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Design and STM Investigation of Intramolecular Folding in Self-Assembled Monolayers on the Surface

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The patterning of surfaces by lithography¹ techniques and μ -contact printing² has now reached the 50 nm regime, but the two-dimensional (2D) spatial positioning of functional groups at 0.2–20 nm length scales is still a major challenge in nanotechnology and surface science.³ A powerful approach is the decoration of interfaces with organic molecules that form regular 2D patterns by self-assembly, and recently this strategy has been exploited to organize discrete molecular features.⁴ It remains however a challenge to design systems which combine flexibility in the implementation of chemical functionalities, size, and symmetry.

In proteins, exact positioning of functionality (in 3D) is achieved from linear sequences of monomers that adopt very specific folded conformations.⁵ The observation that linear alkyl fragments featuring amide or urea groups form lamellar structures reminiscent of the β -sheets found in nature upon adsorption at the solid–liquid interface of HOPG⁶ prompted us to introduce a β -turn mimic in these systems as a next logic step. A 2D turn mimic should obey the requirements that (i) the entire structure is flat, (ii) the alkyl groups are spaced by approximately 5.0 Å, that is the optimal distance for H-bonding,⁷ and (iii) the amide moieties are kept in registry, with respect to position as well as orientation.

Here we report on the design of such a 2D turn mimic, which fulfills all the requirements. The general structure is depicted in Figure 1a. We envisage that connection of multiple units will render true minimal foldamers⁸, which, in principle, will give ultimate control over the position of integrated functionality in a 2D crystalline lattice.

The confinement in 2D space greatly reduces conformational degrees of freedom, which facilitates rational design by means of molecular modeling.⁹ The catechol moiety (Figure 1a) is flat, bifunctional, and derivatives are synthetically accessible; the ortho-substitution pattern endows the structure with the necessary geometry for making turns. A systematic conformational search identified the conformation most likely to fold in a plane involving the formation of an intramolecular hydrogen bond (Figure 1b,c). Modeling showed that folding is facilitated by a dissymmetry with respect to the spacers. Best results are obtained for combinations $n = m + 1$ or $n = m + 3$. The longer spacer is bending away from the catechol moiety. Comparison between a symmetric (**1**, $n = m = 10$, Figure 1b) and a nonsymmetric (**2**, $n = m + 1$; $m = 10$, Figure 1c) derivative shows that **1** adopts a twisted conformation when folding in the constrained environment defined by the graphite, while **2** can adopt the favorable all-trans conformation. This renders **2** the more likely candidate for our purposes because this conformation allows for efficient adsorption onto graphite, as

Figure 1. (a) Chemical structure of the turn mimics. Optimized conformations of (b) **1** ($n = m = 10$), (c) **2** ($m = 10, n = 11$), and (d) **3** ($m = 3, n = 6$). (e) Demonstration of the concept showing extended and folded conformations.

the zigzag plane of both alkyl groups is almost parallel to the surface of graphite. This is also reflected in the energy differences between folded and extended conformations for these derivatives. The relative energy-difference for **2** is 4.7 kcal/mol larger than for **1**, indicating a higher propensity to fold for the former. In both cases the folded conformation is more favorable than the extended one.

To test the predictions of our model, self-assembled monolayers at the liquid-HOPG interface were investigated by scanning tunneling microscopy (STM). STM images of the monolayers of these compounds are shown in Figure 2a,d. The bright spots correspond to the catechol groups and the darker rods to the alkyl chains. The H-bonding sites, via the amide groups appear as bright spots in the middle of the alkyl chains in the monolayers of **1** and **2** (blue dotted lines). The apparent molecular lengths are in agreement with the models. The distance between adjacent alkyl chains was measured to be 0.47 ± 0.01 nm.

Compound **1** gives rise to head-to-head, tail-to-tail as well as head-to-tail lamella structures. On the basis of the line profile analysis as shown in Figure 2b, it indeed does not adopt a folded conformation in the plane of the graphite (one alkyl chain per catechol group): possibly only one alkyl chain is adsorbed on the

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Figure 2. (a) STM image of monolayer from **1**. $I_{\text{set}} = 0.6$ nA. $V_{\text{bias}} = -0.90$ V. (b) Line profiles along the dashed lines in part a. (c) Packing model of **1** at the interface. (d) STM image of monolayer from **2**. $I_{\text{set}} = 1.0$ nA. $V_{\text{bias}} = -0.82$ V. (e) Line profiles along the lines in part d. (f) Packing model of **2** according to the information derived from part e. Only one alkyl tail is visible for the molecule in green. (g) STM image of monolayer from **3**. $I_{\text{set}} = 0.8$ nA. $V_{\text{bias}} = -0.93$ V. Insets: line profiles and a tentative model of packing.

surface while the other one is pointing into the solution (Figure 2c). This may seem counterintuitive, but it has been observed previously.¹⁰ The extended conformation was not observed. In contrast, the catechol groups appear more isolated in monolayers of **2** (Figure 2d). Folded as well as unfolded conformations are observed in coexistence on the surface: both the alkyl chains of molecules **i**, **iii**, and **iv** (Figure 2e,f) are adsorbed on the surface, while one of the alkyl chains of molecule **ii** points into the solution (Figure 2e,f). Since the amide groups are located in the middle of the aliphatic part of the molecule, there is no preference for the catechol groups to be aligned at the same side, as intermolecular hydrogen bonding is still possible.

To corroborate the initial results and test the $n = m + 3$ case, derivative (**3**, $n = m + 3$; $m = 3$) was synthesized. The shorter spacers were chosen to remove the symmetry in the aliphatic part by placing the amide groups off-center. The choice of spacers also dictates the directionality of the H-bonding array (Figure 1d).

Modeling indicated that the minimum-energy conformation for **3** obeyed all the criteria (vide supra). As can be seen in Figure 1d, the all-trans conformation is similar to that of compound **2**. Although this is a smaller molecule (less methylene groups), and can therefore not a priori be compared to compounds **1** and **2**, folding of **3** is again favorable with respect to extended conformations. This compound formed much more stable and well-ordered monolayers with a head-to-head type interaction (Figure 2g). Here the amide groups appear dark, which suggests that the in-plane orientation of the H-bonding site is different from the other derivatives. The line profile analysis clearly indicates that every molecule adopts the folded conformation on the surface as illustrated with a model (superimposed on the image in Figure 2g; two alkyl chains per catechol group).

In conclusion, we successfully designed a 2D turn element for oligo-amide sequences. The length of the spacers between the catechol and amide moieties plays an important role in the folding process. As forecasted by the calculations, derivatives obeying the rule $n = m + 1$ or $n = m + 3$ give folded structures upon adsorption at the liquid/solid interface. These results constitute a promising approach toward surface patterning and extension of the concept toward derivatives incorporating multiple turns is underway.

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Supporting Information Available: Schemes showing the reactions and text giving details on synthesis and characterization of **1–3**, molecular modeling, and STM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Wang, X. J.; Hu, W. C.; Ramasubramaniam, R.; Bernstein, G. H.; Snider, G.; Lieberman, M. *Langmuir* **2003**, *19*, 9748–9758.
- (2) Xia, Y. N.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153–184.
- (3) (a) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030–1034. (b) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541–548. (c) Watson, M. D.; Jäckel, E.; Severin, N.; Rabe, J. P.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 1402–1407. (d) Miura, A.; Chen, Z. J.; Uji-i, H.; De Feyter, S.; Zdanowska, M.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W.; Würthner, F.; De Schryver, F. C. *J. Am. Chem. Soc.* **2003**, *125*, 14968–14969. (e) Hla, S. W.; Rieder, K. H. *Annu. Rev. Phys. Chem.* **2003**, *54*, 307–330. (f) Lewis, P. A.; Donhauser, Z. J.; Mantoosh, B. A.; Smith, R. K.; Bumm, L. A.; Kelly, K. F.; Weiss, P. S. *Nanotechnology* **2001**, *12*, 231–237. (g) Maoz, R.; Frydman, E.; Cohen, S. R.; Sagiv, J. *Adv. Mater.* **2000**, *12*, 725–731.
- (4) (a) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619–621. (b) Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. *Nature* **2003**, *424*, 1029–1031. (c) Hoepfner, S.; Wonnemann, J.; Chi, L.; Erker, G.; Fuchs, H. *ChemPhysChem* **2003**, *4*, 490–494. (d) Barth, J. V.; Weckesser, J.; Trimarchi, G.; Vladimirova, M.; De Vita, A.; Cai, C.; Brune, H.; Günter, P.; Kern, K. *J. Am. Chem. Soc.* **2002**, *124*, 7991–8000. (e) De Feyter, S.; Larsson, M.; Schuurmans, N.; Verkuijl, B.; Zorinants, G.; Gesquiere, A.; Abdel-Mottaleb, M. M.; van Esch, J.; Feringa, B. L.; van Stam, J.; De Schryver, F. C. *Chem.—Eur. J.* **2003**, *9*, 5, 119–1206.
- (5) (a) Saven, J. G. *Chem. Rev.* **2001**, *101*, 3113–3130. (b) Koonin, E. V.; Wolf, Y. I.; Karev, G. P. *Nature* **2002**, *420*, 218–223.
- (6) van Esch, J.; De Feyter, S.; Kellogg, R. M.; De Schryver, F. C.; Feringa, B. L. *Chem.—Eur. J.* **1997**, *3*, 1238–1243.
- (7) Jeffrey, G. A. Distance between two carbonyl carbons in the respective chains. *Hydrogen bonding in biological structures*; 1991.
- (8) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893–4011.
- (9) Materials Studio package has been used. See www.accelrys.com.
- (10) Gorman, C. B.; Touzov, I.; Miller, R. *Langmuir* **1998**, *14*, 3052–3061.

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