

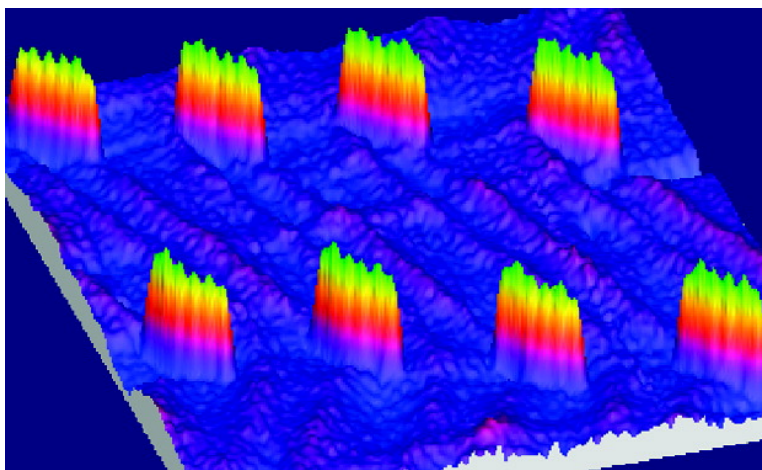
Communication

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## Azo Supramolecules on Au(111) with Controlled Size and Shape

Yongfeng Wang,<sup>\*,†</sup> Xin Ge,<sup>†</sup> Guillaume Schull,<sup>†</sup> Richard Berndt,<sup>†</sup> Claudia Bornholdt,<sup>‡</sup> Felix Koehler,<sup>‡</sup> and Rainer Herges<sup>‡</sup>

*Institut für Experimentelle und Angewandte Physik and Institut für Organische Chemie, Christian-Albrechts-Universität, D-24098 Kiel, Germany*

Received November 18, 2007; E-mail: yfwang@physik.uni-kiel.de

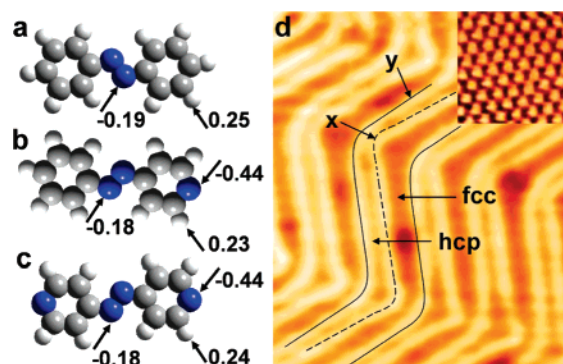
Supramolecular aggregation is controlled by directional, selective, and noncovalent interactions between neighboring molecules.<sup>1</sup> Densely packed molecular networks on single-crystal surfaces have been widely investigated.<sup>2</sup> However, for local control of the movement of the molecules, such as switching or rotation, a compact arrangement does not appear ideal.<sup>3</sup> Therefore, discrete supramolecules on surfaces, held together by strong hydrogen bonds or metal–ligand interactions, have recently begun to receive attention.<sup>4</sup> These strong intermolecular interactions induce the formation of a supramolecule with a maximized size, like extended chains.<sup>5</sup> Reducing the size of supramolecules is a prerequisite for the realization of device arrays with a high density.

We introduce the weak C–H···N hydrogen bond to reduce the size of the supramolecular aggregates. Azobenzene-related (azo) molecules (Figure 1) are chosen as building blocks because they are good candidates for molecular switches and light-controlled motion devices.<sup>6</sup> Dimers and triangular trimers on Au(111) have been successfully prepared. Moreover, we have also obtained peculiar ordered arrays of linear trimers and tetramers for the first time via the subtle balance between weak intermolecular C–H···N hydrogen bonds and molecule–surface interactions.

The measurements were performed in a home-built ultrahigh vacuum scanning tunneling microscope (STM) at 5.8 K. Au(111) surfaces and etched polycrystalline W tips were cleaned by cycles of Ar<sup>+</sup> sputtering and heating. The Au(111) substrate is reconstructed and exhibits a herringbone pattern (Figure 1d), which consists of adjacent pairs of partial dislocation lines.<sup>7</sup> Every type-*x* dislocation line contains a point dislocation at each elbow site, while the type-*y* dislocation line is free of this defect. The *x* and *y* lines separate the reconstructed surface into areas with hcp and fcc stacking, as marked in Figure 1d. High-purity azobenzene, 4-phenylazopyridine, and 4,4'-azopyridine (Figure 1) were separately dosed onto Au surfaces at room temperature. In our calculations, an azo oligomer was treated as a single molecule confined to a plane using Gaussian 03 at the B3LYP/6-31g(d) level of density functional theory. Quantum effects of hydrogen bonding thus are included in the model. Atomic natural bond orbital (NBO) charges of free molecules were calculated with the same method.

Azobenzene forms straight tetramer (Figure 2a, e, i) arrays at a coverage of  $\theta \approx 0.2$  monolayer (ML) in contrast to monomers and long chains reported earlier.<sup>8</sup> The partially negatively charged atoms (Figure 1a) determine the supramolecular side-by-side arrangement, whereas the width of the fcc area prevents the tetramers from growing longer (Figure 3a). Parallel straight chains appear to repel each because the tetramer is surrounded by positively charged hydrogen atoms.

To obtain less dense structures compared to the relatively compact azobenzene tetramer, we synthesized 4-phenylazopyridine



**Figure 1.** Schematic molecular structures of (a) azobenzene, (b) 4-phenylazopyridine, and (c) 4,4'-azopyridine. White, gray, and blue balls represent H, C, and N atoms, respectively. NBO charges of atoms which are crucial in forming H-bonds are indicated. (d) STM image of reconstructed Au(111) (45.0 nm × 55.0 nm, with an atomically resolved image as an inset). Sample bias  $V = 0.6$  V, current  $I = 0.06$  nA.

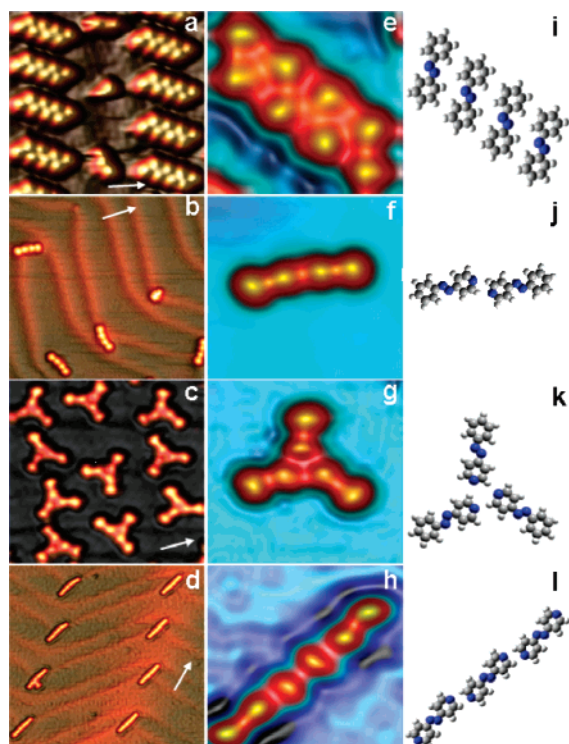
and 4,4'-azopyridine which expose either one or two partially negative charged N atoms. At low coverage,  $\theta \approx 0.02$  ML, 4-phenylazopyridine forms dimers at elbow sites (Figure 2b). A close-up image (Figure 2f) reveals a four-leaved shape which we attribute to a dimer arranged in a head-to-head fashion. This structure is consistent with the NBO charge distribution. The N atom of the pyridine group carries the largest negative charge (−0.44) while peripheral H atoms are positively charged (0.23) (Figure 1b). The dimer is stabilized by double C–H···N hydrogen bonds leading to the optimized structure (Figure 2j). At high coverage,  $\theta \approx 0.3$  ML, the molecules assemble into triangular trimers with the C–H···N hydrogen bonds (Figure 2c, g, k). In manipulation experiments (Supporting Information, Figure S2), the trimer moved as a whole.

4,4'-Azopyridine comprises an additional negatively charged nitrogen atom and forms linear aggregates as expected (Figure 2d). There are four H bonds in the linear trimer (Figure 2h, l) leading to increased stability compared to triangular trimers of 4-phenylazopyridine which involve three H bonds. The unusual linear trimer originates from the fine balance between weak C–H···N hydrogen bonds and molecule–surface interactions. A first molecule attaches to an elbow of type-*x* dislocation line and then captures one molecule at each side to form the linear trimer (Figure 3b). Adjacent to the longitudinal sides of the trimer, the defect-free surface does not favor the adsorption of molecules and the weak C–H···N hydrogen bonds cannot stabilize another molecule at either side. This is why we observe individual linear clusters in contrast to extended chains bonded by strong hydrogen bonds.<sup>5</sup>

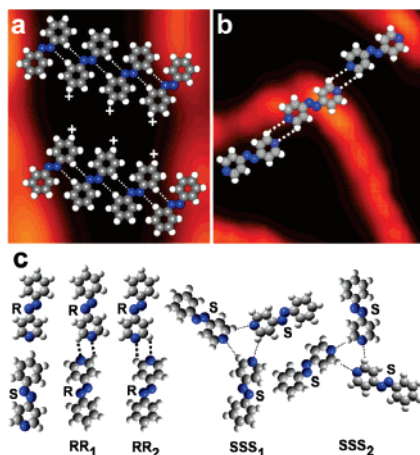
Generation of chirality through surface adsorption of achiral molecules is a widely studied phenomenon.<sup>9</sup> Two enantiomers “R” and “S” of 4-phenylazopyridine are shown in Figure 3c. In dimers, three combinations, “RR”, “RS”, and “SS”, are possible, each in

<sup>†</sup> Institut für Experimentelle und Angewandte Physik.

<sup>‡</sup> Institut für Organische Chemie.



**Figure 2.** Pseudo-three-dimensional STM topographs and optimized models of supramolecules on Au(111). Azobenzene tetramers (a,  $12 \times 12 \text{ nm}^2$ ) and 4-phenylazopyridine dimers (b,  $19 \times 19 \text{ nm}^2$ ) adopt side-by-side and head-to-head configurations, respectively. 4-Phenylazopyridine trimer (c,  $12 \times 11 \text{ nm}^2$ ) and 4,4'-azopyridine trimers (d,  $32 \times 32 \text{ nm}^2$ ) arrange in the triangular and linear way separately. High-resolution STM images and optimized molecular models: azobenzene tetramer (e, i,  $3.1 \times 3.1 \text{ nm}^2$ ); 4-phenylazopyridine dimer (f, j,  $4.2 \times 4.2 \text{ nm}^2$ ); 4-phenylazopyridine trimer (g, k,  $3.8 \times 3.8 \text{ nm}^2$ ); 4,4'-azopyridine trimer (h, l,  $3.7 \times 3.7 \text{ nm}^2$ ). White arrows point to the [110] direction.  $I = 0.06 \text{ nA}$ ,  $V = -0.8 \text{ V}$  for 4-phenylazopyridine and  $V = 1.0 \text{ V}$  elsewhere.



**Figure 3.** (a) Two azobenzene tetramers at an fcc area. “+” near hydrogen atoms indicates positive charge. (b) Schematic structure of 4,4'-azopyridine trimer at the elbow site on Au(111). (c) Two 4-phenylazopyridine enantiomers: R and S. Dimers  $RR_1$ ,  $RR_2$  of R enantiomer and trimers  $SSS_1$ ,  $SSS_2$  of S enantiomer are also depicted.

two different geometries. For example, two “R” molecules could form two kinds of dimers “ $RR_1$ ” and “ $RR_2$ ” by changing the position of C–H $\cdots$ N hydrogen bonds, as shown in Figure 3c. In total, six geometries of 4-phenylazopyridine dimers are conceivable on Au(111) (Supporting Information, Figure S4). In the trimer case, combinations “RRR”, “RRS”, “RSS”, and “SSS” are possible.

Again each combination allows for two geometries by changing the position of the cyclic C–H $\cdots$ N hydrogen bonds, such as “ $SSS_1$ ” and “ $SSS_2$ ” (Figure 3c). Therefore, eight kinds of trimers exist on the surface (Supporting information, Figure S5). For 4,4'-azopyridine, 20 kinds of trimers on the surface are expected, the reason being that the linear stacking allows for more structures than the triangular arrangement (Supporting Information, Figure S6). The multiformity of azo supramolecules determines their diversity in STM images, as evident from Figure 2. Different from dimers and trimers discussed above, azobenzene tetramers display spontaneous quasi chiral separation. Only four kinds of tetramers (Supporting Information, Figure S7) are observed. Repulsion between positively charged hydrogen atoms renders tetramers with azobenzenes of mixed handedness less stable.

Azo molecules prefer to lie flat on the surface because of the interplay between the surface and the  $\pi$ -electrons of the molecules. Ordered supramolecular arrays indicate sufficient mobility of the adsorbates at room temperature. The low coverage of azo molecules used in our experiments allows them to diffuse freely and to form the most stable oligomers on Au(111).<sup>10</sup>

In summary, arrays of dimers, triangular trimers, linear trimers, and tetramers of azo molecules have been prepared by tuning the strength and position of C–H $\cdots$ N hydrogen bonds and molecule–surface interactions. Theoretical modeling based on first-principles calculations was performed to elucidate the formation mechanism of the supramolecular structures. Relatively weak hydrogen bonds are instrumental in achieving individual clusters in contrast to extended chains bonded by strong hydrogen bonds.<sup>5</sup> This method provides an opportunity to assemble superstructures containing a small number of subunits and could be easily adapted to a wide range of molecules. The application of these ordered structures as single supramolecular switches is in progress.

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**Supporting Information Available:** Side view of Figure 2, NBO charge distributions of molecules and schemes of azo supramolecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Leininger, S.; Olenyuk, B.; Stang, P. J. *J. Chem. Rev.* **2000**, *100*, 853.
- (2) (a) Wan, L. J. *Acc. Chem. Rev.* **2006**, *39*, 334. (b) Smith, R. K.; Lewis, P. A.; Weiss, P. S. *Prog. Surf. Sci.* **2004**, *75*, 1. (c) De Feyter, S.; De Schryver, F. C. *Chem. Soc. Rev.* **2003**, *32*, 139. (d) Néel, N.; Kröger, J.; Berndt, R. *Adv. Mater.* **2006**, *18*, 174. (e) Bléger, D.; Kreher, D.; Mathevet, F.; Attias, A. J.; Schull, G.; Huard, A.; Douillard, L.; Fiorini-Debuschert, C.; Charra, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 7404.
- (3) (a) Wintjes, N.; Bonifazi, D.; Cheng, F.; Kiebele, A.; Stöhr, M.; Jung, T.; Spillmann, H.; Diederich, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 4089. (b) Alemani, M.; Peters, M. V.; Hecht, S.; Rieder, K.-H.; Moresco, F.; Grill, L. *J. Am. Chem. Soc.* **2006**, *128*, 14446.
- (4) (a) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R.; Mauri, F.; Vita, A. D.; Car, R. *Phys. Rev. Lett.* **1999**, *83*, 324. (b) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Wühh, M.; Wöll, C.; Berndt, R. *Surf. Sci.* **2000**, *444*, 199.
- (5) (a) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619. (b) Weckesser, J.; De Vita, A.; Barth, J. V.; Cai, C.; Kern, K. *Phys. Rev. Lett.* **2001**, *87*, 96101.
- (6) (a) Feringa, B. L.; Ed. *Molecular Switches*; Wiley-VCH: Weinheim, 2001. (b) Comstock, M. J.; Levy, N.; Kirakosian, A.; Cho, J.; Lauterwasser, F.; Harvey, J. H.; Strubbe, D. A.; Frechet, J. M. J.; Trauner, D.; Louie, S. G.; Cromptie, M. F. *Phys. Rev. Lett.* **2007**, *99*, 38301.
- (7) Wöll, Ch.; Chiang, S.; Wilson, R. J.; Lippel, P. J. *J. Phys. Rev. B* **1990**, *42*, 9307.
- (8) Kirakosian, A.; Comstock, M. J.; Cho, J.; Cromptie, M. F. *Phys. Rev. B* **2005**, *71*, 113409.
- (9) Charra, F.; Cousty, J. *Phys. Rev. Lett.* **1998**, *80*, 1682.
- (10) Stöhr, M.; Wahl, M.; Galka, C. H.; Riehm, T.; Jung, T.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 7394.

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