Photoisomerization of azobenzene-substituted alkanethiolates on Au(111) substrates in the context of work function variation: the effect of structure and packing density

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Photoisomerization of a series of custom-designed, azobenzene-substituted alkanethiolate (AT) self-assembled monolayers (SAMs) on Au(111) substrates was studied in the context of work function variation, using Kelvin probe measurements as a transduction technique. These SAMs featured variable packing density (by ~14%; due to the odd–even effects) and, as an option, were additionally decorated with the electron donating/withdrawing –CH₃ and –CF₃ tail group, respectively, which induce additional dipole moments. The efficiency of photoisomerization and the respective extent of work function variation (ΔΦ) were found to be quite low and independent of the packing density in the SAMs, within the given odd–even packing density variation. They could only be increased, up to ca. 40 meV for ΔΦ, by mixing the azobenzene-substituted ATs with shorter “matrix” molecules, which were introduced for a partial release of the sterical constraints. The ΔΦ values for the SAMs decorated with the –CH₃ and –CF₃ tail groups were found to be lower than those for the monolayers without such a decoration, which correlated well with the theoretical estimates for the change of the dipole moment of the relevant molecules upon the photoisomerization.

1 Introduction

Stimuli-responsive self-assembled monolayers (SAMs) enjoy a growing popularity among the scientific community, in view of a variety of potential applications in nanotechnology, molecular and organic electronics, creation of active recognition systems, sensor fabrication, etc.1-4 A useful functional moiety in this regard is azobenzene, which possesses distinct photochromic behavior, viz. a change between the planar trans conformation and the twisted cis conformation upon the exposure to UV (trans–cis) and visible (cis–trans) light. In the latter case, so called back isomerization, i.e. a spontaneous cis–trans transformation, is possible as well, since the trans conformation is thermodynamically favorable. Azobenzene can serve as or be flexibly integrated into the backbone of the SAM constituents, with such examples as substituted aliphatic films5-17 and purely aromatic monolayers based on biphenyl azobenzene.18-25 The efficiency of photoisomerization in these films varies quite strong from system to system and is frequently very low, which is generally explained by a negative effect of several factors, such as sterical constraints imposed by the neighbor molecules upon the sterically demanding trans–cis transformation,18 the quenching of the pre-isomerization excited state by interaction with the substrate,26 and excitonic coupling among the azobenzene chromophores.27 The first factor, considered usually as the major one, can be partly released by increasing the separation between the azobenzene moieties in the SAMs, which can be achieved by either a large molecular footprint28,29 or by diluting the azobenzene-bearing SAM constituents in a “matrix” of shorter molecules.30-33

Recently we have reported on the synthesis of novel azobenzene-substituted alkanethiols (ATs) and SAMs thereof on Au(111) and Ag(111) substrates, characterized in very detail.34 The azobenzene moiety in these molecules is linked to the thiol anchoring group via a short aliphatic spacer of variable length, i.e. (CH₃)ₙ or (CH₂)ₙ, corresponding to a different parity of n (Fig. 1; R = –H). These molecules form well-ordered SAMs on the above substrates, exhibiting a small but distinct odd–even variation in the packing density and molecular inclination, viz. a higher packing density (by ~14%) and smaller inclination (by ~17°) of the azobenzene moieties for n = odd as compared to n = even on Au(111) and reversed but less pronounced behavior on Ag(111). This behavior

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is associated with the well-known odd–even effects in monomolecular self-assembly, reported previously for a variety of SAMs, included those with the thiolate anchoring group.\textsuperscript{34–41}

Here we test the photoisomerization ability of the above novel azobenzene-substituted ATs, assembled on the Au(111) substrates, studying also the systems in which the azobenzene moiety is additionally decorated with the dipolar \(-\text{CH}_3\) or \(-\text{CF}_3\) tail groups (Fig. 1). The goals are (i) to test the suitability of these systems for the stimuli-responsive work function variation; (ii) to understand whether the variation in the packing density, even though quite small (see above), affects the efficiency of the photoisomerization; (iii) to see whether the specific molecular arrangements in the R-AZO-C\(_n\) SAMs hinder or favor the photoisomerization, as was reported for some systems (cooperative behavior);\textsuperscript{18,20} and (iv) to monitor the effect of the dipolar tail groups, above all in the context of the work function variation. In addition to the single-component R-AZO-C\(_n\) SAMs, we also studied mixed monolayers, in which the R-AZO-C\(_n\) moieties were combined with different matrix molecules (Fig. 1), \textit{viz}. C6, C8, PT, and P-C3. Such a mixture should result in a larger separation between the azobenzene moieties and, thus, in at least partial release of sterical constraints hindering the photoisomerization.

The photoisomerization of the single-component and mixed R-AZO-C\(_n\) SAMs was monitored using the work function, which, at the same time, is the parameter that we would like to vary in a controlled fashion by external stimuli (light in the given case). R-AZO-C\(_n\) SAMs represent potentially a suitable system in this regard, as schematically illustrated in Fig. 2. Note that according to the theoretical estimates, the dipole moment of non-substituted and substituted azobenzene (R-AZO) changes upon the \textit{trans}–\textit{cis} transformation: from 0 to 3.17 D for H-AZO, from 0.81 to 3.63 D for CH\(_3\)-AZO, and from 3.64 to 2.66 D for CF\(_3\)-AZO.\textsuperscript{22} Accordingly, one can expect work function variation upon exposure of the R-AZO-C\(_n\) SAMs to the UV and visible light, as far as the azobenzene moieties in these monolayers are aligned upright, which is the case,\textsuperscript{14} and capable of photoisomerization, which will be addressed in the present study. Apart from the above photoisomerization part, the SAM-induced work function offset with respect to the clean Au(111) substrate is generally determined by a combined effect of the S–Au interface (bond dipole; lowers the work function) and the dipolar tail groups.\textsuperscript{42–45} Comparing the R-AZO-C\(_n\) films with other non-substituted and substituted thiolate SAMs,\textsuperscript{45–47} one can then expect that the assembly of the H-AZO-C\(_n\) and CH\(_3\)-AZO-C\(_n\) SAMs should lower the work function of the Au(111) substrate, whereas the deposition of the CF\(_3\)-AZO-C\(_n\) monolayers should increase it.

Note that azobenzene-based SAMs have already been used for stimuli-responsive work function modulation,\textsuperscript{22,48–50} including their implementation in model organic field effect transistors.\textsuperscript{2,51} In particular, the SAMs of asymmetric azobenzene disulfides on gold, with either non-substituted or nitrile-substituted azobenzene, exhibited a consecutive work function variation of 50–100 meV upon the photoisomerization.\textsuperscript{49} Similar values were also obtained for the pure aromatic azobenzene SAMs (70–116 meV),\textsuperscript{22} which presumably have a close-to-100% isomerization efficiency,\textsuperscript{18–20} and perfluorinated azobenzene-based SAM (80–100 meV).\textsuperscript{50} Interestingly, these values are quite close to the theoretical estimates for the given systems, which are \(\sim 100 \text{ meV}\)\textsuperscript{22} and \(\sim 220 \text{ meV}\)\textsuperscript{39} for the former and latter monolayers, respectively. Note that the former value was corrected later to 60 meV relying on a more sophisticated, state-of-the-art theoretical approach.\textsuperscript{52} It was stated that the \textit{cis}–\textit{trans} shift in the work function is qualitatively quite robust with respect to the details of the SAM. However, the exact value of this shift should be sensitive to these details.\textsuperscript{52}

2 Experimental

The R-AZO-C\(_n\) compounds were synthesized according to the literature protocols.\textsuperscript{53} C6, C8, and PT compounds were purchased...
from Sigma-Aldrich and used as received. The P-C3 compound was custom-synthesized according to an established route, as described below. To a solution of 1-bromo-3-phenylpropane (1.1 g, 5.4 mmol, purchased from Sigma-Aldrich) in ethanol (50 mL) NaHS (0.60 g, 11 mmol) was added at once and the mixture was stirred at room temperature for 3 h. The solution was acidified with diluted HCl, DCM was added and the aqueous phase was separated. The solvent was evaporated and the residue was purified by column chromatography (hexane:ethyl acetate/SiO2 99:1) to yield the product as a colorless liquid. Yield: 0.20 g, 24%. 1H NMR (400 MHz, CDCl3) δ 7.30–7.11 (m, 5H), 2.75–2.66 (m, 2H), 2.51 (dd, J = 14.7, 7.4 Hz, 2H), 1.97–1.85 (m, 2H), 1.33 (t, J = 7.8 Hz, 1H).

The gold substrates were purchased from Georg Albert PVD, Silz, Germany. They were prepared by thermal evaporation of 100 nm of gold (99.99% purity) onto polished single crystalline silicon (100) wafers (Silicon Sense) primed with a 5 nm titanium adhesion layer. The evaporated films were polycrystalline, with a predominant (111) orientation and a grain size of 20–50 nm.

The single component R-AZO-Cn SAMs were formed by immersion of freshly prepared substrates into 1 mmol solutions of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute ethanol for 24 h at room temperature. The mixed, R-AZO-C of the respective compounds in absolute alcohol for 24 h at room temperature.

The photoisomerisation of the R-AZO-Cn compounds in solution (0.1 mM in ethanol) was monitored by UV/vis spectroscopy using a Jasco V 650 spectrometer. The spectra were successively recorded upon the exposure of the dissolved compounds to UV light (365 nm).

The photoisomerisation of the R-AZO-Cn SAMs was monitored on the basis of the work function, getting, at the same time, direct information on its variation, which was the major goal of the present study. Work function measurements were carried out in ultra-high vacuum (UHV) using a UHV Kelvin Probe 2001 system (KP technology Ltd, UK). The pressure in the UHV chamber was ~10−9 mbar. As reference, we used a C16 SAM with the work function value of 4.32 eV according to literature. The latter value was additionally verified by its referencing to the work function of freshly sputtered gold set to 5.2 eV, close to the literature value (5.12 eV). The SAMs were successively exposed to UV (365 nm; ~6.5 mW cm−2; epi-SPOT-365-C) and visible (440 nm; ~3.0 mW cm−2; LEDIL CA11663 HEIDI-RS) light via an UHV quartz window. In each case, the exposure time was set to 15 min based on the preliminary experiments monitoring the progressing photoisomerization. The time required for the subsequent work function measurement was ca. 3 min, which included the placement of the Kelvin Probe tip, retracted during the exposure of the sample to UV/visible light (to avoid shadowing), and the measurement itself. The complete irradiation cycle, including irradiation by UV light, first work function measurement, irradiation by visible light, and second work function measurement, was usually repeated several times to
verify the observed changes and to get representative values for the extent of the work function variation.

3 Results and discussion

3.1 H-AZO-C\textsubscript{n} SAMs

UV-vis spectra recorded upon the exposure of H-AZO-C3 and H-AZO-C4, dissolved in ethanol, to UV light are shown in Fig. 4. The spectra of the dissolved substances are characteristic of the \textit{trans}-isomer of azo-compounds,\textsuperscript{58,59} showing an intense $\pi-\pi^*$-transition band around $\lambda = 344$ nm and a weaker (forbidden) $n-\pi^*$-band around $\lambda = 450$ nm. Irradiation of these substances with UV light of a suitable wavelength (see Section 2) results in a progressive decrease in the intensity of the $\pi-\pi^*$-band and an increase in the intensity of the $n-\pi^*$-band, leveling off at the spectra characteristic of the \textit{cis}-isomer of azo-compounds.\textsuperscript{58,59} Thus, both, H-AZO-C3 and H-AZO-C4, are well capable of the photoisomerization in molecular state.

After the successful isomerization in solution, single-component H-AZO-C3 and H-AZO-C4 SAMs were investigated. The photoisomerization in the SAMs was monitored by using the work function as a fingerprint parameter but also as the parameter which we intend to control by the light-responsive azobenzene-based SAMs of this study. The work function of the as-prepared, single-component H-AZO-C3 and H-AZO-C4 SAMs was estimated at $4.45 \pm 0.1$ eV and $4.5 \pm 0.1$ eV, respectively, with the higher packing density of the former monolayer having only a moderate effect on the work function. These values varied to some extent, but not significantly, upon diluting the H-AZO-C\textsubscript{n} moieties with the shorter “matrix” molecules (see Fig. 1) in the mixed SAMs. A typical variation of the work function upon consecutive exposure of the above SAMs, both single-component and mixed, to UV and visible light is shown in Fig. 5, by the example of the mixed H-AZO-C3/PT and H-AZO-C4/PT monolayers with two different compositions, corresponding to the different time of the reaction exchange between the primary, “matrix” PT SAM and the H-AZO-C\textsubscript{n} molecules in solution (see Section 2).

For these SAMs, pronounced and systematic variations of the work function upon the UV/vis exposure are observed, with the lower values for the as-prepared films and the films exposed to the visible light and the higher values for the films exposed to the UV light. This agrees well with the directions of the dipole moment for the assembled H-AZO-C\textsubscript{n} molecules in the \textit{trans} and \textit{cis} conformations (see Fig. 2; the contribution of the R group is absent in the given case): one expects a lower work function for the dipole moment directed from the substrate (\textit{trans}) and somewhat higher work function for the dipole moment directed to the substrate (\textit{cis}), apart from the contribution of the S-Au interface (see Section 1), which is similar for both conformations.

Similar behavior was observed for the single-component H-AZO-C\textsubscript{n} SAMs as well as for all the respective mixed monolayers. The extent of the work function variation ($\Delta \Phi$) in these monolayers is summarized in Fig. 6. According to this figure, the $\Delta \Phi$ values for the single-component H-AZO-C3 and H-AZO-C4 SAMs are $\sim 30$ meV and $\sim 20$ meV, respectively. Both these values are noticeably lower than those for the purely aromatic azobenzene SAMs ($70–116$ meV),\textsuperscript{22} suggesting a lower degree of photoisomerization in the H-AZO-C\textsubscript{n} films of this study. Assuming a close-to-100% isomerization efficiency in the SAMs

![Fig. 4](image-url) UV-vis spectra recorded upon the exposure of R-AZO-C3 (a) and R-AZO-C4 (b) dissolved in ethanol to UV light. The vertical dashed lines mark the characteristic bands.

![Fig. 5](image-url) Work function variation upon the consecutive exposure of the mixed H-AZO-C3/PT (a) and H-AZO-C4/PT (b) SAMs to UV and visible (vis) light; the general accuracy of the measurements could be estimated at 5 meV but larger deviations from the general behavior were observed as well, for particular isomerization cycles within particular datasets. The average $\Delta \Phi$ values are given at the respective curves. The mixed SAMs were prepared by the immersion of the primary PT monolayers in the solution of AZO-C\textsubscript{n} molecules for either 1 h (red circles and dashed lines) or 3 h (blue diamonds and dashed lines); the portion of the AZO-C\textsubscript{n} molecules in these SAMs was 40–75% (see below). A comparably small work function change for the third switching from UV to vis for both datasets with 3 hours immersion is most likely coincidental and related to these particular datasets; such a behavior was not generally observed.
of ref. 22 and taking into account similar molecular orientation and packing density in both systems,18–20 we get ca. 20–30% isomerization efficiency in the present case. We think that such a lower value in our case is mainly related to the sterical constraints, which should be especially strong for the densely packed H-AZO-C₃ SAMs and, obviously, are not released in the less densely packed (by ~14%)49 H-AZO-C₄ monolayer. It looks also that the structures of both H-AZO-C₃ and H-AZO-C₄ SAMs are not as favourable for cooperative isomerization as was reported for some densely packed azobenzene-based monolayers.18–20

The assumption about the role of the sterical constraints is supported by the data for the mixed SAMs since the mixing with shorter molecules results in a larger spacing between the azobenzene moieties protruding over the photoisomerization-neutral “matrix”. Indeed, the mixed H-AZO-C₃/PT and H-AZO-C₄/PT SAMs with a sufficiently large portion of the H-AZO-Cₙ molecules exhibit similar ΔΦ values of ca. 40 meV (Fig. 6), which are noticeably (a factor of 1.5–2) higher than those for the single-component monolayers. Considering that the respective work function variation is mediated by the smaller number of the H-AZO-Cₙ molecules as compared to the single-component SAMs, the photoisomerization efficiency in the best-performing H-AZO-C₃/PT and H-AZO-C₄/PT monolayers can be coarsely estimated at ~80% and ~50%, respectively. Also, the ΔΦ values for the best-performing H-AZO-Cₙ/PT SAMs are comparable to those for the asymmetric azobenzene disulfide monolayers (50–100 meV), in which the portion of the azobenzene-bearing SAM constituents was 50%.49

As to the other mixed SAMs, they give ΔΦ values which are either close to or even smaller than those for the single-component monolayers (Fig. 6). To some extent, such a behavior stems from a small portion of the H-AZO-Cₙ molecules, capable of the photoisomerization, in the SAMs, but such additional factors as exact orientation of these molecules could be of importance as well. The latter assumption is tentatively supported by the lack of exact systematic correlation between the ΔΦ values and the portion of H-AZO-Cₙ in Fig. 6, even though a certain correlation can be probably traced.

An important parameter of the azobenzene-containing SAMs is cis–trans back isomerization, driven by the lower energy of the latter state. The respective process was monitored for the single-component H-AZO-Cₙ SAMs only. The results are presented in Fig. 7. The work function of both H-AZO-C₃ and H-AZO-C₄ SAMs decreases in the exponential fashion, exhibiting pseudo first order kinetics typical of the back isomerization.20 The derived relaxation time is rather short as compared to other azobenzene-based SAMs.30 In view of the specific time necessary to measure the work function with our experimental setup (ca. 3 min; see Section 2), this means that the obtained ΔΦ values are probably slightly (~20%) underestimated, which, however, does not change them noticeably.

3.2 CH₃-AZO-Cₙ and CF₃-AZO-Cₙ SAMs

The work function of the pristine, single-component CH₃-AZO-C₃ and CH₄-AZO-C₄ SAMs was found to be 4.3 ± 0.1 eV and 4.4 ± 0.1 eV, respectively. The lower value for the former monolayer is related to its somewhat higher packing density, as can be expected analogous to the H-AZO-Cₙ SAMs. The effect should be reversed for the opposite direction of the dipole moments, which is indeed the case for the ~CF₃ tail group. Consequently, the work functions of the CF₃-AZO-C₃ and CF₃-AZO-C₄ SAMs was found to be 5.6 ± 0.1 eV and 5.4 ± 0.1 eV.
The single-component and mixed CH$_3$-AZO-C$_n$ SAMs exhibited a photoisomerization behavior similar to that of the H-AZO-C$_n$ monolayers (Fig. 5). The respective values of $\Delta \Phi$ are presented in Fig. 8. The values for the single-component CH$_3$-AZO-C$_3$ and CH$_3$-AZO-C$_4$ SAMs, which are $\sim$ 12.5 meV and 15 meV, respectively, are even smaller than those for the H-AZO-C$_n$ monolayers (Fig. 6). On the one hand, this correlates with the smaller difference between the dipole moments of CH$_3$-AZO in the trans and cis conformation ($\Delta \mu = 2.62$ D; see Section 1) as compared to the H-AZO case ($\Delta \mu = 3.17$ D; see Section 1). On the other hand, this means that the isomerization efficiency of the CH$_3$-AZO-C$_n$ SAMs is quite small.

Similar to the H-AZO-C$_n$ case (Fig. 6), the mixing of CH$_3$-AZO-C$_n$ with the C8, C6, and PT molecules allows to increase the $\Delta \Phi$ values to some extent, up to 25 meV for the best-performing CH$_3$-AZO-C$_3$/PT and CH$_3$-AZO-C$_4$/PT SAMs (Fig. 8), which is not a particularly high absolute value but a relative increase by 65–100% compared to the single-component monolayers. This means that the sterical constraints play a role for the single-components CH$_3$-AZO-C$_n$ SAMs as well. Interestingly, the exchange reaction, used for the fabrication of the mixed SAMs, was more efficient in the CH$_3$-AZO-C$_n$ case as compared to the H-AZO-C$_n$ one: higher portions of CH$_3$-AZO-C$_n$ were achieved for the C6 and C8 matrix (compare Fig. 8 and 6), even though this did not help to increase $\Delta \Phi$.

Along with the CH$_3$-AZO-C$_n$ SAMs, CF$_3$-AZO-C$_3$ monolayer was tested. Representative results for the mixed H-AZO-C$_3$/P-C$_3$, CH$_3$-AZO-C$_n$/P-C$_3$, and CF$_3$-AZO-C$_3$/P-C$_3$ SAMs are presented in Fig. 9, with the matrix molecule P-C$_3$ mimicking the “bottom” part of the R-AZO-C$_3$ moieties upon the assembly of thereof on Au(111). The work function behaviour of the H-AZO-C$_3$/P-C$_3$ and CH$_3$-AZO-C$_n$/P-C$_3$ SAMs is similar to the case of the C6, C8, and PT matrix. First, for both these SAMs, pronounced and systematic variations of the work function upon the UV/vis exposure are observed, with the lower values for the as-prepared films and the films exposed to the visible light and the higher values for the films exposed to the UV light. Second, the extent of the work function variation ($\Delta \Phi$) is larger for the H-AZO-C$_3$/P-C$_3$ SAM as compared to the CH$_3$-AZO-C$_3$/P-C$_3$ monolayer. Third, the absolute values of $\Delta \Phi$, viz. 30–40 meV and 20–25 meV, respectively, agree well with the best values for the C6, C8, and PT matrix.

In contrast, the work function variation in the CF$_3$-AZO-C$_3$/P-C$_3$ case occurs in the inverse fashion as compared to the H-AZO-C$_3$/P-C$_3$ and CH$_3$-AZO-C$_n$/P-C$_3$ SAMs, with the higher values for the as-prepared films and the films exposed to the visible light and the lower values for the films exposed to the UV light. This behaviour is similar to the cases of the azobenzene-based SAMs with nitrile$^{49}$ and perfluorophenyl$^{50}$ tail groups and can be explained by the orientation and strength of the dipole moment of the –CF$_3$ group. Indeed, this group has quite a large

Fig. 8 The extent of the work function variation ($\Delta \Phi$) for the single component (black squares) and mixed CH$_3$-AZO-C$_3$ (a) and CH$_3$-AZO-C$_4$ (b) SAMs upon photoisomerization as a function of portion of CH$_3$-AZO-C$_n$ in the SAMs. As the second component of the mixed SAMs, C8 (red circles), C6 (green up triangles), or PT (blue down triangles) were used. The legend is given in the figure. The values for the single-component SAMs are highlighted by gray dashed lines.

Fig. 9 Work function variation ($\Delta \Phi$) upon the exposure of the mixed H-AZO-C$_3$/P-C$_3$ (a), CH$_3$-AZO-C$_3$/P-C$_3$ (b), and CF$_3$-AZO-C$_3$/P-C$_3$ (c) SAMs to UV and visible (vis) light; the general accuracy of the measurements could be estimated at $\pm 5$ meV but larger deviations from the general behavior were observed as well, for particular isomerization cycles within particular datasets. The portion of H-AZO-C$_3$, CH$_3$-AZO-C$_3$, and CF$_3$-AZO-C$_3$ in the SAMs was about 50%. The work function of the CF$_3$-AZO-C$_3$/P-C$_3$ SAM exhibits some drift. For this SAMs, the absolute values of the work function are lower than that for the single-component CF$_3$-AZO-C$_3$ monolayer, because of the admixture of P-C$_3$ (oppositely directed molecular dipole).
responsive azobenzene-containing SAMs could be assembled in model devices (organic field effect transistors), utilizing stimuli-sensitive molecules. The efficiency could be increased up to 50–80% by mixing the azobenzene-substituted ATs with the shorter “matrix” molecules, with the aromatic molecules performing better in this context. The packing density in the SAMs, varied within the odd–even effects by photoisomerization, coarsely estimated at 20–30%, and the packing lack of cooperative effects. No correlation between the efficiency of the molecular packing and by the constraints associated with a dense molecular packing and by the sterical hindrances associated with a dense molecular packing and by the lack of cooperative effects. No correlation between the efficiency of photoisomerization, coarsely estimated at 20–30%, and the packing density in the SAMs, varied within the odd–even effects by ~14% for the different linker lengths, was observed. However, the DΦ values could be increased up to ca. 40 meV and the photoisomerization efficiency could be increased up to 50–80% by mixing the azobenzene-substituted ATs with the shorter “matrix” molecules, with the aromatic molecules performing better in this context. The highest DΦ values were obtained for the H-AZO-Cn SAMs and the lowest for the CF3-AZO-Cn monolayer, which correlates with the theoretical estimates for the change of the dipole moment of the R-AZO moieties upon the photoisomerization. Consequently, the former films are suited better for the applications, unless an increase in the work function, mediated by the latter films, is required.

The results of this study show that it is quite difficult to get noticeable variation of the work function by external stimuli using azobenzene-containing SAMs and new ideas for rational design of such monolayers are required. The highest DΦ values reported so far are, to the best of our knowledge, about 100 meV, which correlates coarsely with the realistic theoretical estimates (see Section 1 for details). Nevertheless, model devices (organic field effect transistors), utilizing stimuli-responsive azobenzene-containing SAMs could be assembled and successfully tested, which gives hope for the given field of research.

Conflicts of interest

There are no conflicts to declare.

4 Conclusions

Photoisomerization of a series of custom-designed, azobenzene-substituted AT SAMs on Au(111) substrates was studied in the context of work function variation, using Kelvin probe measurements as a transduction technique. A special feature of these SAMs was the variable packing density, which was controlled by the length of the aliphatic linker between the thiolate anchoring group and azobenzene moiety (odd–even effects). The latter moiety was introduced either as-is (H-AZO-Cn) or decorated with dipolar –CH3 or –CF3 tail groups (CH3-AZO-Cn and CF3-AZO-Cn, respectively).

The DΦ values obtained for the single-component SAMs were quite low (20–30 meV) which was explained by the sterical hindrances associated with a dense molecular packing and by the lack of cooperative effects. No correlation between the efficiency of photoisomerization, coarsely estimated at 20–30%, and the packing density in the SAMs, varied within the odd–even effects by ~14% for the different linker lengths, was observed. However, the DΦ values could be increased up to ca. 40 meV and the photoisomerization efficiency could be increased up to 50–80% by mixing the azobenzene-substituted ATs with the shorter “matrix” molecules, with the aromatic molecules performing better in this context. The highest DΦ values were obtained for the H-AZO-Cn SAMs and the lowest for the CF3-AZO-Cn monolayer, which correlates with the theoretical estimates for the change of the dipole moment of the R-AZO moieties upon the photoisomerization. Consequently, the former films are suited better for the applications, unless an increase in the work function, mediated by the latter films, is required.

The results of this study show that it is quite difficult to get noticeable variation of the work function by external stimuli using azobenzene-containing SAMs and new ideas for rational design of such monolayers are required. The highest DΦ values reported so far are, to the best of our knowledge, about 100 meV, which correlates coarsely with the realistic theoretical estimates (see Section 1 for details). Nevertheless, model devices (organic field effect transistors), utilizing stimuli-responsive azobenzene-containing SAMs could be assembled and successfully tested, which gives hope for the given field of research.

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References
