

Large Work Function Shift of Gold Induced by a Novel Perfluorinated Azobenzene-Based Self-Assembled Monolayer

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Dedicated to the memory of Dr. Gianluca Latini

Chemisorption of self-assembled monolayers (SAMs) is a universal method to modify numerous surface properties, which allows interfaces to be optimized for the application of choice.^[1] Because of this reason SAMs are currently widely used as key components in the fabrication of various optoelectronic devices, such as organic thin-film transistors (OTFTs),^[2] organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) and organic memory (OMEM) cells.^[3] When chemisorbed on

metallic surfaces, SAMs can be used for the tuning of both the metal work function and surface wettability,^[4] thus enabling the optimization of the charge injection/extraction at metal–semiconductor interfaces^[5] and the control over the molecular order (including the degree of crystallinity) within the semiconducting layer deposited on top of the SAMs.^[6] The latter is crucial for the optimization of the transfer integral, representing the electronic coupling of neighboring molecules, and the polaronic relaxation energy, to promote the charge transport within the active material and ultimately enhance the device performance. It has been demonstrated that subtle changes in the chemical structure of the molecules forming the SAMs can dramatically change the resulting properties of the device.^[4,7] It is now known and widely exploited for device fabrication that chemisorption of n-alkanethiols and partially perfluorinated thiols on Au electrodes decreases and increases the metal work function, respectively.^[8] The use of one versus the other depends on the nature of the active molecular material, i.e., n-type, p-type, or ambipolar, that is employed to fabricate the specific device.

Azobenzenes are extensively employed photochromic systems because of their accessible and reversible isomerization process that occurs upon illumination with UV and visible light between the *trans* and *cis* states and vice versa, respectively.^[9] Among the vast variety of applications of azobenzene, the photoinduced conformational change of azobenzene-based SAMs has been used for the development of responsive molecular wires,^[10] which were successfully integrated in an organic field-effect transistor to photochemically modulate the charge injection at the metal–semiconductor interface.^[11] One physical property that was found to be photochemically modified is the work function of Au.^[12] Unfortunately, this result was obtained using bi-component SAMs, which thus integrated, in a poorly controlled way, two molecular building blocks featuring diverse electrical and electronic properties. We have recently reported a single-component responsive SAM, based on an azo-biphenyl molecule, exhibiting a photo-modulable work-function when chemisorbed on Au electrodes.^[13] Here, we have designed and synthesized a new thiolated azobenzene molecule exposing a perfluorinated benzene head group. These SAMs obtained by chemisorption on Au exhibit a markedly large shift of the metal work function when compared to the non-fluorinated analog.

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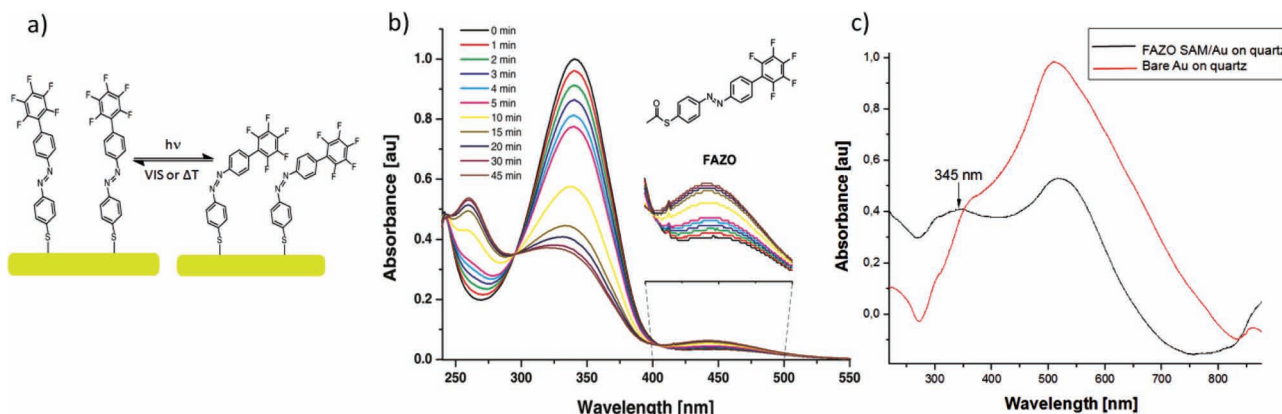


Figure 1. a) Schematic representation of the FAZO-SAM in its *trans* (left) and *cis* (right) state. b) UV-vis spectra of **1** in solution (2.89×10^{-5} M in chloroform) and c) in SAM chemisorbed on gold.

This shift is comparable to other fluorinated SAMs on Au such as those based on pentafluorobenzene thiol (PFBT),^[14] but here due to the presence of an azobenzene moiety, the work function can be later altered by irradiating the SAM at a specific wavelength, thus widening the functionality of the monolayer.

The synthesis of the fluorinated azobenzene compound **1** (FAZO) was accomplished in six steps, as detailed in the Supporting Information. All compounds were characterized by NMR-spectroscopy, mass spectrometry and elemental analysis. Furthermore, single crystals suitable for X-ray analysis were obtained for **1** by slow evaporation of a saturated CDCl₃ solution. The solid-state structure corroborated the identity of **1** in its *trans* form.

The preparation of the SAM of **1** (FAZO-SAM) was accomplished by immersion of a freshly gold evaporated substrate in a 0.1 mM solution in CHCl₃ for 48 hours. The SAM formation was carried out in the dark to obtain the SAM in its *trans* state (Figure 1a). On the contrary, for inducing the adsorption of the *cis* FAZO molecules on the substrate, a 0.1 mM solution of **1** was initially irradiated with UV light for 1 h and then the substrate was immersed in the solution for 23 hours keeping the irradiation ON during the formation of the SAM.^[15] After the corresponding immersion time, the functionalized substrates were removed from the solution, vigorously rinsed with CHCl₃ and dried under a N₂ stream.

The reversible isomerisation process between *trans* and *cis* forms of **1** in solution was followed by UV-vis absorption spectroscopy. Figure 1b shows the evolution of the absorption spectrum upon irradiation with UV light (366 nm), which clearly demonstrates the photo-induced isomerisation of **1** after ca. 45 minutes. The peak at 340 nm corresponds to the *trans* form, which decreases upon irradiation. Conversely, 15 minutes of white light irradiation were sufficient to induce the complete back isomerization. The same technique was employed to characterize the SAM prepared on a transparent 25 nm thick gold film evaporated on quartz. In Figure 1c the UV-vis absorption spectrum of the non-functionalized gold on quartz substrate (red) and that of the AZO modified one (black) are reported. The bare gold substrate shows a non-symmetric broad absorption band centered at approximately 510 nm that can be attributed to the gold surface plasmon resonance (SPR).^[16] Upon

chemisorption of the AZO molecules the intensity of this band decreases as a result of the formation of the Au-S bond, and a new band with a maximum centered at 345 nm appears, which is attributed to the π - π^* transition in the *trans* state, indicating the formation of the FAZO-SAM.

The water contact angle (CA) measurement of a freshly prepared FAZO-SAM revealed a strongly hydrophobic nature of the *trans* FAZO-SAM (CA = $94.0^\circ \pm 2.3^\circ$). This value is in agreement with other reported fluorinated SAMs,^[17] hence supporting the successful SAM formation observed by UV-vis absorption measurements. To investigate the *trans* to *cis* isomerisation of the chemisorbed molecules, the same sample was rinsed with water and ethanol, dried under N₂ stream and exposed for one hour to UV (365 nm) irradiation. The obtained CA value of the irradiated sample featured a larger error bar ($91.6^\circ \pm 7.3^\circ$), and most importantly did not reveal a significant difference when compared to the initial *trans* SAM. To avoid any possible damage of the surface during the first CA measurement which could affect the yield of isomerization, a freshly prepared *trans* SAM was illuminated with UV for two hours: in this case, the obtained value was $88.0^\circ \pm 0.8^\circ$. The small difference observed between CA values measured before and after irradiation does not unambiguously prove the occurrence of the *trans* to *cis* isomerisation in chemisorbed molecules forming the SAM on Au but on the contrary it does not exclude the possibility that this change is observable. Taking into account that the molecule has a terminal perfluorinated benzene ring, one hypothesis to explain the last measurement is that although the molecules are in their *cis* state, the fluorine atoms are not completely hidden and hence do not promote a significant change in the final wettability. This observation is confirmed by calculated optimized geometries (see the Supporting Information), providing evidence for the exposure of some of the fluorine atoms in the *cis* SAM. Atomic force microscopy (intermittent contact mode) images were acquired on both *trans* and *cis* based SAMs. Although relevant structural information of the monolayer could not be extracted the measured root mean square roughness (R_{rms}) showed an increase from 2 ± 1 Å to 4 ± 1 Å when comparing the uncoated surface of Au(111) with the same surface once coated with the FAZO-SAM.

The electronic properties of the gold coated with a FAZO-SAM in its *trans* and *cis* isomer, and in particular its work function (Φ), were experimentally studied by macroscopic Kelvin Probe measurements (KP), Kelvin Probe Force Microscopy (KPFM), Photoelectron Spectroscopy (PS) under atmospheric conditions, and by Electroabsorption (EA) spectroscopy.^[18] Theoretical calculations were also performed to achieve a better understanding of the influence of the SAM in the two isomeric forms on the Au work function.

The change in the Φ of Au upon formation of the SAM was studied by EA^[19] measurements, performed on an LED incorporating the *trans* FAZO-SAM, with the following structure: ITO/Au(5 nm)/FAZO-SAM/F8BT(100 nm)/Al(50 nm). A detailed experimental description can be found in reference.^[13,18] All measurements were carried out at room temperature by irradiating with a monochromated beam (from a Xe-lamp) at $\lambda = 505$ nm, while applying a sinusoidal voltage $V_{AC} = 0.5$ V at a frequency $f = 2$ kHz, and with the optical probe entering the LED through the semitransparent ITO/Au electrode. For calculating the work function of the modified gold, we consider the possibility of pinning unlikely since the LUMO of F8BT is accepted to lie in the range 3.2–3.5 eV and the Al work function only decreases below 3.5 eV upon exposure to significant amount of oxygen during or after evaporation (the work function of Al in UHV is ~4.1–4.2 eV).^[20] In addition, previous KP measurements of our evaporated Al electrodes gave an average Al work function in our diodes of 3.70–3.80 eV. Assuming a work function of the cathode of 3.75 ± 0.05 eV, we calculated the work function of the functionalized gold electrode, Φ_{anode} , by using the equation $V_{null} = (\Phi_{anode} - \Phi_{cathode})/e$, where V_{null} is the zero-crossing voltage of the EA signal and e is the electronic charge. The obtained V_{null} was 2.02 ± 0.06 V, which corresponds to a Φ_{anode} of 5.77 ± 0.1 eV for the FAZO functionalized gold electrode. Figure 2a shows the EA signal as a function of the applied DC bias, which is compared with the recently reported non-fluorinated AZO SAM^[13] to show the large Φ shift caused by the fluorinated terminal benzene ring.

Macroscopic KP measurements revealed a large Au work function shift compared with bare gold ($\Phi = 5.12$ eV^[13]): freshly prepared *trans* FAZO-SAMs on Au/glass were found to display a Φ shift up to 5.78 ± 0.02 eV, in perfect agreement with the EA results (with 0.02 being the standard deviation).

Upon sample irradiation with UV light (365 nm) for ~1 hour only a small decrease in Φ (30 meV) was monitored (see measurements in Supporting Information). The relatively modest difference observed prompted us to study two independent systems, i.e. the separate functionalization of the gold with FAZO molecules in their *trans* and *cis* state. Ambient PS measurements, done on “ex situ” freshly prepared *trans* and *cis*-FAZO-SAMs on Au(111)/mica, revealed $\Phi_{trans-FAZO/Au(111)} = 5.36 \pm 0.02$ eV and $\Phi_{cis-FAZO/Au(111)} = 5.25 \pm 0.02$ eV, providing evidence for a large Φ variation between the two isomers, with a $\Delta\Phi_{trans-cis}$ of ~110 meV (see measurements in Supporting Information). As expected the Φ values obtained by PS are few hundreds of meV lower than those measured by KP; this is due to the fact that the KP method measures an average of all Φ values found in potentially different (and/or non-homogenous) domains existing under the probe head. Differently, PS is most sensitive to the lowest work function in the probed area, as the secondary electrons with the lowest kinetic energy are used for the determination.^[21] Interestingly, KPFM revealed a similar work function shift when a *trans* FAZO-SAM was irradiated with UV light (i.e., $\Delta\Phi_{trans-cis}$); this shift amounts to 90 meV with $\Phi = 5.50 \pm 0.01$ eV and 5.41 ± 0.01 eV for the *trans*- and *cis*- states, respectively. KPFM measurements were used to monitor the Φ variation of the sample during in situ UV light/dark cycles (Figure 2b). Differently from the previously studied non-fluorinated AZO-SAM,^[13] the two switching kinetics are similar showing a simple exponential behaviour with a characteristic time of ~100 min. The simple exponential decay suggests that the switching can be described in terms of a single mechanism and that all FAZO molecules chemisorbed within an area of about $100 \mu\text{m}^2$ are activated at the same time, i.e. no serial activation as observed in the case of AZO-SAM.

All techniques consistently displayed higher Φ values for the *trans* isomer based SAM compared to the corresponding *cis*. This trend, which is opposite compared to our previous findings on a non-fluorinated azobenzene derivative, is due to the presence of a perfluorinated terminal phenyl ring featuring strong electron-withdrawing characteristics. Interestingly, our result on the FAZO-SAM is in line with previously reported works on other azobenzene based SAMs having an ending CN group exposed to the surface.^[12]

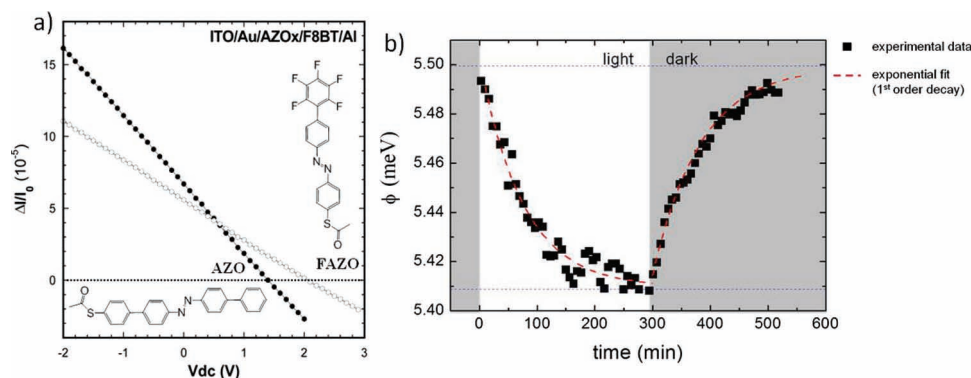


Figure 2. (a) DC voltage scan of the EA signal towards positive bias. The zero crossing voltages are 1.39 V (5.15 ± 0.10 eV) for AZO (black circles) and 2.02 V (5.77 ± 0.1 eV) for FAZO (white circles). (b) KPFM on the FAZO-SAM on Au(111). The work function variation is monitored in situ while irradiating the initial *trans* SAM and then following the thermal back conversion (in dark) from the *cis* to the *trans* SAM.

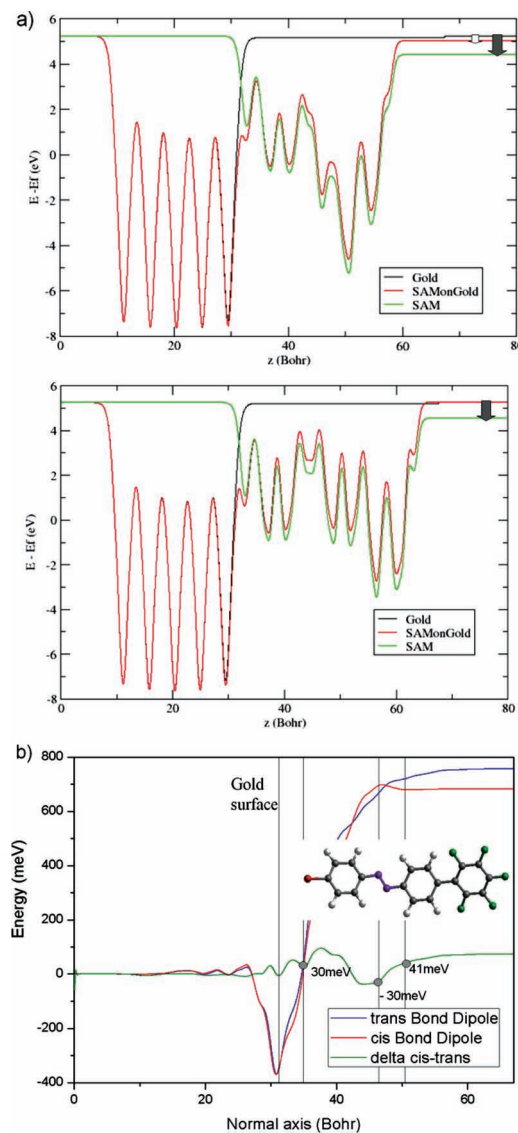


Figure 3. (a) Plane averaged potentials of the *cis* (top) and *trans* (middle) SAMs on the gold (111) surface. The zero energy is set at the Fermi level so that the work function is directly readable. We display curves for the bare Au(111) gold surface in its relaxed state (black), the gold surface covered by the SAM (red), and the free SAM layer (green). In the left part, we can identify the five gold layers and the SAM contribution moving away from the surface (see Supporting Information for more details). The two arrows on the right side points to the work function shift of the full system (light grey) and of the contribution arising from the free SAM (red). The difference between these shifts corresponds to the bond dipole. (b) Evolution of the bond dipole at the metal/SAM interface from the left to the right side. The blue and red lines correspond to the *trans* and *cis* isomers, respectively. Reference vertical lines correspond to the gold surface and different positions along the molecular backbone in the superimposed *trans* geometry. The bond dipole first decreases in the vicinity of the Au-S bond due to the repulsion of the gold electronic cloud at the surface by the atoms of the deposited molecule (i.e., pillow effect), then grows to reach its final value. The green solid line corresponds to the difference between the bond dipoles of the two isomers. This shows that the bond dipole is not confined in the Au-S bond region.

Figure 3a displays the calculated plane averaged potential profiles associated to the optimized structures of the unit cell for the *cis* and *trans* isomers. For both isomeric forms, the unit cell

contains two independent molecules chemisorbed within a herringbone packing on a slab made five layers of gold; the chosen number of gold layers ensures a good convergence of the results when varying the thickness of the slab (details about the theoretical methodology and geometry optimizations are reported in the supporting information). The work function of gold modified with the *cis* and *trans* isomers are 5.06 eV and 5.28 eV, respectively, which represents a decrease by -0.20 eV and an increase of $+0.02$ eV with respect to the clean metal surface. The higher Φ observed for the *trans* form is consistent with the experimental data although the calculated $\Delta\Phi$ (220 meV) is higher than the experimental one (90 meV) measured with the KPFM. The comparison of the absolute Φ values is most likely hampered by the actual nature of the gold sample and by the presence of contaminants, which can shield the intrinsic Φ of the sample surface both in the KP and the KPFM measurements.

In order to investigate the bond dipole versus molecular contributions to this shift, we have also computed the potential profile of the free SAM in Figure 3a. For the *cis* form, the molecular contribution is -0.85 eV, leading to a bond dipole of $+0.65$ eV. A close value of -0.72 eV is obtained for the *trans* form, which translates into a bond dipole about $+0.74$ eV. According to our calculations, the shift of the work function is thus driven by the two counter-acting contributions.

In Figure 3b we have plotted the evolution of the generated bond dipole when moving from the left to the right side of the interface for both isomers as well as the difference between *cis* and *trans* isomers. This difference is zero on the left side and amounts to a total value of 96 meV on the right side. This graph illustrates that the bond dipole does not build up exclusively in the vicinity of the Au-S bond since the dipole is significantly growing from the sulfur atom to the middle part of the molecule. The bond dipole difference between *cis* and *trans* forms is about 30 meV near the sulfur atom to be compared with the final difference of about 96 meV. The bond dipole stops increasing in the *cis* isomer when the second phenyl ring is reached, while it grows until the fluorinated ring is reached in the *trans* configuration.

The contribution of the molecular backbone to $\Delta\Phi$ arises from its dipole moment. For the *cis* isomer, the dipole moment of the radical evolves from 3.20 D in the gas-phase optimized geometry (as calculated in a large unit cell to avoid intermolecular interactions) to 3.24 D and 3.12 D for isolated radical molecules adopting the structure of the non-equivalent units in the SAM; the dipole changes for the *trans* isomer from 2.86 D to 2.58 D and 2.46 D, respectively. Depolarization effects next come into play to modify these individual dipoles when accounting for the intermolecular interactions between the two inequivalent molecules within the SAM.^[22] The total dipole of the unit cell based on the two independent radical molecules is 4.66 D for *cis* and 3.75 D for *trans*, thus showing a depolarization of about 30% compared to the isolated molecules ($3.24 + 3.12 = 6.36$ D for *cis* and $2.58 + 2.46 = 5.04$ D for *trans*). The use of periodic conditions further reduce the dipole of the cell by up to 70%, leading finally to a similar dipole value of 1.41 D for *cis* and 1.21 D for *trans* per cell, thus rationalizing the larger ΔV_{SAM} contribution for the *cis* form.

In summary, we have demonstrated that the modulation of the gold work function can be easily achieved following an

ad-hoc design of the functional molecules forming the SAM, as it is the case for the novel fluorinated azobenzene reported here. In addition to the significant modification of the energetics and wettability properties of the metal surface, the photoactive azobenzene unit can be used for further photochemical modification of these surface characteristics. Theoretically, the Φ shift between the two isomeric forms of the compound on the Au(111) surface has been found to be ~ 220 meV. The higher shift predicted for the *trans* isomer is in full accordance with the experimental data obtained by PS, macroscopic KP and KPFM. In spite of the small variation observed for this system in the in situ experiment, the present experimental and theoretical results demonstrate that this is a promising and versatile approach for the dynamic tuning of the work function of metal electrodes for organic electronic applications.

Experimental Section

Details on the synthetic procedures, compound characterization, and information on the techniques are available in the Supporting Information.

Supporting Information

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

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