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Radical self-assembled monolayers on Au(111) formed by the adsorption of closed-shell molecules†Ferdinand Rissner,^{‡a} ZhongYun Ma,^{‡bc} Oliver T. Hofmann,^a Christian Slugovc,^d Zhigang Shuai^e and Egbert Zojer^{*a}

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Using density-functional theory band-structure calculations, we show how the exothermic adsorption of conjugated closed-shell organic semiconductor molecules on an Au(111) surface can turn them into radicals. For this to happen, we suggest the use of a thiocarbonyl docking group instead of the commonly applied thiols. The radicalisation of the adsorbed molecules resulting from the formation of the Au–S bond leads to reduced electron- and hole-injection barriers. The calculations predict two energetically close solutions for the adsorbed monolayer, one being non-magnetic and metallic and another being magnetic with reduced density of states at the Fermi energy.

In the field of molecular electronics,¹ the alignment of the molecular electronic states with respect to the Fermi level of the metal, E_F , is the key quantity for understanding and tuning the characteristics of molecular junctions.² Unfortunately, it cannot be easily predicted, as it is sensitively determined by several factors besides the electronic levels of the molecule. Most generally, these are substrate–adsorbate interactions and intermolecular interactions within the adsorbate layer.³ Both depend on the exact geometry of the interface, as collective phenomena⁴ and depolarization effects⁵ determine the properties of well-ordered densely packed self-assembled monolayers (SAMs), but do not occur in isolated molecules. Consequently, individual molecules and such surrounded by like molecules in the form of a SAM can differ greatly in their electronic properties.⁶ Understanding and controlling the relevant factors is thus of considerable interest in order to tune, *e.g.*, charge-injection barriers. A

relatively easy prediction of the barriers is possible if the highest occupied (lowest unoccupied) states in the organic material were above (below) the metal Fermi energy in the hypothetical case of no metal/molecule interaction, *i.e.*, vacuum level alignment. Then, so-called Fermi level pinning takes place and fixes occupied (unoccupied) states close to E_F .⁷

Only relatively recently, also the properties of metal/organic interfaces involving radical molecules/SAMs have become a topic of heightened interest (see ref. 8 and references therein). The conductance of radicals at small bias voltages was found to be orders of magnitude larger than that of closed-shell molecules.^{9,10} This can be easily understood in a spin-restricted picture, *i.e.*, when assuming α - and β -spin states to be identical. Then, because the highest occupied orbital of the radical is only singly occupied, in the corresponding SAM one is dealing with a half-filled valence band that in thermodynamic equilibrium must align with E_F . In that case, the metallic character extends onto the SAM.^{10,11} The overall situation can be somewhat modified when relaxing the above-mentioned conditions of forcing α - and β -spin states to be equal, as discussed below, but it has been argued (see ESI of ref. 10) that also in a situation with uncompensated spins small injection barriers are realized for electrons and holes simultaneously. Another peculiar feature of such radical monolayers is that they can be easily chemically oxidized or reduced. This lead to the development of redox-sensitive, surface-confined molecular optical and magnetic switches.¹²

In the present contribution we describe how a radical character can be realized in a SAM consisting of closed-shell molecules. This is achieved by using a docking group whose bonding situation is fundamentally altered by the reaction with the metal. For that purpose, we propose the thiocarbonyl group, where binding to Au(111) results in the formation of a new bond rather than the replacement of an existing one. The latter is the case, for example, when replacing the S–H bond by an S–Au bond in thiols, the most commonly used docking groups in molecular electronics. To investigate thiocarbonyl-bonded SAMs, we studied densely packed layers of the three closed-shell molecules 1–3 shown in Fig. 1. They are all characterized by a quinoidal backbone and bear either electron accepting (1 and 2) or electron donating (3) tail groups. Although the molecules under investigation to the best of our knowledge have not yet been studied in experiments (while 1 has been considered in a theoretical study¹³), their synthesis or the synthesis of closely related species should be feasible.¹⁴

^aInstitute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria. E-mail: egbert.zojer@tugraz.at

^bKey Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, People's Republic of China

^cSchool of Aerospace and Materials Engineering, National University of Defense Technology, 410073 Changsha, People's Republic of China

^dInstitute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, 8010 Graz, Austria

^eKey Laboratory of Organic Opto-Electronics and Molecular Engineering, Department of Chemistry, Tsinghua University, 100084 Beijing, People's Republic of China

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‡ These authors have contributed equally to this work

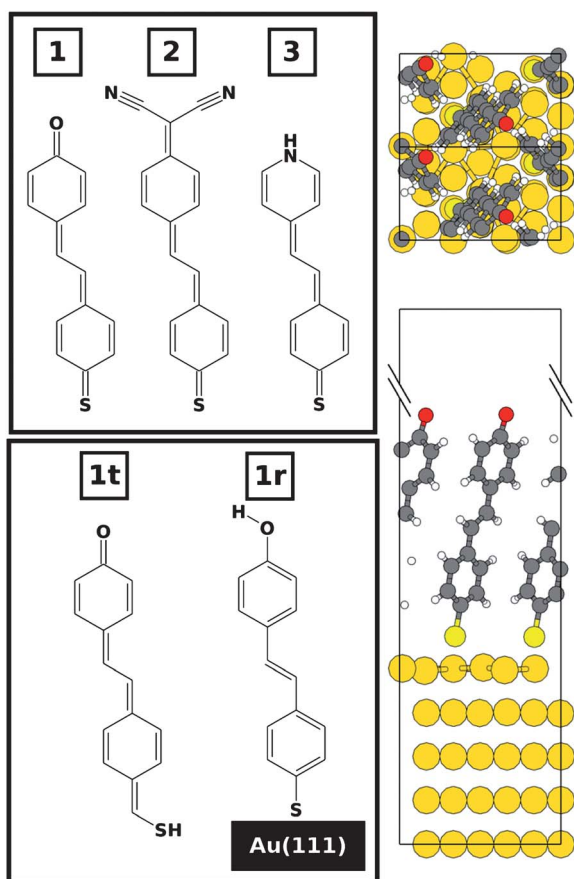


Fig. 1 Left: chemical structures of the closed-shell molecules **1–3**; **1t** is analogous to **1**, but bearing a mercaptomethylene docking group; **1r** is the reduced version of **1** after it has been bonded to the Au(111) surface. Right: top and side view of the unit cell used in the periodic calculations.

Our computational work relies on density-functional theory (DFT) based band-structure calculations using the VASP code^{15–17} and the PW91 functional. Electronic states were broadened by 0.2 eV, a dipole layer was placed in the vacuum region between neighboring slabs to compensate for the net dipole, and spin-unrestricted results were obtained by suitable initial guesses for the magnetization (for further details, see ESI†). We studied molecules **1–3** arranged in a herringbone-packed, upright-standing monolayer on Au(111) infinitely extended in two dimensions, where the metal substrate is represented by five Au layers. Since we lack corresponding experimental information, we chose a $(3 \times \sqrt{3})$ surface unit-cell containing two molecules (see Fig. 1), as this is often found for aromatic thiol-docked SAMs;¹⁸ this implies that no large-scale reconstructions are considered here. We chose relatively extended molecules, as for them a higher degree of order can be expected.¹⁹ The adsorption energy per molecule is defined as $E_{\text{ads}} = \frac{1}{2} \{E_{\text{Au(111)+SAM}} - (2E_{\text{mol}} + E_{\text{Au(111)}})\}$, *i.e.*, the difference in energy between the bonded and isolated subsystems. Despite neglecting van der Waals contributions for methodological reasons (see ESI†), we find sizable exothermic values of -0.58 eV (-56.0 kJ mol⁻¹), -0.56 eV (-54.0 kJ mol⁻¹) and -0.33 eV (-31.8 kJ mol⁻¹) per molecule for **1**, **2** and **3**, respectively. This indicates that such monolayers can indeed be formed and will be reasonably stable. Here, it should be mentioned that for thiols, replacing the S–H with an S–Au bond is calculated to be even slightly

endothermic using the same methodology (while breaking the finally formed thiolate–Au bond again costs a considerable amount of energy in excess of 1 eV (96.5 kJ mol⁻¹)).²⁰

For the adsorbed SAMs consisting of molecules **1–3**, the densities of states projected onto the molecular layers (PDOS) at energies close to E_{F} are shown in Fig. 2. The spin-restricted calculations (shown as black areas) are characterized by peaks around E_{F} that are only half-filled, a result expected for radicals under these conditions (*vide supra*); only in **1**, a somewhat more complex situation occurs, as there are overlapping peaks in the DOS close to E_{F} . The real-space representations (local density of states, LDOS) of the states contributing to this half-filled peak are shown as the inset for **1** integrated between E_{F} and $E_{\text{F}} \pm 0.1$ eV, respectively. They are reminiscent of the closed-shell molecular LUMO, which is also observed for **2** and **3** (see ESI†).

As radicalisation implies the existence of unpaired electrons, relaxing also the spin degree of freedom can lead to a spin-polarized

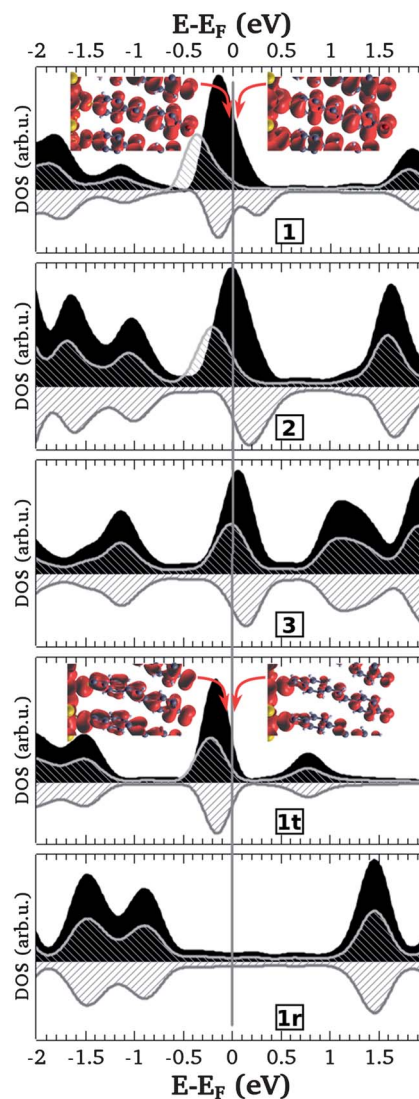


Fig. 2 Spin-restricted (black) and spin-unrestricted (up/down: light/dark grey) PDOS of all investigated adsorbed monolayers, aligned at the Fermi energy E_{F} (vertical grey line). In the insets for **1** and **1t**, the LDOSs integrated between E_{F} and $E_{\text{F}} \pm 0.1$ eV are shown.

solution at lower energy. Indeed, using a proper initial guess for the magnetisation (see ESI†) we find such solutions with different α - and β -spin densities of states, shown in light and dark grey colour in Fig. 2. The calculated stabilisation of the α - and destabilisation of the β -states are quite small, which is why both peaks remain close to E_F and very similar injection barriers are found for electrons and holes. Note, however, that the extent of the predicted splitting depends on the chosen density functional and we find it to increase when using a hybrid functional (*cf.*, discussion in the ESI†). In this context it is, however, worth remembering that Crivillers *et al.*⁹ did observe a huge increase in the low-bias conductivity in related radical molecules compared to their closed-shell counterparts, which supports the notion that radical formation significantly reduces the transport gap. The fundamental difference between the study in ref. 9 and the present one is that Crivillers *et al.* adsorbed radicals directly onto a properly primed Au surface, while we here suggest a strategy to start with closed-shell systems and then form the radical through the binding to the substrate.

The different number of electrons in the α - and β -spin manifolds in the spin-unrestricted calculations also implies that the closed-shell molecules **1–3** change their magnetic properties upon adsorption. Each of the unit cells is characterized by an uncompensated spin, which in the case of the PW91 based calculations amounts to 1.70 (**1**), 1.55 (**2**), and 0.65 μ_B (**3**), respectively. The exact values for these magnetic moments should be considered with some caution, as a larger splitting between the α - and β -manifolds as expected, *e.g.*, for hybrid functionals (*vide supra*), would most likely modify these values. They are also to some extent influenced by the chosen broadening of the electronic states (see ESI†). Independent of these technical details, each molecule bears a non-vanishing magnetic moment, *i.e.*, the monolayer is calculated to be ferromagnetic. Ferromagnetic organic materials are indeed known,^{21,22} but it has to be kept in mind that the periodic boundary-conditions in the band-structure calculation enforce parallel alignment of the spins in all unit cells. Thus, on the basis of our calculations it also cannot be excluded that the actual monolayer displays paramagnetic properties (*cf.* ref. 12). As a side note, we also mention that magnetic phenomena at the Au–S interface have been discussed in various contexts in the literature (see for instance refs. 23–25).

An interesting observation is also that for the investigated systems, the spin-unrestricted solutions are lower in energy by only 0.04 eV (**1**), 0.02 eV (**2**) and <0.01 eV (**3**) than the spin-restricted ones. These values are in the order of $k_B T$, suggesting that for the present molecules both spin-unrestricted solution (ferro/paramagnetic with a non-vanishing transport gap) as well as spin-restricted solution (diamagnetic with the highest bands half-filled by electrons of opposite spins rendering the system metallic—*vide supra*) might well coexist at room temperature. Their relative stability (and thus the fundamental magnetic and electronic properties of the SAMs) could then very well be controlled by chemical substitution or external stimuli like applying a magnetic field. These observations certainly warrant further investigations.

To illustrate that the formation of a radical SAM (be it ferro/paramagnetic or not) upon adsorption of molecules **1–3** is solely due to the thiocarbonyl docking group and not a consequence, for example, of the quinoidal backbone of the studied molecules, we also calculated the PDOS for molecule **1t** (Fig. 1) on Au(111). Apart from the thiocarbonyl group being replaced by a mercaptomethylene group, this (closed-shell) system is identical to **1** and we assumed the same

unit cell in the calculation.²⁶ The corresponding PDOS around E_F and the related LDOS are also shown in Fig. 2. We observe pinning of the fully occupied HOMO-derived peak at E_F (*cf.* also ref. 7) and find the empty LUMO-derived states well above E_F .²⁷ Moreover, no spin-unrestricted solution is found (see grey curves for **1t** in Fig. 2).

The mechanism responsible for the generation of the radical upon bonding is sketched in Fig. 3a for molecule **1**: the formation of the new Au–S bond causes a decrease of electron density in the S=C bond and, thus, leads to a significant elongation of this bond. The new situation can be essentially described as an Au–S–C unit, in which one electron of the S=C bond is used for the formation of the Au–S bond. Consequently, an unpaired electron is generated and accommodated all over the molecule, which now bears an increased aromatic character (see bond length changes in Fig. 3a). This delocalization of the uncompensated spin can be seen in the calculated spin-density (*i.e.*, the difference between α - and β -charge densities) of the adsorbed molecules shown in panel b of Fig. 3. This shows that the quinoidal/aromatic nature of the backbone is important for the radical's delocalization, while its formation is a consequence of using a thiocarbonyl docking group (see comparison between **1** and **1t**).

As mentioned, redox-switching of the optical and magnetic properties of closely related molecules has been found experimentally.¹² To show the effect of chemical reduction on the interfacial electronic structure, we studied also a variant of the Au(111)/**1** interface in which the carbonyl groups were reduced (*i.e.*, where the carbonyl groups were replaced by hydroxyl groups). This yielded the SAMs denoted as **1r** in Fig. 1. The resulting bond-length changes indicate a further increase of the aromatic character of the backbone (see ESI†) and the molecules adopt a closed-shell structure now also on the surface. As a result, the gap between the (now fully occupied) HOMO- and the LUMO-derived states drastically increases (bottom panel of Fig. 2). The absence of Fermi-level pinning (that is still observed for **1t**, *vide supra*) implies an equally drastic increase of the charge-injection barriers, consistent with above mentioned experimental observations.^{12,9}

To summarise, we propose the thiocarbonyl group as a potentially interesting docking group for use in self-assembled monolayers on noble metals. A radicalisation of closed-shell molecules is induced upon bonding to the substrate, for which we find clearly exothermic adsorption energies of 0.33–0.58 eV (32–56 kJ mol⁻¹) per molecule.

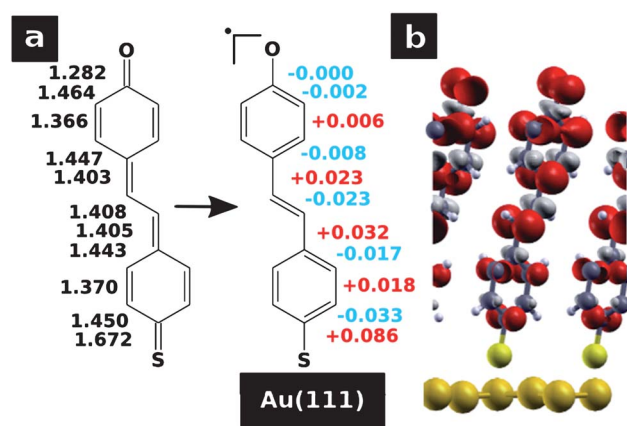


Fig. 3 (a) Mechanism of radicalisation upon adsorption: gas phase bond lengths and bond length changes are indicated. (b) Spin density of the adsorbed molecules (red: excess α -spin; light grey: excess β -spin).

The electronic and magnetic properties of the resulting SAMs are fundamentally different from thiolate-bonded but otherwise analogous molecules. Charge-injection barriers are modified and energetically extremely close solutions for non-magnetic metallic and magnetic monolayers with reduced density of states at E_F are found. We speculate that one of these solutions could be stabilised with respect to the other by a molecular design approach, and further show how level-alignment and magnetic properties in such SAMs can be switched by redox-reactions.

Acknowledgements

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- We note that upon adsorption, the hydrogen might actually reduce the molecule rather than being desorbed as H_2 , rendering also **1t** a radical. We do not consider this possibility here as our intention is to demonstrate the role of only the docking group on the interfacial electronic structure.
- Note that this band gap can be viewed only as a lower limit, as semi-local functionals such as PW91 are known to underestimate the band gap of semiconductors.