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Neutral Organic Radical Formation by Chemisorption on Metal Surfaces

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Abstract: Organic radical monolayers (r-MLs) bonded to metal surfaces are potential materials for the development of molecular (spin)electronics. Typically, stable radicals bearing surface anchoring groups are used for generating r-MLs. Following a recent theoretical proposal based on a model system, we report the first experimental realization of a metal surface induced r-ML where a rationally chosen closed-shell precursor 3,5-dichloro-[bis-(2,4,6-trichlorophenyl)methylen]cyclohexa-2,5-diene-1-one (**1**) transforms into a stable neutral open-shell species (**1'**) via chemisorption on Ag(111) surface. X-ray photoelectron spectroscopy reveals that the $>C=O$ group of **1** reacts with the surface forming a C-O-Ag linkage which induces an electronic rearrangement that transforms **1** to **1'**. Importantly, Au is inert towards **1**, while Cu surface leads to dehalogenation reactions. The radical nature of the monolayer was further confirmed by angle-resolved photoelectron spectroscopy and electronic structure calculations which provide evidence for the emergence of the singly occupied molecular orbital (SOMO) of **1'**.

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KEYWORDS: Self-assembled monolayers, chemisorption, X-ray photoelectron spectroscopy, angle-resolved photoelectron spectroscopy, stable radicals, density functional theory.

Molecular functionalization of substrates has been shown to be a promising route to confer novel properties to a surface. In particular, organic radicals exhibiting spin as well as redox activity constitute attractive functional building blocks in the fields of molecular electronics and spintronics.¹⁻⁸ The generation of radical anions/cations physisorbed on surfaces has been achieved by inducing a charge transfer between a neutral molecule and a metal substrate or by the application of an electrical stimulus to locally reduce/oxidize the molecules.^{9,10} Stable neutral organic radicals have also been physisorbed on surface showing the Kondo effect.¹¹⁻¹³ In order to better stabilize such systems for potential applications, direct chemical bonding of the molecules with the surface can be realized to prepare organic radical monolayers (r-MLs).^{14,15} The realization of such r-MLs requires the rational design and synthesis of neutral organic radicals (R) with appropriate surface anchors (A) (Fig. 1A). Importantly, the radicals need to be highly stable to survive the harsh and multi-step reaction conditions required to provide these species with sufficient synthetic tailorability. However, the scarcity of suitable highly persistent radicals hampers the development of novel and versatile r-MLs. To circumvent this problem, recently, Rissner et. al.¹⁶ proposed an alternative pathway to r-MLs based on theoretical calculations showing how closed-shell organic molecules could convert into a neutral open-shell (radical) species by chemisorption on a metal surface. These calculations are based on molecules which would lead to rather reactive adsorbed radical species upon chemisorption and as such, at first sight, the proposed concept appears to be rather analogous to substrate-induced formation of unstable organic radical cation/anions.^{9,17-22} Our approach addresses three crucial challenges necessary in order to experimentally implement the predicted closed-shell to neutral radical principle to generate a stable neutral r-ML (Fig. 1B): i) rational design of a stable closed-shell molecule which chemisorbs on a given metal surface in a programmed manner, ii) controlling

the surface reaction, and iii) stabilizing the resulting neutral organic radical on the metallic surface to ensure persistency. To overcome these challenges and to provide a proof of concept, we have chosen tris(2,4,6-trichloro-phenyl)methyl (TTM) based radicals as the target entities to be formed on the desired metal surface (Fig. 1C).^{23,24} Note that TTM and the perchlorotriphenylmethyl (PTM) analogue radicals are very stable under ambient conditions and have been successfully deployed in r-MLs²⁵⁻²⁷ and molecular junctions.^{28,29} However, the chemistry required for tailoring such PTM or TTM systems directly with appropriate anchors (A) remains challenging due to their limited tolerance to physical and chemical conditions during processing.³⁰ For this reason, starting from a closed-shell molecule, with high stability under synthesis/processing conditions, which can transform into a relatively stable radical upon metal-surface reaction, is extremely appealing.

Here, we demonstrate the selective reactivity of the carbonyl functionalized TTM-monomer **1**,³¹ a closed-shell molecule with a mono $>C=O$ moiety, on metal surfaces such as Au(111), Ag(111) and Cu(111) in a rational way as shown in Fig. 1B. This molecule has been designed with an exposed carbonyl group able to react with a metal surface, and a bis(2,4,6-trichlorophenyl)methylene unit capable of sterically protecting the central methylene carbon (αC). Under ultra-high vacuum (UHV) conditions, **1** is sublimated to form molecular monolayers on the metal substrates. Importantly, X-ray photoelectron spectroscopy (XPS) provided strong evidence that **1** is chemisorbed on Ag surface through a direct interaction of the $>C=O$ group and the metal surface establishing a localized Ag-O-C linkage. This interaction triggers an electron rearrangement in **1** which causes the generation of the neutral open-shell **1**[•] based r-ML (Fig. 1C). This overall mechanism, with molecules that are stably chemisorbed on the Ag(111) surface in a tilted edge-on manner, has been further supported by electronic structure calculations. It was

found that Au remained inert towards **1**, whereas Cu reacted in an undesired manner promoting dehalogenation of **1**. In both Au and Cu cases no r-ML were formed and, thus, this result confirmed that the surface reactivity of the metal has a pivotal role in governing this phenomenon. Angle-resolved ultraviolet photoemission spectroscopy (ARUPS), with the aid of electronic structure calculations, confirmed the spin active nature of the r-ML through detection of the singly occupied molecular orbital (SOMO) of **1**[•].

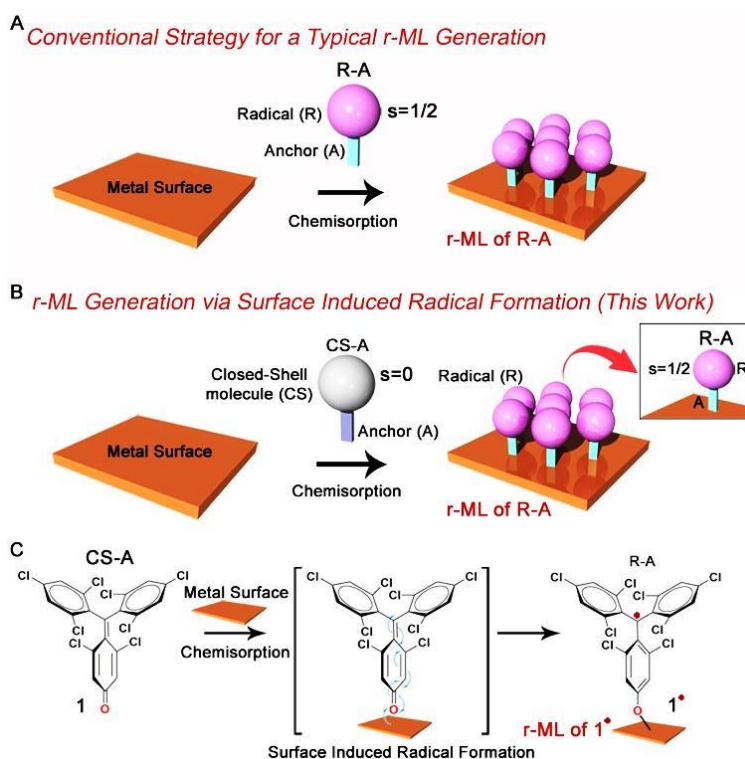


Figure 1. A) Conventional reaction of radical-anchor (R-A) molecules on a metal substrate. B) A closed-shell molecule with an appropriate anchor (CS-A) adsorbs on a metal surface generating r-ML of R-A. C) A plausible mechanism that describes the formation of r-ML of **1**[•] via surface induced radical formation of **1**: Molecule **1** is chemisorbed on a suitable metal surface in an edge-on fashion and, subsequently, transformed to **1**[•] based r-ML.

The choice of TTM derivatives to form stable neutral r-ML was based on the need to incorporate steric protection to the central alpha carbon where most of the spin density would reside upon radical formation. Thus, a precursor with sufficient bulky substituents was essential for providing sufficient stability to the target radical. Following this principle, a TTM derivative with six chlorine atoms in the ortho positions, was designed as a potential candidate to explore the surface-induced radical formation. We note that the widely used fully chlorinated PTM derivatives were not employed since the Cl atoms in meta positions could strongly sterically hinder the accessibility of the anchoring groups with the surface. As anchoring groups, we selected $>C=O$, $>C=S$ and $>C=NH$, as each have been theoretically predicted to react with metallic surfaces leading to the corresponding open-shell derivatives.¹⁶ Following this principle, compound 3,5-dichloro-[bis-(2,4,6-trichlorophenyl)methylen]cyclohexa-2,5-diene-1-one (**1**) was synthesized and purified (Fig. 1C and SI).¹⁶ Attempts to synthesize the analogue compounds with $>C=S$ and $>C=NH$ as anchoring groups (see SI) were also pursued. However, such target molecules were not stable.

Compound **1** was then sublimated under UHV over the metal (111) surfaces of Au, Ag and Cu. The interaction of **1** with these surfaces (**1**/Au, **1**/Ag and **1**/Cu) was investigated with XPS. The Cl 2p emission spectrum was fitted with $2p_{3/2}$ - $2p_{1/2}$ spin-orbit doublets separated by 1.6 eV with the intensity ratio of 2:1 (Fig. 2A). In **1**/Au, the spectrum shows a single doublet with the Cl $2p_{3/2}$ peak at 200.2 eV (high binding energy component, Cl-C). In the case of **1**/Ag and **1**/Cu, component Cl-C appears at 200.3 (78%) and 199.8 eV (41%), respectively, along with an additional Cl contribution, which appears at 197.7 (22%) and 198.1 eV (59%), respectively. This second component (low binding energy component, Cl-Ag) is small in **1**/Ag, but dominates for **1**/Cu. In the three cases, the high energy component Cl-C can be attributed to Cl atoms involved

in a covalent Cl-C bond in **1**.³²⁻³⁷ The lower binding energy contribution Cl-Ag, on the other hand, is most likely related to Cl atoms directly interacting with the metallic surface arising from C-Cl bond dissociations in **1** (see Section 2.1 of the SI for further details).^{32,33,35, 38} By comparing Cl 2p of **1**/Au, **1**/Ag and **1**/Cu, it is evidenced that interaction of **1** with the Au does not alter its molecular structure, whereas C-Cl bond cleavage occurs on Ag (22%) to a lesser extent, and Cu (59%) to a major extent.

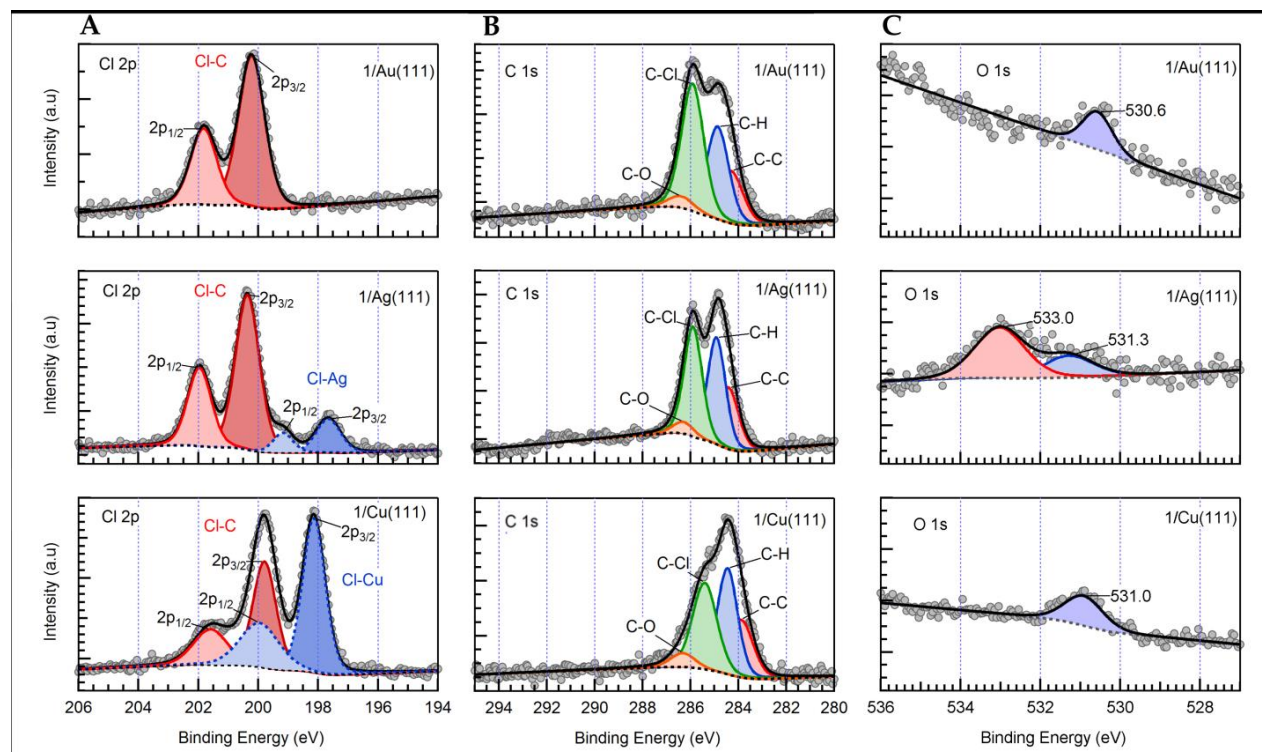


Figure 2. Cl 2p, C 1s and O 1s XPS spectra of **1** on (111) surfaces of Au, Ag and Cu. Raw data is displayed by grey dots and the fitting results and subcomponents by solid lines.

The C 1s spectra of **1**/Au, **1**/Ag and **1**/Cu were also analysed (Fig. 2B). The C 1s spectrum of **1**/Au showed an emission peak that can be fitted taking into account four components centred at 284.3, 284.9, 285.9 and 286.4 eV^{34,39,40} consistent with C at C-C, C-H, C-Cl and C-O bonds,

respectively. In the fitting procedure, the relative peak areas were initially fixed to the stoichiometric ratio between different carbon components (C-C:C-H:C-Cl:C-O 4:6:8:1), and the ratio constraint was released in a second step. A significant and gradual decrease of C-Cl bond intensity was noticed from the inspection of **1**/Ag and **1**/Cu C 1s spectra, which is in line with the Cl 2p analysis. In detail, the C 1s emission of **1**/Ag and **1**/Cu can be fitted to four components, where the stoichiometry was corrected assuming the loss of Cl estimated by the Cl 2p spectra, i.e., the C-Cl dissociation intensity was reduced by 22% for **1**/Ag and 59% for **1**/Cu.

From Cl 2p and C 1s spectral analysis it is almost clear that **1** molecularly physisorbs on Au, whereas surface reactions occur on Ag and Cu involving a proportion of the adsorbed molecules which undergo dehalogenation. However, the possible surface induced radical formation and the concomitant emergence of r-MLs is yet to be confirmed. Since the expected radical formation involves the interaction of >C=O group in **1** with the respective metallic surfaces, we have inspected the O 1s core-level region (Fig. 2C). Notably, **1**/Au and **1**/Cu exhibit emissions in the 530-531 eV range, characteristic of C atoms in the >C=O bond.⁴¹ The absence of any other peak related to Au-O and Cu-O bonds indicates that no chemisorbed species, and hence no radical formation, can be detected within our experimental resolution. The preservation of the >C=O double bond indicates the absence of Au-O and Cu-O bonds and, hence, no radical formation and r-ML can be expected. Remarkably, **1**/Ag shows an intense peak at 533 eV along with the 531.3 eV peak. The new peak at 533 eV is consistent with Ag-O bond formation,^{42,43} which we tentatively assign to the organic molecule in an edge-on type adsorption configuration (Fig. 1C). A quantitative evaluation of the 'edge-on' vs. 'flat' configurations of **1** is estimated from the intensity of Ag-O-C (68%) and >C=O ratio (32%). In other words, we find an efficiency for radical formation of 68%. It is reasonable to assume that the tilted configuration, where the

interaction of Cl atoms with surface atoms is minimized, protect the chemical integrity of the radical species by preventing dehalogenation. In fact, in the absence of interactions, dehalogenation of aryl halides is highly endothermic, with reaction energies in the order of 3-4 eV.⁴⁴ The reaction, however, becomes exothermic with relatively low energy barriers when exposed to noble metal surfaces, as it occurs in the case of the flat lying molecules. In fact, if we attribute the observed 22% of overall dehalogenation to the 32% of flat lying molecules exclusively, we obtained a dehalogenation ratio of 5.5/8. This is a reasonable ratio considering that in the flat configuration three Cl atoms clearly stand away from the surface and are hence expected to be protected from cleavage (Fig. 4 A).

Once the chemisorption of **1** on Ag via the Ag-O-C bond formation was confirmed, to gain insight into the mechanism, the electronic properties of **1**/Au, **1**/Ag and **1**/Cu were examined by angle-resolved ultraviolet photoemission spectroscopy (ARUPS). Fig. 3 shows the ARUPS spectra of the clean and one monolayer covered metal surfaces. Close to the Fermi energy (EF), the Shockley-type surface states (SS) with parabolic dispersion are clearly visible in the three cases (Fig. 3 A-C). Due to their strong localization at the surface, Shockley states represent a sensitive probe for surface modifications, adsorption processes, and interactions between adsorbate and substrate.⁴⁵ The SS parabola in clean Au (Fig. 3A) has the band bottom at ~ 0.4 eV below the EF. In clean Ag, the parabolic dispersion of the SS is hardly discernible due to its proximity to the Fermi level (the band bottom is at less than 0.1 eV below the EF) (Fig. 3B). In both these cases, the SS appears strongly quenched and at approximately the same energy after the deposition of a monolayer of **1**. From the lack of energy shift and the strong intensity decrease, we attribute the signal as coming from molecule-free patches in an unsaturated monolayer. More interestingly, in **1**/Ag we can identify a new peak at around 1.2 eV which, in

line with previous experimental work,⁴⁶ we attribute to the SOMO of the TTM based radical (**1**[•]).³⁰ The substrate-induced character of this new peak is confirmed by its absence in the spectra acquired with multilayer films (Fig. S5 in SI). Its lack of dispersion reveals the local character of the molecular orbital, excluding the formation of any dispersing hybrid interface state. The energetic coincidence of the rest of molecular peaks as compared to multilayer films also indicates the absence of any sizeable charge transfer related to the interaction with the metal surface (Fig. S4 and S5), which is further confirmed by a similar comparison with the spectra acquired with the charge neutral monolayer TTM on Au(111). This neutral radical scenario is fully reproduced by DFT calculations, as discussed later. Therefore, as designed, our results strongly support that the electronic structure of **1** becomes open-shell like, i.e., **1** transforms to **1**[•] as a result of chemisorptive Ag-O-C formation, and thereby forms a **1**[•]-based r-ML. This mechanism was not possible on Au due its inert reactivity towards **1**. In contrast, the SOMO peak does not show up the **1**/Cu binding energy plot, which we attribute to the higher reactivity of Cu compared to Au and Ag, thus leading to different, highly dehalogenated surface species. Considering all the above, both XPS and ARUPS confirm the appearance of a r-ML generated by the interaction of **1** with the Ag(111) surface. Experiments also reveal that Au is inactive towards **1** and that Cu is likely too reactive. Thus, Ag(111) appears to selectively induce the change in the electronic structure of the isolated closed-shell **1** compound into an open-shell adsorbed radical, which thereafter generates the desired r-ML.

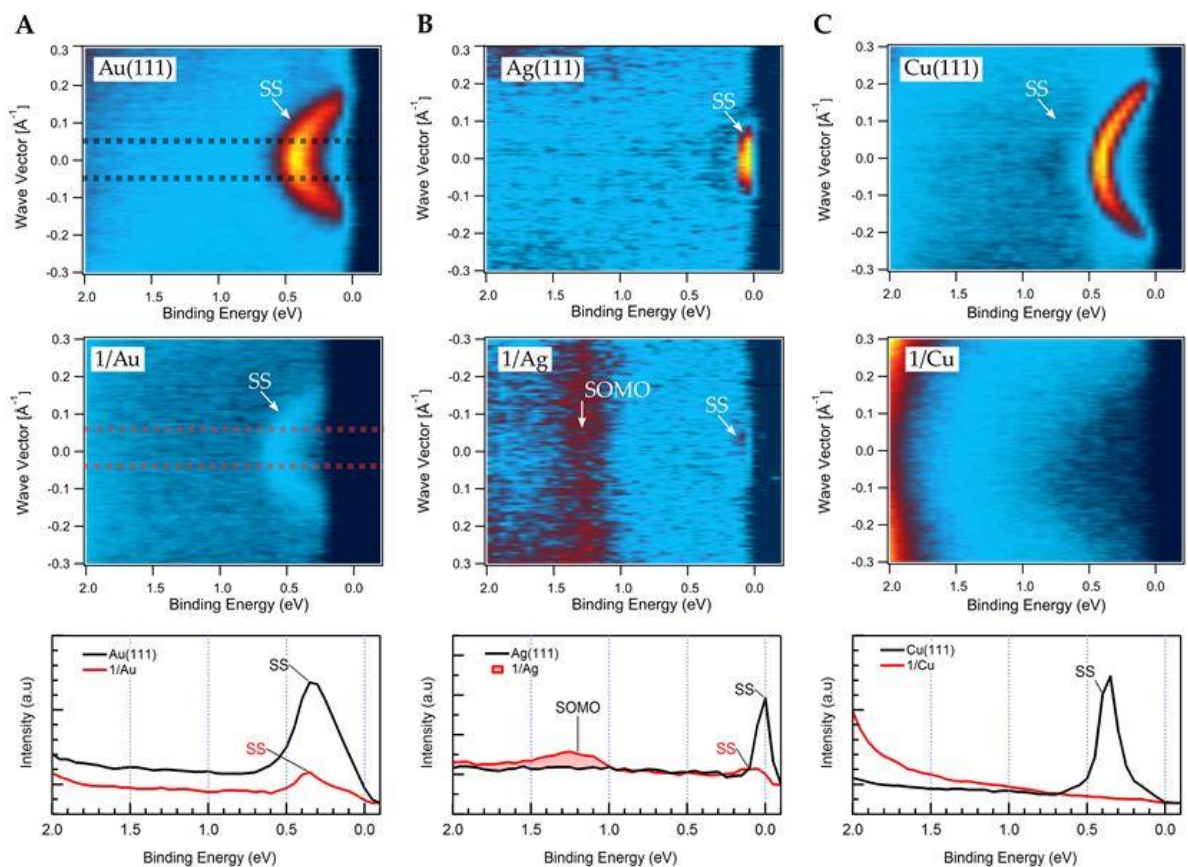


Figure 3. (Top) ARUPS of clean Au, Ag and Cu (111) surfaces (A-C, respectively) and of the same surfaces covered by a molecular monolayer. (Bottom) Profiles of the top spectra at emission angles around the SS band minima as indicated by the dotted lines in A.

To gain further detailed insight into the adsorption configurations and the electronic structure of **1** on the three different metal substrates we carried out first principles periodic density functional theory (DFT) based calculations. The actual systems in experiment consist of layers of many molecules interacting with one another and with various metal substrates. Due to the very high

complexity involved (e.g. molecular configurational and packing possibilities) our calculations are mostly focused on establishing whether the proposed radical formation mechanism is viable and, if so, for which combinations of metal substrate and molecule adsorption configurations this is most likely. As such, to reduce the number of degrees of freedom, our calculations mainly deal with the situation where intermolecular interactions are minimal. We note that, even under such an assumption, the set-up and analysis of the calculations requires careful scrutiny. In the SI a full description and discussion of the calculations, and relevant data derived therefrom (e.g. structural, charge and spin changes upon adsorption).

For all three considered metals, the calculations showed that an ideal upright edge-on configuration (i.e. that shown in Fig. 1) was found to be energetically metastable to flat or ‘tilted edge-on’ configurations (see Fig. 4 and SI). In the cases of Ag(111) and Cu(111) upright edge-on configurations were at least 0.47 eV and 0.73 eV less stable than tilted edge-on configurations, respectively, and are thus unlikely to be prominent species in experiment. In the case of Au(111), **1** could not be stabilized in an ideal upright edge-on configuration and spontaneously relaxed into a tilted configuration which was slightly metastable to the flat configuration by 0.07 eV (see SI). The most stable adsorbed configurations of **1** on the three considered metal surfaces from the DFT calculations are shown to the left in Fig. 4A.

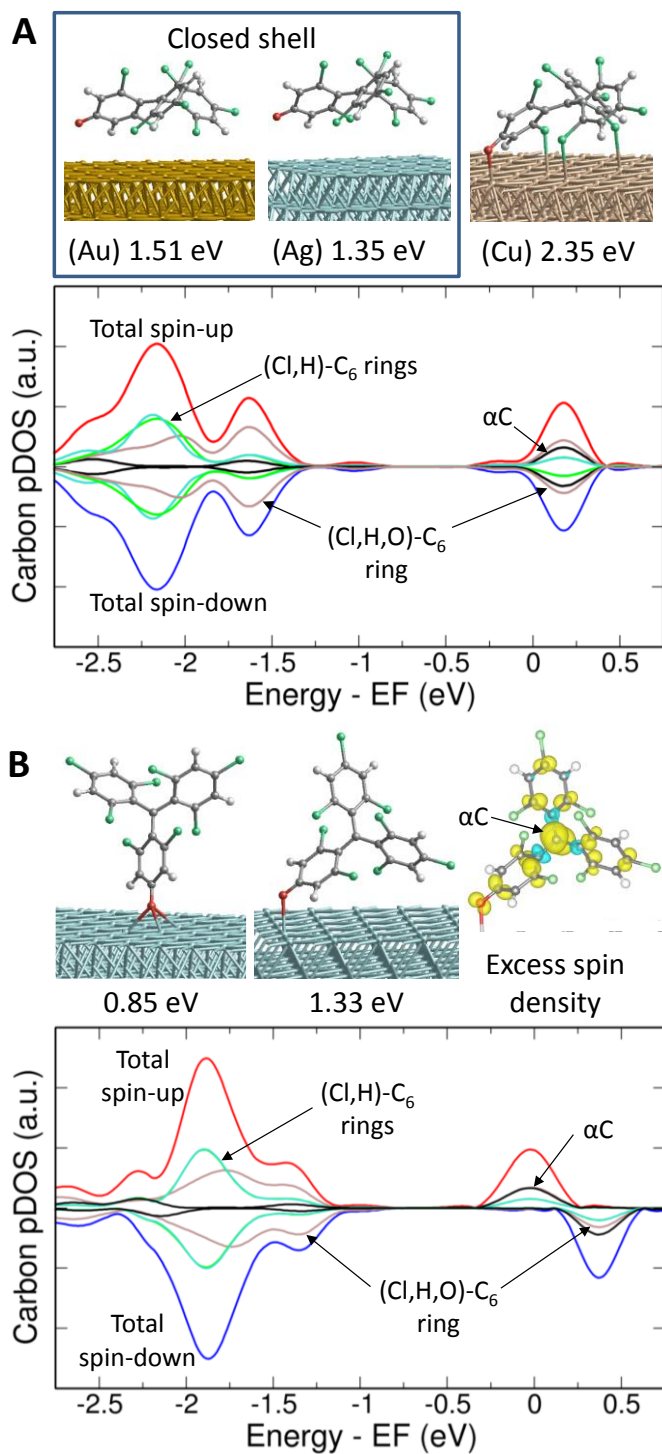


Figure 4. A) Upper, low energy flat adsorption configurations for **1** when closed shell and physisorbed on Au(111) and Ag(111) surfaces, and chemisorbed on Cu(111). Lower, spin-resolved pDOS of all carbon atoms for the Ag(111) case with contributions shown for each

functionalized aryl ring and the α C separately. B) Upper, low energy spin-polarised edge-on and tilted edge-on adsorption configurations for **1** chemisorbed on Ag(111) and the corresponding excess spin density for the tilted edge-on case (yellow – up-spin, blue – down spin). Right, corresponding spin-resolved carbon pDOS for the edge-on case, with contributions shown for each functionalized aryl ring and the α C separately. In both A) and B) molecular adsorption energies of the isolated species relative to the respective surface are shown below each figure. In the carbon pDOS plots the energy is shown relative to the Fermi energy (EF).

For both Au(111) and Ag(111) we found a similar low energy physisorbed closed-shell configuration with **1** lying flat to the surface (see Fig. 4A, left), with both possessing three close Cl-metal interatomic distances and one O-metal interatomic distance all within a 2.7 – 3.2 Å range. In Fig. 4A we also show the calculated spin-resolved projected density of states (pDOS) of all carbon atoms in the Ag(111) physisorbed case. Here, we identify three main closed-shell (i.e. with equal up and down spin populations) peaks. The fully unoccupied peak centered at ~0.2 eV is found to be mainly associated with the C atoms involved in the (Cl,H,O)-functionalized aryl ring and the central α C atom. The occupied peak centered at -1.7 eV is dominated by a component from the (Cl,H,O)-C₆ aryl ring. The larger lowest energy peak at -1.9 eV is found to be associated with C atoms in the other two (Cl,H)-functionalised aryl rings. Chemically speaking, the latter two aryl rings can be thought of as more aromatic than the (Cl,H,O)-C₆ aryl ring, which has a more quinoidal character in the free molecule (see S10 in the SI).

Although for Au(111) we could only find closed-shell solutions for all configurations, for Ag(111) edge-on chemisorbed configurations with the formation of an O-Ag bond of 2.4 Å were

found to have a spin-polarized character. Specifically, the previously fully unoccupied peak mainly due to the α C atom and the (Cl,H,O)-functionalized aryl ring splits to yield some spin-up occupation (the equivalent pDOS for the tilted edge-on case is provided in the SI). This new SOMO peak clearly confirms the emergence of a Ag-bound radical species in line with the ARUPS data. Examination of the calculated excess spin density reveals that, as expected, the spin is mainly localized on the α C (~50% of the total, see Fig. 4B and section 3.3 in SI) also confirming the radical nature of the Ag-bound molecule. We also note that, with respect to the pDOS in Fig. 4A, the pDOS in Fig. 4B shows a diminishment of the -1.7 eV peak associated with the (Cl,H,O)-C₆ aryl ring and an increase in the -1.9 eV peak. This change indicates that chemisorption of **1** on Ag(111) leads to a decrease in the quinoidal character of (Cl,H,O)-C₆ aryl ring making it chemically more similar to the other two (Cl,H)-functionalised aryl rings – see also SI. The sum of atomically partitioned charges of **1** when bound to the Ag(111) surface reveals that the molecule remains very close to being charge neutral (see section 3.4 in SI)^{46,47} confirming that the interaction of **1** with the Ag surface leads to a localized Ag-O bond formation with no significant overall charge transfer between **1** and the substrate.

As an isolated species the Ag-bound tilted edge-on radical configuration has almost the same adsorption energy as the corresponding closed-shell flat configuration (see Fig. 4) and thus both would be expected to be observed. Although an exploration of the huge number of possible coverage/packing possibilities is beyond the scope of the present work, we have performed some DFT calculations at an increased coverage on the Ag(111) surface. These calculations (see details in SI) confirm that increased intermolecular interactions can increase the effective adsorption energies of **1** in all configurations. However, we find that the effective adsorption

energy of molecules in the tilted edge-on configuration is most enhanced by intermolecular interactions. This results in tilted edge-on molecules having higher effective adsorption energies than those in the flat configuration for higher packings. In addition, we note that as molecules in the tilted edge-on configuration occupy approximately 12% less surface area than when flat to the metal substrate, for increased coverages the higher potential density of the former will also lead to more stable MLs which would likely favour its increased prevalence. Overall, in a r-ML, for which relatively high density packing is quite likely, we would thus expect tilted configurations to be more prevalent than flat configurations, as is also confirmed by the analysis of the XPS data (see above). We further note that the tilted edge-on configuration has two closest Cl-Ag distances which are both $>3.6 \text{ \AA}$, whereas the flat configuration has three closest Cl-Ag distances which are all $\leq 3.2 \text{ \AA}$. This large structural difference in the adsorption geometry is likely to contribute to a significantly lower susceptibility of the tilted edge-on configuration with respect to surface-induced dehalogenation reactions, in line with the experimental XPS analysis above.

Although qualitatively in line with the ARUPS data, we note that the calculated energy of the SOMO peak (Fig. 4B) is upshifted in energy by approximately 1 eV with respect to the experimentally observed SOMO. This mismatch likely reflects well known limitations of periodic DFT calculations with respect to metal-bound organic molecular systems. This is partly due to the use of generalized gradient functionals which, although qualitatively good, often do not fully capture the detailed features of the electronic structure of organic molecules.⁴⁸ More generally, the disparity is due to the fundamental shortcoming of DFT based methods in recovering screening of adsorbate electronic structure due to the metal support.⁴⁹ This issue is

discussed in more detail in the SI where we also provide an estimated correction to the position of the calculated SOMO peak.

Finally, the interaction of **1** with the Cu(111) surface always leads to strongly chemisorbed species with Cl-Cu bonds of 1.75 Å. Although we find that such configurations are also spin-polarized, the very strong interaction with the surface strongly suggests that this system will be very reactive and susceptible to dehalogenation, as also indicated from the ARUPS data.

In conclusion, our experimental and theoretical analyses consistently confirm that, as proposed by Rissner et al.,¹⁶ the interaction of suitably designed closed-shell quinoidal monomers with metallic surfaces may induce the formation of neutral radical species chemically bonded on the surface (i.e., r-MLs). The successful experimental realization of this appealing concept to generate a stable r-ML, however, is far from straightforward. Through meeting the challenges of rationally designing a suitable stable closed-shell precursor which can chemisorb on metal surfaces in a programmed manner, and choosing the appropriate surface to precisely induce the required effect, we were able to produce a stable r-ML of neutral organic radicals on a metal surface. Specifically, we chose compound **1** as a TTM-related molecule, where the eventually formed unpaired electron is protected by the six ortho chlorine atoms on each of the three aryl rings bonded to the eventually generated radical centre. At the same time, the carbonyl group anchors **1** to the surface and triggers the electronic reorganization. Indeed, our results consistently support that the radical species is formed at the Ag(111) surface is persistent enough to generate a stable r-ML. Our on-surface experimental results and DFT calculations also show that not all metallic substrates are good candidates to form the r-MLs. In fact, XPS and ARUPS

measurements and DFT calculations for **1** adsorbed on the Au(111) surface indicate physisorption only, whereas the interaction with Cu(111) is much stronger and leads to undesired species at the surface. We note that upon interaction of **1** with Ag(111), a proportion of the adsorbed molecules also undergo some chemical transformation. However, the ARUPS peaks at 1.2 eV of binding energy is a clear indication of the appearance of an unpaired electron on the organic units, which is also consistent with the results of our DFT based calculations.

To summarize, we provide strong experimental and theoretical evidence to confirm that rationally designed closed shell molecules interacting with suitably reactive metal surfaces can generate chemically adsorbed persistent neutral radicals eventually resulting in r-MLs. This work paves the way for the synthetic design of new closed-shell precursors that can generate stable r-MLs with an improved reaction yield, which is of great importance for the implementation of organic radicals into organic (spin)electronic devices.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, extended data sets, and extended figures.

AUTHOR INFORMATION

§ These authors equally contributed to the manuscript.

Notes

The authors declare no competing financial interests.

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