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Self-assembled monolayers of polar molecules on Au(111) surfaces: distributing the dipoles

David A. Egger,^a Ferdinand Rissner,^a Gerold M. Rangger,^a Oliver T. Hofmann,^a Lukas Wittwer,^a Georg Heimel,^{*b} and Egbert Zojer^{*a}

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Quantum-mechanical calculations are performed to investigate the interface between Au(111) surfaces and self-assembled monolayers (SAMs) of π -conjugated molecules. Dipolar pyrimidine units act as building blocks to systematically tune the molecular dipole moments via the number of repeat units. The resulting work-function modifications and the energetic alignment of the frontier electronic states in the SAM with the Fermi level are analyzed. Compared to SAMs where strong dipole moments are realized only by end-group substitutions on otherwise non-polar molecules, an entirely different evolution with backbone length is found for the present systems, where dipoles are built directly into the backbone. In particular, the achievable work-function modifications depend on peculiarities in the relative alignment of the energy levels in the SAM and in the metal. We thus introduce an additional degree of freedom for tuning surface and interface electronic properties with functional self-assembled monolayers.

In organic electronic devices, the alignment of the electrodes' Fermi-level relative to the frontier orbitals of the adjacent organic semiconductors critically influences device performance.¹ The most important parameter in this context is the electrode work function, Φ . One approach to adjust Φ is the adsorption of self-assembled monolayers (SAMs) of dipolar molecules.^{2,3,4,5,6,7} In-depth quantum-mechanical studies on the effect of various molecules have led to a microscopic understanding of the processes governing the electronic structure of the metal/SAM interface.^{8,9,10,11}

So far, the focus has been largely on the effect of end-group substituents, e.g., dipolar donor- or acceptor-groups^{4,10,12} or fluorinated segments^{2,3,4,5} attached to a non-polar backbone. Here, we propose a novel approach: distributing a series of dipoles along the molecular backbone. This provides an additional "chemical" handle for tuning interfacial properties, especially when adapting the number of polar repeat units in each molecule. Furthermore, it should modify the interaction between the SAM-forming molecules,

and differences in the electric field distribution within the SAM can be expected to affect parameters like charge transport through the layer. The quantities of interest in the present computational study are the work-function modification, $\Delta\Phi$, due to the SAM and the alignment, ΔE_{HOPS} , between the Fermi level of the system and the HOMO-derived π -states (the HOPS) of the SAM. Specifically, we show that the distributed-dipole approach results in modifications of the

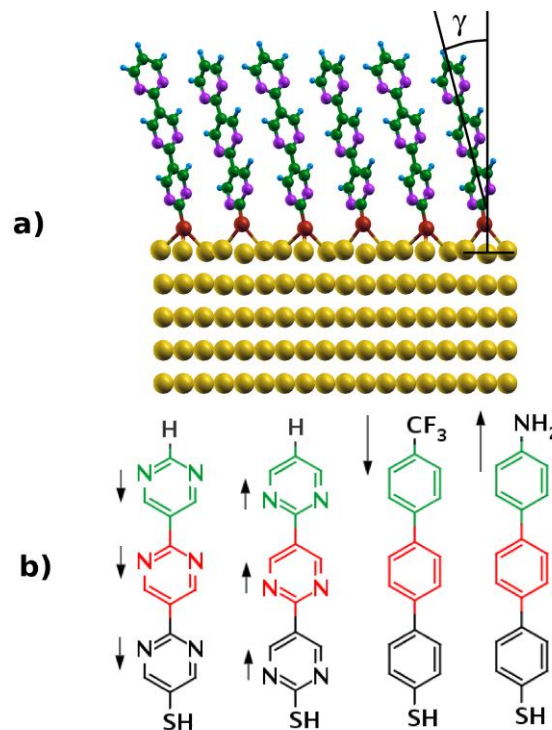


Fig. 1 (a) Schematic representation of "N-down" terpyrimidinethiol SAM adsorbed on Au(111). The tilt angle γ of the molecule relative to the surface normal is indicated. (b) Chemical structures of the four investigated molecules (from left to right): "N-up" oligopyrimidinethiol (-SH attached at the 5 position); "N-down" oligopyrimidinethiol (-SH attached at the 2 position); CF₃-substituted oligophenylthiol and NH₂-

substituted oligophenylthiol. For each system 1, 2, and 3 rings were considered. The arrows schematically indicate the relevant molecular dipole moments.

interface energetics that differ significantly from those in conventional SAMs. This is especially true as far as the evolution of the aforementioned physical quantities of interest with the length of the backbone is concerned.

The calculations rely on density-functional theory (DFT) within the repeated-slab approach, applying the PW91 exchange-correlation functional and using the VASP code.¹³ Geometry relaxations were performed in internal coordinates using the optimizer GADGET.¹⁴ The applied methodology follows Ref. 15 and is presented in the supplementary information.⁸ Three-dimensional representations of the systems were generated with XCrysDen.¹⁶

We investigated thiols adsorbed on the Au(111) surface (Fig. 1a) in a $p(\sqrt{3}\times 3)$ surface forming a herringbone pattern in analogy to what was found experimentally for biphenylthiols.¹⁷ This procedure also ensures comparability with our previous calculations.^{10,12,15} We chose (mono, bi, and ter) pyrimidines as backbones, with the dipolar pyrimidine moieties linked in a head-to-tail fashion. Here, one has to distinguish between two possible orientations of the nitrogens relative to the docking group (and, thus, in the SAM relative to the metal substrate), referred to as “N-up” (thiol group in 5-position) and “N-down” (thiol group in 2-position), as shown in Fig. 1b. In this way, the resulting molecular dipole moment points either towards (“N-up”) or away from the metal surface (“N-down”). As reference systems with non-polar backbones we chose oligophenylthiols^{10,12,15} (considering 1, 2, and 3 rings) bearing donor or acceptor head groups (Fig. 1b). From the large pool of possible substituents, we chose the donor amine (-NH₂) and the acceptor trifluoromethyl (-CF₃) substituent as the resulting SAMs for two-ring backbones (the intermediate length case amongst the ones considered here) give rise to work-function modifications similar to the “N-down” and “N-up” bipyrimidines.

Conceptually, changing an electrode’s work function by means of dipolar molecules results from two different microscopic origins:¹² First, the molecular dipole moments give rise to a step in the electrostatic potential energy across the (non-bonded) monolayer, referred to as ΔE_{vac} . As it is proportional to the component of the dipoles perpendicular to the substrate surface, the molecular orientation plays a decisive role.¹⁸ Furthermore, electrostatic interactions between the molecules forming the monolayer induce coverage-dependent depolarization effects,^{9,19} typically resulting in a sub-linear increase of the magnitude of ΔE_{vac} with the packing density.²⁰ Second, an additional shift in the potential energy (with amplitude ΔE_{BD}) is caused by interfacial charge rearrangements upon Au-SAM bond formation. To sum up, $\Delta\Phi = \Delta E_{\text{vac}} + \Delta E_{\text{BD}}$.

We first analyze the electrostatics of the isolated monolayers (with the sulphur atoms saturated by hydrogens). Figs. 2a and 2b show the plane-averaged electron potential energy across “N-down” terpyrimidinethiol and NH₂-substituted terphenylthiol. For the non-polar backbone, all rings are at virtually the same potential; the potential drop

responsible for ΔE_{vac} is confined to the region of the NH₂ substituent. In contrast, for “N-down” terpyrimidinethiol, a continuous decrease of the potential across the entire backbone is found, as each polar ring introduces a step in the potential energy landscape. When comparing the “N-up” conformations with the CF₃-substituted oligophenylthiol SAMs, an analogous situation with different sign of ΔE_{vac} is observed (not plotted). The total potential step across the monolayer, ΔE_{vac} , is plotted in Fig. 2c as a function of the number of pyrimidine/phenyl rings.[†] As expected,¹⁹ this potential energy step changes only slightly with the length of the backbone in the head-group substituted reference systems. In fact, also previous studies^{21,22} have found a small variation of the work function with the length of the adsorbed molecules in SAMs of (fluorinated) alkylthiolates, which could be largely attributed to changes in the geometry of the

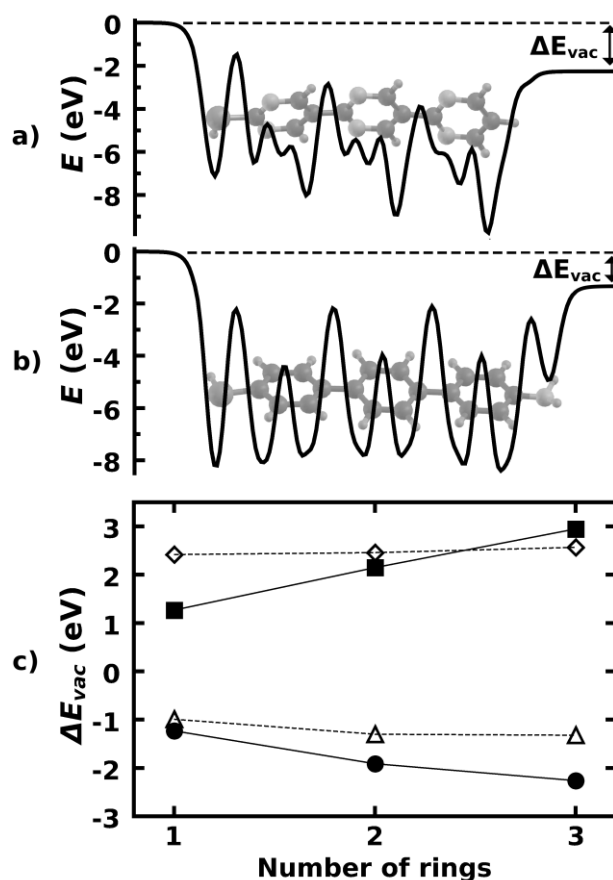


Fig. 2 Plane-averaged electron potential energy of (a) “N-down” terpyrimidinethiol and (b) NH₂-substituted terphenylthiol. The left vacuum energy is chosen as the energy reference (c) Backbone length dependence of ΔE_{vac} for “N-up” oligopyrimidinethiol (filled squares), “N-down” oligopyrimidinethiol (filled circles), CF₃-substituted (open diamonds), and NH₂-substituted terphenylthiol (open triangles).

alkyl backbone.²² The (minor) length dependence of ΔE_{vac} in the case of the -NH₂ substituent is in part due to a slight increase of the molecular dipole moment, similar to what has been observed for nitro-substituted phenylenevinylene.¹⁹ The main origin, however, is purely geometric: The tilt angle γ (Fig. 1a) of the NH₂-substituted phenylthiols decreases with chain length (Table 1), which results in an increase of the

component of the dipole moment perpendicular to the surface. Importantly, a pronounced dependence on the backbone length is found for the oligopyrimidinethiols, where every additional ring significantly contributes to a further change in the potential energy. Moreover a close to linear evolution is observed. While this is what one might have expected for molecules resembling a linear series of dipoles, it is actually far from trivial as (i) the intra-molecular interaction between the rings changes upon elongating the backbone[‡] (ii) the inter-

molecular interactions (including depolarization) can be expected to change with chain length and (iii) significant changes of the backbone orientation (and thus of the component of the dipole moment perpendicular to the surface) are found with increasing length of the backbone, i.e., the tilt angle γ decreases with increasing number of repeat units (see Table 1).

The second contribution to the SAM-induced work-

Table 1 DFT-calculated work-function modification, $\Delta\Phi$, magnitude of the induced potential energy shift due to the bond dipole, ΔE_{BD} , potential step across the saturated monolayer, ΔE_{vac} , difference between E_F of the system and the HOPS of the SAM, ΔE_{HOPS} , and tilt angle, γ , of the long molecular axes relative to the surface normal; as there are two inequivalent molecules in the unit cell, average values are reported for γ .

monolayer	number of rings	$\Delta\Phi$ (eV)	ΔE_{BD} (eV)	ΔE_{vac} (eV)	ΔE_{HOPS} (eV)	γ (°)
“N-up” pyrimidine	1	0.35	-0.94	1.27	-0.91	37.2
	2	1.09	-1.07	2.15	-0.17	26.7
	3	0.98	-1.99	2.94	-0.15	19.1
“N-down” pyrimidine	1	-1.96	-0.74	-1.23	-1.67	31.5
	2	-2.58	-0.68	-1.91	-1.44	26.7
	3	-3.11	-0.85	-2.26	-1.37	24.0
“CF ₃ ” phenyl	1	1.34	-1.08	2.42	-1.06	16.2
	2	1.33	-1.13	2.46	-1.01	13.7
	3	1.39	-1.18	2.57	-0.97	12.2
“NH ₂ ” phenyl	1	-2.21	-1.23	-0.99	-0.83	25.2
	2	-2.48 ^a	-1.18 ^a	-1.30 ^a	-0.86 ^a	17.1
	3	-2.49	-1.17	-1.32	-0.86	15.7

^a These values differ slightly from those reported in Ref. [10] due to a different geometry-optimization scheme used for the present work.

function modification, ΔE_{BD} , is obtained by analyzing the adsorption under the assumption of hydrogen removal and Au-S bond formation.¹⁵ Table 1 lists the values for all twelve systems. ΔE_{BD} primarily depends on the docking chemistry.¹⁰ Accordingly, a similar value of ΔE_{BD} is found for all phenylthiol-docked SAMs independent of the end-group substituent, as the latter does not affect the docking group side of the SAM (cf., Table 1).¹⁰

For the “N-down” pyrimidinethiol SAMs, ΔE_{BD} is somewhat decreased compared to the biphenylthiols, and its magnitude is almost independent of the number of repeat units.[†] Consequently, the evolution of ΔE_{vac} from Fig. 2c is translated into an almost linear dependence of the work-function modification on the number of “N-down” oriented pyrimidines as shown in Fig. 3. This indicates that distributing dipoles throughout the molecular entity indeed provides a strategy to tune the work-function modification over a wide range in a systematic way. One might even be tempted to think that arbitrarily large work-function changes could be realized as long as one merely synthesized a long-enough

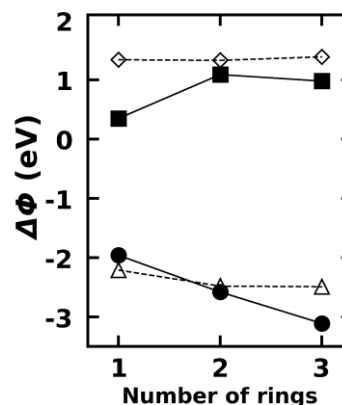


Fig. 3 Backbone length dependence of the work-function modification $\Delta\Phi$ for “N-up” oligopyrimidinethiol (filled squares), “N-down” oligopyrimidinethiol (filled circles), CF₃-substituted (open diamonds) and NH₂-substituted terphenylenethiol (open triangles).

backbone (provided that such molecules would actually form closely packed SAMs). That assessment, however, is put into perspective by the results for the pyrimidine “N-up” configuration (cf., Fig. 3). There, no linear evolution of $\Delta\Phi$ with the number of repeat units is observed. It rather saturates at two rings and never exceeds the value for the CF₃-substituted biphenylthiol (actually, for three rings even a slight decrease is observed). From Table 1, it becomes obvious that the saturation of $\Delta\Phi$ for the 3-ring pyrimidine “N-up” SAM is the consequence of the exceedingly large ΔE_{BD} in that system.

In order to understand the ΔE_{BD} value of the “N-up”

terpyrimidine it is necessary to consider the energetic alignment between the molecular states and the Fermi-level of the system. As shown in Table 1, ΔE_{HOPS} (defined as the energy difference between the HOPS peak and E_{F}) amounts to -0.91 eV in “N-up” monopyrimidine. Upon elongating the backbone, the HOMO-LUMO gap decreases, as does the ionisation potential of the SAM at the side of the docking group; together with ΔE_{BD} , the latter determines the level alignment.^{10,12} Consequently, also ΔE_{HOPS} becomes smaller and reaches a value of -0.17 eV. If that trend continued for terpyrimidine, its HOPS would come to lie above the Fermi level, which would be inconsistent with a population of the electronic states according to the Fermi-Dirac statistics. Instead, as soon as the tail of the HOPS-related density of states crosses E_{F} , electrons are redistributed within SAM and metal, resulting in a sizeable extra interfacial dipole layer. This essentially pins the HOPS of the SAM at E_{F} , as can be inferred from the fact that ΔE_{HOPS} in terpyrimidinethiol is only slightly smaller than in bipyrimidinethiol. The pinning-induced interface dipole then manifests itself in the very large ΔE_{BD} for the terpyrimidine SAM in the “N-up” configuration. In fact, a closer look at the ΔE_{BD} values in Table 1 indicates that already in the two-ring system, weak Fermi-level pinning is at work. An important conclusion from this finding is that there is a natural limit for the maximum achievable $\Delta\Phi$ within the distributed-dipole approach, which is determined by the energies of the frontier electronic states in the SAM. That is, $\Delta\Phi$ can be increased by elongating the molecular backbone only as long as Fermi-level pinning can be avoided.

As for the work-function modification and ΔE_{vac} , a qualitatively different behaviour is observed also for the level alignment in the “N-down” systems: Already for the one-ring system, the absolute value of ΔE_{HOPS} is by 0.76 eV larger than for the corresponding “N-up” structure. This is insofar remarkable, as one is dealing with an identical molecular backbone that is merely attached in a different orientation to the sulphur docking groups bonded to the metal. The difference in ΔE_{HOPS} between the “N-up” and “N-down” configurations further increases for bipyrimidinethiol, where it reaches the maximum value of 1.27 eV. This behaviour is in sharp contrast to what is seen in the two reference systems, CF_3 - and NH_2 -substituted biphenylthiol. In spite of the fact that they yield work-function modifications equivalent to the “N-up” and “N-down” bipyrimidinethiol SAMs, the differences between their ΔE_{HOPS} are very minor, as observed in all end-group substituted systems studied so far.^{10,18} The reason for these qualitatively different trends is rooted in the fact that, in the absence of Fermi-level pinning, the level alignment is determined by the ionisation potential of the (non-bonded) SAM on that side of the layer, which is eventually docked to the metal. This quantity is virtually unaffected by the dipoles induced by end-group substituents which, naturally, are attached to the opposite side of the SAM.¹² It is, however, of course modified by dipoles distributed within the backbone and by dipoles close to or at the docking group.

In summary, we discussed a novel approach to tuning the interface energetics of metal/SAM systems through distributed

dipoles built into the molecular backbones; in the presented prototypical case, this is realized by pyrimidine rings linked in *para* position. The direction of the SAM-induced work-function change can be controlled by the pyrimidine orientation and its magnitude increases linearly with the number of repeat units (as long as one can avoid Fermi-level pinning). This is in sharp contrast to what is known from SAMs in which the work-function is changed by polar end-group substituents on otherwise non-polar backbones. Unlike in these systems, one finds that, for the oligopyrimidine-based SAMs, different work-function modifications go hand in hand with differences in the alignment between the molecular states and the Fermi-level. In fact, we observe differences in the level alignment of up to 1.27 eV for chemically equivalent backbones docked to the substrate in different orientations.

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Notes and references

- ^a Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria Fax: 00433168738466; Tel: 00433168738475; E-mail: egbert.zojer@tugraz.at
- ^b Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, D-12489 Berlin, Germany Fax: 00493020937632; Tel 00493020937713; E-mail: georg.heimel@physik.hu-berlin.de
- § Electronic Supplementary Information (ESI) available: Details on the computational methodology. See DOI: 10.1039/b000000x/
- † H-saturation of the thiol group introduces another dipole moment, affecting also the resulting ΔE_{vac} . While the C-S-H bond angle is unambiguous the C-C-S-H dihedral angle is not. Although the position of the saturating hydrogen atoms was chosen in a consistent way for all systems, geometrical differences (such as significantly different molecular tilt angles or the orientation of the axis around which the molecules are actually tilted) result in a different effect of the S-H bond on ΔE_{vac} .
- ‡ However, we stress that ΔE_{vac} is not an experimentally accessible quantity (i.e., there is no “correct” way of determining it), as it characterizes the hypothetical free-standing monolayers. The dependence of ΔE_{vac} on the H positions is fully compensated by ΔE_{BD} , thus keeping $\Delta\Phi$ and ΔE_{HOPS} , of course, independent of the H-position in the saturated monolayer.
- ‡ The three rings are not equivalent. The first carries a thiol group, the centre ring is coupled to two adjacent pyrimidine units, and the third (hydrogen-terminated) ring is coupled to only one pyrimidine unit; a certain amount of charge transfer between these three distinct moieties cannot be excluded a priori.
- 1 N. Koch, *ChemPhysChem* 2007, **8**, 1438.
- 2 I. H. Campbell, S. Rubin, T. A. Zawodzinski, J. D. Kress, R. L. Martin, D. L. Smith, N. N. Barashkov and J. P. Ferraris, *Phys. Rev. B* 1996, **54**, R14321.
- 3 B. de Boer, A. Hadipour, M. M. Mandoc, T. van Woudenberg and P. W. M. Blom, *Adv. Mater.* 2005, **17**, 621.
- 4 B. H. Hamadani, D. A. Corley, J. W. Ciszek, J. M. Tour and D. Natelson, *Nano Lett.*, 2006, **6**, 1303.
- 5 P. Marmont, N. Battaglini, P. Lang, G. Horowitz, J. Hwang, A. Kahn, C. Amato and P. Calas, *Org. Electronics* 2008, **9**, 419.
- 6 C. Bock, D. V. Pham, U. Kunze, D. Käfer, G. Witte and C. Wöll, *J. Appl. Phys.* 2006, **100**, 114517.
- 7 K. Ihm, B. Kim, T. H. Kang, K. J. Kim, M. H. Joo, T. H. Kim, S. S. Yoon and S. Chung, *Appl. Phys. Lett.* 2006, **89**, 033504.
- 8 Q. Sun, A. Selloni and G. Scoles, *J. Phys. Chem. B* 2005, **110**, 3493.
- 9 A. Natan, Y. Zidon, Y. Shapira and L. Kronik, *Phys. Rev. B* 2006, **73**, 193310.

-
- 10 G. Heimel, L. Romaner, E. Zojer and J. L. Bredas, *Nano Lett.* 2007, **7**, 932.
 - 11 M. L. Sushko and A. L. Shluger, *Adv. Funct. Mater.* 2008, **18**, 2228.
 - 12 G. Heimel, L. Romaner, E. Zojer and J. L. Bredas, *Acc. Chem. Res.* 2008, **41**, 721.
 - 13 G. Kresse and J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169.
 - 14 T. Bučko, J. Hafner and J. G. Ángyán, *J. Chem. Phys.* 2005, **122**, 124508.
 - 15 G. Heimel, L. Romaner, J. L. Bredas and E. Zojer, *Surf. Sci.* 2006, **600**, 4548.
 - 16 A. Kokalj, *Comp. Mater. Sci.* 2003, **28**, 155; code available from <http://www.xcrysden.org/>.
 - 17 W. Azzam, C. Fuxen, A. Birkner, H. T. Rong, M. Buck, C. Wöll, *Langmuir* 2003, **19**, 4958.
 - 18 L. J. Wang, G. M. Ranggner, L. Romaner, G. Heimel, T. Bučko, Z.Y. Ma, Q.K. Li, Z. Shuai and E. Zojer, *Adv. Funct. Mater.* 2009, DOI:10.1002/adfm.200900989.
 - 19 D. Cornil, Y. Olivier, V. Geskin and J. Cornil, *Adv. Funct. Mater.* 2007, **17**, 1143.
 - 20 L. Romaner, G. Heimel and E. Zojer, *Phys. Rev. B* 2008, **77**, 045113.
 - 21 S. D. Evans and A. Ulman, *Chem. Phys. Lett.* 1990, **170**, 462.
 - 22 D. Alloway, M. Hofmann, D. L. Smith, N. E. Gruhn, A. L. Graham, R. Colorado Jr., V. H. Wysocki, T. R. Lee and N. R. Armstrong, *J. Phys. Chem. B.* 2003, **197**, 11690.