Self-Assembly

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Dipole Amplification: A Principle for the Self-Assembly of Asymmetric Monomers on Metal Surfaces**

*Owain P. H. Vaughan, Ali Alavi, Federico J. Williams, and Richard M. Lambert**

Fabrication of structures with nanometer-size dimensions is a major research theme, and scanning probe microscopes have played a pivotal role in the discovery, characterization and manipulation of such structures.[1] Maneuvering of individual atoms, molecules or bonds—one at a time—by means of the STM tip has been used to create a variety of structures on solid surfaces.[2,3] Potentially more useful, however, is the versatile and frequently explored approach which involves the spontaneous formation of an architecture by association of its molecular constituents as a result of noncovalent interactions—self-assembly.[4]

Inspired by solid-state and solution-based supramolecular chemistry, self-assembled surface nanostructures have been realized by exploiting noncovalent interactions between adsorbed molecules, thereby relying mainly on hydrogen-bonding or metal–ligand interactions.[5–14] However, the symmetry and electronic structure of the underlying substrate atomic lattice may also play a significant role,[1] for example, leading to the formation of extended periodic structures associated with charge-density waves.[15]

Here, we report the discovery of self-assembled, localized nanostructures of styrene, α-methylstyrene (α-MS), and *trans*-methylstyrene (TMS) (Figure 1) on the Ag(100) surface. There are no possibilities for hydrogen-bonding or metal–-ligand-type interactions in these three cases.

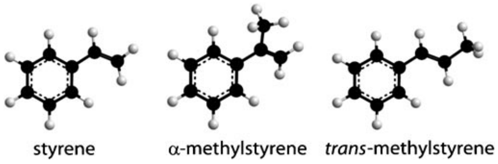

Figure 1. Molecular structures of styrene, α-methylstyrene (α-MS), and *trans*-methylstyrene (TMS). The H and C atoms are shown in white and black, respectively.

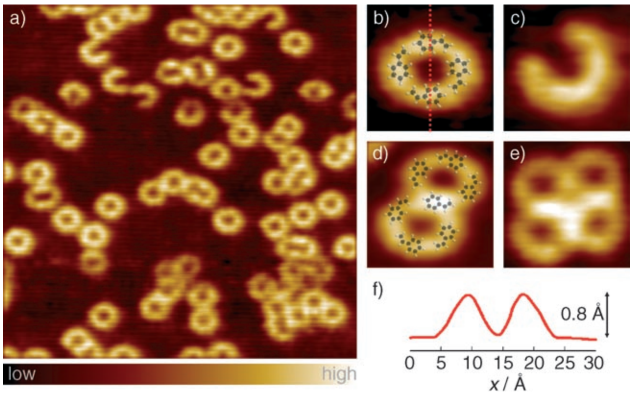

Figure 2. STM images of styrene molecules adsorbed on Ag(100) (taken at 123 K). a) A submonolayer coverage of styrene molecules ($V_{tip} = 0.05$ V, $I = 0.4$ nA, 200×200 Å^2). The styrene molecules self-assemble into a range of discrete nanostructures, the principal form of which is a ring shape. b) A single styrene tetramer ($V_{tip} = 0.05$ V, $I = 0.25$ nA, 26×26 Å^2). The STM image is overlaid with a possible configuration for the four styrene molecules within the tetramer; the H and C atoms are shown in white and black, respectively. c) Three styrene molecules in an incomplete tetramer ($V_{tip} = 0.05$ V, $I = 0.4$ nA, 22×22 Å^2). d) A figure-of-eight structure formed from seven styrene molecules ($V_{tip} = 0.05$ V, $I = 0.25$ nA, 30×30 Å^2). The STM image is overlaid with a possible configuration for the seven styrene molecules within the structure; the H and C atoms are shown in white and black, respectively. e) A four-ringed structure, composed of 12 styrene molecules ($V_{tip} = 0.05$ V, $I = 0.25$ nA, 32×32 Å^2). f) A typical line profile for an individual tetramer (the profile corresponds to a line in the direction indicated by the dotted line of Figure 3 b). The structures exhibit an apparent diameter of about 18 Å and an apparent height of approximately 0.8 Å.

Figure 2 a shows an STM image that corresponds to a submonolayer coverage of styrene molecules adsorbed on Ag(100) at 123 K. The molecules have self-assembled into a variety of different shapes, the principal form being a ring-shaped structure. As we shall show, these rings correspond to the formation of tetramers. The individual rings exhibit an apparent diameter of about 18 Å (see line profile in Figure 2) and are approximately 7 Å wide.

The properties of styrene adsorbed on Ag(100) have previously been studied by Williams et al.[16] It was shown that styrene adsorbs and desorbs from the metal surface at a temperature of about 330 K (enthalpy of adsorption ≈ 73 kJ mol^{-1}) without decomposition, and near edge X-ray absorption fine structure (NEXAFS) analysis carried out at submonolayer coverage and 220 K indicated that the phenyl and vinyl groups are coplanar, with the molecule lying almost flat on the metal surface. In the STM (at 220 K), no nanostructures were observed and the individual styrene molecules could not be imaged, presumably because of their mobility on the surface. However, given the NEXAFS results,[16] and from the observed apparent height and

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[*] Dr. O. P. H. Vaughan, Dr. A. Alavi, Dr. F. J. Williams,
Prof. R. M. Lambert
Department of Chemistry
University of Cambridge
Cambridge CB2 1EW (UK)
Fax: (+44) 1223-336-362
E-mail: rml1@cam.ac.uk

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diameter of the ring structures in comparison to similar systems,[17] we may conclude that in the present case, the styrene molecules also lie almost flat on the silver surface (with which they form no strong chemical bonds). The dimensions of the ring-shaped structures are consistent with the formation of tetramers. A plausible configuration is illustrated in Figure 2 b. This assignment accords well with the van der Waals dimensions of four styrene molecules arranged as shown. The slight elongation in the horizontal direction of Figure 2 b—the scan direction—is likely caused by tip-induced molecular motion.

Figure 2 also illustrates some minority structures observed along with the tetramers, namely, three styrene molecules, which correspond to a partially formed tetramer (Figure 2 c), a figure-of-eight structure (Figure 2 d), and a four-ringed structure (Figure 2 e). The figure-of-eight and four-ringed structures correspond to 7 and 12 styrene molecules, respectively, and the manner in which these structures may be plausibly explained, in terms of defects in the basic tetramer motif, is as follows.

A notable consequence of confining an achiral molecule, such as styrene, to two dimensions is the introduction of a chirality not present in the gas phase, as previously noted by several authors.[18,19] The molecule and its mirror image cannot be superimposed by translation and rotation within the plane of the surface. Consequently, the tetramers, which are formed from an achiral precursor (namely, gaseous styrene), can exist as two enantiomorphic forms. By choosing a direction that runs from the phenyl to the vinyl functionalities of the molecule, we may define a clockwise tetramer as "*R*′" and the opposite anticlockwise tetramer as "*S*". Thus, Figure 2 b illustrates a potential configuration for an *R*-tetramer.

Accordingly, both the figure-of-eight and the four-ringed structures are understandable in terms of "chirality defects" that can occur in the growing styrene chain, such that ring opening (rather than ring closure) is the result. Consider a growing *R*- or *S*-tetramer at the three-molecule stage (see, for example, Figure 2 c). At this point, addition of a fourth styrene molecule with the "wrong" chirality (*S*- or *R*-, respectively) prevents ring closure and causes a switch in the growth direction, thus leading to a figure-of-eight structure. This is shown in Figure 2 d, which also illustrates how the four-ring structure arises as a result of the same "chirality switch" mechanism. These observations show that self-assembly proceeds by stepwise addition of monomers to a growing chain, independently of the details of our chirality defect hypothesis.

To test the hypothesis that tetramer formation is the result of metal-mediated intermolecular electronic interactions (as opposed to direct molecule–molecule interactions), we also examined the behavior of two substituted styrene compounds, namely, α-MS and TMS, which differ significantly in geometric structure from each other and from styrene itself. However, similar to styrene, both these derivatives are also weakly bonded to the silver surface, with adsorption enthalpies of about 75 kJ mol^{-1} (for α-MS) and approximately 78 kJ mol^{-1} (for TMS).[20] Moreover, NEXAFS data taken at a relevant temperature (that is, at 150 K, a temperature at which we can still observe the tetramer structures) show that in both cases, the phenyl and vinyl groups are again essentially coplanar and almost parallel to the silver surface.[21] Thus, in all three cases, the conditions for a significant interaction between the delocalized π-electron system of the molecules and the Ag valence electrons are met.

Figure 3 shows STM results for α-MS and TMS adsorbed on Ag(100) at 123 K. In both cases, self-assembled tetramers are again the principal feature observed, along with a few incomplete tetramers. With α-MS, the tetramers exhibit an apparent diameter of about 20 Å (see Figure 3 b), which is larger than the corresponding value for styrene tetramers (of about 18 Å). Figure 3 c shows the corresponding results for TMS. Again, the dominant features are ring-shaped tetramers, with an apparent diameter of approximately 22 Å—the largest of all (see Figure 3 d). These systematic increases in the tetramer size are consistent with the structural differences between the monomer units, as illustrated in Figure 1.

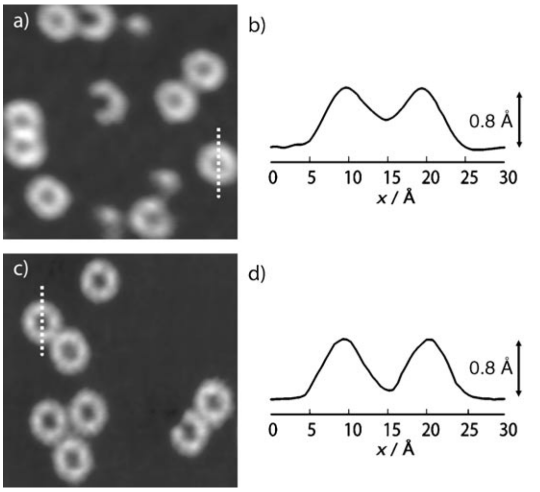

Figure 3. STM images of self-assembled structures composed of adsorbed methylstyrene molecules. a) STM image of α-methylstyrene molecules adsorbed on Ag(100) (taken at 123 K, $V_{tip} = 0.5$ V, $I = 0.25$ nA, 100×100 Å^2). b) A typical line profile for a single α-methylstyrene tetramer (the profile corresponds to a line in the direction highlighted by the dotted line); the tetramers exhibit an apparent diameter of about 20 Å and an apparent height of about 0.8 Å. c) STM image of *trans*-methylstyrene molecules adsorbed on Ag(100) (taken at 123 K, $V_{tip} = 0.75$ V, $I = 0.25$ nA, 100×100 Å^2). d) A typical line profile for a single *trans*-methylstyrene tetramer (the profile corresponds to a line in the direction highlighted by the dotted line); the tetramers exhibit an apparent diameter of about 22 Å and an apparent height of about 0.8 Å.

In the present case, neither intermolecular hydrogen bonding nor metal–ligand interactions can account for the observed behavior. What then is the mechanism that stabilizes these tetramers (and related structures) on the Ag(100) surface? The S4 symmetry of the tetramers and the fourfold symmetry of the Ag(100) surface suggest that the underlying metal lattice plays a critical role in the self-assembly process. In other words, it seems likely that the intermolecular interactions are mediated by coupling of the molecular π-electron systems with the Ag valence electrons. Although substrate-mediated indirect inter-adsorbate interactions have been studied experimentally and theoretically for some time,[22] virtually all work has been confined to atomic or diatomic adsorbates whose behavior have been discussed in terms of either electron-[23] or phonon-mediated indirect coupling.[24] However, there appears to be no precedent for the effects reported here: discrete, localized, nonperiodic self-assembly, which is likely mediated by the valence electrons of the metal.

To gain insight into the effect that leads to an effective substrate-induced attraction between the styrene molecules, we performed periodic density functional calculations.[25] A styrene molecule was allowed to relax on a 4×4 lateral supercell exposing a (100) surface of Ag; the relaxed geometry is shown in Figure 4. Three C atoms—in *ortho*, *meta*, and *para* positions—of the benzyl ring sit closest to the surface, with bond lengths to the nearest surface Ag atoms of about 2.50 Å, whilst the remaining C–Ag distances are substantially larger (>2.80 Å). The closest distance from the vinyl C atoms to the nearest Ag atoms is 3.28 Å, which indicates that the interaction of the molecule with the surface is not uniform, but is locally stronger in part of the benzyl ring. Also shown in Figure 4 is the induced density plot: $\delta\rho = \rho(\mathrm{Ag{+}St}) - \rho(\mathrm{Ag}) - \rho(\mathrm{St})$, that is, the difference between the electron density in the adsorbed state (Ag + St) and the sum of the electron densities of the isolated surface and the styrene molecule in the adsorbed geometry. This plot shows how electrons are redistributed upon adsorption, thus leading to regions of accumulation and depletion. The following features are apparent:

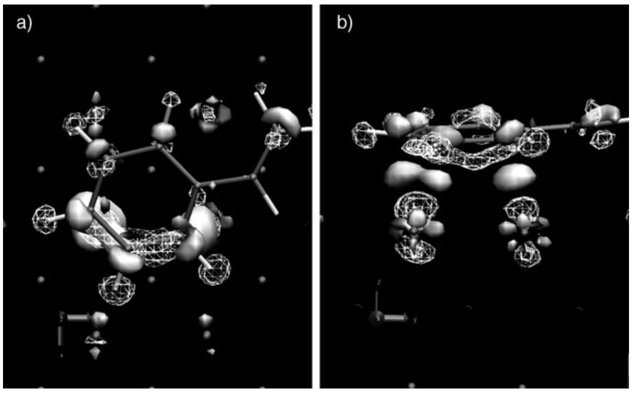

Figure 4. The relaxed styrene molecule on the Ag(100) surface in a 4×4 lateral unit cell, as given by the DFT(LDA) calculations. The induced electron density is shown by the two isosurfaces: electron accumulation (solid grey surface), electron depletion (wireframe). a) Top view: electron depletion at the hydrogen atoms is clearly visible: This leads to an increase in the Löwdin charges (from about +0.13 to around +0.17). b) Side view: electron depletion from the aromatic π system, as well as from the metal d_{z^2} orbitals, is clearly visible. Electron accumulation in the region between the benzyl ring of the molecule and the surface is characteristic of a weak chemisorption bond.

1) There is an asymmetric electron-density depletion from the π system of the aromatic ring, the depletion being strongest at the C atoms located closest to the surface.
2) Two d_{z^2} orbitals on Ag atoms directly below these C atoms also lose electrons.
3) There is a buildup of electron density in the intermolecular region between the depleted aromatic area and the two Ag atoms. Altogether, this implies that localized bonding develops between the close part of the styrene molecule and the surface.
4) A further feature, important in the subsequent discussion, is a depletion of electrons from the H atoms, most notably from those attached to the aromatic ring. Löwdin analysis of the electronic charge indicates that the partial charges on these H atoms change from about $+0.13|e|$ in the isolated molecule to about $+0.16$–$0.17|e|$ (an increase of $+0.04|e|$), whilst the partial charges of the C atoms change from about $-0.07|e|$ to about $-0.02|e|$.

Overall, the dipole moment of styrene changes from approximately 0.15 D (in the gaseous state) to about 1.12 D (in the adsorbed state). We can estimate the corresponding interaction energy (E) between adsorbed styrene molecules as: $E \approx 2\mu^2/(4\pi\varepsilon_o R^3)$. The free molecule dipole moment ($\mu = 0.15$ D) implies an interaction energy of $E/k_b \approx 2$ K (with $R = 5$ Å), which is far too weak to induce self-assembly at a temperature of approximately 100 K. However, the adsorption-induced dipole moment ($\mu = 1.12$ D) yields $E/k_b \approx 110$ K, which is of the required magnitude. Recently, Baber et al. observed the formation of extended periodic arrays, which result from the adsorption of styrene on Au(111) at very low temperatures (namely, at 7 K) and are likely stabilized by ferroelectric interactions.[26] This behavior and its origins are quite distinct from those observed in the present case, in which discrete, nonperiodic entities become stable at much higher temperatures. Given that local density approximation (LDA) calculations lead to over-binding, we checked our findings by performing calculations on the geometry-optimized structure using the Perdew–-Burke–-Ernzerhof (PBE) generalized gradient approximation (GGA).[25] These calculations gave an induced dipole of 1.10 D, which is in good agreement with the LDA value (namely, 1.15 D). Thus, the induced dipole effect is not an artifact of a particular density functional.

It is well known from work-function measurements that adsorption of cyclic hydrocarbons—both saturated and aromatic—results in very significant electron transfer to the metal. Thus, on platinum surfaces, work-function decreases on the order of approximately 1.5–2.0 eV are observed at saturation coverage.[27] The corresponding values for noble metals are somewhat below this one (typically around 1 eV).[28] In the present case, according to the induced density map, this flow of electrons leads to an electron-density depletion from the aromatic ring and the associated hydrogen species, thus leading to a substantially enhanced dipole parallel to the surface. Therefore, the interaction between adjacent styrene molecules acquires a substantial electrostatic component as a result of this adsorption-induced enhancement of the in-plane molecular dipole moment. Self-assembly into the observed pattern of tetramers (and small clusters of fused tetramers) is then expected on electrostatic grounds as a result of the interactions between the induced dipoles and quadrupoles. Once a tetramer has formed, the dipoles of the constituent aggregate screen each other—thereby leaving a weaker, quadrupolar, electric field, which tend to associate in the observed (but rarer) figure-of-eight and four-ringed structures. The tetramers cannot aggregate indefinitely as the assembly acquires an increasing net positive charge, which cannot be counterbalanced by the rapid screening of the attractive electric fields of the higher moments. This result provides an explanation of the observed (finite) sizes of the self-assembled clusters. The same general argument applies to α-MS and TMS, where, if anything, the induced in-plane dipole moment will be somewhat larger than in the case of styrene. It is noteworthy that an increase in the induced in-plane dipole by only about 50 % would result in structures that would be stable at room temperature.

Strikingly, STM observations carried out on the Ag(111) surface showed no formation of self-assembled structures by styrene at 123 K. In agreement with this, corresponding DFT calculations carried out for styrene on Ag(111) predict that the dipole remains essentially unchanged from its gas-phase value (which is of about 0.15 D), thus leading to a dipole–dipole interaction energy of only a few Kelvin. This result implies that dipole-driven self-assembly would occur only at very low temperatures. The differences between the (100) and (111) surfaces can be attributed to discrepancies in the local adsorption geometry, which reflects the surface corrugation. On the (100) surface, styrene interacts principally with two Ag atoms, which leads to the development of a weak chemisorption bond and significant charge redistribution. On the (111) surface, such local charge transfer is much less pronounced, so the induced dipole effect is much weaker. This observation provides further support for our hypothesis that substrate-induced dipole amplification is crucial to increasing the intermolecular interaction energy. Note that adsorbate-to-substrate charge transfer does not necessarily imply dipole amplification (it could also weaken the intrinsic dipole or have essentially no effect.)

Thus, our explanation rests on the observation that the asymmetric charge transfer out of (or into) adsorbed molecules can induce substantial in-plane dipole (and higher) moments, which drive the subsequent self-assembly into tetramers. With this insight, we may expect to devise other systems lacking inversion symmetry (with different side chains or larger aromatic systems), in which this effect is even stronger, thus leading to more stable structures. Experiments are underway.

Experimental Section

Experiments were carried out in an Omicron variable-temperature ultra high vacuum (UHV) STM, which was operated in the constant-current mode using etched tungsten tips. The Ag(100) sample was cleaned by repeated cycles of Ar^+ (99.999 % Messer) sputtering followed by annealing at 600 K until a clean, atomically flat surface was obtained, as observed by low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and STM. Reagent-grade styrene, α-MS, and TMS (Sigma Aldrich) were, prior to dosing, subjected to several freeze–pump–thaw cycles. With the Ag(100) sample in the STM stage, and at 123 K, the styrene species were delivered to the chamber via a high-precision leak valve equipped with a dosing tube aligned directly at the silver crystal; sample purity was monitored by mass spectrometry. Observations at temperatures >150 K were not possible because of thermal drift, whereas temperatures <123 K were not achievable because of instrumental limitations.

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[1] J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671.
[2] D. M. Eigler, E. K. Schweizer, *Nature* **1990**, *344*, 524.
[3] T. A. Jung, R. R. Schlitter, J. K. Gimzewski, H. Tang, C. Joachim, *Science* **1996**, *271*, 181.
[4] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.
[5] M. Böhringer, K. Morgenstern, W. D. Schneider, R. Berndt, F. Mauri, A. De Vita, R. Car, *Phys. Rev. Lett.* **1999**, *83*, 324.
[6] J. V. Barth, J. Weckesser, C. Z. Cai, P. Gunter, L. Burgi, O. Jeandupeux, K. Kern, *Angew. Chem.* **2000**, *112*, 1285; *Angew. Chem. Int. Ed.* **2000**, *39*, 1230.
[7] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **2001**, *413*, 619.
[8] J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029.
[9] G. Pawin, K. L. Wong, K.-Y. Kwon, L. Bartels, *Science* **2006**, *313*, 961.
[10] A. Semenov, J. P. Spatz, M. Moller, J. M. Lehn, B. Sell, D. Schubert, C. H. Weidl, U. S. Schubert, *Angew. Chem.* **1999**, *111*, 2701; *Angew. Chem. Int. Ed.* **1999**, *38*, 2547.
[11] N. Lin, A. Dmitriev, J. Weckesser, J. V. Barth, K. Kern, *Angew. Chem.* **2002**, *114*, 4973; *Angew. Chem. Int. Ed.* **2002**, *41*, 4779.
[12] P. Messina, A. Dmitriev, N. Lin, H. Spillmann, M. Abel, J. V. Barth, K. Kern, *J. Am. Chem. Soc.* **2002**, *124*, 14000.
[13] N. Lin, S. Stepanow, F. Vidal, J. V. Barth, K. Kern, *Chem. Commun.* **2005**, 1681.
[14] O. P. H. Vaughan, F. J. Williams, N. Bampos, R. M. Lambert, *Angew. Chem.* **2006**, *118*, 3863; *Angew. Chem. Int. Ed.* **2006**, *45*, 3779.
[15] S. Lukas, G. Witte, Ch. Wöll, *Phys. Rev. Lett.* **2002**, *88*, 028391.
[16] F. J. Williams, D. P. C. Bird, E. C. H. Sykes, A. K. Santra, R. M. Lambert, *J. Phys. Chem. B* **2003**, *107*, 3824.
[17] L. J. Lauhon, W. Ho, *J. Phys. Chem. A* **2000**, *104*, 2463.
[18] S R. Viswanathan, J. A. Zasadzinski, D. K. Schwartz, *Nature* **1994**, *368*, 440.
[19] M. Böhringer, K. Morgenstern, W.-D. Schneider, R. Berndt, *Angew. Chem.* **1999**, *111*, 832; *Angew. Chem. Int. Ed.* **1999**, *38*, 821.
[20] R. L. Cropley, PhD thesis, University of Cambridge (UK), **2004**.
[21] O. P. H. Vaughan, PhD thesis, University of Cambridge (UK), **2006**.
[22] E. C. H. Sykes, P. Han, S. A. Kandel, K. F. Kelly, G. S. McCarty, P. S. Weiss, *Acc. Chem. Res.* **2003**, *36*, 945.
[23] J. Repp, F. Moresco, G. Meyer, K.-H. Rieder, *Phys. Rev. Lett.* **2000**, *85*, 2981.
[24] S. Junren, B. Wu, X. C. Xie, E. W. Plummer, Z. Zhang, *Phys. Rev. Lett.* **2003**, *91*, 076103.
[25] We used the Car–Parrinello molecular dynamics (CPMD) code, with Troullier–Martin norm-conserving pseudopotentials for all species. The wavefunction cutoff was set to 70 Ry. The slab consisted of three layers of Ag(100) and nine layers of vacuum, which corresponds to 12.77 Å of vacuum. We found an adsorption energy of 1.2 eV from the LDA and 0.1 eV from

the PBE functional, sandwiching the experimental value of about 0.76 eV. This is typical of such DFT calculations, whereby the LDA overbinds and the GGA underbinds. We used LDA because it produces a physical geometry-optimized adsorption structure, which the GGA fails to do. However, the charge analysis we performed on the optimized structure gives similar results with a GGA functional (PBE) as compared to the LDA prediction (with PBE we obtained an induced dipole of 1.10 D, and with LDA 1.15 D, in both cases we observed a significant amplification of the intrinsic molecular dipole). In other words, the charge redistribution is essentially the same in both functionals for a given geometry.

[26] A. E. Baber, S. C. Jensen, E. C. H. Sykes, *J. Am. Chem. Soc.* **2007**, *129*, 6368.

[27] Z. Hlavathy, P. Tétényi, *Appl. Surf. Sci.* **2005**, *252*, 412.

[28] G. Witte, S. Lukas, P. S. Bagus, C. Wöll, *Appl. Phys. Lett.* **2005**, *87*, 263502.