable for the fabrication of high-quality SAMs.

#### References

- 1 F. R. F. Fan, J. P. Yang, L. T. Cai, D. W. Price, S. M. Dirk, D. V. Kosynkin, Y. X. Yao, J. M. Tour and A. J. Bard, *J. Am. Chem. Soc.*, 2002, **124**, 5550–5560.
- 2 C. D. Zangmeister, S. W. Robey and R. D. van Zee, J. Am. Chem. Soc., 2004, 126, 3420–3421.
- 3 R. W. Zehner, B. F. Persons, R. P. Hsung and L. R. Sita, *Langmuir*, 1999, **15**, 1121–1127.
- 4 F. R. F. Fan, Y. R. Lai, J. Cornil, Y. Karzazi, J.-L. Bredas, L. T. Cai, L. Cheng, Y. Yao, J. Price, D. W, S. M. Dirk, J. M. Tour and A. J. Bard, J. Am. Chem. Soc., 2004, **126**, 2568–2573.
- 5 F. R. F. Fan, Y. Yao, L. T. Cai, L. Cheng, J. M. Tour and A. J. Bard, *J. Am. Chem. Soc.*, 2004, **126**, 4035–4042.
- 6 I. H. Campbell, J. D. Kress, R. L. Martin and D. L. Smith, *Appl. Phys. Lett.*, 1997, **71**, 3528–3530.
- 7 A. Dhirani, P. H. Lin, P. Guyot-Sionnest, R. W. Zehner and L. R. Sita, J. Chem. Phys., 1997, 106, 5249–5253.
- J. M. Tour, Acc. Chem. Res., 2000, 33, 791–804.
  K. Walzer, E. Marx, N. C. Greenham, R. J. Less, P. R. Raithby
- and K. Stokbro, J. Am. Chem. Soc., 2004, **126**, 1229–1234. 10 K. Kalyanasundaram and M. Grätzel, Chem. Rev., 1998, **177**,
- 347–414.
- 11 A. J. Bard and M. A. Fox, Acc. Chem. Res., 1995, 28, 141-145.
- 12 T. Nann, U. Kielmann and C. Dietrich, *Anal. Bioanal. Chem.*, 2002, **373**, 749–753.
- 13 D. P. Arnold, D. Manno, G. Micocci, A. Serra, A. Tepore and L. Valli, *Langmuir*, 1997, **13**, 5951–5956.
- 14 A. D. F. Dunbar, T. H. Richardson, A. J. McNaughton, J. Hutchinson and C. A. Hunter, J. Phys. Chem. B, 2006, 110, 16646–16651.
- 15 D. Holten, D. F. Bocian and J. S. Lindsey, Acc. Chem. Res., 2002, 35, 57–69.
- 16 R. K. Lammi, R. W. Wagner, A. Ambroise, J. R. Diser, D. F. Bocian, D. Holten and J. S. Lindsay, *J. Phys. Chem. B*, 2001, 105, 5341–5352.
- 17 A. Ambroise, R. W. Wagner, P. D. Rao, J. A. Riggs, P. Hascoat, R. Diers, J. Seth, R. K. Lammi, D. F. Bocian, D. Holten and J. S. Lindsay, *Chem. Mater.*, 2001, **13**, 1023–1034.
- 18 H. S. Cho, N. W. Song, Y. H. Kim, S. C. Jeoung, S. Hahn and D. Kim, J. Phys. Chem. A, 2000, 104, 3287–3298.
- 19 A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly, Academic Press, California, 1st edn, 1991.
- 20 J. E. Hutchison, T. A. Postlethwaite and R. W. Murray, Langmuir, 1993, 9, 3277–3283.
- 21 K. Shimazu, M. Takechi, H. Fujii, M. Suzuki, H. Saiki, T. Yoshimura and K. Uosaki, *Thin Solid Films*, 1996, 273, 250–253.
- 22 A. A. Yasseri, D. Syomin, L. V. Malinovskii, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, J. Am. Chem. Soc., 2004, 126, 11944–11953.
- 23 M. S. Boeckl, A. L. Bramblett, K. D. Hauch, T. Sasaki, B. D. Ratner and J. W. Roger, *Langmuir*, 2000, 16, 5644–5653.
- 24 A. L. Bramblett, M. S. Boeckl, K. D. Hauch, B. D. Ratner, T. Sasaki and J. W. Roger, *Surf. Interface Anal.*, 2002, 33, 506–515.
- 25 K. M. Roth, D. T. Gryko, C. Clausen, J. Li, J. S. Lindsay, W. G. Kuhr and D. F. Bocian, J. Phys. Chem., 2002, 106, 8639–8648.

- 26 H. Imahori, H. Norieda, Y. Nishimaru, I. Yanmazaki, K. Higuchi, N. Kato, T. Motohiro, H. Yamada, K. Tamaki, M. Arimura and Y. Sakata, *J. Phys. Chem. B*, 2000, **104**, 1253–1260.
- 27 J. Zak, H. Yuan, M. Ho, L. K. Woo and M. D. Porter, *Langmuir*, 1993, 9, 2772–2774.
- 28 H. Imahori, T. Hasobe, H. Yamada, Y. Nishimaru, I. Yamazaki and S. Fukuzumi, *Langmuir*, 2001, **17**, 4925–4931.
- 29 A. M. Rawlett, T. J. Hopson, I. Amlani, R. Zhang, J. Tresek, L. A. Nagahara, R. K. Tsui and H. Goronkin, *Nanotechnology*, 2003, 14, 377–384.
- 30 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103–1169.
- 31 M. Zharnikov, S. Frey, H.-T. Rong, Y.-J. Yang, K. Heister, M. Buck and M. Grunze, *Phys. Chem. Chem. Phys.*, 2000, 2, 3359–3362.
- 32 H.-T. Rong, S. Frey, Y.-J. Yang, M. Zharnikov, M. Buck, M. Wühn, C. Wöll and G. Helmchen, *Langmuir*, 2001, 17, 1582–1593.
- 33 A. Shaporenko, M. Brunnbauer, A. Terfort, M. Grunze and M. Zharnikov, J. Phys. Chem. B, 2004, 108, 14462–14469.
- 34 P. Cyganik, M. Buck and C. Wöll, J. Phys. Chem. B, 2004, 108, 4989–4969.
- 35 A. Shaporenko, J. Muller, T. Weidner, A. Terfort and M. Zharnikov, J. Am. Chem. Soc., 2007, **129**, 2232–2233.
- 36 M. J. Tour, L. Jones, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh and S. V. Atre, J. Am. Chem. Soc., 1995, **117**, 9529–9534.
- 37 D. Nilsson, *PhD Thesis*, Chalmers University of Technology, 2007.
- 38 A. Shaporenko, M. Brunnbauer, A. Terfort, L. S. O. Johansson, M. Grunze and M. Zharnikov, *Langmuir*, 2005, 21, 4370–4375.
- 39 M. Zharnikov and M. Grunze, J. Phys.: Condens. Matter, 2001, 13, 11333–11365.
- 40 O. Lavastre, S. Cabioch, P. H. Dixneuf and J. Vohlidal, *Tetra*hedron, 1997, 53, 7595–7604.
- 41 T. Ljungdahl, K. Pettersson, B. Albinsson and J. MÅrtensson, Eur. J. Org. Chem., 2006, 2006, 3087–3096.
- 42 D. T. Gryko, C. Clausen, K. M. Roth, N. Dontha, D. F. Bocian, W. G. Kuhr and J. S. Lindsey, J. Org. Chem., 2000, 65, 7345–7355.
- 43 J. M. Tour, A. M. Rawlett, M. Kozaki, Y. X. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C. W. Zhou, J. Chen, W. Y. Wang and I. Cambell, *Chem.-Eur. J.*, 2001, 7, 5118–5134.
- 44 J. J. Hwang and J. M. Tour, Tetrahedron, 2002, 58, 10387-10405.
- 45 F. Köhn, Diploma Thesis, Universität Heidelberg, 1998.
- 46 K. Heister, PhD Thesis, Universität Heidelberg, 2001.
- 47 M. H. Dishner, M. M. Ivey, S. Gorer, J. C. Hemminger and F. J. Feher, J. Vac. Sci. Technol., A, 1998, 16, 3295–3300.
- 48 M. H. Schoenfisch and J. E. Pemberton, J. Am. Chem. Soc., 1998, 120, 4502–4513.
- 49 H. Rieley, N. J. Price, T. L. Smith and S. H. Yang, J. Chem. Soc., Faraday Trans., 1996, 92, 3629–3634.
- 50 Surface chemical analysis-X-ray photoeletron spectrometers-Calibration of the energy scales, ISO 15472, International Organization for Standardization, Geneva, Switzerland, 2001.
- 51 G. K. Wertheim, M. A. Butler, K. W. West and D. N. E. Buchanan, *Rev. Sci. Instrum.*, 1974, 45, 1369–1371.
- 52 D. A. Shirley, Phys. Rev., 1972, 5, 4709-4714.
- 53 J. Thome, M. Himmelhaus, M. Zharnikov and M. Grunze, Langmuir, 1998, 14, 7435–7449.
- 54 C. L. A. Lamont and J. Wilkes, *Langmuir*, 1999, **15** 2037–2042.
- 55 J. Stöhr, NEXAFS Spectroscopy, Springer Series in Surface Science 25, Springer-Verlag, Berlin, 1992.
- 56 O. Lavastre, L. Ollivier and P. H. D. Sibandhit, *Tetrahedron*, 1996, **52**, 5495–5504.
- 57 A. K. Flatt, Y. X. Yao, F. Maya and J. M. Tour, J. Org. Chem., 2004, 69, 1752–1755.
- 58 J. Kajanus, S. B. van Berlekom, B. Albinsson and J. Mårtensson, Synthesis-Stuttgart, 1999, 7, 1155–1162.
- 59 M. P. Eng, T. Ljungdahl, J. Andreasson, J. Mårtensson and B. Albinsson, J. Phys. Chem. A, 2005, 109, 1776–1784.
- 60 R. P. Hsung, J. R. Babcock, C. E. D. Chidsey and L. R. Sita, *Tetrahedron Lett.*, 1995, 36, 4525–4528.

- 61 K. Tomizaki, L. Yu, W. Lingyun, D. F. Bocian and J. S. Lindsey, J. Org. Chem., 2003, 68, 8199–8207.
- 62 P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh and R. G. Nuzzo, J. Am. Chem.Soc., 1991, 113, 7152–7167.
- 63 M. Zharnikov, S. Frey, K. Heister and M. Grunze, *Langmuir*, 2000, 16, 2697–2705.
- 64 R. G. Nuzzo, B. R. Zegarski and L. H. Dubois, J. Am. Chem. Soc., 1987, 109, 733–740.
- 65 M. Himmelhaus, I. B. M. Gauss, F. Eisert, C. Wöll and M. Grunze, J. Electron Spectrosc. Relat. Phenom., 1998, 92, 139–149.
- 66 C. D. Bain, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1989, **5**, 723–727.
- 67 D. G. Castner, K. Hinds and W. Grainger, *Langmuir*, 1996, 12, 5083–5086.
- 68 J. J. Yeh and I. Lindau, Atomic Data and Nuclear Data Tables, 1985, 32, 1–155.
- 69 H. Morita, R. Nozawa, Z. Bastl, J. Subrt and J. Pola, J. Photochem. Photobiol., A, 2006, 179, 142–148.
- 70 P. W. Wang, S. Bater, L. P. Zhang, M. Ascherl and J. H. Craig, Jr, *Appl. Surf. Sci.*, 1995, **90**, 413–417.
- 71 T. M. Owens, T. Nicholson, M. M. B. Holl and S. Suzer, J. Am. Chem. Soc., 2002, 124, 6800–6801.
- 72 T. M. Owens, S. Suzer and M. M. B. Holl, J. Phys. Chem. B, 2003, 107, 3177–3182.
- 73 K. Heister, M. Zharnikov, M. Grunze and L. S. O. Johansson, J. Phys. Chem. B, 2001, 105, 4058–4061.
- 74 A. Shaporenko, P. Cyganik, M. Buck, A. Terfort and M. Zharnikov, J. Phys. Chem. B, 2005, 109, 13630–13638.
- 75 A. Shaporenko, A. Ulman, A. Terfort and M. Zharnikov, J. Phys. Chem. B, 2005, 109.
- 76 T. Weidner, A. Shaporenko, J. Muller, M. Höltig, A. Terfort and M. Zharnikov, J. Phys. Chem. B, 2007, 111, 11627–11635.
- 77 D. Nilsson, S. Watcharinyanon, M. Eng, L. Li, E. Moons, L. S. O. Johansson, M. Zharnikov, A. Shaporenko, B. Albinsson and J. Mårtensson, *Langmuir*, 2007, 23, 6170–6181.
- 78 S. Frey, V. Stadler, K. Heister, W. Eck, M. Zharnikov and M. Grunze, *Langmuir*, 2001, 17, 2408–2415.
- 79 K. Heister, H.-T. Rong, M. Buck, M. Zharnikov, M. Grunze and L. S. O. Johansson, J. Phys. Chem. B, 2001, 105, 6888–6894.
- 80 C. M. Whelan, C. J. Barnes, C. G. H. Walker and N. M. D. Brown, *Surf. Sci.*, 1999, **425**, 195–211.
- 81 A. Gölzhäuser, S. Panov, A. Schertel, M. Mast, C. Wöll and M. Grunze, *Surf. Sci.*, 1995, **334**, 235–247.
- 82 P. G. Gassman, A. Ghosh and J. Almlöf, J. Am. Chem. Soc., 1992, 114, 9990–10000.

- 83 D. M. Sarno, L. J. Matienzo and W. E. Jones, Jr, *Inorg. Chem.*, 2001, 40, 6308–6315.
- 84 Z. Zhang, R. Hu and Z. Liu, Langmuir, 2000, 16, 1158-1162.
- 85 A. Ghosh, J. Fitzgerald, P. G. Gassman and J. Almlöf, *Inorg. Chem.*, 1994, 33, 6057–6060.
- 86 D. H. Karweik and N. Winograd, Inorg. Chem., 1976, 15, 2336–2342.
- 87 J. M. Gottfried, K. Flechtner, A. Kretschmann, T. Lukasczyk and H.-P. Steinruck, J. Am. Chem. Soc., 2006, 128, 5644–5645.
- 88 T. Ikame, K. Kanai, Y. Ouchi, A. Fujimori and K. Seki, *Chem. Phys. Lett.*, 2005, **413**, 373–378.
- 89 A. Ferri, G. Polzonetti, G. Iucci, G. Paolucci, A. Goldoni, P. Parent, C. Laffon, G. Contini and V. Carravetta, *Surf. Interface Anal.*, 2000, **30**, 407–409.
- 90 A. Dhirani, R. W. Zehner, R. P. Hsung, P. G. Sionnest and L. R. Sita, J. Am. Chem. Soc., 1996, 118, 3319–3320.
- 91 J. J. Stapleton, P. Harder, T. A. Daniel, M. D. Reinard, Y. Yao, D. W. Price, J. M. Tour and D. L. Allara, *Langmuir*, 2003, **19**, 8245–8255.
- 92 G. H. Yang, Y. L. Qian, C. Engtrakul, L. R. Sita and G. Y. Liu, J. Phys. Chem. B, 2000, 104, 9059–9062.
- 93 C. Fuxen, W. Azzam, R. Arnold, G. Witte, A. Terfort and C. Wöll, *Langmuir*, 2001, **17**, 3689–3695.
- 94 K. Kilså, J. Kajanus, J. Mårtensson and B. Albinsson, J. Phys. Chem. B, 1999, 103, 7329–7339.
- 95 N. Katsonis, J. Vicario, T. Kudernac, J. Visser, M. M. Pollard and B. L. Feringa, J. Am. Chem. Soc., 2006, 128, 15537–15541.
- 96 M. M. Williamson and C. L. Hill, *Inorg. Chem.*, 1987, 26, 4155–4160.
- 97 B. Jiang, S.-W. Yang and W. E. Jones, Jr, Chem. Mater., 1997, 9, 2031–2034.
- 98 C. A. Hunter and J. K. M. Sanders, J. Am. Chem. Soc., 1990, 112, 5525–5534.
- 99 Y. Tai, A. Shaporenko, H.-T. Rong, M. Buck, W. Eck, M. Grunze and M. Zharnikov, J. Phys. Chem. B, 2004, 108, 16806–16810.
- 100 Y. Jeong, C. Lee, E. Ito, M. Hara and J. Noh, Jpn. J. Appl. Phys., Part 2, 2006, 45, 5906–5910.
- 101 A. Marchenko, N. Katsonis, D. Fichou, C. Aubert and M. Malacria, J. Am. Chem. Soc., 2002, 124, 9998–9999.
- 102 N. Katsonis, A. Marchenko, S. Taillemite, D. Fichou, G. Chouraqui, C. Aubert and M. Malacria, *Chem.-Eur. J.*, 2003, 9, 2574–2581.
- 103 C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371–1448.