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Biofunctional Electrolyte-Gated Organic Field-Effect Transistors

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In the past few years, substantial research effort has been devoted to the development of organic biosensors, since they combine general merits of electronic sensors, like speed, size and system integration, with the ones of organic semiconductors, such as low cost production, facile integration with flexible substrates, and biocompatibility.[1–8] In this respect, organic transistors are particularly interesting devices for food monitoring or health care applications.[3,7] These transistor-based organic sensors operating in aqueous environments are usually divided into two classes: organic electrochemical transistors and field-effect transistors (FETs).[3,7] The conductivity of the active material (usually a polymer) in the former devices is modulated using an electrochemical doping or dedoping effect, which necessitates a charge transfer process occurring across the electrolyte/polymer interface.[9] FETs, on the other hand, operate via the formation of a conductive channel by a shift of the quasi-Fermi level due to an applied electric field. The potential necessary for the accumulation of sufficient charge carriers at the interface depends thereby on the defect density in the semiconductor and the capacitance of the dielectric. In order to operate FETs at the low potentials required for in-electrolyte operation it is necessary to use a dielectric with a sufficiently large capacitance. Therefore, materials like high-k dielectrics,[10] ultra-thin polymers[6] or electrolytes[11–13] have been investigated in the past. We and others have shown previously that the double-layer capacitance formed when the organic semiconductor is in direct contact with an aqueous electrolyte can be used to fabricate devices which can be operated at low voltages and are sufficiently stable.[12,13] This approach is especially interesting for sensor applications as the conductive channel is in direct contact with the electrolyte containing the analytes, in contrast to the usually reported back-gated devices. Furthermore, it has previously been shown that thick passivation layers separating the organic semiconductor and the electrolyte diminish the sensitivity of organic sensors towards species in the electrolyte.[14] Thus, the complete absence of such a layer should improve the sensitivity. Besides the requirements of sensitivity, sensors are expected to exhibit high selectivity towards specific analytes. In order to render the transistor sensitive to a certain analyte, specific recognition elements are usually grafted to the surface exposed to the electrolyte. Typical examples for this approach are the grafting of antibodies in order to detect the corresponding antigen[4] or the functionalization of the surface with enzymes, which catalyze specific reactions.[15,16]

In the particular case of FET sensors based on inorganic semiconductors, enzyme-modifed FETs (ENFETs) have been successfully applied to the detection of a large variety of analytes by combining the intrinsic pH sensitivity of inorganic-based ion-sensitive field effect transistors with the surface functionalization of suitable enzymes.[15–18] Upon the specific reaction of such enzymes with particular analytes, the pH is locally modified in the vicinity of the sensor's surface and, as a result, the presence of the analyte is detected in terms of a pH variation. This sensing scheme opens the way to the selective detection of many biologically relevant analytes such as glucose, penicillin, urea, lactose, sucrose, maltose, etc. (see the review of Schöning and references therein).[17] In the case of organic FET biosensors, to the best of our knowledge such an approach has not yet been reported.

In this work, we report on a novel sensor platform based on enzyme-modified organic field effect transistors. To this end, we have functionalized α-sexithiophene (α6T)-based solution-gated field-effect transistors (SGFETs) with the enzyme penicillinase. α-Sexithiophene has been chosen as one of the prototypical organic semiconductors stable in an aqueous electrolyte, which does not require any further surface passivation.[19] Penicillinase, on the other hand, has been broadly used in inorganic ENFETs and can, thus, be used for benchmarking. This enzyme hydrolyzes the amide bond of the *β*-lactam ring of penicillin. During this reaction a proton is generated, locally changing the pH of the electrolyte, which in turn is detected by the transistor. Since, however, the pH sensitivity of bare α6T is rather low,[13] an additional surface treatment is necessary in order to increase the sensitivity towards the pH of the electrolyte. We show that, after a controlled oxidation of the surface, the response of the SGFET is increased at low pH as expected for oxygen related surface species. On the other hand, the pH sensitivity is increased in more neutral buffer solutions after modification of the α6T thin film with (3-aminopropyl)triethoxysilane (APTES). Furthermore, the amino group of the APTES molecule serves as an anchoring site for the subsequent immobilization of enzymes, which we exemplarily demonstrate using penicillinase (PEN), resulting in sensors able to specifically detect penicillin in the μM range.

The transistors were fabricated on sapphire substrates onto which metallic source and drain contacts were evaporated. Subsequently, these contacts were partially covered with a

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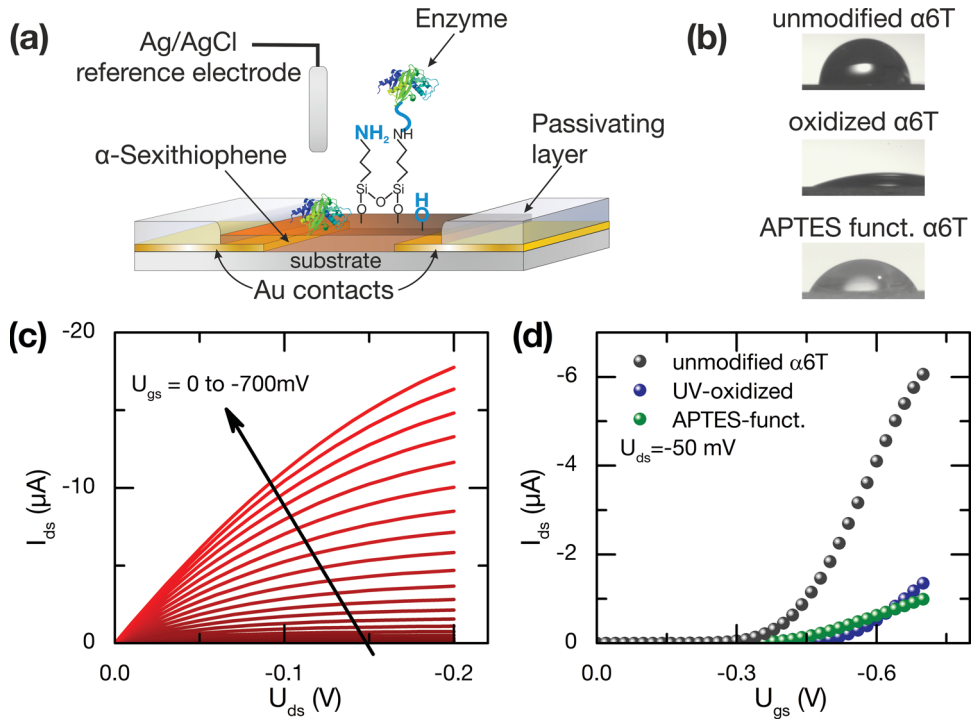

Figure 1. a) Schematic drawing of the transistor layout, including the different functionalization steps investigated in this work. b) Static water contact angle measurements of differently treated α-sexithiophene thin films. c) Typical output characteristic of a transistor with a width-to-length ratio of 4900 recorded at pH 5. d) Transfer curves of untreated, oxidized (5 min UV illumination) and APTES-functionalized transistors, measured at pH 5.

chemically stable photoresist in order to minimize the exposure of the metal to the electrolyte. Only in the channel region, a 5 μm part of the metal is still exposed and serves as the contact to the 100 nm thin polycrystalline α6T film (see the schematic in **Figure 1**a and the experimental section for further information). A Ag/AgCl reference electrode immersed in the electrolyte is used to modulate the channel conductivity by applying a voltage between the electrode and the source contact and thereby shifting the Fermi level in the organic semiconductor. As previously shown,[13] this configuration ensures field-effect operation without significant charge transfer between the electrolyte and the organic semiconductor in the potential window of the organic layer.

The electrical double layer induced at the interface between the aqueous electrolyte and the organic semiconductor leads to the formation of an interfacial capacitance with values of around 2 μFcm^{-2}. As a result, the output transistor characteristics (see Figure 1c and 1d) show the typical behavior of a field-effect transistor already at gate voltages below 1 V. The on/off ratio at U_{ds} = –50 mV is of the order of 10^2–10^3 and the extracted field-effect mobility reaches up to 4×10^{-2} $cm^2V^{-1}s^{-1}$. This mobility is about an order of magnitude lower as has been reported for back-gated devices operated in aqueous environment, which might be due to the rough interface between the organic layer and the electrolyte in our case, as compared to the smooth surface of the polymer dielectric in the work of Roberts et al.[19] All these values are deduced from transistor measurements in a 10 mM phosphate-buffered saline (PBS) solution, with a pH of 5 and its total ionic strength adjusted to 50 mM by KCl. It is worth to recall that in these devices the organic semiconductor is in direct contact with the electrolyte and no passivation layer is used. Even under these conditions, we have previously found that the devices are stable during continuous operation in the electrolyte.[13] To enhance the lifetime of the devices, a proper selection of the bias operation within the electrochemical potential window is crucial.

A typical limitation to the stability of organic thin film transistors is the oxidation of the material upon exposure to atmospheric oxygen or ozone in combination with UV illumination.[20,21] We used this mechanism in order to introduce oxygen-related species at the surface, which will be later used to control the chemistry and sensitivity response of the organic FET sensors. To this end, the samples were kept in a closed container under a pure oxygen atmosphere and then illuminated for varying durations with an UV lamp. As a result, the characteristics of the transistor were affected as follows: upon exposure to the oxidizing environment we observed a decrease in the transconductance and a shift of the threshold voltage U_{th} towards more negative gate voltages (see supporting information and the blue dots in Figure 1d). This effect is tentatively attributed to the formation of oxygen-related trap states at the interface, which are expected to decrease the effective mobility in accordance with the multiple trap and release model.[22] In addition, the oxygen-related surface moieties are positively charged and thereby shift U_{th} to more negative values.

A similar behavior can be observed for APTES modified transistors (green dots in Figure 1d). The surface functionalization was conducted by exposing the untreated α6T films to APTES

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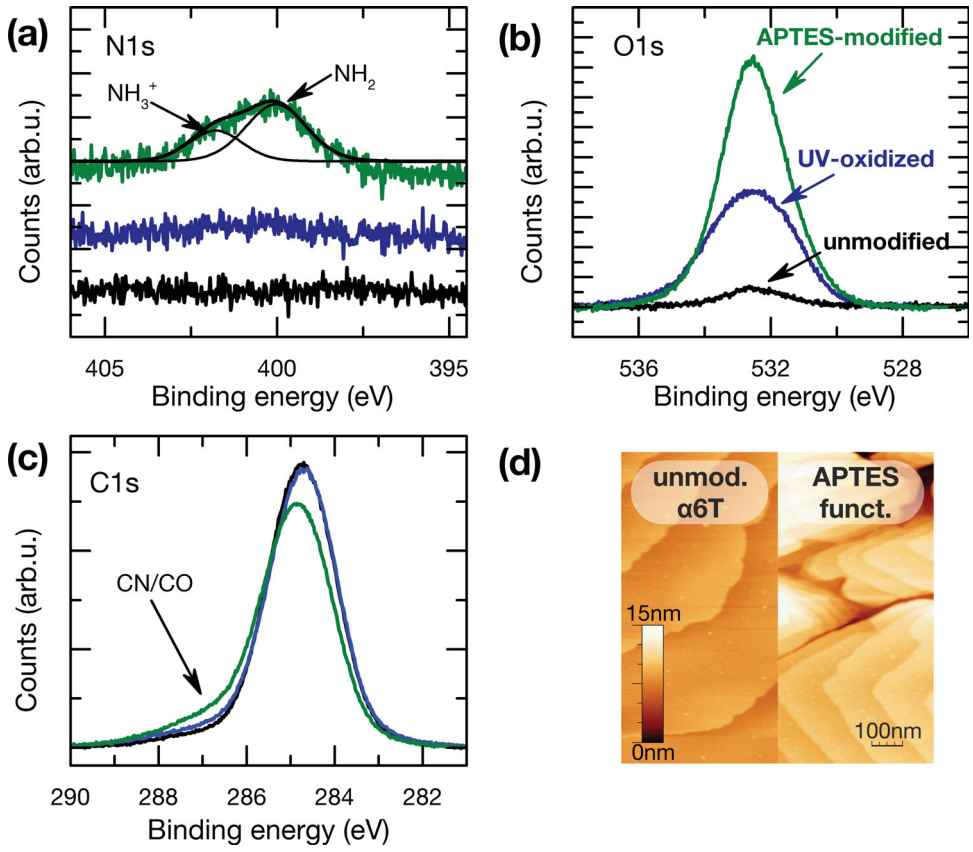

Figure 2. a) XPS core level spectra of the N1s peak, showing the presence of nitrogen on the surface of APTES-modified α6T films (green), while no nitrogen is detected on untreated films (black) or on films illuminated with UV under oxygen atmosphere (blue). Deconvolution of the peak for the APTES modified sample reveals the presence of NH_2 and NH_3^+. b) XPS spectra in the O1s region showing the presence of oxygen species on both the UV treated as well as the APTES modified samples, while only little oxygen can be detected for the untreated α6T films. c) XPS core level spectra of the C1s peak of bare α6T (black), APTES modified α6T (green), and an oxidized film (blue), showing the emergence of a shoulder related to CN/CO bonds. d) AFM pictures of an untreated and a α6T film functionalized with APTES.

vapor in a previously evacuated vacuum vessel, as reported by Calhoun et al.[23] During this process, the ethoxysilane groups of the APTES molecules are expected to hydrolyze when coming in contact with the water film adsorbed on the surface of the transistors, and one of the three silane groups binds to oxidized α6T molecules. Additional APTES molecules can subsequently bind the other two silanol groups, forming a silane network on top of the α6T thin film. Static water contact angle measurements serve as a quick check to confirm the modification of the film surface. As can be seen in Figure 1b, the contact angle decreases from the 87 ± 3° for untreated α6T films to 21 ± 3° upon partial oxidation of the surface. The decreased hydrophobicity of the organic semiconductor results from the increased density of oxygen-related moieties at its surface, as was confirmed by X-ray photoemission spectroscopy (XPS). The further attachment of APTES molecules onto the previously oxidized surface increases the contact angle again to around 61 ± 3°, as usually observed for amine-terminated surfaces.[24]

In order to assess the successful attachment of APTES molecules onto the surface of α6T we conducted X-ray photoemission spectroscopy (XPS). **Figure 2**a depicts the XPS spectrum in the region of the nitrogen 1s core level for untreated, oxidized, and APTES-modified α6T samples. Only for the latter a clear N1s signal can be observed, which can be resolved into a dominant peak at 400 eV and a shoulder at 401.7 eV. These peaks are usually observed for APTES modified surfaces and attributed to NH_2 and NH_3^+ groups, respectively.[25,26] The functionalization of the surface with APTES molecules does not only introduce amino groups to the surface, but also increases the amount of oxygen, as can be seen in Figure 2b. This figure, depicting the O 1s spectral region, further reveals the increase of oxygen species at the surface of α6T films upon UV treatment for 5 minutes under oxygen atmosphere. This increase, however, is lower than the one observed after APTES functionalization. The small amount of oxygen present on the untreated sample might be due to adsorbed water or to unintentionally oxidized α6T molecules. The emerging shoulder in the C1s spectra at a binding energy around 287 eV is related to CO or CN bonds (see Figure 2c). Its presence is expected in the case of the APTES modified sample, resulting from the CN bonds present in the molecules. For the UV treated samples the signal in this region suggests the oxidation to take place on the carbon atoms of the thiophene ring. From the attenuation of the thiophene-related S2p peak signal (see supporting information), one can estimate

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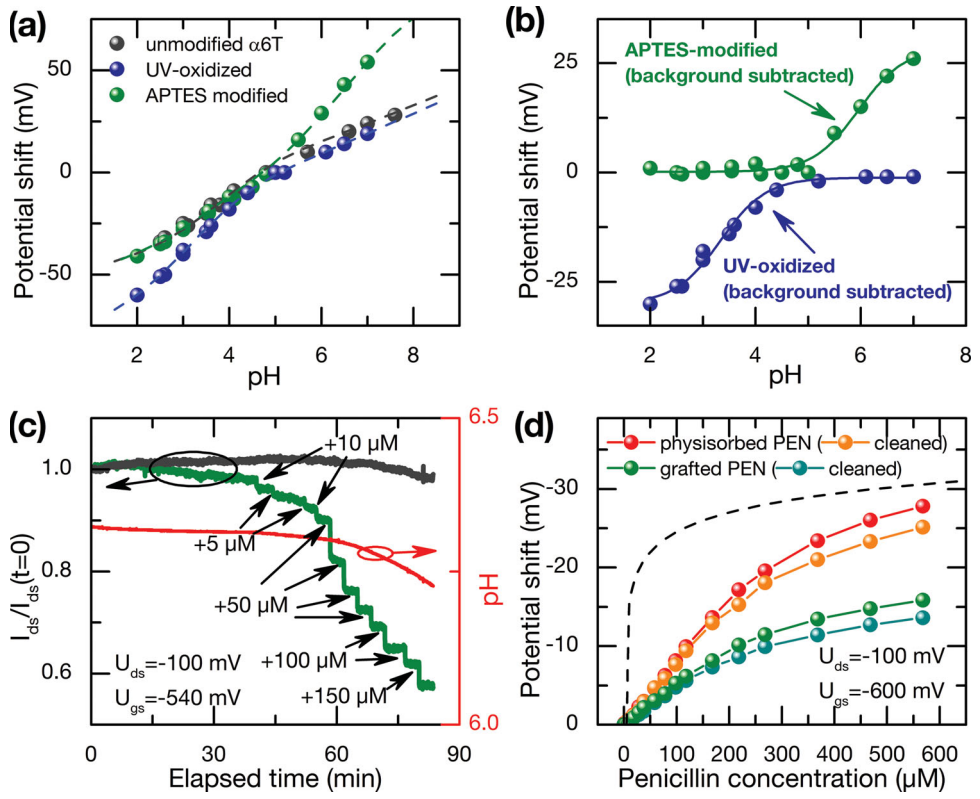

Figure 3. a) Threshold voltage shift of untreated α6T films, APTES-functionalized and UV-oxidized samples upon a change in the pH of the electrolyte, obtained by titration measurements. The shift is calculated with respect to the threshold voltage at pH 5. The dashed lines correspond to fits using the amphifunctional model (see text). b) The graph depicts the threshold voltage shift of the APTES-treated sample and the oxidized samples after the subtraction of the response of untreated α6T. The solid lines are fits to the data. c) Time-lapse of I_{ds} during a penicillin titration experiment conducted in a 0.5 mM PBS buffer. The ionic strength was adjusted to 50 mM using NaCl. The green line corresponds to the response of a device functionalized with APTES and penicillinase, while the grey line depicts the I_{ds} response of an untreated α6T OFET. The pH of the electrolyte is shown in red. d) Plot of the calculated threshold voltage shift due to a change in penicillin concentration of the electrolyte for as-prepared devices with physisorbed enzymes and chemisorbed enzymes and after three washing steps. The dashed line shows the simulated response due to pH variations in an unbuffered electrolyte.

an APTES film thickness of around 1 nm, which agrees well with the theoretical value of a monolayer of 8.5 Å. However, this value should be taken with care due to uncertainties in the attenuation length and the azimuth angle.[27] In summary, the XPS data confirms the successful introduction of amino- or oxygen-related groups to the surface after the respective functionalization steps.

Figure 2d shows an atomic force microscopy (AFM) image of an untreated α6T film, featuring the typical thin film morphology of α6T layers with the expected step height of around 2.2 nm.[28] The film morphology is not substantially altered upon the functionalization with APTES, as can be seen in the right side of the image. Only small features are visible on the film, which might stem from local multilayer formation on certain spots. This is not surprising considering that harsh cleaning methods usually employed to remove any physisorbed species cannot be used for organic thin films without disrupting their film quality.

Titration experiments were performed in order to assess the effect of the surface modification on the pH sensitivity of the α6T SGFETs. As previously reported, the transistors respond to variations of the pH with a shift in their threshold voltage U_{th}, while the mobility remains constant.[13] Therefore, the shift of U_{th} can be directly measured in the constant source-drain current (I_{ds}) mode, in which the transistor is biased with a continuous source-drain voltage while a feedback loop controls the gate voltage in order to keep I_{ds} constant. **Figure 3**a summarizes the pH sensitivity of unmodified, UV-oxidized, and APTES-functionalized organic SGFETs. According to this figure, all samples exhibit a negative shift of the threshold voltage when going from neutral towards acidic electrolyte conditions. For untreated α6T transistors, a sensitivity of 14 mV pH^{-1} is obtained up to a pH of 5, decreasing to around 10 mV pH^{-1} for more neutral solutions. Upon oxidation (300 s) the sensitivity in the region below pH 5 increases to 26 mV pH^{-1}, while it remains unchanged for higher pH values. A similar behavior can be observed for the transistors functionalized with APTES. In this case, however, the sensitivity increases to 21 mV pH^{-1} in the neutral region, while no changes are visible for more acidic electrolyte conditions. Figure 3b depicts the threshold voltage shift for the two modified surfaces (UV oxidation and APTES-functionalized) for which the response of the untreated α6T film were subtracted,

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Table 1. Values used to fit the data in Figure 3a using the amphifunctional model and Equation (1).

Sample	N_0 [cm^{-2}]	Q^* [meV]	N_s [cm^{-2}]	pK_a	$N_{s,2}$ [cm^{-2}]	$pK_{a,2}$
untreated α6T	$3.6 * 10^{14}$	250	$1.8 * 10^{13}$	3.5		
UV-treated	$3.6 * 10^{14}$	250	$3 * 10^{13}$	3.1		
APTES-functionalized	$2.4 * 10^{14}$	250	$1.1 * 10^{13}$	3.0	$1.5 * 10^{14}$	5.3

rendering the change in the sensitivity upon surface modification clearly visible. Measurements at more basic electrolyte conditions were not possible for these samples: for higher pH values, the electrochemical potential of the oxygen redox-couple shifts towards less negative gate potentials and thereby reduces the potential window available for stable transistor operation. pH sensitivity measurements reaching higher pH values are provided in the supporting information, and were performed in samples exhibiting lower U_{th}.

The shift of the threshold voltage with the pH of the electrolyte can be understood in terms of a pH-dependent surface charge. The behavior of this surface charge upon variations of the pH is described using the so-called amphifunctional model, which is a modification of the site-binding model.[29–31] Based on this model (see supplementary information for a detailed description), we assume that functional groups present at the device surface, for instance introduced by the different surface modification methods, can either be protonated or deprotonated depending on their pK_a value. However, a problem arises when trying to fit the data for the untreated α6T devices: the sensitivity of 10 mV pH^{-1}, far below the theoretical Nernstian limit of 59 mV pH^{-1}, cannot be modeled over a large range of pH values using only one type of surface species with a density N_s. Thus, a different model has to be used to describe the observed change of the surface potential. It is generally reported that hydrophobic organic materials feature a negative surface charge in contact with aqueous solution, and it has been suggested that either hydroxyl ions specifically adsorb on this kind of surfaces,[32] or that the surface charge is due to a water ordering effect at the interface.[33,34] In the case of specific adsorption, a Langmuir adsorption isotherm is typically used to describe the surface coverage for homogeneous surfaces. If, as for the polycrystalline α6T films, the surface is more heterogeneous and the adsorption energy Q is not the same on different surface sites but follows an exponential distribution with a decay constant Q^*, the surface charge due to the specific adsorption of OH^- can be described using the Freundlich isotherm[35]:

$$\sigma_{ads} = -e N_0 \left({c_{OH^-}^{surf}}/{c_0} \right)^{{kT}/{Q^*}} \quad (1)$$

Here N_0 is the maximum site density available for adsorption and $c_{OH^-}^{surf}$ the concentration of hydroxyl ions close to the surface, which is related to its bulk concentration via a Boltzmann term (see supporting information). The maximum OH^- concentration in aqueous electrolytes $c_0 = 1$ mol/L serves as a normalization term. The parameters of this specific adsorption isotherm can be obtained from a fit of the titration curve of the untreated α6T devices (grey dots in Figure 3a) and are given in **Table 1**. The value for N_0 corresponds to a monolayer of hydroxyl ions including their hydration shell. This fit includes the response of surface bound species with a density N_s and a pK_a of 3.5. By increasing the density N_s (now with a pK_a of 3.1), while keeping the parameters related to specific adsorption constant, the data for the oxidized sample can be modeled (see Figure 3a). It seems reasonable to assume that the surface groups with pK_a around 3 are related to oxygen species, like OH, which increase from a low amount present on the untreated α6T films by deliberate oxidation. However, when comparing the values given in Table 1 with the estimation obtained from the XPS O1s core level spectrum in Figure 2b, the increase of the oxygen moieties upon UV-oxidation appears to be higher in the case of the samples investigated with XPS. This might stem from the oxidation of the samples when exposed to the electrolyte; which was avoided for the films measured in XPS. For the samples treated with APTES, additional surface groups with a $pK_{a,2}$ value of 5.3 and a density $N_{s,2}$ have to be added to the model. This is the typically measured pK_a value for APTES-modified surfaces and is usually attributed to silanol groups. The amino groups in the APTES molecule also contribute with a $pK_{a,2}$ value around 9,[36] but this is out of the pH range investigated in Figure 3a.

In order to demonstrate the potential of organic SGFETs for biosensing applications, penicillinase was grafted to the transistor surface, which should render the device specifically sensitive to penicillin. More details on the grafting protocol can be found in the experimental section. Immobilized on the device surface, penicillinase catalyzes the decomposition of penicillin into penicilloic acid and a proton, which can be subsequently detected by the pH sensitive surface. Figure 3c depicts the response of untreated α6T and PEN-modified devices to the subsequent addition of varying amounts of penicillin to a 0.5 mM PBS solution at pH 6.4. As can be clearly seen, only the PEN-modified device shows a clear response to the addition of penicillin, with a sensitivity limit of around 5 μM. A new stable current level is reached several seconds after the addition of penicillin (see supporting information). The bare device only shows a small response at higher penicillin concentration, which is due to the pH change in the bulk solution.

Considering that the device response stems from a pH variation, a logarithmic relation between the threshold voltage shift and the penicillin concentration would be expected (as depicted by the dashed line in Figure 3d). The linear behavior at low concentrations commonly observed in the calibration curves of ENFETS is the result of the interplay of the kinetics of the buffer, the enzyme kinetics and the diffusion between the enzyme layer and the surrounding electrolyte.[37]

The response of the device with PEN grafted to the surface using APTES, as explained above, has been compared to that

of a device with PEN physisorbed onto the untreated α6T surface. Interestingly, no substantial advantages for the APTES-treated devices have been observed concerning both the signal and the stability (see Figure 3d). The sensitivity of the device derived from the region of low penicillin concentration with physisorbed enzymes is of the order of 80 μV/μM and about 50 μV/μM for the APTES-treated thin films. Nevertheless, these values compare well with those obtained with different inorganic ENFETs, despite the lower pH sensitivity of the organic devices.[15,16,38,39] In order to assess whether the enzymes are more strongly bound to the APTES-functionalized surfaces compared to the physisorbed samples, both devices were cleaned in a shaker in 1 M KCl solution for 2 h at 600 rpm, a cleaning procedure commonly used to remove physisorbed enzymes.[40] After the cleaning process the response decreased similarly for both devices, suggesting that a complex immobilization process might not be necessary to achieve stable ENFETs, at least for rather robust enzymes like penicillinase. These results are in sharp contrast to typical inorganic semiconductors used for this kind of application, in which a clear stability enhancement was observed for covalently grafted proteins.[15] It thus appears that the surface energetics and the morphology of the organic thin films favor a strong physisorption of the enzymes.

In summary, we report the modification of organic solution-gated field-effect transistors with different surface treatments, leading to an increased sensitivity to the pH of the electrolyte. This behavior is explained using an amphifunctional model and the specific adsorption of hydroxyl ions to the untreated hydrophobic organic semiconductor surface. Furthermore, by modifying the organic SGFETs with enzymes we have demonstrated the operation of organic ENFET biosensors which are specific to certain analytes (in our example to penicillin). The sensitivity of these devices is comparable to or even exceeds the sensitivity of inorganic devices. Combined with the low-cost production of organic semiconductors and the stable attachment of enzymes by simple physisorption, these results emphasize the potential of organic SGFETs as disposable biosensors.

Experimental Section

Transistor fabrication: The α6T (Sigma Aldrich) thin films were deposited onto pre-patterned sapphire substrates at a substrate temperature of 50 °C and an evaporation rate around 1 Å/min. The background pressure in the chamber was 2×10^{-8} mbar. The photolithographically defined source and drain contacts (Ti (5 nm)/Au (45 nm)) contacts with a spacing of 20 μm create an interdigitated transistor with an effective channel width of 98 mm. The largest part of the contacts (besides 5 μm in direct contact to the channel, see Figure 1a) was covered with SU-8 2002 (Microchem) resist.

Surface modification: In order to oxidize the α6T films in a controlled fashion, the devices were exposed to oxygen in a sealed chamber and illuminated with UV light (5 W emission with a maximum at 254 nm). After the exposure, the chamber was immediately flushed with dry nitrogen to remove any remaining ozone. The silanization of the samples was conducted by exposing the films to fumes of APTES (Sigma Aldrich) in a homemade setup similar to the one reported by Calhoun *et al*.[23] In order to graft penicillinase (enzyme nr. EC 3.5.2.6, Sigma Aldrich), the amino group of the APTES molecule was first converted to a carboxyl group. This was achieved by immersing the sample in 50 mM Na-based PBS buffer with a pH of 6.2 and subsequently adding small quantities of succinic anhydride (Sigma Aldrich) (2 M in acetone). The *pH* was kept constant by titration with NaOH until a total amount of 4 ml succinic anhydride solution was added.[41] The carboxyl group is activated using 400 mM 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and 100 mM N-hydroxy-succimide (NHS) in 100 mM MES buffer.[41] In a final step the sample was stored for 12 h in 0.2 mg/ml PEN dissolved in 50 mM Na-based PBS at pH 6.2 at 4 °C. For the physisorbed samples only this last step was employed.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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