J|A|C|S
COMMUNICATIONS

Mounting Freestanding Molecular Functions onto Surfaces: The Platform Approach

Belinda Baisch,[†] Diego Raffa,[†] Ulrich Jung,[†] Olaf M. Magnussen,*[,†] Cyril Nicolas,[‡] Jerome Lacour,[‡]
Jens Kubitschke,[§] and Rainer Herges*[,§]

*Institute of Experimental and Applied Physics, Christian-Albrechts-University Kiel, 24098 Kiel, Germany,
Department of Organic Chemistry, University of Geneva, 1211 Geneva, Switzerland, and Otto-Diels-Institute of
Organic Chemistry, Christian-Albrechts-University Kiel, 24098 Kiel, Germany*

Received October 7, 2008; E-mail: rherges@oc.uni-kiel.de; magnussen@physik.uni-kiel.de

Attaching reversibly switchable molecular functions, such as molecules that undergo photo-, redox-, or electric field-induced isomerization, to surfaces is a topic of major interest for the preparation of advanced nanosystems.[1−3] A key requirement for preserving these functions in an adsorbed monolayer film is sufficient free volume availability for the functional group as well as an adsorption geometry that avoids direct contact of this group with the surface. In particular on metal substrates the latter can result in a strong degradation or even complete quenching of the desired function.[4] The most commonly employed strategy to overcome these problems is incorporation of the functional entities into a matrix of nonfunctional spacer molecules, such as alkane thiols.[1] However, in such mixed adlayers the distribution and adsorption geometry of the functional groups on the surface is ill-defined and a high, temporally stable density of functional groups is difficult to obtain due to 2D phase separation.[5] More recently, alternative approaches have been suggested, such as increasing the free volume of molecules in the self-assembled monolayer by integrated bulky spacer groups[6,7] or employing large tripod-shaped molecules,[8] resulting in clearly improved switching properties. Nevertheless, also in these cases structurally well-defined, ordered adlayers, as desirable for the preparation of sophisticated nanosystems, are still difficult to obtain.[8i]

Here we introduce a novel concept where molecules are attached to metal surfaces via customizable molecular platforms with a defined adsorption geometry. These platforms act as pedestals that enforce a controlled orientation of the functional groups relative to the surface and determine by their size the spacing between these groups, resulting in arrays of free-standing functional molecules (Figure 1).

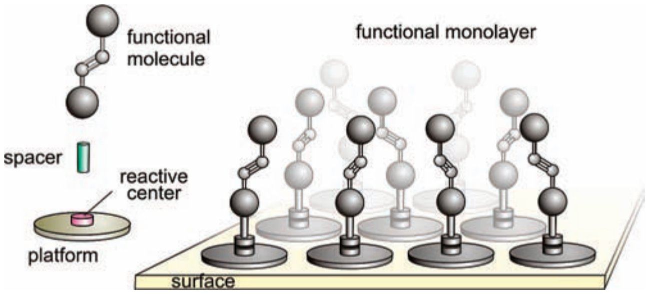

Figure 1. Schematic view of the platform approach. The size of the platform determines the distance between the functional molecules, the length of the spacer defines the distance from the surface, and the reactive center allows a "click type" attachment.

To this end, we developed a molecular construction set by using triazatriangulenium (TATA) ions as the platform, ethinyl or phenyl units as the spacer, and a simple polar C−C bond formation to attach the functional units R′ to the platform (Figure 2). TATA platforms can be easily prepared with various side chains R of different steric demand, which determine the size of the platform.[9,10] As shown in the following, both the TATA platform and the functionalized platforms form close-packed chemisorbed layers on Au(111) surfaces upon self-assembly from solution.

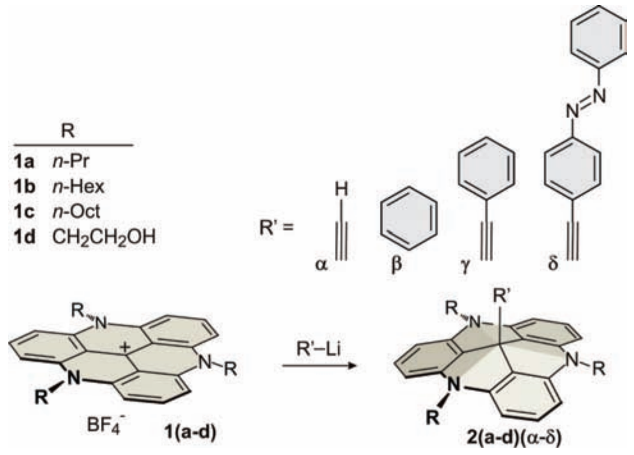

Figure 2. Attachment of functional groups to the TATA platform.

Characteristic scanning tunneling microscopy (STM) images of **1** (Figure 3a and b) reveal that these novel molecular platforms form hexagonally ordered adlayers with a defined in-plane orientation relative to the Au substrate lattice and typical domain sizes of several ten of nanometers. This is in accordance with a planar adsorption geometry where the molecules bind, similar to the case in porphyrin or phthalocyanine monolayers,[11] via interactions between the π-system and the metal substrate. Based on the unit cell parameters of the molecular adlayer and on high-resolution images, which reveal the triangular shape of the TATA moiety (see, e.g., insets in Figure 3), an in-plane arrangement as shown in Figure 3c is proposed. Here the molecules form a commensurate ($\sqrt{13} \times \sqrt{13}$)R13.9° superstructure (unit cell indicated in Figure 3c) on the Au(111) substrate with all molecules being oriented in the same direction. Although the molecular orientation cannot be unambiguously identified, the tips of the TATA triangles seem to point preferentially toward the centers of the sides of three neighboring molecules in the high-resolution images. The position of the propyl chains is currently unclear. However, the space requirements of the molecules in this tightly packed structure cannot be fulfilled by complete planar adsorption of these chains on the Au

---

[†] Institute of Experimental and Applied Physics, Christian-Albrechts-University Kiel.
[‡] University of Geneva.
[§] Otto-Diels-Institute of Organic Chemistry, Christian-Albrechts-University Kiel.

10.1021/ja807923f CCC: $40.75 © 2009 American Chemical Society

surface, suggesting that the latter extend at least partially into the adjacent solution.

With increasing side chain length from propyl (**1a**) to octyl (**1c**) the intermolecular spacing increases from 1.10 ± 0.05 (Figure 3a) to 1.30 ± 0.05 nm (Figure 3b), which corresponds to an ~40% change in the area per molecule. Although this change is somewhat smaller than that expected for direct adsorption of the additional hydrocarbon groups on the Au surface, an effect that again is attributed to partial extension of side chains into the solution, it demonstrates clearly that the surface density of the platforms can be controlled by the molecular architecture. Even larger intermolecular distances should be achievable by stiffer aromatic side chains.

Adlayer structures with a very similar in-plane molecular arrangement are found for the functionalized, nonplanar species of type **2**, which carry groups that are perpendicularly oriented with respect to the platform.[12] This is illustrated in Figure 3d−f for molecules bearing phenyl (**2a*γ***) and azobenzene (**2a*δ***) substituents, respectively, fixed to the platforms by ethinyl spacers. Obviously, these adlayers also are hexagonally ordered, although the domain sizes are noticeably smaller. Furthermore, the intermolecular distances of 1.14 ± 0.05 nm for propyl (**2a*γ***, Figure 3d,f) and 1.35 ± 0.05 nm for octyl (**2c*γ***, Figure 3e) side chains, respectively, are almost identical to those found in adlayers of the corresponding bare TATA molecules **1a** and **1c**. These STM data strongly suggest a similar adsorption geometry as that for the type **1** species, i.e., a surface-parallel adsorption of the TATA platform with the functional group pointing away from the surface. Further support for this comes from spectroscopic data and photoelectrochemical measurements, which reveal for **2a*δ*** reversible electrochemical and light-induced switching of the azobenzene unit.[13] The resulting molecular adlayers consist of a forest of perpendicularly oriented phenyl or azobenzene units, respectively, with a uniform nearest neighbor spacing that is clearly larger than that found in analogous thiol bound self-assembled monolayers and obviously directly controlled by the space requirement of the molecular platform rather than by packing of the functional groups.

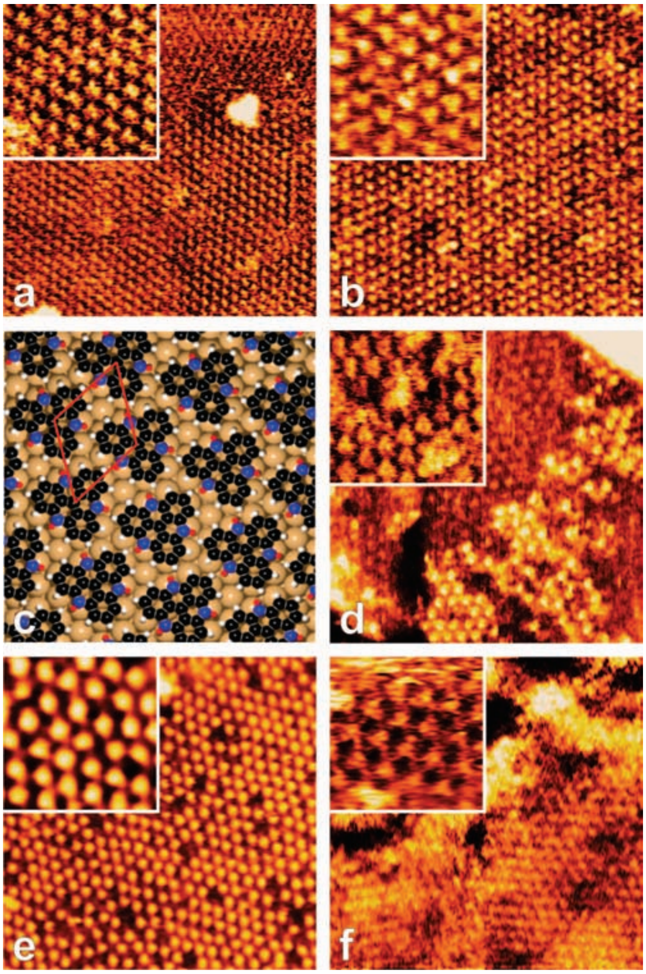

Figure 3. (a,b,d-f) STM images (30×30 nm^2, inset 7.5×7.5 nm^2) of adlayers of TATA platforms (a) **1a** (R = *n*-Pr) and (b) **1c** (R = *n*-Oct) on Au(111). (c) Structural model for adlayers of **1a**. (d) **2a*γ*** (R = *n*-Pr, R′ = phenyl ethinyl) and (e) **2c*γ*** (R = *n*-Oct, R′ = phenyl ethinyl) as well as of (f) the azobenzene-functionalized TATA platform **2a*δ*** on Au(111).

Adlayers of the bare (type **1**) as well as functionalized (type **2**) TATA molecules on Au(111) were found to be stable for at least several hours in air, solvents, and aqueous solutions of various pH's, supporting a strong adsorption. This was also supported by electrochemical studies in 0.1 M H_2SO_4 solutions using cyclic voltammetry and *in situ* STM, where identical adlayers were observed over a wide potential range from the onset of hydrogen evolution up to ~0.7 V_{SCE}.[13]

In conclusion, we have proposed a novel, highly versatile concept for the preparation of well-defined functional adsorbate layers on metal surfaces using triazatriangulenium cations as basic building blocks. Contrary to previous approaches, the requirements for maintaining chemical functionality in terms of free volume and orientation are not achieved by packing constrains within the self-assembled monolayer, but by a broad molecular stand that allows (i) fixing of the functional group at a given angle to the surface as well as (ii) precise tuning of the intermolecular distances between the adsorbates, allowing preparation of adlayers with an optimized surface density of the functional units. Due to its inherent great degree of control and flexibility, our approach appears to be a promising, novel route toward functional molecular nanostructures.

Acknowledgment. We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft via SFB 677.

Supporting Information Available: General preparation procedure for the functionalization of the TATA platforms, and the preparation and STM analysis of the monolayers. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421.
(2) Balzani, V.; Credi, A.; Venturi, M. *ChemPhysChem* **2008**, *9*, 202.
(3) Kondo, T.; Uosaki, K. *J. Photochem. Photobiol. C* **2007**, *8*, 1.
(4) Morin, J.-F.; Shirai, Y.; Tour, J. M. *Org. Lett.* **2006**, *8*, 1713.
(5) (a) Tamada, K.; Akiyama, H.; Wei, T. X.; Kim, S.-A. *Langmuir* **2003**, *19*, 2306. (b) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, *8*, 1330.
(6) Lahann, J.; Mitragotri, S.; Tran, T. N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371.
(7) Ito, M.; Wei, T. X.; Chen, P. -L.; Akiyama, H.; Matsumoto, M.; Tamada, K.; Yamamoto, Y. *J. Mater. Chem.* **2005**, *15*, 478.
(8) (a) Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Jin, C.; Keana, J. F. W. *J. Org. Chem.* **2003**, *68*, 4862. (b) Kittredge, K. W.; Minton, M. A.; Fox, M.-A.; Whitesell, J. K. *Helv. Chim. Acta* **2002**, *85*, 788. (c) Kitagawa, T.; Idomoto, Y.; Matsubara, H.; Hobara, D.; Kakiuchi, T.; Okazaki, T.; Komatsu, K. J. *Org. Lett.* **2006**, *71*, 1362. (d) Katano, S.; Kim, Y.; Matsubara, H.; Kitagawa, T.; Kawai, M. *J. Am. Chem. Soc.* **2007**, *129*, 2511. (e) Jian, H.; Tour, J. M. *J. Org. Chem.* **2003**, *68*, 5091. (f) Zhu, L.; Tang, H.; Harima, Y.; Yamashita, K.; Aso, Y.; Otsubo, T. *J. Mater. Chem.* **2002**, *12*, 2250. (g) Sakata, T.; Maruyama, S.; Ueda, A.; Otsuka, H.; Miyahara, Y. *Langmuir* **2007**, *23*, 2270. (h) Takamatsu, D.; Yamakoshi, Y.; Fukui, K. *J. Phys. Chem. B* **2006**, *110*, 1968. (i) Wei, L.; Tiznado, H.; Liu, G.; Padmaja, K.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. *J. Phys. Chem. B* **2005**, *109*, 23963.
(9) Laursen, B. W.; Krebs, F. C. *Chem.−Eur. J.* **2001**, *7*, 1773.
(10) Nicolas, C.; Lacour, J. *Org. Lett.* **2006**, *8*, 4343.
(11) De Feyter, S.; De Schryver, F. *Top. Curr. Chem.* **2005**, *258*, 205.
(12) Lofthagen, M.; Chadha, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 8785. Mobian, P.; Nicolas, C.; Francotte, E.; Bürgi, T.; Lacour, J. *J. Am. Chem. Soc.* **2008**, *130*, 6507.
(13) Jung, U. Dissertation, University of Kiel, 2008.

JA807923F