

# Chemical Engineering of Gallium Arsenide Surfaces with 4'-Methyl-4-mercaptobiphenyl and 4'-Hydroxy-4-mercaptobiphenyl Monolayers

K. Adlkofer,<sup>†</sup> A. Shaporenko,<sup>‡</sup> M. Zharnikov,<sup>‡</sup> M. Grunze,<sup>‡</sup> A. Ulman,<sup>§</sup> and M. Tanaka<sup>\*,†</sup>

*Lehrstuhl für Biophysik E22, Technische Universität München, James-Frank-Strasse, D-85748 Garching, Germany, Lehrstuhl für Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany, and Department of Chemical Engineering, Chemistry and Materials Science, and the NSF MRSEC for Polymers at Engineered Interfaces, Polytechnic University, Six Metrotech Center, Brooklyn, New York*

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Stable chemical engineering of stoichiometric GaAs [100] surfaces was achieved by deposition of two types of mercaptobiphenyls: 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl, which can render the surface hydrophobic and hydrophilic, respectively. Topography of the engineered surface was studied by atomic force microscopy (AFM), and the covalent binding between the thiolate and surface arsenide was confirmed by high-resolution X-ray photoelectron spectroscopy (HRXPS). Total surface free energies of the engineered surfaces as well as its dispersive and polar components were calculated from contact angle measurements. Electrochemical properties of the engineered GaAs in aqueous electrolytes were measured by impedance spectroscopy at a cathodic potential (−350 mV), demonstrating that both types of mercaptobiphenyls can form stable monolayers with high electric resistances,  $R > 2 \text{ M}\Omega \text{ cm}^2$ . The surface engineering method established here allows for control of surface free energies toward deposition of model biomembranes on GaAs-based device surfaces.

## Introduction

Surface engineering of semiconductors with bio-functional molecular assemblies has been drawing increasing attention.<sup>1–4</sup> Especially, organic self-assembled monolayers,<sup>5</sup> which can prevent the decomposition of semiconductors in aqueous electrolytes as well as provide various surface functions. Although there have been several reports on the passivation of GaAs surfaces with various types of sulfides and mercaptos in contact with air or with metals<sup>6–9</sup> to overcome the intrinsic instability of GaAs, systematic studies on the passivation of GaAs surfaces under physiological conditions (in aqueous electrolytes, near neutral pH conditions) are still missing. Previously, we reported the electrochemical passivation of GaAs surfaces under physiological conditions, i.e., at neutral pH in aqueous electrolytes, by deposition of octadecylthiol (ODT) monolayers,<sup>10,11</sup> which has further been transferred onto near-surface indium arsenide quantum dots.<sup>12,13</sup> Electrochemical stability of the engineered surface in electrolytes was significantly improved by enrichment of elemental arsenide, which serves as a binding site for sulfide, via a “photochemical etching” procedure. However, this surface pretreatment under UV irradiation often caused roughening or chemical damage of the surface. To avoid this preparation step, we recently achieved the coating of stoichiometric GaAs [100] by deposition of 4-mercaptobiphenyls, which has a more rigid and bulkier aromatic backbone.<sup>14</sup> Synchrotron-based high-resolution X-ray photoelectron spectroscopy (HRXPS) and near-edge X-ray

absorption fine structure (NEXAFS) spectroscopy further revealed that 4-mercaptobiphenyl molecules form well-ordered and densely packed self-assembled monolayers on GaAs with an upright orientation with an average tilt angle of  $\Theta \sim 31^\circ$ .<sup>15</sup>

Another advantage of 4-mercaptobiphenyl derivatives is that 4'-substitution allows for surface engineering with various functions.<sup>16–19</sup> This paper deals with stable surface coating of stoichiometric GaAs [100] surfaces with 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl monolayers, which can render the surface hydrophobic and hydrophilic, respectively. The surface topography was studied by atomic force microscopy (AFM), while the covalent coupling between the thiolate and surface arsenide was confirmed by high-resolution X-ray photoelectron spectroscopy (HRXPS). Contact angle measurements yielded the total surface free energy and the dispersive and polar components for each surface. Electrochemical stability of the monolayer-coated GaAs substrates was carefully examined by impedance spectroscopy in the wide frequency region between 50 kHz and 1 mHz for more than 20 h.

## Experimental Section

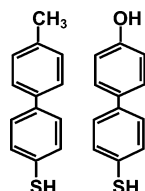
**Materials.** Single-crystalline Si-doped n-type GaAs [100] wafers with a doping ratio of  $(2.2\text{--}3.4) \times 10^{18} \text{ cm}^{-3}$  were purchased from American Xtal Technology Inc. (Fremont, CA). For electrochemical studies, an Ohmic contact was established from the backside of the wafer by electron beam vapor deposition of Ni (100 Å), Ge (200 Å), and Au (2500 Å). Synthesis of 4'-substituted-4-mercaptobiphenyl (Figure 1) was reported elsewhere.<sup>16</sup> All the other chemicals were purchased from Aldrich (Steinheim, Germany) and used without further

\* Corresponding author. E-mail: mtanaka@ph.tum.de.

<sup>†</sup> Technische Universität München.

<sup>‡</sup> Universität Heidelberg.

<sup>§</sup> Polytechnic University.



**Figure 1.** Chemical structures of 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl.

purification. Freshly distilled ultrapure water (Millipore, Molsheim, France) was used throughout this study.

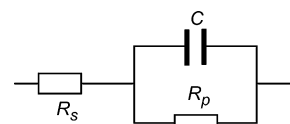
**Sample Preparation.** Prior to the surface modification, the samples were briefly sonicated in acetone (~3 min) and rinsed with ethanol. The native oxide of GaAs was stripped by soaking the sample in concentrated HCl for 1 min, resulting in a stoichiometric GaAs [100] surface. Self-assembled monolayers were deposited by immersing freshly prepared substrates into 0.1 mM 4'-substituted-4-mercaptobiphenyl solution in dry ethanol at 50 °C for 20 h. The reactions were carried out under nitrogen ( $N_2$ ) atmosphere to avoid surface oxidation. After deposition, the sample was taken out from the reactor, sonicated briefly (~1 min) in ethanol, and dried by a  $N_2$  flow.

**Atomic Force Microscopy (AFM).** Topography of the monolayer-coated surfaces was characterized by atomic force microscopy (Nanoscope IIIa, Digital Instruments, Mannheim, Germany). A silicon cantilever with a spring constant of about 40 N/m was used to scan an area of  $1 \mu m^2$  in tapping mode. Typical modulation amplitude and frequency were in the order of 10 nm and 300 kHz, respectively.

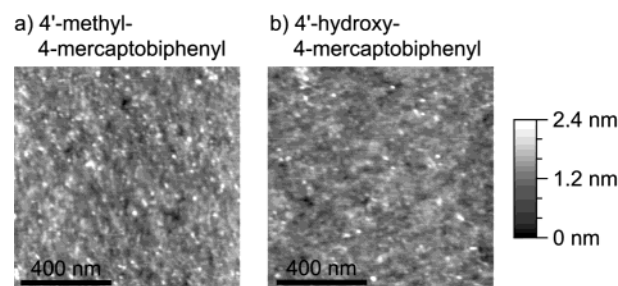
**Contact Angle Measurements.** Contact angles of water, diiodomethane, and glycerol were measured using a G10 contact angle meter (Krüss GmbH, Hamburg, Germany). Measurements were carried out in an ambient atmosphere at room temperature forming a sessile drop (volume ~ 10  $\mu L$ ) at the end of a blunt-ended needle and placing it on the substrates. The total surface free energy ( $\gamma$ ), as well as its dispersive ( $\gamma_s$ ) and polar ( $\gamma_p$ ) components, was calculated with an aid of DSA1 droplet shape analysis program based on the Owens-Wendt method<sup>20</sup> using the static contact angles of water, diiodomethane, and glycerol. The overall accuracy throughout the calculation of surface free energy was within  $\pm 3$  mN/m.

**High-Resolution X-ray Photoelectron Spectroscopy (HRXPS).** The HRXPS measurements were performed at the D1011 beamline of the synchrotron radiation facility MAX-Lab in Lund, Sweden. The beamline was equipped with a Zeiss SX-700 plane-grating monochromator and a two-chamber UHV experimental station with a SCIENTA analyzer. For both studied systems, the S 2p and As 3d spectra were acquired at photon energies of 350 and 130 eV, respectively. The spectra were fitted using Voigt peak profiles and a Shirley background. To fit the 2p and 3d doublets, we used two peaks with the same fwhm, the spin-orbit splitting close to a handbook value of ~1.2, and branching ratios of 2:1 ( $p_{3/2}/p_{1/2}$ ) and 3:2 ( $d_{5/2}/d_{3/2}$ ). The resulting accuracy of the binding energies and fwhm's reported here is 0.04–0.05 eV. Further details can be found elsewhere.<sup>15,21,22</sup>

**Electrochemical Measurements.** Electrochemical properties of the freshly prepared surface and the surface coated with the biphenyl monolayers were measured by impedance spectroscopy at room temperature (VoltaLab 40, Radiometer Analytical, Lyon, France). The contact area of the surface to the electrolyte was 0.28 cm<sup>2</sup>, and volume inside the chamber was about 1.5 mL. A Ag/AgCl electrode was used as the reference electrode, and a Au electrode as the counter electrode, respectively. Instead of using a rotating disk electrode, a constant flow of degassed 10



**Figure 2.** Simplified equivalent circuit model used for the analysis of impedance spectra. Details about simplification of the circuit model were described elsewhere.<sup>11</sup> Serial resistance  $R_s$  corresponds to Ohmic contributions from the electrolyte and contacts. Parallel resistance  $R_p$  is attributed to Ohmic behavior of the interface, whereas capacitance  $C$  to the interface capacitance.



**Figure 3.** Tapping mode AFM images of GaAs coated with (a) 4'-methyl-4-mercaptobiphenyl and (b) 4'-hydroxy-4-mercaptobiphenyl monolayers. Roughness rms values calculated within  $1 \mu m^2$  are (a) 3.1 Å and (b) 2.7 Å, respectively, which are comparable to that of a freshly etched GaAs, 3.3 Å (data not shown).

**TABLE 1: Total Surface Free Energies  $\gamma$ , Dispersive Components  $\gamma_s$ , and Polar Components  $\gamma_p$  of the Functionalized GaAs Surfaces**

surface coating	total surface free energy $\gamma$ [mN/m]	dispersive component $\gamma_s$ [mN/m]	polar component $\gamma_p$ [mN/m]
4'-methyl-4-mercaptobiphenyl	35	30	5
4'-hydroxy-4-mercaptobiphenyl	48	33	15

mM phosphate buffer with 10 mM NaCl (pH = 7.5) was applied. Impedance spectra were taken between 50 kHz and 1 mHz under sinusoidal potentials with an amplitude of  $|U| = 10$  mV. To estimate the electrochemical parameters quantitatively from the measured impedance data, the whole system was represented by simple ideal elements of a simplified equivalent circuit model composed of serial resistance  $R_s$ , interface capacitance  $C$ , and interface resistance  $R_p$  (Figure 2). The fitting errors through the data analysis were kept below 10%. Details of the fitting routine were described elsewhere.<sup>11,23</sup>

## Results and Discussion

**Surface Homogeneity.** Surface topography of a GaAs [100] substrate was characterized by AFM at several different locations within an area of  $1 \times 1 \mu m^2$ . The HCl-stripped GaAs surface showed a roughness rms of 3.3 Å, which agrees well with our previous report.<sup>14</sup> Figure 3 shows the tapping mode AFM images of GaAs coated with (a) 4'-methyl-4-mercaptobiphenyl and (b) 4'-hydroxy-4-mercaptobiphenyl monolayers. The roughness rms values within the scanned area were 3.1 Å for the GaAs with 4'-methyl-4-mercaptobiphenyl (Figure 3a) and 2.7 Å for the GaAs with 4'-hydroxy-4-mercaptobiphenyl (Figure 3b). Although the AFM measurement of an intact (freshly prepared) GaAs surface is difficult because of the fast oxidation of GaAs surfaces in ambient atmosphere,<sup>11</sup> both of the obtained rms values are comparable to that for the freshly etched surface and indicate that both grafting reactions did not increase the surface roughness.

**Surface Free Energy.** Table 1 gives the calculated surface free energies for the GaAs surfaces coated with 4'-substituted-

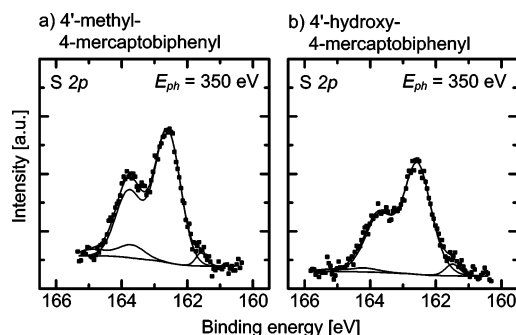
4-mercaptobiphenyls. A total surface free energy of GaAs coated with 4'-methyl-4-mercaptobiphenyl was calculated to be  $\gamma_{\text{CH}_3} = 35 \text{ mN/m}$ , indicating that the surface was rendered hydrophobic. The dispersive and polar components of the free energy could be obtained as  $\gamma_s = 30 \text{ mN/m}$  and  $\gamma_p = 5 \text{ mN/m}$ , respectively. Coating of GaAs with 4'-hydroxy-4-mercaptobiphenyl resulted in a hydrophilic surface, whose total surface free energy was  $\gamma_{\text{OH}} = 48 \text{ mN/m}$ . The dispersive and polar components of the engineered surface could also be calculated as  $\gamma_s = 33 \text{ mN/m}$  and  $\gamma_p = 15 \text{ mN/m}$ , respectively.

In comparison to the surface free energies of the same biphenyls on Au surfaces,  $\gamma_{\text{CH}_3} = 40 \text{ mN/m}$  and  $\gamma_{\text{OH}} = 68 \text{ mN/m}$ ,<sup>16</sup> the total surface free energies obtained here are smaller. This can partially be explained by the different tilt angles that biphenyl backbones take with respect to the surface normal, which were obtained by NEXAFS: e.g.,  $\Theta \sim 31^\circ$  on GaAs<sup>15</sup> and  $\Theta < 20^\circ$  on Au for nonsubstituted mercaptobiphenyls.<sup>18,24,25</sup> In fact, the lattice spacing of As on the GaAs [100] surface (5.6 Å) is larger than that for Au on Au [111] ( $\sim 5.0 \text{ Å}$ ), suggesting the different grafting densities on these two surfaces. Even though the absolute values of free energies are different, the calculated dispersive and polar components on GaAs showed good agreement with the previous results on Au,<sup>16</sup> that is, the functional groups influence the dispersive components but not the polar components.

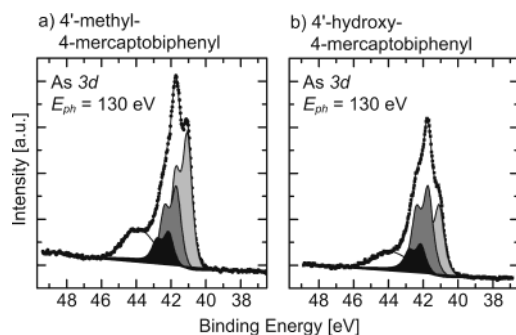
**Chemical Identity.** The chemical identities of the coated GaAs surfaces were studied by HRXPS. The S 2*p* core level spectra of GaAs coated with 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl measured at a photon energy of  $E_{\text{ph}} = 350.0 \text{ eV}$  are presented in Figures 4a and 4b, respectively. A dominant S 2*p* doublet at a binding energy of 162.6 eV (S 2*p*<sub>3/2</sub>) is characteristic for thiolate species and verifies the covalent attachment of mercaptobiphenyls onto GaAs.<sup>21,26</sup> A minor contribution at 161.7 eV (S 2*p*<sub>3/2</sub>) was also observed for GaAs with a 4-mercaptobiphenyl monolayer and can be attributed either to atomic sulfur or to Ga 3*s* emission.<sup>27</sup> Figures 5a and 5b represent the As 3*d* core level spectra of GaAs coated with 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl, respectively. As the effective sampling depth at the given photon energy (130 eV) is about 2 nm,<sup>28,29</sup> with a larger contribution from the topmost layers, these spectra are mainly representative for the GaAs surface. The spectra can be decomposed into the individual contributions related to stoichiometric GaAs (light gray), elemental arsenide (As<sup>0</sup>, gray), and arsenide bound to sulfur (black). The presence of the latter component also provides clear evidence for the covalent attachment of mercaptobiphenyls to surface arsenides.

In addition to the above-mentioned spectral components, there is a broad shoulder at a high binding energy ( $\sim 44 \text{ eV}$ ) in the spectra in Figure 5, which can be assigned to arsenide oxide. The respective extent of oxidation was comparable to that of a freshly etched GaAs (ca. 15–18%), although the samples were kept for several days in ambient atmosphere after the grafting reaction.<sup>15</sup> Since the bare GaAs is severely oxidized in ambient atmosphere within 1–2 h,<sup>11,30</sup> we concluded that grafting of both mercaptobiphenyls results in a high surface coverage and protects the surface from further oxidation.

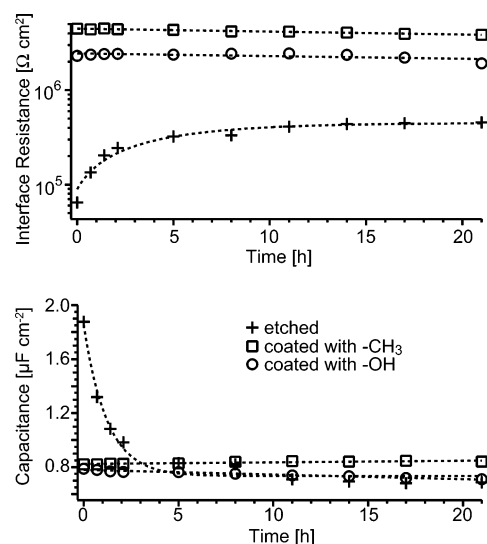
**Electrochemical Characteristics, Stability in Aqueous Electrolytes.** From the previous cyclic voltammetry experiments on an intact (freshly etched) GaAs,<sup>14</sup> a bias potential of  $-350 \text{ mV}$  was applied throughout the impedance spectroscopy experiments in order to minimize the electrochemistry at interface. Interface resistance,  $R_p$ , and interface capacitance,  $C$ , can be calculated from the measured spectra using the simplified



**Figure 4.** S 2*p* HRXPS spectra of (a) 4'-methyl-4-mercaptobiphenyl- and (b) 4'-hydroxy-4-mercaptobiphenyl-coated GaAs acquired at a photon energy of  $E_{\text{ph}} = 350 \text{ eV}$ . A dominant doublet at 162.6 eV (S 2*p*<sub>3/2</sub>) suggests the presence of thiolate on the surface.



**Figure 5.** As 3*d* HRXPS spectra of GaAs with a (a) 4'-methyl-4-mercaptobiphenyl monolayer and (b) 4'-hydroxy-4-mercaptobiphenyl acquired at a photon energy of  $E_{\text{ph}} = 130 \text{ eV}$ . A decomposition of distinct spectral features by doublets related to individual chemical species is shown: light gray, GaAs; gray, elemental As; black, As bound to sulfur. The shoulders at a high binding energy side of the shadowed doublets correspond to As oxides. The appearance of the sulfur-bonded As (black) confirmed the covalent attachment of biphenyl monolayers.



**Figure 6.** Changes in (a) interface resistance  $R_p$  and (b) interface capacitance  $C$  versus time for GaAs functionalized with 4'-methyl-4-mercaptobiphenyl (□) and 4'-hydroxy-4-mercaptobiphenyl (○). In contrast to freshly etched GaAs (+), deposition of monolayers resulted in stabilization of the GaAs/electrolyte interface for more than 20 h. The lines are given to guide the eye.

equivalent circuit model (Figure 2). Changes in the interface resistance and capacitance versus time were plotted for GaAs covered with 4'-methyl-4-mercaptobiphenyl (□) and 4'-hydroxy-4-mercaptobiphenyl (○) in Figure 6a and 6b, respectively. For comparison, the corresponding results for freshly etched GaAs



(+) are also given in the figure. As can be seen, freshly etched GaAs exhibited a continuous increase in interface resistance from  $R_{p0} = 64 \text{ k}\Omega \text{ cm}^2$  at  $t = 0 \text{ h}$  (first measurement) to  $R_{p1} = 0.46 \text{ M}\Omega \text{ cm}^2$  at  $t \sim 20 \text{ h}$ . Interface capacitance also decreased continuously from  $C_0 = 1.9 \mu\text{F cm}^{-2}$  ( $t = 0$ ) to  $C_1 = 0.69 \mu\text{F cm}^{-2}$  ( $t \sim 20 \text{ h}$ ), reflecting the formation of an insoluble surface layer.<sup>31</sup> In contrast, GaAs functionalized with both types of mercaptobiphenyls showed stable interface resistance for more than 20 h,  $R_{p\text{CH}_3} = 4.2 \text{ M}\Omega \text{ cm}^2$  and  $R_{p\text{OH}} = 2.3 \text{ M}\Omega \text{ cm}^2$ . The comparison of these values to that of freshly etched GaAs,  $R_{p0} = 64 \text{ k}\Omega \text{ cm}^2$  implies that the deposition of a biphenyl monolayer caused a significant increase in interface resistance by a factor of  $50 \pm 15$ . Monolayer-coated GaAs also showed very stable interface capacitance,  $C_{\text{CH}_3} = 0.83 \mu\text{F cm}^{-2}$  and  $C_{\text{OH}} = 0.75 \mu\text{F cm}^{-2}$ . All the electrochemical parameters obtained here are comparable to those obtained for GaAs with nonsubstituted 4-mercaptobiphenyl,  $R_{p\text{BPT}} = 3.2 \text{ M}\Omega \text{ cm}^2$  and  $C_{\text{BPT}} = 0.45 \mu\text{F cm}^{-2}$ .<sup>14</sup> Previously, Allara and his colleagues reported the deposition of ODT monolayers on stoichiometric GaAs [100] surfaces, which prevented the surface reoxidation.<sup>6,8</sup> However, in our previous accounts, we found that the ODT monolayer on stoichiometric GaAs [100] could not stabilize the GaAs/electrolyte interface effectively, probably due to the large distance between surface arsenides.<sup>10,11</sup> In contrast, 4-mercaptobiphenyls with more rigid and bulkier aromatic backbones could accomplish the stable surface passivation even in aqueous electrolytes.<sup>14</sup> The results obtained here also confirmed that both of the functional biphenyl monolayers can realize effective passivation against electrochemical degradation in electrolytes.

## Conclusions

We demonstrated engineering of GaAs [100] surfaces by deposition of 4'-methyl-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl monolayers. As demonstrated in our previous studies, the surface of chemically robust organic monolayers can be used as a platform for deposition of ultrathin ( $d < 10 \text{ nm}$ ) biocompatible polymer films<sup>3,32,33</sup> and model biomembranes.<sup>2,4,33</sup> For this purpose, the important criteria we should fulfill are (a) smooth surface coating, (b) controlled wetting conditions (for deposition of polymers and membranes), (c) stable (covalent) coupling between the monolayer and substrate, and (d) chemical/electrochemical stability in ambient as well as in aqueous electrolytes. AFM measurements demonstrated that the grafted monolayer did not cause roughening of the surface. Total surface free energies and their dispersive and polar components could quantitatively be estimated by contact angle measurements, showing a strong dependence of the dispersive component on 4'-substitutions. The covalent attachment of biphenyl monolayers to GaAs was confirmed by S 2p and As 3d HRXPS spectra. Electrochemical stability of the functionalized GaAs was carefully examined by impedance spectroscopy at a current-minimum potential ( $-350 \text{ mV}$ ). Both  $\text{CH}_3$ - and  $\text{HO}$ -substituted biphenyl monolayers were found to be electrochemically insulating and able to stabilize the GaAs/electrolyte interface for more than 20 h. Further experiments such as Mott-Schottky analysis and photoluminescence measurements will provide deeper insight of the influence of the monolayer deposition on the electronic structures of GaAs. On metal surfaces, it has been demonstrated that 4-mercaptobiphenyls with different 4'-substitutions have large potentials toward versatile modifications of surface functions.<sup>16–19</sup> For example, aromatic backbones can be cross-linked with low-energy electrons,<sup>34,35</sup> while the functional groups attached to these backbones can

chemically be modified.<sup>36,37</sup> The first approach is promising to stabilize the surface coating in aqueous electrolytes furthermore, while the second allows for "local" conversion of surface functions. More detailed spectroscopic characterization (FTIR, NEXAFS) are being carried out to reveal more exact structures in molecular scales. Moreover, the surface engineering protocol established here can directly be transferred onto various semiconductor heterostructures in the proximity of GaAs surfaces,<sup>12,13</sup> which would realize novel organic–semiconductor hybrids.

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