Effect of the Molecular Polarizability of SAMs on the Work Function Modification of Gold: Closed- versus Open-Shell Donor-Acceptor SAMs

Valentin Diez-Cabanes, Dayana C. Morales, Manuel Souto, Markos Paradinas, Francesca Delchiaro, Anna Painelli, Carmen Ocal, David Cornil, Jérôme Cornil, Jaume Veciana,* Imma Ratera**

Valentin Diez-Cabanes, Dr. David Cornil, Dr. Jérôme Cornil
Laboratory for Chemistry of Novel Materials, University of Mons—UMONS, Place du Parc
20, 7000 Mons, Belgium.
e-mail: jerome.cornil@umons.ac.be

Dr. Dayana C. Morales, Dr. Manuel Souto, Dr. Markos Paradinas, Dr. Carmen Ocal, Prof.
Jaume Veciana, Dr. Imma Ratera
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193
Bellaterra, Spain
Dr. Manuel Souto, Prof. Jaume Veciana, Dr. Imma Ratera
CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), 08193 Bellaterra,
Spain
e-mail: iratera@icmab.es; vecianaj@icmab.es

Dr. Dayana C. Morales
Universidad Técnica de Ambato, Facultad de Ciencia e Ingeniería en Alimento, Av. Colombia
y Chile, Ambato, Tungurahua, EC180105 Ecuador

Dr. Francesca Delchiaro, Prof. Anna Painelli
Department of Chemistry, Life Science and Environmental Sustainability, University of
Parma & INSTM UdR-Parma, I-43124, Parma, Italy

Dr. Markos Paradinas
Current address: Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and
BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain

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Abstract

Charge injection barriers at metal/organic interfaces can be tuned by modifying the work function of metallic electrodes using Self-Assembled Monolayers (SAMs) of polar molecules. An interesting example of polar molecules is offered by donor-acceptor (D-A) dyads based on ferrocene (Fc) as electron-donor unit and either a polychlorotriphenylmethyl (PTM) radical or a polychlorotriphenylmethane (α HPTM) as electron-acceptor units, connected by a π -conjugated vinylene bridge. The D-A radical exhibits high chemical and thermal stability and present different electronic, optical, and magnetic properties with respect to the closed-shell form. The magnitude of the shift in the charge injection barriers for these two D-A systems has been estimated by means of surface potential measurements performed by Kelvin Probe Force Microscopy (KPFM). The experimental data have been compared with Density Functional Theory (DFT) calculations, which evidence the importance of the molecular dipole moments and polarizabilities to understand the experimental values. This work points out that in order to achieve high work function shifts of metals upon SAM formation, the molecules forming the SAM have to exhibit both a high permanent dipole moment and a low polarizability along the direction normal to the substrate. In presence of polarizable molecules, the work function shifts can be enhanced by reducing the intermolecular interactions; this can be achieved by adding some intermolecular spacers in the design of the molecules or by using mixed SAMs with active molecules embedded into a passive matrix.

1. Introduction

Surface engineering by means of Self-Assembled Monolayers (SAMs) is often exploited in different applications when a fine control of surface structure and physico-chemical properties is pivotal. Such overlayers are typically made of molecules covalently attached to a substrate via a tailored anchoring group to form a densely packed and well-ordered two-dimensional phase.^[1,2] Interestingly, a small change in the chemical structure of the SAM-

forming molecules can translate into significant changes of macroscopic properties, such as the contact angle of a wetting solution or the work function of the underlying substrate.^[3]

Over the last years, significant research efforts in the field of organic electronics have focused on understanding and controlling the interface energetics between metals (electrodes) and organic molecules.^[4,5,6] Such interfaces play a key role in the device operation and efficiency since they dictate the amplitude of the charge injection barriers, defined as the difference between the work function of the electrode and the ionization potential (electron affinity) of the (macro) molecules in the active organic layer for hole (electron) injection.^[4,7] Minimizing the injection barriers is highly desirable and can be achieved in practice by depositing on the metallic electrodes a SAM based on dipolar molecules to modulate their work function. In classical electrostatics, the change in the work function $\Delta\phi$ induced by dipolar molecules is expressed by the Helmholtz formula:

$$\Delta\phi = -\frac{\mu_z}{\varepsilon_0 \varepsilon A} \quad (1)$$

where ε_0 is the vacuum permittivity, ε is the medium dielectric constant of the SAM, μ_z is the normal component of the total dipole of a single molecule within the SAM and A the surface area occupied by a single molecule.

The normal component of the dipole entering into the Helmholtz formula is typically casted down in two different contributions.^[8,9,10]

$$\Delta\phi = \Delta V_{SAM} + BD \quad (2)$$

where BD is the bond dipole arising from the charge reorganization at the interface between the metal and the molecule, induced by a charge transfer and/or electronic polarization effects

and ΔV_{SAM} is the normal component of the intrinsic dipole moment of the molecular backbone. In the case of thiol-based molecules deposited on gold, previous theoretical studies have indicated that the bond dipole is very small when depicting the chemisorption process as the attachment of the thiolate radical form (without the hydrogen atom) on the gold substrate, *i.e.*, the so-called radical scenario.^[11,12,13]

Depending on the sign of the dipole along the normal to the surface, the SAM would induce a vacuum level shift at the interface of opposite sign which, in principle, raises or reduces the work function shift of the metal, and hence allows modulating the charge injection barriers.^[14] For example, the sign of the dipole can be reversed going from alkanethiols to fluorinated alkanethiols deposited on gold or silver.^[15] Experimentally, the work function shift can be measured by Ultraviolet Photoelectron Spectroscopy (UPS) and the related electrostatic surface potential can also be accessed by Kelvin Probe Force Microscopy (KPFM) which can be measured with no disturbance of the surface and is a comparatively simple method. Conversely to UPS that provides average properties of the surface, KPFM gives information about the local properties of the scanned area with a lateral resolution from tens to hundreds of nanometers in ambient conditions. However, in both cases, the measured work function shift is dependent on specific molecular characteristics (dipole, polarizability, coverage...) that are not directly accessible. In this respect, quantum-chemical calculations are useful to shed light on the electronic properties that control the metal/organic interfaces at the molecular level.

Recently, the concept of incorporating photoswitchable molecules in SAMs has been introduced to generate bistable systems providing a dynamic control over the work function shift and hence on the charge injection barriers.^[16,17,18,19] Prototypical molecules are azobenzene derivatives that can be switched reversibly between the *trans* and *cis* states under illumination. Interestingly, the switching process is preserved in the dense SAM medium thanks to a cooperative switching mechanism, although so far, only relatively small work

function shifts on the order of 100 meV have been obtained for azobenzene derivatives deposited on Au(111).^[16,17] It is there of prime interest to assess from the theoretical point of view the molecular parameters responsible for the changes in the work function and to find strategies to maximize the amplitude of the changes, not only for the work function but also for other interesting properties such as wetting contact angles.

Another compound with interesting physical properties is a D-A dyad based on ferrocene (Fc) as donor unit and polychlorotriphenylmethyl (PTM) radical as an acceptor unit, connected by a conjugated vinylene bridge.^[20,21,22,23] This D-A radical dyad exhibit high chemical and thermal stability and present very different electronic, optical, and magnetic properties compared to the corresponding closed-shell form where the PTM radical unit is replaced by a polychlorotriphenylmethane (α HPTM) one.^[24] Interestingly, both PTM-based SAMs sandwiched between two metallic electrodes display a very different conductivities.^[25,26] This conductivity difference has been attributed to the participation of the Singly Unoccupied Molecular Orbital (SUMO) level in the charge transport for the open shell form which is absent in the corresponding closed-shell SAM. Very recently, some of us have reported the charge transport measurements of Fc-PTM and Fc- α HPTM based SAMs on gold observing different rectification behavior when the acceptor unit is in the open- or closed-shell form,^[27] but there is no report on the use of such dyad-based SAMs for modulating the charge injection barriers.

In this study, we report a joint experimental and theoretical characterization of the work function shift of a gold surface when depositing SAMs based on the Fc-PTM D-A dyad in the electronic closed-shell and radical open-shell, respectively (see molecular structures **S2** and **S3** in Figure 1). The two compounds are functionalized by a (CH₂)₄ carboxylic chain terminated by a disulfide group (DS) to promote chemisorption on the gold substrate.^[27] The SAM including only the ferrocene moiety (Structure **S1**) has been also studied for comparison.

The work function shifts have been measured by KPFM technique. The interpretation of experimental data is supported by Density Functional Theory (DFT) calculations, highlighting the role played by the molecular dipole moment and polarizability of the closed- and open-shell molecule-based SAMs.

Figure 1. Molecular structures of the donor-acceptor (D-A) dyad in the non-radical (**S2**) and radical (**S3**) forms as well as of the reference compound (**S1**).

2. Results and discussion

SAMs S1, S2, and S3 have been prepared on Au/glass substrates and characterized as previously reported.^[27] The Ultraviolet Photoelectron Spectroscopy (UPS) data applying -10 V bias to the sample were previously reported obtaining similar values for SAMs **S2** and **S3**, observing only a small difference of 0.05 eV in the work function. The values of the work function were obtained by measuring the onset of the slope of the secondary electron cutoff (SECO). Despite the lack of statistics, the difference in the work function of **S2** and **S3** is significant.^[27]

In order to gain additional insight into the different properties of the open- versus closed-shell D-A systems, the surface contact potential was also measured by Kelvin Probe Force Microscopy (KPFM). The methodology employed is schematically shown in Figure 2. Since KPFM measures the local contact potential difference between the tip and the sample ($CPD = \phi_{tip} - \phi_{sample}$), the use of in-situ references is convenient to eliminate tip effects as well as to obtain reliable relative CPD values (see Supporting Information). Therefore, we used engineered surfaces consisting on SiO_2 substrates partially covered with 30 nm thick gold deposits evaporated on it (inset in Figure 2) so that the uncovered SiO_2 constituted a common in-situ reference for all samples. A non-functionalized sample (control) was measured to know the contact potential difference between bare gold and SiO_2 ($CPD_{Au-SiO_2} = \phi_{SiO_2} - \phi_{Au}$) (bottom left in Figure 2). After gold functionalization (bottom right Figure 2), the contact potential difference between SAM regions and SiO_2 being $CPD_{SAM-SiO_2} = \phi_{SiO_2} - \phi_{SAM}$.

The CPD values of bare gold, **S1**, **S2** and **S3** with respect to the respective unmodified SiO_2 regions were measured at room temperature and in low humidity (less than 5% under a continuous flux of nitrogen) conditions. To ensure reliability, systematically CPD measurements on the control sample were performed before and after characterization of each SAM sample. By following the described procedure, the variation of the surface potential of each SAM with respect to gold was estimated as follows (See Supporting Information for more details):

$$CPD_{SAM-Au} = CPD_{SAM-SiO_2} - CPD_{Au-SiO_2} \quad (3)$$

Table 1 summarizes the work function changes obtained for the different functionalized surfaces from the CPD histograms (Figure 3) of the corresponding KPFM images. The

separation between Gaussian curves for each sample provides the corresponding $CPD_{SAM-SiO_2}$
 $= \phi_{SiO_2} - \phi_{SAM}$ while the value of CPD_{Au-SiO_2} was 240 mV for all cases.

Figure 2. Schematics of the methodology used for the KPFM experiments. The inset at the top shows the pattern of the Au deposits on the SiO₂ substrates. Bottom left: Control sample consisting of SiO₂ and bare Au deposits. Bottom right: Upon gold functionalization, the CPD of each SAM relative to the SiO₂ in-situ reference is obtained and compared to that of the bare gold in the control sample (equation 3 in the text).

Table 1. Work function shifts ($\Delta\phi$) extracted from the KPFM Contact Potential Difference data of bare Au and in presence of the SAMs **S1**, **S2** and **S3**, along with the normal components of the dipole (μ_z), in Debyes) and polarizabilities (α_{zz}) for the isolated molecules constituting the **S1**, **S2**, and **S3** SAMs, as calculated at (U)PBE/6-31G(d) level.

Sample	KPFM	Calculated magnitudes in isolated molecules	
		$\Delta\phi$ (mV)	μ_z (D)

S1	-400	2.01	39.7
S2	55	-0.3	120.7
S3	20	-1.24	151.6

Figure 3. Histograms or distribution plots of KPFM images containing two surface regions (insets) of the analyzed samples: a) Au vs. SiO₂; b) **S1** vs. SiO₂; c) **S2** vs. SiO₂ and c) **S3** vs. SiO₂. Note that lower CPD value in the images (in darker brown color) indicates higher work function (see Supporting Information). Inset scale bar corresponds to 5μm.

KPFM measurements reflect the work function change of gold functionalized with **S1**, **S2**, and **S3** SAMs. Interestingly, this technique shows that the orientation of the interface dipole changes when going from **S2** and **S3** to **S1**. The negative sign of $\Delta\phi$ for **S1** implies that the system work function decreases upon gold functionalization and hence that the surface dipole layer is oriented with the negative pole close to the metal surface and the positive one further away toward the monolayer/air interface (Figure S1). Oppositely, the work function increases for **S2** and **S3** so that the dipole has a positive pole close to the metal surface and a negative pole at the monolayer/air interface. The top location of the partial negative charge is expected from the strong electron-withdrawing character of the 14 chlorine atoms present in the PTM and α HPTM subunits, as previously shown for fluorinated monolayers.^[28,29] In **S2** and **S3**, the smaller amplitude of the work function shift thus reflects a compensation between the dipole associated to the bottom part of the SAM and the dipole of the top D-A dyad, both pointing in opposite directions.

When comparing the **S2** and **S3** monolayers, the higher electron acceptor ability of the PTM radical moiety induced by the presence of a low in energy singly unoccupied molecular orbital (SUMO) and the high in energy highest occupied molecular orbital (HOMO), located on the Fc, are expected to promote a larger dipole moment in **S3** than in the closed-shell form **S2**. Thus, this should give rise to a larger modification of the work function in **S3** which is not observed experimentally. Recently, quantum-chemical calculations performed by Egger and Zojer have found an anti-correlation between the work function change and the dipole of the molecules assembled on a gold surface.^[30] Contrary to intuition, the authors showed that increasing the molecular dipole moment can reduce the change of the work function. Actually, the coexistence of adjacent large dipoles can drive the interface into a thermodynamically unstable situation which is compensated by a charge reorganization weakening the molecular dipoles (i.e., the so-called depolarization effects). The dipole moment and polarizability of the

isolated molecules are the prime parameters that must be taken into account to rationalize this anti-correlation between **S2** and **S3**.

In order to rationalize the complex behavior of these systems, we have computed first the molecular dipole and polarizability of the isolated molecules and next the work function shift of the Au(111) gold surface upon deposition of the three SAMs. In the latter case, we have also analyzed the impact of two highly relevant parameters, namely the nature of the contact geometry and the degree of surface coverage (See Supporting Information for details on the calculations). At this point, it must be taken into account that the values that we compare with theory are not absolute values but always changes. Indeed, one of the reasons for using relative values for sake of comparison results from the different magnitudes of the work function of the pristine surface obtained at theoretical and experimental level. The theoretical value of the Au work function represents the work function of atomically clean Au. In order to achieve this work function value (~5.2 eV) at the experimental level, it is necessary working under Ultra High Vacuum (UHV) conditions, which is not the case in our set of experiments.

The calculated behavior of the molecular dipoles in the gas phase follows the same trend as the expected scheme in Figure S4 (see Table 1): positive dipole for **S1** ($\mu_{z-S1}=2.01D$) and negative dipoles for **S2** and **S3** ($\mu_{z-S2}= -0.3D$ and $\mu_{z-S3}= -1.24D$), showing larger values for the radical form as expected. Note that the experimental estimate by Near Edge X-ray Absorption Fine Structure (NEXAFS) of the tilt angle of the molecular backbone with respect to the normal to the surface for **S1** (53.8°) allows us to extract the Z component of the dipole of the individual molecules. However, the charge distribution of the molecules changes upon interaction with their neighbors in the SAMs (see Figure S4) and consequently their dipoles readjust. This effect is governed by the molecular polarizability α , reflecting the charge reorganization induced by an external electric field E (see Equation 4).

$$\vec{\mu}_i = \bar{\alpha}_{ij} \vec{E}_i$$

In our case, we are interested in the dipole component in the direction normal to the surface (μ_z) and to the relevant component of the polarizability α_{zz} . The calculated components of the polarizability (see Supporting Info for details) are also reported in Table 1.

With this information, we can use the Helmholtz equation (Equation 1) to relate the work-function modification to the chemical nature of the SAM, where the medium dielectric constant ε has been defined as:^[31]

$$\varepsilon = 1 + \alpha F A^{-1.5} \quad (5)$$

Where F is a factor characteristic of the geometrical packing. By assuming a hexagonal arrangement of the molecules, we set F=8.892 in the following.^[32] The last required information is the area per molecule, that we estimate as $\sim 40 \text{ \AA}^2$ for **S1** (see Section 4 in Supporting Info) and set to the experimental value of $\sim 111 \text{ \AA}^2$ for **S2** and **S3** taken from ref. 27. Accordingly, we estimate $\Delta\phi = -791 \text{ mV}$, $+53 \text{ mV}$, and 196 mV for **S1**, **S2** and **S3**, respectively, in semi-quantitative agreement with experimental results, in part due to the neglect of the bond dipole contribution.

In order to provide a yet deeper analysis, the work function modification has been directly computed for several anchoring geometries, while neglecting at this stage the influence of intermolecular interactions and setting up the molecular geometry from experimental measurements (see Supporting Info). The formation of covalent bonds between the sulphur and gold may lead to a breaking of the original S-S bond in the disulphide moiety. There are thus four possible anchoring configurations: two varying by the number of anchored S atoms (one or two) and another two depending on whether there is an S-S bond breaking (b) or not

(a), (Figure S4). The values of $\Delta\phi$, ΔV_{SAM} , and BD calculated for each configuration are collected in Table S1. Note also that an extra hydrogen atom has been added to the unbounded sulfur atom of the molecules for the b-type anchoring with only one sulphur atom covalently bonded to Au. The influence of the anchoring group (a-type or b-type) on the charge transfer at the interface has been analyzed by considering only the disulfide anchoring group (DS) on the same Au slab. (See Supporting Information.) In fact, the origin of the very different behaviours of the a- versus b-type geometries arises from the larger charge transfer at the interface in the case of the a-anchoring type (see Figure S5). (0.168 |e| for a-type versus 0.04 |e| for b-type), which promotes higher BD values for the first anchoring group. On the other hand, despite the fact that the values of the molecular contribution ΔV_{SAM} and bond dipoles BD differ depending on the number of sulfurs attached to the surface (see Table S1), the total work function shift $\Delta\phi$ is almost independent of it. These results thus show that $\Delta\phi$ is more affected by the breaking or not of the S-S bond than by the number of sulfur atoms bound to the gold surface.

The large interfacial charge transfer induced by the original S-S bond (see Figure S6) leads to high BD values (300-400 meV) and hence work function shifts far from the experimental measurements, thus strongly suggesting that this bond breaks during the SAM formation (see Section 7 in Supporting Info), in full consistency with the calculated total energies of different contact geometries (see Table S2). The resulting anchoring geometries give rise to small BD values (0-100 meV) in agreement with previous theoretical^[33-37] and experimental^[38] works. The shift in the work function linked to the introduction of the dipole of the Fc-PTM dyad is reflected by the difference in ΔV_{SAM} between **S1** and **S2** or **S3**. As a result, the evolution of the work function shift appears to be mainly driven by the molecular component (i.e. ΔV_{SAM} in Equation 2).

The theoretical results yield a smaller work function for **S2** compared to **S3** (with a difference of 63 meV) whereas the opposite holds true for the KPFM (a difference of 35

meV) measurements. The calculations are thus consistent with the view that the dipole moment of the D-A dyad is larger for the radical form, as illustrated for the isolated molecules. However, since all values described so far make reference to SAMs without intermolecular interactions, we investigate in the next section the influence of the degree of coverage.

Previous experimental and theoretical studies have indicated that intermolecular interactions in SAMs can lead to a reduction in the magnitude of the dipole moment of the individual molecules, referred to as depolarization effects.^[39,40,41] Accordingly, we have studied here the evolution of the total work function shift and its components as a function of coverage θ , defined as the ratio between the number of molecules in the unit cell and the number of molecules corresponding to a full surface coverage ($\theta=1$). To do so, we have used the same unit cell as before with two ($\theta=0.5$), three ($\theta=0.75$), and four ($\theta=1$) molecules, adopting systematically the same geometry as that used for the single molecule (see Figure S5).

As expected, the difference observed in the evolution of the work function shift as a function of coverage for the three molecules is primarily ascribed to the molecular contribution. Figure 4 shows the evolution of the averaged dipole (*i.e.*, intrinsic dipole of the unit cell divided by the number of molecules) for the bottom part of the attached molecule (*i.e.*, the dyad formed by Fc and DS anchoring group attached to the surface) and for the top part of the attached molecule (*i.e.*, the Fc-PTM dyad) of **S2** and **S3** as a function of the surface coverage. The interaction of the neighboring DS-Fc units is weak due to their large spatial separation, thus explaining in both cases the small reduction of the averaged dipole (0.33D) with growing coverage. In contrast, the Fc-PTM units are more polarizable and the interaction of the neighboring units is more pronounced in view of their close contact, resulting in a significant decrease in the averaged dipole, by 0.66 D and 0.85 D respectively for the closed and open-shell forms. In other words, the short distances between the closest Cl atoms of neighboring PTM units, partly responsible for the permanent dipole moment of the Fc-PTM

part, also help enhancing the depolarization effects. The larger drop calculated for **S3** reflects the larger polarizability of the open-shell form, as discussed before for the isolated molecules. Fc-PTM is more polarizable than Fc-PTMH due to its larger charge-transfer character. PTM radical acts a good electron acceptor with respect to Fc (a good electron donor), as demonstrated by the appearance of a CT transition in the near-IR.^[42] This transition is missing in Fc-PTMH, where the non-radical hydrogenated PTM unit has a weaker electron-accepting character. Low-frequency CT transitions contribute to the molecular polarizability, particularly along the long molecular axis, thus justifying the observed result. Thus, the Fc-PTM dyad dipole for the open-shell ($\mu_{\text{Fc-PTM}}$) drops much faster than the dipole of the closed-shell form ($\mu_{\text{Fc-PTMH}}$) upon increasing the coverage. Note that the differences in the drop of the dipoles cannot be ascribed to different contact geometries since they are found to be very similar for **S2** and **S3** (see Figure S4 and Tables S3-S4). Interestingly, the results further demonstrate that the difference between the dipole of the D-A dyad in **S2** and **S3** quickly drops when the intermolecular interactions are switched on due to depolarization effects. This partly explains the discrepancy observed between the amplitude of the calculated dipole moment of the D-A part in the isolated **S2** and **S3** with respect to the experimentally measured work function shifts, thereby highlighting the clear absence of correlation between these two quantities. Rationalizing in absolute values the experimental work function shifts would require a precise knowledge of the surface organization of the molecules in the SAM, which is hard to estimate and is beyond the scope of the present paper.

Figure 4. Evolution of the averaged dipoles of the bottom part ($\mu_{\text{DS-Fc}}$) and top part ($\mu_{\text{Fc-PTM(H)}}$) of the attached molecules for **S2** (left) and **S3** (right) as a function of the coverage ratio.

3. Conclusion

In summary, we have reported here a joint theoretical and experimental study of the Au(111) work function modification upon adsorption of D-A (Fc-PTM) based SAMs. In a first stage, we have measured the surface potential by KPFM technique. The results point to the coexistence of two opposite dipoles: one formed by the anchoring DS and Fc (DS-Fc) and the other by the Fc-PTM dyads. In contrast to our expectations, the work function shift of the closed-shell form is higher than that of the open-shell form as concluded by KPFM measurements, in spite of a larger dipole for the open form in the isolated state supported by our theoretical calculations. Calculations of the work function shifts associated to the deposition of the molecules on gold showed that the evolution among the three compounds is dominated by the molecular dipoles of the SAMs. Moreover, the calculations evidence that the open-shell form undergoes more pronounced depolarization effects, in full consistency with the higher molecular polarizability calculated for the isolated systems. This rationalizes the anti-correlation between the measured work function shifts and the calculated properties of the isolated molecules and demonstrates the intertwined influence of the molecular dipole

moment and polarizability. This anti-correlation phenomenon implies that, in order to achieve high work function shifts upon SAM formation, the molecules forming the SAM have to exhibit both a high permanent dipole moment and a low polarizability along the direction normal to the substrate. In presence of polarizable molecules, the work function shifts can be enhanced by reducing the intermolecular interactions; this can be achieved by adding some intermolecular spacers in the design of the molecules or by using mixed SAMs with active molecules embedded into a passive matrix.

Supporting Information

General synthetic and characterization procedures, Ultraviolet photoemission spectroscopy (UPS) data, Kelvin probe microscopy (KPFM) data, Surface coverage estimation by Cyclic Voltammetry (CV), Computational methods, Supporting Figures and Tables, discussion on the verification of the theoretical methodology.

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The table of contents entry

A modification in the Au work function is observed upon absorption of D-A closed- and open-shell SAMs. Theoretical calculations provided an understanding of the role played by the molecular polarizability and depolarization effects in the magnitude of these work function shifts providing practical hints to attain high work function shifts of metals upon SAM formation.

Keywords:

Self-Assembled Monolayers; Donor-Acceptor; PTM radical; KPFM; Density Functional Theory (DFT) calculations

Valentin Diez-Cabanes, Dayana C. Morales, Manuel Souto, Markos Paradinas, Francesca

Delchiaro, Anna Painelli, Carmen Ocal, David Cornil, Jérôme Cornil, Jaume Veciana,**

*Imma Ratera **

Effect of the Molecular Polarizability of SAMs on the Work Function Modification of Gold: Closed- versus Open-Shell Donor-Acceptor SAMs

ToC figure