Branched Substituents Generate Improved Supramolecular Ordering in Physisorbed Molecular Assemblies

10 AUTHORS, INCLUDING:

Mathieu Linares
Linköping University
63 PUBLICATIONS **982** CITATIONS

SEE PROFILE

Benjamin Isare
Pierre and Marie Curie University - Paris 6
22 PUBLICATIONS **301** CITATIONS

SEE PROFILE

Victor Geskin
Université de Mons
75 PUBLICATIONS **1,782** CITATIONS

SEE PROFILE

Roberto Lazzaroni
Université de Mons
400 PUBLICATIONS **9,357** CITATIONS

SEE PROFILE

Article

Branched Substituents Generate Improved Supramolecular Ordering in Physisorbed Molecular Assemblies

F. Vonau, M. Linares, B. Isare, D. Aubel, M. Habar, L. Bouteiller,
G. Reiter, V. Geskin, F. Zerbetto, R. Lazzaroni, and L. Simon

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Branched Substituents Generate Improved Supramolecular Ordering in Physisorbed Molecular Assemblies

F. Vonau,[†] M. Linares,[‡] B. Isare,[§] D. Aubel,[†] M. Habar,[†] L. Bouteiller,[§] G. Reiter,[∥] V. Geskin,[⊥] F. Zerbetto,[#] R. Lazzaroni,[⊥] and L. Simon*,[†]

Institut des Sciences des Matériaux de Mulhouse, CNRS-LRC 7228, Université de Haute Alsace, 4, rue des Frères Lumière 68093 Mulhouse, France, Department of Physics, Chemistry and Biology, IFM, Linköpings Universitet, SE-58183 Linköping, Sweden, UPMC Univ Paris 06, UMR 7610, Chimie des Polymères, F-75005 Paris, France, and CNRS, UMR 7610, Chimie des Polymères, F-75005 Paris, France, Physikalishes Institut, Universitat Freiburg, Hermann-Herder-Str. 3, 79104 Frieberg, Germany, Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut/Materia Nova, Place du Parc, 20, B-7000 Mons, Belgium, and Dipartimento di Chimica G. Ciamician, Universit 2, 40126 Bologna, Italy

We present an experimental study supported by molecular simulations of the influence of the shape of alkyl side groups on the interactions and self-organization of supramolecular assemblies, built from bis-urea-substituted toluene molecules deposited on Au(111) surfaces. In particular, we demonstrate the crucial importance of the presence of branched alkyl groups (i.e., ethylhexyl) that allow two adjacent supramolecular polymers to arrange closer to each other, leading to the formation of molecular "zippers". Thus, steric constraints at the level of individual molecules can generate improved ordering between neighboring supramolecular polymers interacting with a planar substrate.

Introduction

The generation of nanostructured functional materials with hierarchical levels of supramolecular organization relies on a set of molecular building units that interact through relatively weak, noncovalent forces (e.g., hydrogen bonds, coordinative bonding, van der Waals and electrostatic interactions, etc.)[1−5] Various organized patterns resulting from such noncovalent, reversible bonds have been realized and studied, often in bulk and solution[6−8] but also on surfaces (2D).[9−16] The physicists' goal is to reveal and to predict how these forces govern self-assembly processes so that chemists would be able to design and synthesize new, even more versatile, functional molecules for the generation of artificial functional systems. In this context, the question arises if and how the shape of the basic building units can influence the molecular organization, in particular on surfaces. Therefore, we focused on the consequences of small modifications of a molecular subunit, which are not supposed to alter the various intermolecular forces driving the self-organization process. In particular, we draw the attention on how minor changes of the shape of side groups in a functional molecule can lead to drastic changes of molecular ordering on multiple length-scales. As in our previous studies,[17,18] we investigated bis-urea-substituted toluene compounds deposited on the Au(111) surface with scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions. The full names of theses molecules are given in the Experimental part at the end of the paper but simplified names will be used in the text for more clarity. These molecules were designed for their
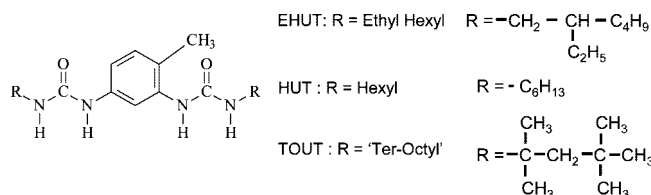

Figure 1. Molecular structure of the three bis-urea compounds. Full names are available in the Experimental Section.

strong association ability and consist of a central aromatic core (i.e., a toluene ring T) connected to two urea groups (U) which provide four directional hydrogen bonds. Linking such molecules via these hydrogen bonds can lead to the formation of rather rigid polymeric chains, characterized by a large persistence length.[19] Molecules having 2-ethyl-hexyl (EH) side groups, as used previously, are compared to molecules with linear hexyl(H) side groups or with ter-octyl(TO) (i.e., 1,1,3,3-tetramethylbutyl) groups attached to the ureas (see structures in Figure 1). It must be noted that those three groups have the same chemical properties and almost the same number of atoms (from 6 to 8 carbons); only their shape is different: the hexyl group is simply linear; the "ter-octyl" group has four methyl groups attached on the backbone, and the ethyl-hexyl group has an ethyl branch along a hexyl backbone. All molecules were deposited via sublimation in UHV on Au (111) surfaces. As documented previously,[17,18] well-organized patterns of molecular chains, i.e., supramolecular polymers, can be formed after adequate annealing in layers of 2-ethylhexylureidotoluene (EHUT) deposited on crystalline, planar gold surfaces. Surprisingly however, these supramolecular polymers of EHUT were always paired, i.e., two polymers "zipped" together, which leads to the formation of twin rows with a central "zip" line. What is more surprising is that such "zipping" occurs as well at extremely low surface coverage[18] as at saturated coverage (more than a monolayer), which hints at the presence of a specific

* To whom correspondence should be addressed. E-mail: L.Simon@uha.fr.
† Institut des Sciences des Matériaux de Mulhouse.
‡ Linköpings Universitet.
§ UPMC Univ Paris 06.
∥ Universitat Freiburg.
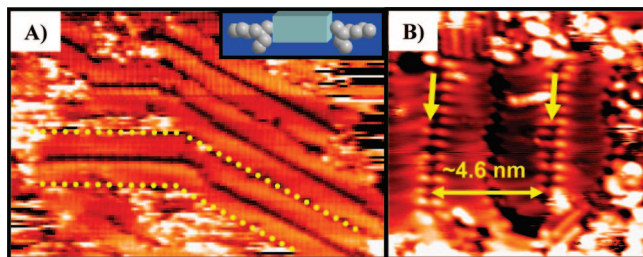⊥ Université de Mons-Hainaut.
Dipartimento di Chimica G. Ciamician.

Figure 2. STM image of EHUT molecules deposited on Au(111) (A) 30 × 20 nm², (B) 11 × 11 nm². The molecules (orange sticks) self-assemble in a twin-rows structure delimited by the yellow dotted lines in part A. In part B, the central bright parts of the twin rows ("zippers") are indicated with arrows and correspond to the alkyl chains interactions. The distance of 4.6 nm between two zippers corresponds to the length of 2 single molecules. A schematic representation of the molecule shows the carbon atoms in the lateral ethyl hexyl groups; the central rectangle represents the aromatic core with the urea groups: no contrast is visible in the images because of the nonplanar position of the aromatic core.
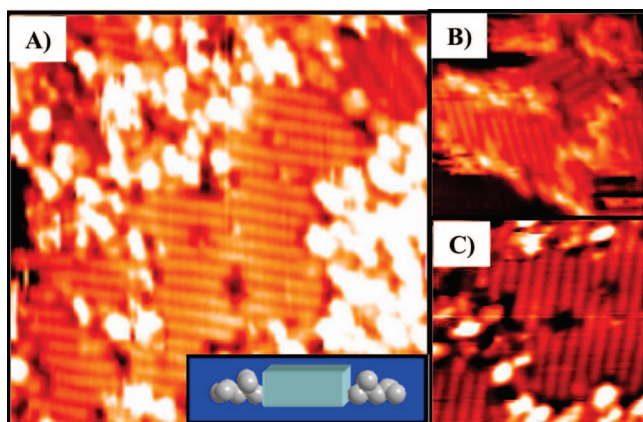

Figure 3. STM images of a deposit of TOUT on the Au(111) surface and schematic representation of the molecule. (A) 13.5 × 13.5 nm², (B) 10.5 × 10.5 nm², and (C) 7.5 × 7.5 nm². No zip line could be observed.

interaction between two individual supramolecular chains. Moreover this has been observed at the same hierarchical level as the formation of hydrogen bonds of the self-organization process which has been followed step by step.[17] Such ordering cannot be linked to either specific interactions like hydrogen bonds or nonspecific van der Waals interactions. The formation of such "zippers" thus raises the question about the origin of the interaction between chains and the role of the "zipper" in the self-organization process. Hence, here, we examine the influence of the shape of the basic submolecular building unit, i.e., whether the arrangement of individual atoms and groups on the side of the bis-urea-substituted toluene core has consequences on the interaction between molecules.

Results and Discussion

STM Study of the Self-Assembly. In the first experiment, we compare 1,1,3,3-tetramethylbutyl-3-[3-(3-(1,1,3,3-tetramethylbutyl)ureido)-4-methylphenyl]urea (TOUT) and EHUT, which have alkyl side groups with the same number of carbon atoms but different shape. After deposition and a few hours of annealing at about 60 °C, STM revealed a distinctly different organization for these most similar molecules; see the STM images of EHUT and TOUT in Figures 2 and 3, respectively. While both compounds clearly exhibit the formation of supramolecular assemblies with a periodic distance of 0.49 nm
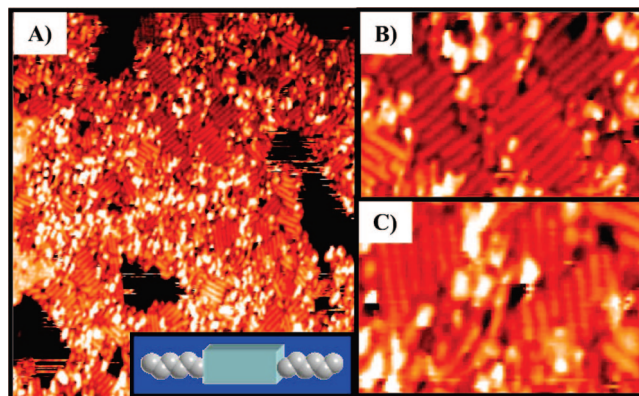

Figure 4. (A) STM images of a deposit of HUT on Au(111) and schematic representation of the molecule. No zip line could be observed on large scanned area (50 × 50 nm²); details of the structure are shown in (B) 13 × 8.5 nm² and (C) 10 × 6.5 nm².
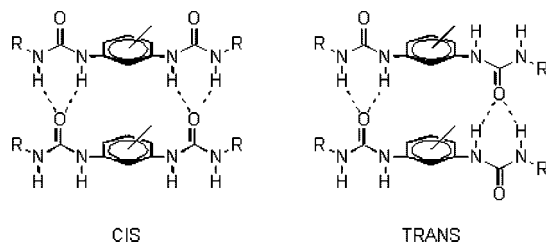
between molecules along the assembly, i.e., normal to the long axis of the molecules, a "zipper" is only observed for EHUT. In addition, after the same thermal history (annealing either at 60 ± 5 °C or at room temperature), TOUT is not able to organize on large length scale (Figure 3). This clearly demonstrates that the "zipper" formation depends on the structure of the alkyl side groups.

One may argue that the bulky "ter-octyl" side group could prevent any possibility for intermolecular interactions between neighboring supramolecular polymers. Thus, in order to be closer to the molecular structure of EHUT, we then examined hexyl urea toluene (HUT), a molecule different from EHUT but only by the missing ethyl branch on the alkyl side group. The hexyl group is expected to be linear (rather than coiled) when participating to dense assemblies. HUT has been deposited and annealed in the same way as EHUT and TOUT and the resulting surface patterns have been visualized by STM, as shown in Figure 4.

Rod-shaped structures with a length of 2.6 nm were observed, but they were arranged in a rather disordered fashion. No "zipper" formation was ever observed (see Figure 4), and no extended well-organized areas were detected in large scale images (Figure 4A). Obviously, under the same conditions as employed for studies of EHUT, HUT molecules are not able to form patterns possessing long-range order, neither in the direction along the supramolecular polymers nor perpendicular to this direction. This result is remarkable because linear alkyl chains usually yield better packing than branched alkyl chains. This is well-known in the case of monolayers, and also in the case of crystals where for instance linear alkanes have higher melting points than their branched isomers.

Molecular Modeling of the Supramolecular Polymers on the Surface. To understand these experimental observations, we performed molecular modeling simulations on supramolecular assemblies. Two possible conformations exist that allow for a self-assembly process via urea−urea H-bonds between neighboring molecules: the two urea groups of a given molecule can either point in the same direction (cis) or they can point in opposite directions (trans) according to scheme 1. Note that, while the urea groups are almost coplanar, the toluene rings have to rotate sufficiently out of the urea plane; the conformational flexibility of urea-substituted toluene units will be addressed in the next section.

The structure and stability of the corresponding assemblies for HUT and EHUT molecules on the Au(111) surface were investigated with a molecular mechanics/molecular dynamics

Substituents Generate Improved Supramolecular Ordering

J. Phys. Chem. C, Vol. 113, No. 12, 2009 **4957**

SCHEME 1: Two Conformations for the Self-Assembly Process via Urea−Urea H Bonds: Cis and Trans

(MM/MD) approach (see computational details below). To identify the main driving forces at play in the formation of linear assemblies of such molecules, we first built two linear chains of HUT molecules (with either all-cis or all-trans configuration of the urea groups), with alternating orientation of the methyl group on the toluene ring to reduce the steric hindrance, and placed them on the gold surface. In both systems, the distance between adjacent toluene units in the assembly is about 0.47 ± 0.02 nm, in excellent agreement with the periodicity measured experimentally. It appears clearly that the cis arrangement is more stable, by 3.4 kcal/mol per molecule, than the trans arrangement, due to the presence of a constraint between the toluene ring and the urea groups in the latter system.

The obtained conformations on the gold surface show a strong tilting of the phenyl core with respect to the surface plane; in other words, the phenyl ring is not adsorbed flat on the surface but rather "edge-on" (see Figure 5A). The entire hexyl side groups are in contact with the gold substrate, and no interdigitation of hexyl groups from neighboring supramolecular polymers is noticed. The optimized relaxed arrangement yields a period of 5.1 nm for a double row, which is consistent with the expected length of two HUT molecules aligned end-to-end but is distinctly larger than the average width of "zipper" lines experimentally observed for EHUT (4.6 nm).

The presence of the ethyl branch opens new possibilities of generating regular assemblies for EHUT. On one hand, the hexyl group can be fully adsorbed, as in the HUT assemblies. On the other hand, the MD simulations indicate that EHUT molecules can also arrange with the ethyl branch adsorbed and the extremity of the hexyl group away from the surface (as marked by the red arrow in Figure 5B). Regular double arrays of EHUT molecules in that conformation can be formed and are highly stable (Figure 5C). In that structure, the average width of the double rows is 4.7 nm, very close to experimental width of the "zipper" line, which indicates that the structure of Figure 5C is the most appropriate model for the "zipper".

Such conformation causes a weakening of interactions between the molecular layer and the surface by about 1 kcal/mol per molecule (because of the smaller contact area between the alkyl group and the surface). However this loss is almost fully compensated by van der Waals interactions between the freely suspended parts of the hexyl segments arising from the reduced distance between two supramolecular polymers (from 5.1 to 4.7 nm). Thus, if one attempts to separate two polymers forming a "zipper", one has to overcome the van der Waals attractive interactions between the hexyl branches of the adjacent rows. The fact that in our experiments we never observed isolated supramolecular polymers from EHUT molecules suggests that this attraction may be comparatively strong. This type of side group interaction cannot take place in HUT assemblies (because the linear hexyl groups fully adsorb on the surface) or in TOUT assemblies (because the parts of the alkyl groups directed away from the surface are too short to allow for
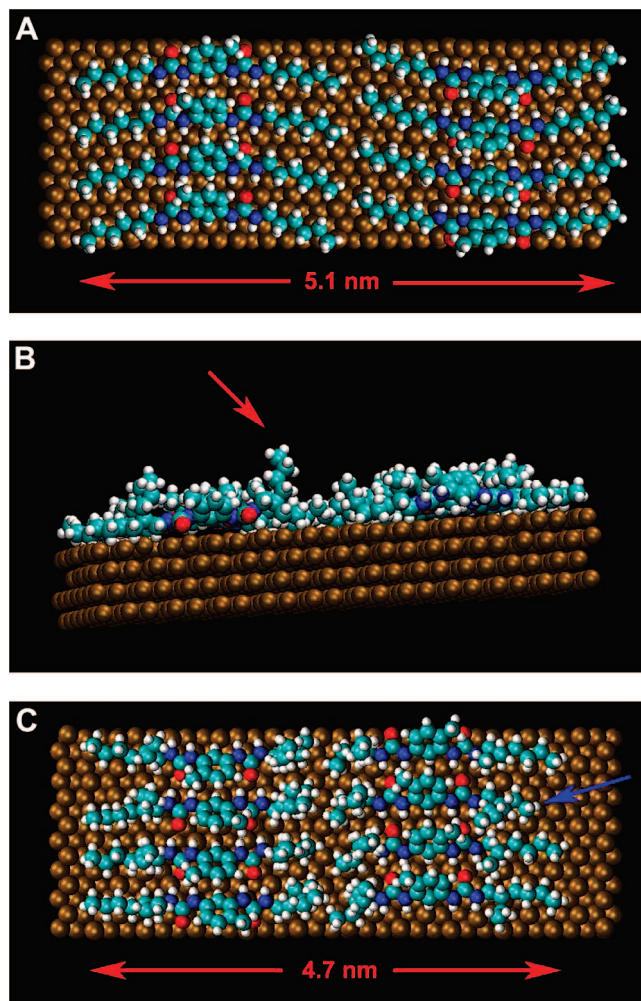
Figure 5. Top views of a section of a double row of HUT (A) and EHUT (B and C) molecules on the gold surface. Gold atoms are displayed in ochre, carbon in light blue, nitrogen in dark blue, oxygen in red, and hydrogen in white. In the HUT assembly, the linear hexyl groups are fully adsorbed on the surface and the calculated width of the double row is 5.1 nm. In simulations of EHUT assemblies, the ethyl-hexyl group can arrange so that the ethyl branch is adsorbed and the end of the hexyl branch is pointing away from the surface (as indicated by the red arrow in image B). Considering a regular assembly on the basis of that conformation yields double rows with a width of 4.7 nm (structure C), in good agreement with the experimental data (see Figure 6).

interactions with neighboring supramolecular polymers). It must also be noticed that the ethyl-hexyl groups located in the external parts of the double rows may also take different possible conformations (such a group with its ethyl branch adsorbed is marked with a blue arrow in Figure 5C). As a consequence, the local width of the double row fluctuates, which is consistent with the fact that the external profiles of the "zipper" are not regular (see Figure 6).

Theoretical Study of the Molecular Conformation. In the previous section, it was indicated that the formation of intermolecular hydrogen bonds between the urea groups requires a strongly nonplanar conformation of the urea-substituted toluene (UT) units. Such a conformation is a priori not favorable for an isolated molecule as the conjugation between the aromatic core and the ureas is smaller compared to the fully planar molecule. To investigate the energetic cost of that molecular distortion, we performed a quantum-chemical study of the rotational energy curves of the two urea groups around the toluene core (their behavior is expected to be different because
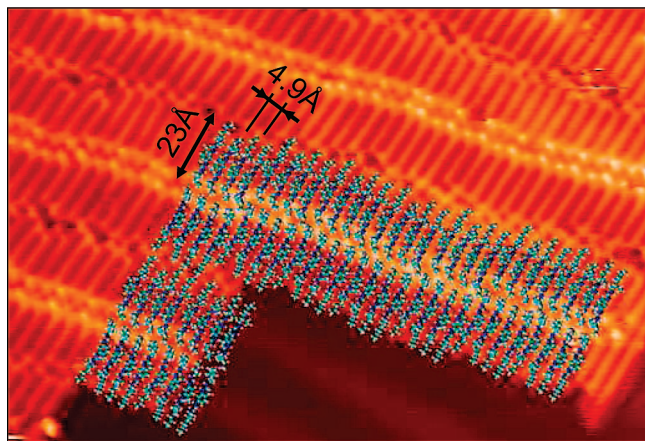
Figure 6. STM image of an EHUT monolayer on Au(111) 20 × 13.5 nm². The substrate with the herringbone reconstruction is visible in the lower part of the image. EHUT molecules self-organize via H bonds in supramolecular twin rows as depicted by the superimposed molecular model of Figure 5C): bright features correspond to alkyl chains pointing out of the substrate plane in interaction to form a "zipper" line. The regular orange contrast along the molecule confirms the nonplanar position of the toluene core. The second endgroup of each molecule can have different conformations and explains the apparent varying length of the molecules.
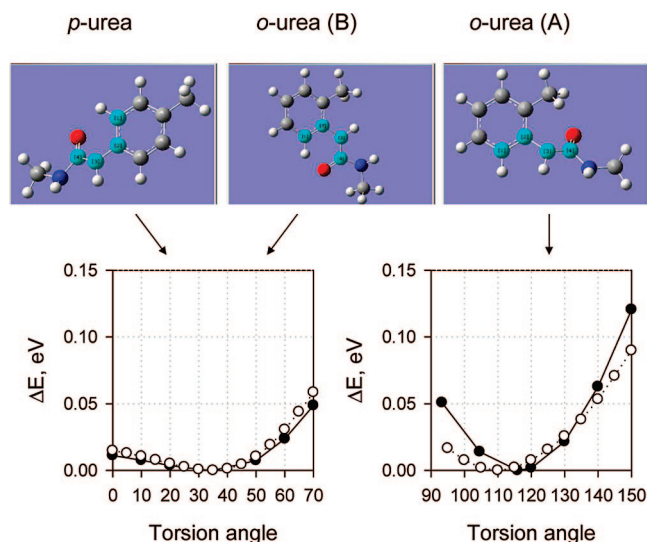

Figure 7. Conformational analysis for each urea group (with a methyl end group) of UT: the stationary structures (optimized with MP2/6-31 g(d,p)) are in the upper three panels, and the energy (correlated ab initio MP2/6-31g(d,p), full symbols; semiempirical AM1, hollow symbols) relative to the minimum vs the relevant dihedral angle (among the atoms highlighted in light blue) are in the lower two panels. The rotational curves around the *p*-urea and *o*-urea (B) minima are practically identical.

of the presence of the methyl group on the aromatic ring). This conformational analysis was carried out for an isolated molecule with ab initio (perturbationally corrected post-Hartree−Fock MP2/6-31g(d,p)), as well as semiempirical (AM1) methods. The results are presented in Figure 7 for the monosubstituted molecule, in which the urea group is capped with a methyl group (this reduces the computational effort without affecting the rotational behavior of the urea moiety).

Note that, even though the N-CO-N skeleton of urea is planar in its ground state, it is well established[20,21] that the entire urea group is not, as the three bonds around each nitrogen atom form a pyramid. Transitions between its different conformations are achieved by low-barrier rotations and inversions; this is taken

into account in the rotational curves, always showing the lowest energy for every torsional angle. In the UT system, the urea skeletons would tend to be coplanar with the aromatic core to maintain conjugation, which is opposed by steric factors.

For the *p*-urea system (i.e., the urea is opposite to the methyl group of toluene), the equilibrium conformation is nonplanar because of steric repulsion from the adjacent hydrogen atoms on the aromatic core; however, this repulsion is weak, as evidenced by the very low barrier at 0°. Practically the same curve is obtained for *o*-urea in the B conformation, as the presence of the methyl group of the toluene is not felt in this case. Still, this methyl group breaks the symmetry of the whole molecule by generating more repulsion for the *o*-urea group in the A conformation. This is reflected by the steeper rotational curve and the increased deviation of the equilibrium torsion angle from planarity in the A conformation (by 180° − 115° = 65°), as compared to the curve for *o*-urea (B) and *p*-urea, which shows a minimum at 35°, cf. the lower right and left panels of Figure 7, respectively.

Therefore, the A conformation of the isolated molecule is closer to the shape required for intermolecular hydrogen bonding in the supramolecular assembly than the B conformation, but for the latter the rotational potential curve is more shallow. Nevertheless, the energy cost of large amplitude rotations does not exceed 0.05 eV (ca. 1 kcal/mol) per group in both cases; this clearly allows the molecule to explore its conformational space even at low temperature, which is essential for self-organization on the surface.

Furthermore, this cost is to be compared with the energy of one hydrogen bond in a dimer involving the oxygen atom of one urea and two hydrogen atoms of the other, which is estimated at 0.2−0.3 eV (ca. 4−6 kcal/mol; cooperative effects are likely to modify this value).[21] The energy gain upon hydrogen bonding largely exceeding the energy cost of rotation proves that the intermolecular bonding that leads to the ribbon formation is favorable indeed.

Conclusions

In summary, our STM measurements have shown that supramolecular assembly at the surface crucially depends on minor changes in the molecular structure: while twin rows with a central "zipper" line are formed on a gold substrate from bis-urea-toluene molecules with branched ethyl-hexyl side groups, this is not the case for its close analogs bearing linear hexyl groups or bulky "ter-octyl" groups. Molecular simulations help to rationalize how steric constraints at the level of the individual molecule (intramolecular constraints) but also between supramolecular polymers (intermolecular constraints) may have consequences at several hierarchical steps of the self-organization process of supramolecular assemblies. Such effects may cause a reduction of molecular flexibility, induce torsion and direct H bonds, and may also generate attraction between neighboring supramolecular polymers when molecules are interacting with a planar substrate. Moreover, these results indicate that branched alkyl groups can actually yield better packing than linear alkyl groups.

Experimental Section

Synthesis. The synthesis of bis-ureas EHUT (2-ethylhexyl-3-[3-(3-(2-ethylhexyl)ureido)-4-methylphenyl]urea)[22] and TOUT (1,1,3,3-tetramethylbutyl-3-[3-(3-(1,1,3,3-tetramethylbutyl)ure-ido)-4-methylphenyl]urea)[23] was reported previously. HUT (hexyl-3-[3-(3-(hexyl)ureido)-4-methylphenyl]urea) was synthesized similarly, by reaction between toluene diisocyanate and

Substituents Generate Improved Supramolecular Ordering

J. Phys. Chem. C, Vol. 113, No. 12, 2009 **4959**

hexylamine. Purification was performed by recrystallization in methanol. ^1H NMR (200 MHz, D_6-DMSO): δ (ppm) = 8.24/7.67 (2s, 2H, Ar-NH), δ = 7.44 (s, 1H, Ar−H), δ = 7.08/6.87 (2d, J = 8.3 Hz, 2H, Ar−H), δ = 6.47/5.92 (2t,2H,C−NH), δ = 3.02 (q, 4H, NH-CH), δ = 2.04 (s,3H, Ar-CH₃), δ = 1.24 (m, 16H, CH), δ = 0.84 (t, 6H, CH₃). ^{13} CNMR(75 MHz, D_6-DMSO): δ (ppm) = 159.2/159.1(C=O), δ = 142.6/142.2/133.8/122.9/115.3/113.8(Ar), δ = 42.9(2)(N-CH), δ = 33.8/33.7/30.1/30.0/26.1(2)/21.2(2)(CH₂), δ = 17.9(Ar-CH₃), δ = 14.0 (CH₃).

Layer Deposition and STM Measurements. Experiments were performed in UHV with a commercial low temperature STM from Omicron. All measurements were carried out at 77 K with both the tip and the sample being at the same temperature. Molecules were evaporated with a Knudsen cell at 80 °C.

Theoretical Methodology. *MM/MD Simulations.* The MM/MD simulations have been performed with the approach developed by the Bologna group.[24] In this approach, the gold substrate is represented using the "glue" model approximation.[25] The molecule−substrate interaction is optimized using a charge equilibrium procedure[26] and a repulsive potential,[27] while the molecule−molecule interactions are described with the MM3 force field.[28,29] This model was previously used to investigate a variety of processes such as (i) the different reconstruction patterns induced by C_{60} on the Au(110) surface,[30] (ii) the adsorption of alkanes and 1-alkenes on Au(111),[24] where the adsorption energies of short chains, up to C_{10}, were reproduced with an average deviation from the experiments of less than 1 kcal mol^{-1} and the unexpected transition to disorder that occurs for the deposition of alkyl chains between 18 and 26 carbon atoms was explained, (iii) the apparent symmetry breaking of a macrocyle on the Au surface,[31] (iv) the substitution kinetics and dynamics of thiols in self-assembled monolayers,[32,33] (v) the mechanochemistry of a polymer on the Au surface,[34] and (vi) the adsorption and dynamics of DNA bases on Au(111) where the energies of adsorption were also within 1 kcal mol^{-1} from the experimental values.[35]

The approach does not impose a priori the definition of bonds between the atoms of the molecules and those of the metal. Molecules are free to drift on the surface, which, in turn, can reconstruct. MM and MD calculations of adsorbed HUT and EHUT assemblies have been performed on a surface with 4 layers of gold atoms, each layer containing 22 × 7 atoms. The two top layers were allowed to relax while the two bottom layers remained fixed. Periodic Boundary Conditions have been used in order to simulate an infinite surface. The MD simulations have been performed within the canonical ensemble at a temperature of 300 K; after a time of equilibration of 100 ps, the geometrical parameters are followed and recorded every 0.1 ps during 100 ps.

The conformational analysis of the bis-urea-substituted toluene unit has been performed both at the semiempirical AM1 level, with the AMPAC program,[36] and at the ab initio MP2 level, with the Gaussian 03 package.[37]

References and Notes

(1) Lehn, J. M. *Supramolecular Chemistry: Concept and Perspectives*; VCH: Weinheim, 1995.

(2) Lehn, J. M. *PNAS* **2002**, *16*, 4763.

(3) Whitesides, G. M.; Boncheva, M. *PNAS* **2002**, *16*, 4769.

(4) Stupp, S. I; Lebonheur, V; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384.

(5) Binder, W. H. *Monatsh. Chem.* **2005**, *136*, 1.

(6) Folmer, L.; Meijer, B. J. B.; Sijbesma, E. W., R. P. *Chem. Rev.* **2001**, *101*, 4071.

(7) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3644.

(8) Descalzo, A. B.; Rarinez-Manez, R.; Sancenon, F.; Hoffmann, K.; Rurack, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 5924.

(9) Rosei, F.; Schunack, M.; Naitoh, Y.; Jiang, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. *Prog. Surf. Sci.* **2003**, *71*, 95.

(10) Lin, N.; Stepanow, S.; Vidal, F.; Kern, K.; Alam, M. S.; Strömsdorfer, S.; Dremov, V.; Muller, P.; Landa, A.; Ruben, M. *Dalton Trans.* **2006**, 2794.

(11) De Feyter, S.; De Schryver, F. C. *J. Chem. Phys. B* **2005**, *109*, 4290.

(12) 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.

(13) Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. *Nature* **2003**, *424*, 1029.

(14) Gesquière, A.; De Feyter, S.; De Schryver, F. C.; Schoonbeek, F.; Van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Nano Lett.* **2001**, *1*, 201.

(15) Hameren, R. van; Schön, P.; Buul, A.M. van; Hoogboom, J. T. V.; Lazarenko, S. V.; Gerritsen, J. W.; Engelkamp, H.; Christianen, P. C. M.; Heus, H. A.; Maan, J. C.; Rasing, T.; Speller, S. E.; Rowan, A. E.; Elemans, J.A.A.W.; Nolte, R. J. M. *Science* **2006**, *314*, 1433.

(16) Barth, J. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 375–407.

(17) Vonau, F.; Suhr, D.; Aubel, D.; Bouteiller, L.; Reiter, G.; Simon, L. *Phys. Rev. Lett.* **2005**, *94*, 066103.

(18) Vonau, F.; Aubel, D.; Bouteiller, L.; Reiter, G.; Simon, L. *Phys. Rev. Lett.* **2007**, *99*, 096103.

(19) Bouteiller, L.; Colombani, O.; Lortie, F.; Terech, P. *J. Am. Chem. Soc.* **2005**, *127*, 8893.

(20) Godfrey, P. D.; Brown, R. D.; Hunter, A. N. *J. Mol. Struct.* **1997**, *405*, 413–414.

(21) Masunov, A.; Dannenberg, J. J. *J. Phys. Chem A* **1999**, *103*, 178–184.

(22) Lortie, F.; Boileau, S.; Bouteiller, L.; Chassenieux, C.; Demé, B.; Ducouret, G.; Jalabert, M.; Laupr, P. *Langmuir* **2002**, *18*, 7218–7222.

(23) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148.

(24) Baxter, R.; Teobaldi, G.; Zerbetto, F. *Langmuir* **2003**, *19*, 7335.

(25) Ercolessi, F.; Parrinello, M.; Tosatti, E. *Philos. Mag. A* **1988**, *58*, 213.

(26) Rappe, A.; Goddard, W. A. *J. Phys. Chem.* **1991**, *95*, 3358.

(27) Born, M. V.; Mayer, J. E. *Z. Phys.* **1933**, *75*, 1.

(28) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(29) Ma, B.; Lii, J.; Allinger, N. L. *J. Comput. Chem.* **2000**, *21*, 813.

(30) Baxter, R. J.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Chem. Phys. Chem.* **2004**, *5*, 245.

(31) Whelan, C. M.; Cecchet, F.; Baxter, R. J.; Zerbetto, F.; Clarkson, G. J.; Leigh, D. A.; Rudolf, P. *J. Phys. Chem. B* **2002**, *106*, 8739.

(32) Montalti, M.; Prodi, L.; Zaccheroni, N.; Baxter, R. J.; Teobaldi, G.; Zerbetto, F. *Langmuir* **2003**, *19*, 5172.

(33) Rapino, S.; Zerbetto, F. *Small* **2007**, *3*, 386.

(34) Duwez, A.-S.; Cuenot, S.; Jérôme, C.; Gabriel, S.; Jérôme, R.; Rapino, S.; Zerbetto, F. *Nature Nanotechnol.* **2006**, *1*, 122.

(35) Rapino, S.; Zerbetto, F. *Langmuir* **2005**, *21*, 2512.

(36) *AMPAC Version 6.55*; Semichem. Inc.: Shawnee, KS, 1997.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. ; Montgomery J.A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J.C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al.Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, ReVision C.02*, revision C.02; Gaussian, Inc., Wallingford, CT, 2004.