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**Interfacial Systems Chemistry: Out of the Vacuum, Through the Liquid, Into the Cell**

**Guest Editors:** Professor Armin Göltzhaus (Bielefeld) & Professor Christof Wöll (Karlsruhe)

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**Editorial**

**Interfacial systems chemistry: out of the vacuum—through the liquid—into the cell**


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**Perspective**

**The role of inert surface chemistry in marine biofouling prevention**


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**Self-assembled monolayers of polar molecules on Au(111) surfaces: distributing the dipoles**


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**Bending of purple membranes in dependence on the pH analyzed by AFM and single molecule force spectroscopy**


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**Polymer confinement effects in aligned carbon nanotubes arrays**


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DOI: 10.1039/b923700c

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DOI: 10.1039/b923789p

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DOI: 10.1039/b923858c

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DOI: 10.1039/b924246p

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Christof Christophis, Michael Grunze and Axel Rosenhahn, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/b924304f

Lipid coated mesoporous silica nanoparticles as photosensitive drug carriers
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DOI: 10.1039/b924370d

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DOI: 10.1039/b924409c

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DOI: 10.1039/b924657f

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Nanocomposite microstructures with tunable mechanical and chemical properties
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Is there a Au–S bond dipole in self-assembled monolayers on gold?†

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Self-assembled monolayers (SAMs) of functionalized thiols are widely used in organic (opto)electronic devices to tune the work function, \( \Phi \), of noble-metal electrodes and, thereby, to optimize the barriers for charge-carrier injection. The achievable \( \Phi \) values not only depend on the intrinsic molecular dipole moment of the thiols but, importantly, also on the bond dipole at the Au–S interface. Here, on the basis of extensive density-functional theory calculations, we clarify the ongoing controversy regarding the existence, the magnitude, and the nature of that bond dipole.

The work function, \( \Phi \), of a metal is defined as the energy difference between its Fermi level, \( E_F \), and the energy of an electron at rest directly outside the metal surface, \( E_{\text{vac}} \). Thus, to modify \( \Phi \) by an amount \( \Delta \Phi \), a SAM must introduce a potential energy step between metal and vacuum. To allow for the rational design of molecules that induce a desired \( \Delta \Phi \), the latter is commonly split into two additive components. The first, \( \Delta E_{\text{vac}} \), arises from the molecular ad-layer only and the second, \( \Delta E_{\text{BD}} \), reflects the interfacial charge rearrangements upon molecule–metal bonding. Disregarding atomic-scale lateral inhomogeneities in the SAM, each potential energy step is linked to a corresponding plane-averaged charge (re)distribution, \( \rho(z) \), via the Poisson equation,

\[
\nabla^2 E(z) = \frac{\rho(z)}{\varepsilon_0} 
\]

(1)

where \( e \) denotes the (by definition positive) elementary charge and \( \varepsilon_0 \) the vacuum permittivity. As only a net dipole moment perpendicular to the surface leads to a non-vanishing \( \Delta E \), eqn (1) is commonly replaced by the heuristic Helmholtz equation, where two contributions to \( \Delta \Phi \) are regarded as arising from two laterally homogenous dipole layers.1–9

\[
\Delta \Phi = \Delta E_{\text{vac}} + \Delta E_{\text{BD}} = -\frac{en}{\varepsilon_0} \left[ \frac{|\mu| \cos(\beta)}{\varepsilon_0(\varepsilon r + \varepsilon_0)} + \mu_{\text{BD}}(n) \right] 
\]

(2)

Here, \( n \) denotes the molecular packing density, \( |\mu| \) is the dipole moment of the free molecule, and \( \beta \) is the angle between the dipole axes of the molecules in the SAM and the surface normal. Generally, the depolarization factor \( \varepsilon_{\text{eff}} \) and the bond dipole at the Au–S interface, \( \mu_{\text{BD}} \), depend on the coverage in a non-trivial manner,10 but the same \( n \) (full coverage) is assumed for all SAMs considered here.

For many adsorbates, the conceptual partitioning of \( \Delta \Phi \) into a purely molecular part (first term in eqn (2)) and a bonding-induced part (second term in eqn (2)) is unambiguously defined.2 However, for SAMs formed by thiols, two different partitioning schemes appear in the literature. For the molecular contribution to \( \Delta \Phi \), thiols (i.e., \( \text{R–SH} \) species) are considered in the first1–5 and \( \text{R–S}^* \) radical species in the second.6–9 These correspond to two conceptually different points of view,

\[
\begin{align}
\text{R–SH} + \text{Au} &\rightarrow \text{R–S–Au} + \text{H}_2 & (3a) \\
\text{R–S}^* + \text{Au} &\rightarrow \text{R–S–Au} & (3b)
\end{align}
\]

(3)

where the first regards the bonding of the SAM to the metal as replacing \( \text{S–H} \) bonds with \( \text{S–Au} \) bonds and the second as forming new bonds between \( \text{R–S}^* \) radicals and gold. Naturally, appreciably different molecular dipole moments are found for the saturated and the radical species and, consequently, by virtue of eqn (2), also different \( \Delta E_{\text{vac}} \) values (see ESI†). As, however, the final situation is identical in both approaches, i.e., a thiolate SAM on a gold surface (\( \text{R–S–Au} \)) with one given \( \Delta \Phi \), eqn (2) implies that then also the bonding-induced contribution to the work-function modification, \( \Delta E_{\text{BD}} \), must differ between the two approaches. In density-functional theory (DFT) calculations, the latter is obtained by applying eqn (1) to the plane-averaged charge-density differences, \( \rho_{\text{diff}} \), that are associated with the processes indicated in eqn (3).1–3

\[
\rho_{\text{diff}}^{\text{rad}} = \rho_{\text{sys}}^{\text{rad}} - \rho_{\text{ref}}^{\text{rad}} \rho_{\text{diff}}^{\text{syst}} = \rho_{\text{sys}}^{\text{syst}} - \rho_{\text{ref}}^{\text{syst}} \]

(4)

(4a)

Here, the subscripts sys, \( \text{Au}, \text{rad}, \text{sat}, \text{and} \text{H} \) refer to the entire metal/SAM system, the pristine metal, the free-standing molecular monolayer of radical and \( \text{H} \)-saturated species, and the layer of saturating \( \text{H} \)-atoms, respectively. Experimentally, \( \Delta E_{\text{BD}} \) can be extracted from \( \Delta \Phi \) measurements on a series of molecules with the aid of their calculated dipole moments and reasonable estimates for all other quantities in eqn (2).4–7

Notably, DFT calculations pursuing the saturated approach have found values of \( \Delta E_{\text{BD}} \approx -1.2 \text{ eV} \) for SAMs of biphenylthiols on \( \text{Au(111)} \),1–3 while negligible values (\( \sim 0.01 - 0.08 \text{ eV} \))

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have been reported for SAMs of alkythiols following the radical scheme. Even more strikingly, experimental studies on thiolns with an aromatic ring adjacent to the –SH group have reported a ∆UBD of −0.85 eV when relying on μ values calculated for saturated molecules, while a ∆UBD between +0.6 and +1.0 eV has been found using μ values calculated for radicals. Thus, the bond dipole of thiols on gold appears to depend not only on the chemical structure of the molecular backbone but, rather unsatisfactorily, also on the chosen partitioning scheme. It is the purpose of the latter, however, to permit correlating the chemical structure of the SAM-forming molecules with the achievable ∆Φ, thus allowing for the rational design of suitable molecules. Therefore, the question arises which of the two possibilities is better suited to provide a chemically and physically insightful picture of the relevant interfacial processes.

To elucidate this question, we performed slab-type DFT band-structure calculations for a series of functionalized thiols on Au(111) using VASP, the internal-coordinate geometry optimizer GADGET, and XCRYSDEN (for details see ESI†). As shown in Fig. 1a, each molecule is endowed with a strongly polar head-group substitution that either lowers Φ in the case of the electron-donating amino group (–NH2) or increases Φ in the case of the electron-accepting cyano group (–CN), note that the total dipole moments of these molecules are composed of the contributions from the head groups on one side and from the thiol groups on the other side, the latter pointing roughly in the direction of the S–H bonds (vide infra). An in-depth analysis of the electronic properties of the molecules shown in Fig. 1a as well as the corresponding SAMs is provided in ref. 14. For the sake of comparability, the same rectangular p(√3 × 3) unit cell containing two molecules is assumed for all monolayers (Fig. 1b). To individually access all components in eqn (4), separate calculations were performed on the corresponding sub-systems listed there.

As it appears more natural and chemically intuitive (in contrast to R–S2 radicals, the –SH terminated molecules are readily accessible to experiment), the saturated scenario is discussed first. There, when setting up the system for the free-standing molecular monolayer in order to determine ∆EVac in eqn (2) and ρvac in eqn (4a), one is faced with the choice of where to place the hydrogen atom relative to the sulfur (Fig. 1c). Two positions can be identified, where the hydrogen lies in the plane defined by the sulfur and the two nearest carbon atoms. As the S–C bond is inclined to the surface normal, the projection of the local dipole moment around the –SH group onto the surface normal (vide supra), the corresponding plot is shown in Fig. 2.† This indicates that, using the saturated partitioning scheme, ∆UBD also reflects the position of the saturating H-atoms and, thus, the orientation of the S–C bond and the molecular plane with respect to the surface normal (Fig. 1c).

To further test the ability of the saturated approach to provide chemically and physically insightful information, we also examined a different quantity, namely the “left-sided” ionisation potentials (IPs) of the free-standing saturated monolayers, which are defined as the energy difference between its highest occupied π-states (the highest fully delocalized σ-states in the case of C1) and Evac on the thiol side, as the latter obviously differs from Evac above the head-group substituents by ∆Evac. Again, the IPleft values in Table 1 reflect the chemical nature adjacent to the sulfur to some extent, i.e., larger values are observed for more polarisable backbones. Notably, the value for the alkyl backbone C1 is non-zero. Also listed are the ∆UBD values for hydrogen position II. Not only are they markedly different, but closer inspection of Table 1 reveals that the difference to the H-position I values increases essentially linearly with the height difference, ∆z1,2, between the two saturating hydrogens in the two positions (Fig. 1c), i.e., with the projection of the local dipole moment around the –SH group onto the surface normal (vide supra); the corresponding plot is shown in Fig. 2.† This indicates that, using the saturated partitioning scheme, ∆UBD also reflects the position of the saturating H-atoms and, thus, the orientation of the S–C bond and the molecular plane with respect to the surface normal (Fig. 1c).
of the molecular backbones, i.e., lower values are found for structures with a more extended conjugation. Similarly to $\Delta z_{C1}$, the height difference between the saturating hydrogen atoms in position I and II; the dashed line is a linear fit through the origin.

Table 1 DFT-calculated vertical distance, $\Delta z_{C1}$, between the saturating hydrogen atoms in positions I and II; left-sided ionisation potential, $IP_{\text{left}}$, energy perturbation of the highest occupied delocalized orbitals upon metal–molecule bonding, $E_{\text{corr}}$, and potential energy step due to the bond dipole, $\Delta E_{\text{BD}}$, for hydrogen position I as well as $\Delta E_{\text{BD}}$ for hydrogen position II obtained for the saturated partitioning scheme

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta z_{C1}$/Å</th>
<th>$IP_{\text{left}}$/eV</th>
<th>$E_{\text{corr}}$/eV</th>
<th>$\Delta E_{\text{BD}}$/eV</th>
<th>$\Delta E_{\text{BD}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–NH$_2$</td>
<td>1.919</td>
<td>7.74</td>
<td>0.03</td>
<td>−1.27</td>
<td>0.16</td>
</tr>
<tr>
<td>C1–CN</td>
<td>1.880</td>
<td>8.17</td>
<td>−0.01</td>
<td>−1.00</td>
<td>0.13</td>
</tr>
<tr>
<td>C2–NH$_2$</td>
<td>0.675</td>
<td>5.03</td>
<td>0.14</td>
<td>−1.14</td>
<td>−0.69</td>
</tr>
<tr>
<td>C2–CN</td>
<td>0.515</td>
<td>5.13</td>
<td>0.17</td>
<td>−1.20</td>
<td>−0.85</td>
</tr>
<tr>
<td>C3–NH$_2$</td>
<td>1.894</td>
<td>3.89</td>
<td>0.16</td>
<td>−1.87</td>
<td>−0.78</td>
</tr>
<tr>
<td>C3–CN</td>
<td>2.067</td>
<td>3.74</td>
<td>0.16</td>
<td>−2.06</td>
<td>−0.88</td>
</tr>
<tr>
<td>T1–NH$_2$</td>
<td>0.821</td>
<td>4.26</td>
<td>0.14</td>
<td>−1.54</td>
<td>−1.01</td>
</tr>
<tr>
<td>T1–CN</td>
<td>0.788</td>
<td>4.30</td>
<td>0.14</td>
<td>−1.57</td>
<td>−1.07</td>
</tr>
<tr>
<td>T2–NH$_2$</td>
<td>1.269</td>
<td>4.04</td>
<td>0.12</td>
<td>−1.70</td>
<td>−0.94</td>
</tr>
<tr>
<td>T2–CN</td>
<td>1.266</td>
<td>4.10</td>
<td>0.13</td>
<td>−1.71</td>
<td>−0.95</td>
</tr>
<tr>
<td>T3–NH$_2$</td>
<td>1.173</td>
<td>3.99</td>
<td>0.13</td>
<td>−1.70</td>
<td>−0.98</td>
</tr>
<tr>
<td>T3–CN</td>
<td>1.160</td>
<td>4.01</td>
<td>0.13</td>
<td>−1.72</td>
<td>−1.02</td>
</tr>
</tbody>
</table>

Table 2 DFT-calculated potential energy step due to the bond dipole, $\Delta E_{\text{BD}}$, left-sided ionisation potential, $IP_{\text{left}}$, and energy perturbation of the highest occupied delocalized orbitals upon metal–molecule bonding, $E_{\text{corr}}$, obtained for the radical partitioning scheme

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{\text{BD}}$/eV</th>
<th>$IP_{\text{left}}$/eV</th>
<th>$E_{\text{corr}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–NH$_2$</td>
<td>−0.04</td>
<td>8.95</td>
<td>−0.02</td>
</tr>
<tr>
<td>C1–CN</td>
<td>−0.04</td>
<td>9.07</td>
<td>−0.09</td>
</tr>
<tr>
<td>C2–NH$_2$</td>
<td>1.11</td>
<td>6.07</td>
<td>−1.11</td>
</tr>
<tr>
<td>C2–CN</td>
<td>0.96</td>
<td>6.08</td>
<td>−1.08</td>
</tr>
<tr>
<td>C3–NH$_2$</td>
<td>1.33</td>
<td>6.11</td>
<td>−0.86</td>
</tr>
<tr>
<td>C3–CN</td>
<td>1.28</td>
<td>6.14</td>
<td>−0.83</td>
</tr>
<tr>
<td>T1–NH$_2$</td>
<td>1.28</td>
<td>5.89</td>
<td>−1.11</td>
</tr>
<tr>
<td>T1–CN</td>
<td>1.19</td>
<td>5.88</td>
<td>−1.07</td>
</tr>
<tr>
<td>T2–NH$_2$</td>
<td>1.22</td>
<td>5.81</td>
<td>−1.07</td>
</tr>
<tr>
<td>T2–CN</td>
<td>1.17</td>
<td>5.81</td>
<td>−1.08</td>
</tr>
<tr>
<td>T3–NH$_2$</td>
<td>1.27</td>
<td>5.89</td>
<td>−0.99</td>
</tr>
<tr>
<td>T3–CN</td>
<td>1.23</td>
<td>5.89</td>
<td>−0.99</td>
</tr>
</tbody>
</table>

SAM formation, one obviously needs not be concerned with the position of a saturating hydrogen atom on the sulfur. The results obtained with the radical partitioning scheme are listed in Table 2. In agreement with previous studies following this approach, a vanishing $\Delta E_{\text{BD}}$ is found for the alkyl backbone C1 and, for all other molecular structures, $\Delta E_{\text{BD}}$ changes sign compared to the saturated scheme (Table 1); a potential dependence on the orientation of the S–C bond is hard to assess. Notably, the $IP_{\text{left}}$ values in the radical case (Table 2) all lie within the narrow range of 5.8 – 6.1 eV (cf. ref. 8); the exception is again C1 due to the different nature ($\sigma$-orbital vs. $\pi$-orbital) of the highest occupied delocalized states. Additionally, the $E_{\text{corr}}$ values are on the order of 1 eV, yet again with the exception of C1 (vide infra). This leads to the conclusions that, in the radical partitioning scheme, chemical information on the nature of the backbone is largely lost and that the electronic structure of the free-standing radical layer is significantly perturbed upon bonding to the metal.

The reason for these observations is that the radical character of the –S$^*$ termination dominates the electronic structure of the free-standing monolayer on the docking-group side and, consequently, also the interfacial charge redistributions upon metal–molecule bond formation. Removing the hydrogen from the sulfur in the thiol and, thus, converting the closed-shell molecule into a radical, induces major charge rearrangements on that side of the molecule. The latter can be expressed as $(\rho_{\text{rad}} + \rho_{\text{th}}) - \rho_{\text{sat}}$ and are shown in the left panels of Fig. 3. For all conjugated systems (C2–T3), the charge redistributions resulting from hydrogen removal reach far onto the molecular backbones, as the sulfur is strongly coupled to their $\pi$-electron system. A qualitatively different behaviour is observed in the case of the alkylthiol (C1), where both the $\pi$-system and the radical character are strongly localized on the sulfur alone and, therefore, the delocalized $\sigma$-states are hardly affected by radical formation. When the bonds between radicals and gold are formed, i.e., when charges are shifted according to eqn (4b), the molecule is essentially converted back to a closed-shell species and the aforementioned charge redistributions are largely reversed in the spatial region of the SAM (left panels in Fig. 3), but not quite. The actual chemical and physical information regarding the Au–S bonding lies hidden in the difference between the processes of removing the hydrogen atoms from the sulfur and “adding” the gold surface.
instead. Exactly this difference (right panels in Fig. 3), which actually corresponds to $\rho_{\text{diff}}$ in the saturated partitioning scheme (eqn (4a)), is obscured in the radical approach. To summarize, we have identified and discussed two distinctly different ways of defining the Au–S bond dipole in thiol SAMs on Au(111), the saturated and the radical scheme. With a well-defined choice for the positions of the saturating hydrogen atoms on the sulfur, the former conserves information on the chemical structure of the thiols, reflects the orientation of the S–C bond, and provides revealing insights into the interfacial charge rearrangements that occur upon metal–molecule bonding. In particular, a considerable negative $\Delta E_{\text{BD}}$ is found for a wide range of molecules, including alkythiols. On the other hand, when considering unsaturated R–S$^+$ species as the origin of the molecular contribution to the work-function modification, chemical information on the SAM electronic structure is largely lost and the relevant bonding-related charge redistributions at the metal–molecule interface are not accessible, which clearly renders this second approach less appealing.

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**Notes and references**

† As there are two inequivalent molecules per unit cell (Fig. 1b), the average $\Delta z_{1,2}$ values are reported.