Determination of Photoswitching Dynamics through Chiral Mapping of Single Molecules Using a Scanning Tunneling Microscope

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Single-molecule-resolved scanning tunneling microscopy of tetra-*tert*-butyl azobenzene (TTB-AB) molecules adsorbed onto Au(111) reveals chirality selection rules in their photoswitching behavior. This observation is enabled by the fact that *trans*-TTB-AB molecules self-assemble into homochiral domains. *Cis*-TTB-AB molecules produced via photoisomerization are found in two distinct conformations with final state chirality determined by the initial *trans* isomer chirality. Based on these observations and *ab initio* calculations, we propose a new inversion-based dynamical photoswitching mechanism for azobenzene molecules at a surface.

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Converting light to mechanical motion at the single-molecule level offers exciting new possibilities for controlling nanomachine and nanoelectronics elements [1–3]. Azobenzene-derived molecules are particularly promising in this regard because their photoisomerization capability allows them to reversibly switch between two structural isomers, *trans* and *cis*, when irradiated by UV and visible light [4]. The internal molecular motions associated with this switching process have been well studied for molecules in solution, where different bond angles have been observed to undergo rotation and inversion at picosecond time scales [5–9]. Many potential nanotechnology applications, however, require contact between such molecules and a surface, leading to an environment where the molecular potential energy surface and dynamical pathways are not known. While this is an important regime for applications, it is largely unexplored due to the difficulty of performing ultrafast time-resolved optical measurement of adsorbate-coated surfaces. Recently, some investigations have been performed that explore surface-based molecular photoswitching using surface analysis techniques [10–12], but these measurements reveal little about the actual dynamical motion of molecules as they switch. Here we describe a new technique for extracting dynamical switching information from surface-bound molecules by spatially mapping their chirality state before and after a photoswitching event. This technique is applicable when different dynamical switching pathways transition a molecule between states of well-determined chirality.

We find that this type of situation exists for 3,3',5,5'-tetra-*tert*-butyl-azobenzene (TTB-AB) molecules adsorbed onto Au(111) [10]. While the isolated molecule is not chiral, the adsorbed molecule *is* chiral due to the breaking of mirror symmetry by the presence of the surface [13–16]. Using scanning tunneling microscopy (STM) we observe that *trans*-TTB-AB on Au(111) assembles into monolayer-high islands composed uniformly of either right-handed (RH) or left-handed (LH) enantiomers [17]. When these *trans* molecules are illuminated with light, we observe that they can switch into two possible *cis* isomer states (“type 1” and “type 2”). The chirality of the resulting *cis* isomers is not random, but rather follows a chirality-dependent photoswitching selection rule: RH (LH) *trans* isomers on Au(111) almost exclusively switch to either LH (RH) type 1 *cis* isomers or RH (LH) type 2 *cis* isomers (the chirality convention is defined below). Using density-functional theory we have determined the geometrical structure of the type 1 and type 2 *cis*-TTB-AB isomers. Armed with these structures and the chirality-dependent selection rule, we are able to place symmetry constraints on the possible dynamical pathways involved in *trans*-to-*cis* switching. This provides evidence for a new surface-based dynamical mechanism for *trans*-to-*cis* photomechanical switching of TTB-AB molecules on Au(111).

Our measurements were performed using a home-built variable-temperature ultrahigh vacuum STM with optical access to the sample. TTB-AB molecules were synthesized via oxidative coupling reactions of 3,5-di-*tert*-butyl-aniline [18]. 0.1 monolayer (ML) of the *trans* isomer of TTB-AB was deposited via Knudsen cell onto clean Au(111) substrates held at 30 K. Samples were then annealed at room temperature for 10 minutes in order to achieve ordered monolayer-high islands of *trans* molecules. STM images were acquired in the temperature range of 30 to 35 K using tunnel currents below 50 pA for stable imaging. A cw laser aligned at an external viewport provided UV (375 nm) radiation at the sample surface with an average intensity of 92 mW/cm^2. During laser exposures the STM tip was retracted 0.2 mm away from the surface and the sample temperature was maintained between 28 and 35 K.

Self-assembly of *trans*-TTB-AB molecules into monolayer-high domains having pure chiral flavor can be seen in the mirror-image lattice chiral domains of Fig. 1. Single *trans*-TTB-AB molecules appear as four lobes arranged at the vertices of a parallelogram [the lobes correspond to the location of the *tert*-butyl (TB) functional groups, as indicated by the molecular model overlays in Fig. 1(a)]. *Trans*-TTB-AB molecules in RH vs LH domains appear slightly sheared to the right and left, respectively. The difference between molecules in the RH vs LH domains is more clearly observed by averaging the location of the highest point of the TB lobes for molecules within like domains, as shown in Fig. 1(b). The resulting average parallelograms for RH and LH domains are mirror images of each other with the edges of the parallelograms angled by 2° from the horizontal and vertical.

When the chiral *trans*-TTB-AB islands are illuminated with UV light, the molecules begin photoswitching into a *cis* isomer structure [19]. High-resolution STM images of the resulting *cis* isomers, as shown in Fig. 2(a), reveal that there are two distinct types of isomers [labeled type 1 and type 2 in Fig. 2(a)]. Each has the appearance of a bright (taller) lobe surrounded by three dimmer (lower) lobes, but the location of the bright lobe with respect to the dim lobes differs between the two types. For type 1 *cis* isomers the bright lobe lies closer to the center line between the two far opposite dim lobes, whereas for type 2 *cis* isomers the bright lobe lies further from this center line and closer to the diagonal point opposite the dim corner lobe (see Fig. 3). Type 1 and type 2 *cis*-TTB-AB are both chiral, and their RH and LH enantiomers can be seen in the images of Fig. 3 using our chirality convention. The photoreaction yields of type 1 *cis* and type 2 *cis* are not equal: type 1 *cis* occur approximately twice as frequently as type 2 *cis*. Type 1 *cis*-TTB-AB has been previously reported in STM images of molecules switched using light [10] and using tip-based interactions [20–22], but type 2 *cis* isomers have gone unnoticed until now because they occur less frequently and require exceptional imaging conditions to be distinguished from type 1.

When a *trans*-TTB-AB molecule on Au(111) is photoswitched to a *cis* isomer, the chirality of the final state is not random. This was determined from careful examination of 338 photoswitched *cis* isomers. We find that *trans* isomers in LH domains produce predominantly either RH type 1 or LH type 2 *cis* isomers (with a 9% defect rate), while *trans* isomers in RH domains produce predominantly either LH type 1 or RH type 2 *cis* isomers (with a 5% defect rate). A

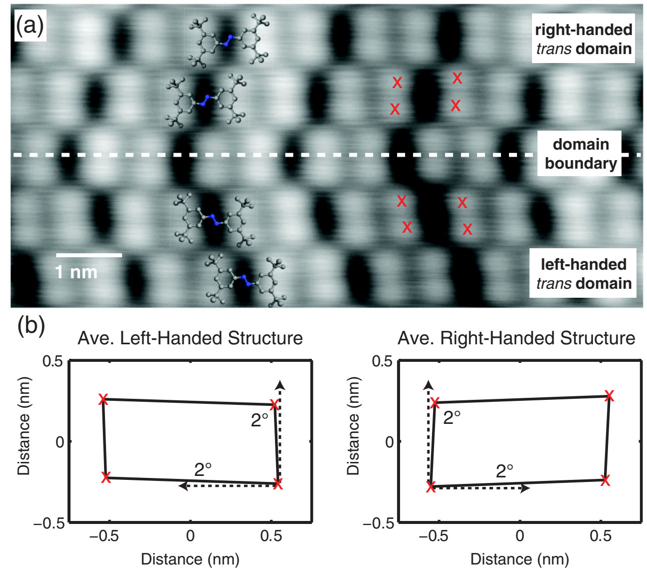

FIG. 1 (color online). (a) Image of *trans*-TTB-AB island composed of two mirror-image chiral domains (domain boundary indicated by dashed white line). *Trans*-TTB-AB single-molecule structural models are superimposed on right-handed and left-handed configurations. Red crosses indicate locations of TB lobe maxima. (b) Average locations of *trans*-TTB-AB TB lobes averaged over 394 left-handed domain molecules (left plot) and 125 right-handed domain molecules (right plot). Left-handed and right-handed domain *trans*-TTB-AB molecules form parallelograms that are angled by 2° from the horizontal and vertical.

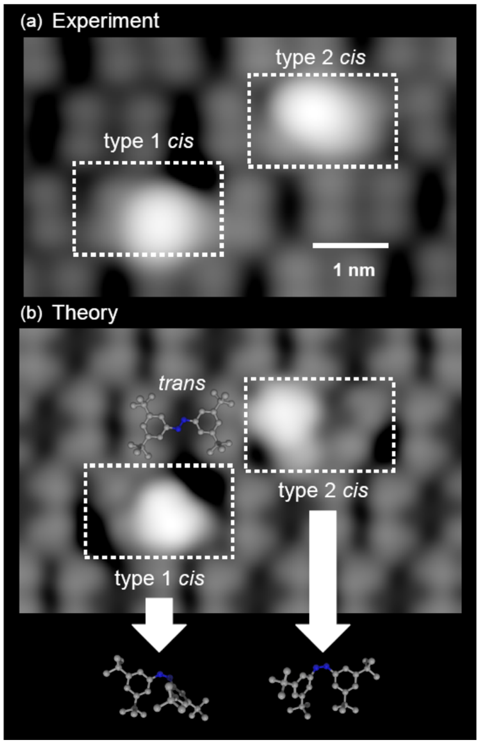

FIG. 2 (color online). (a) High-resolution STM image shows structure of two distinct types of photoswitched *cis*-TTB-AB isomers: a left-handed Type 1 *cis* and a right-handed Type 2 *cis*, contained within dashed white boxes. (b) *Ab initio* DFT simulated STM image of the two *cis*-TTB-AB types surrounded by *trans*-TTB-AB molecules, with structural models shown of *trans*-TTB-AB as well as *cis* type 1 and *cis* type 2 molecules used to calculate simulated STM image.

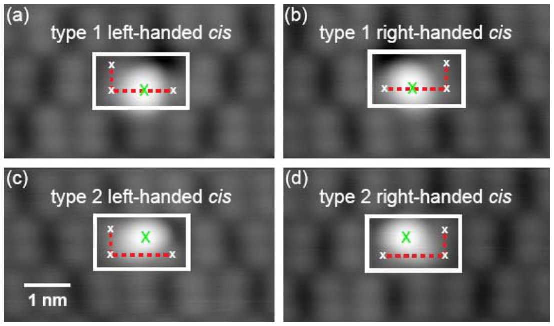

FIG. 3 (color online). STM images showing different chiral states of single *cis*-TTB-AB molecules (within white boxes): (a) *cis* type 1, left-handed (within right-handed *trans* domain), (b) *cis* type 1, right-handed (within left-handed *trans* domain), (c) *cis* type 2, left-handed (within left-handed *trans* domain), and (d) *cis* type 2, right-handed (within right-handed *trans* domain). Location of single bright lobe indicated by green cross and the locations of three dim peripheral lobes indicated by white crosses. Dotted lines are guides to the eye.

clear chirality-dependent photoswitching selection rule is thus observed.

In order to determine the specific constraints placed on molecular photoswitching dynamics by the selection rule above, it is critical to determine the geometrical structure of the *cis* and *trans* molecules imaged by our STM. This determination was performed by calculating topographs from the electronic local density of states (LDOS) of different TTB-AB molecular structures by density-functional theory (DFT) and comparing them to our STM images. DFT calculations were performed using the SIESTA code [23] as in Ref. [10]. Structures of isolated molecules of each type were initially relaxed and then assembled into a monolayer of molecules (without surface atoms) according to the experimentally observed surface lattice parameters [24]. The simulated *trans*-TTB-AB molecules [Fig. 2(b)] show four lobes at the corners of a parallelogram angled from the horizontal and vertical by 2°, as observed in the STM images (Fig. 1), confirming the existence of two enantiomers of *trans*-TTB-AB on the surface. We find two local minima in the DFT potential energy surface that produce LDOS topographs corresponding to the *cis*-TTB-AB type 1 and type 2 STM images, thus yielding the underlying molecular structure for these *cis* types [see Fig. 2(b)]. In both *cis* structures the phenyl ring lying on the surface has a CCNN dihedral bond angle $\approx 30°$. The two *cis* types differ in that the CCNN dihedral angle for the lifted ring is 50° for type 1 and $-60°$ for type 2, leading to the different bright lobe positions observed in the STM images. The type 1 *cis* molecular structure has been experimentally reported in the past [10,20–22]. The type 2 molecular structure, however, while suggested by previous theoretical work [25], has never been observed experimentally until now.

We are now in a position to determine the surface dynamical pathways explored by TTB-AB molecules as they photomechanically switch from one isomeric structure to another. While the photoswitching mechanism for molecules in solution remains controversial [5–9,25–27], two commonly considered mechanisms involve (i) pure rotational motion [5,7,25–27], and (ii) concerted inversion [7,28]. We are able to rule these mechanisms out for TTB-AB on Au(111) using our experimentally determined chiral selection rule and molecular structures. The rotational pathway, for example, leads to *trans* → *cis* conversion via out-of-plane rotation of a phenyl ring as the CNNC dihedral angle is swept. For a RH (LH) *trans* isomer on a surface this motion *always* yields a RH (LH) type 1 *cis* isomer. Because this violates our observed chirality-dependent selection rule, we rule it out as a significant dynamical pathway for TTB-AB photoswitching on gold. The concerted inversion pathway, on the other hand, yields *trans* → *cis* conversion through a mechanism involving synchronous inversion of the phenyl rings as the two NNC bond angles are simultaneously swept. Here the TTB-AB molecule goes through a transition state in which the CNNC atoms are nearly collinear, a configuration that by symmetry is expected to lead to either RH or LH *cis* conformations with nearly equal probability. This too violates our chirality-dependent selection rule, and so we rule it out as a significant dynamical pathway for TTB-AB switching on gold.

The question now arises if there exists any reasonable dynamical pathway to convert *trans*-TTB-AB to *cis*-TTB-AB on Au(111) that is consistent with the observed chirality-dependent selection rule. Here an affirmative answer can be made via a new dynamical mechanism that is a variant of the inversion pathway [5–7,9,26]. We propose that isomerization begins with the in-plane inversion of one phenyl ring and proceeds until the moving phenyl ring makes contact with the stationary ring (see Fig. 4 for a sketch of the mechanism starting from RH *trans*-TTB-AB). A branch in the dynamics occurs at this point. In the first branch (lower left-hand side of Fig. 4) the inverting phenyl ring lifts out of the plane starting from the point away from contact, yielding a type 2 *cis* configuration of the proper chirality. In the second branch (lower right-hand side of Fig. 4) the stationary phenyl ring lifts out of plane starting from the point of contact, yielding a type 1 *cis* configuration of the proper chirality. This mechanism is supported by the fact that it should be energetically more favorable for portions of the molecule to slide along the surface (as in inversion) rather than completely unbind and lift off of the surface (as in rotation).

In conclusion, we have discovered that *trans*-TTB-AB molecules self-assemble into chiral domains on Au(111), and that there are two distinct *cis* isomer structures resulting from TTB-AB *trans* → *cis* surface photoisomerization. Most significantly, we observe a chirality-dependent

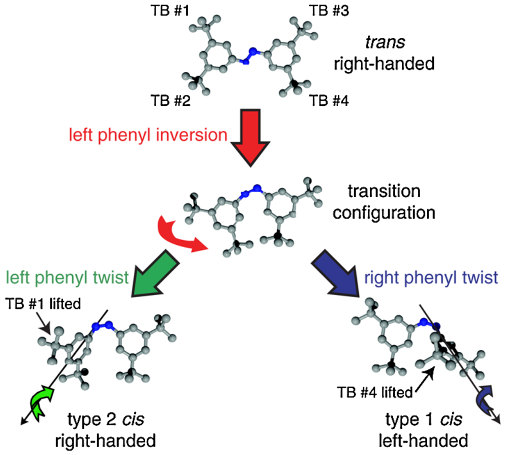

FIG. 4 (color online). Proposed photoisomerization dynamical pathway for TTB-AB on Au(111). A photoexcited right-handed *trans*-TTB-AB molecule (top center, TB legs numbered) begins the isomerization process with an in-plane inversion of the left phenyl ring (middle center). With continuing inversion, steric repulsion due to contact between the phenyl rings forces either: left phenyl to twist out of plane, lifting TB #1 and producing right-handed type 2 *cis*-TTB-AB (bottom left), or right phenyl to twist out of plane, lifting TB #4 and producing left-handed type 1 *cis*-TTB-AB (bottom right).

photoswitching selection rule that imposes a strong correlation between the chirality of initial and final states for photoisomerization of TTB-AB molecules on a surface. This constrains the possible switching dynamics and supports a new inversion-based dynamical pathway for molecular photoswitching on Au(111).

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[1] V. Balzani, A. Credi, F. M. Raymo, and J. F. Stoddart, Angew. Chem., Int. Ed. **39**, 3348 (2000).
[2] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. deJong, T. N. Bowden, J. van Esch, B. L. Feringa, and B. J. van Wees, Phys. Rev. Lett. **91**, 207402 (2003).
[3] C. Zhang, Y. He, H.-P. Cheng, Y. Xue, M. A. Ratner, X. G. Zhang, and P. Krstic, Phys. Rev. B **73**, 125445 (2006).
[4] H. Rau, in *Photochromism: Molecules and Systems*, edited by H. Durr and H. Bouas-Laurent (Elsevier, Amsterdam, 1990).
[5] N. Tamai and H.Miyasaka, Chem. Rev. **100**, 1875 (2000).
[6] T. Fujino, S. Y. Arzhantsev, and T. Tahara, J. Phys. Chem. A **105**, 8123 (2001).
[7] C. W. Chang, Y. C. Lu, T. T. Wang, and E. W. G. Diau, J. Am. Chem. Soc. **126**, 10 109 (2004).
[8] I. K. Lednev, T.-Q. Ye, L. C. Abbott, R. E. Hester, and J. N. Moore, J. Phys. Chem. A **102**, 9161 (1998).
[9] C. M. Stuart, R. R. Frontiera, and R. A. Mathies, J. Phys. Chem. A **111**, 12 072 (2007).
[10] M. J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J. H. Harvey, D. A. Strubbe, J. M. J. Fréchet, D. Trauner, S. G. Louie, and M. F. Crommie, Phys. Rev. Lett. **99**, 038301 (2007).
[11] L. Ovari, M. Wolf, and P. Tegeder, J. Phys. Chem. C **111**, 15 370 (2007).
[12] A. S. Kumar, T. Ye, T. Takami, B.-C. Yu, A. K. Flatt, J. M. Tour, and P. S. Weiss, Nano Lett. **8**, 1644 (2008).
[13] S. M. Barlow and R. Raval, Surf. Sci. Rep. **50**, 201 (2003).
[14] C. J. Eckhardt, N. M. Peachey, D. R. Swanson, J. M. Takacs, M. A. Khan, X. Gong, J. H. Kim, J. Wang, and R. A. Uphaus, Nature (London) **362**, 614 (1993).
[15] G. P. Lopinski, D. J. Moffatt, D. D. Wayner, and R. A. Wolkow, Nature (London) **392**, 909 (1998).
[16] K.-H. Ernst, Top. Curr. Chem. **265**, 209 (2006).
[17] Enantiomers are defined as two nonsuperimposable chiral molecules which are mirror images of each other.
[18] N. Pozhidaeva, M. E. Cormier, A. Chaudhari, and G. A. Woolley, Bioconjugate Chemistry **15**, 1297 (2004).
[19] Our ability to observe the same spot before and after photoirradiation and the reversibility of the observed photoisomerization excludes any defect-mediated conformation change or photolysis (see Ref. [10]). The photoswitching yield increases linearly with laser fluence, indicating that we are observing a single-photon process.
[20] M. Alemani, M. V. Peters, S. Hecht, K.-H. Rieder, F. Moresco, and L. Grill, J. Am. Chem. Soc. **128**, 14 446 (2006).
[21] M. Alemani, S. Selvanathan, F. Ample, M. V. Peters, K.-H. Rieder, F. Moresco, C. Joachim, S. Hecht, and L. Grill, J. Phys. Chem. C **112**, 10 509 (2008).
[22] C. Dri, M. V. Peters, J. Schwarz, S. Hecht, and L. Grill, Nature Nanotech. **3**, 649 (2008).
[23] D. Sanchez-Portal, P. Ordejon, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[24] Our calculations show that including the surface atoms has little effect on the simulated STM topographs of TTB-AB molecules.
[25] M. L. Tiago, S. Ismail-Beigi, and S. G. Louie, J. Chem. Phys. **122**, 094311 (2005).
[26] H. Rau and E. Luddecke, J. Am. Chem. Soc. **104**, 1616 (1982).
[27] C. R. Crecca and A. E. Roitberg, J. Phys. Chem. A **110**, 8188 (2006).
[28] E. W. G. Diau, J. Phys. Chem. A **108**, 950 (2004).