# Controlled Switching within an Organic Molecule Deliberately Pinned to a Semiconductor Surface

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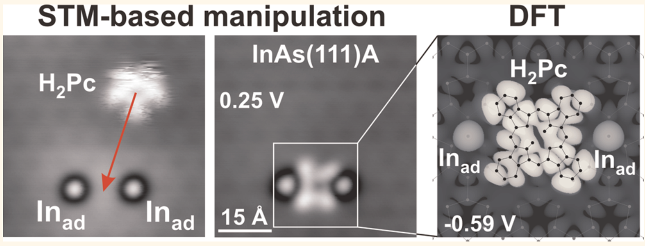
## ABSTRACT



Bistable organic molecules were deposited on a weakly binding III—V semiconductor surface and then pinned into place using individual native adatoms. These pinning atoms, positioned by atomically precise manipulation techniques in a cryogenic scanning tunneling microscope (STM) at 5 K, stabilize the $\pi$-conjugated molecule against rotation excited by the tunneling electrons. The pinning allows triggering of the molecule's intrinsic switching mechanism (a hydrogen transfer reaction) by the STM tunnel current. Density-functional theory calculations reveal that the energetics of the switching process is virtually unaffected by both the surface and the pinning atoms. Hence, we have demonstrated that individual molecules with predictable, predefined functions can be stabilized and assembled on semiconductor templates.

**KEYWORDS:** scanning tunneling microscopy · density-functional theory · semiconductor surfaces · indium arsenide · STM manipulation of single molecules

The proposal of future electronics with organic molecules as device components[1] has stimulated considerable research effort aiming at single-molecule function in a solid-state environment.[2,3] Scanning tunneling microscopy (STM) has proven to be a powerful experimental tool in this context because it combines imaging and spectroscopic means with the capability to manipulate matter at the atomic scale.[4−6] To explore model cases of single-molecule function in an environment compatible with existing device technologies, it is of interest to employ semiconductor materials as templates. On semiconductor surfaces with unsaturated dangling bonds, such as Si surfaces, organic molecules are generally chemisorbed[7,8] or even fragmented[9] upon adsorption. Nonetheless, STM studies of single molecules covalently linked to Si surfaces revealed a reversible conductance switching due to rotational movements between stable adsorption configurations[10] and biconformational switching[11,12] driven by the tunneling electrons. On the other hand, a concept utilizing molecular building blocks with predefined properties that are not quenched, or even significantly perturbed, upon adsorption would require a molecule—semiconductor system characterized by a moderate electronic coupling. Maintaining and controlling an unperturbed functionality inherent to the free molecular state has not yet been demonstrated for single molecules adsorbed on a semiconductor surface.

In this article we describe a weakly coupled molecule—semiconductor hybrid system involving a III—V semiconductor surface with fully saturated dangling bonds and a planar $\pi$-conjugated molecule that exists in two tautomers due to an internal hydrogen transfer reaction. As a consequence of the weak coupling, the adsorbed molecule is highly sensitive to inelastic excitations by the tunneling electrons, inducing an in-plane rotation about its center. To stabilize the molecule, we applied STM-based manipulation techniques and assembled adatom—molecule complexes in which the rotational degree of freedom is sterically hindered. The STM data, in combination with first-principles total-energy calculations, reveal that the intrinsic hydrogen transfer (experimentally evident from a conductance switching by 1 order of magnitude) remains unperturbed by both the substrate and the adatoms that prevent rotation of the molecule.

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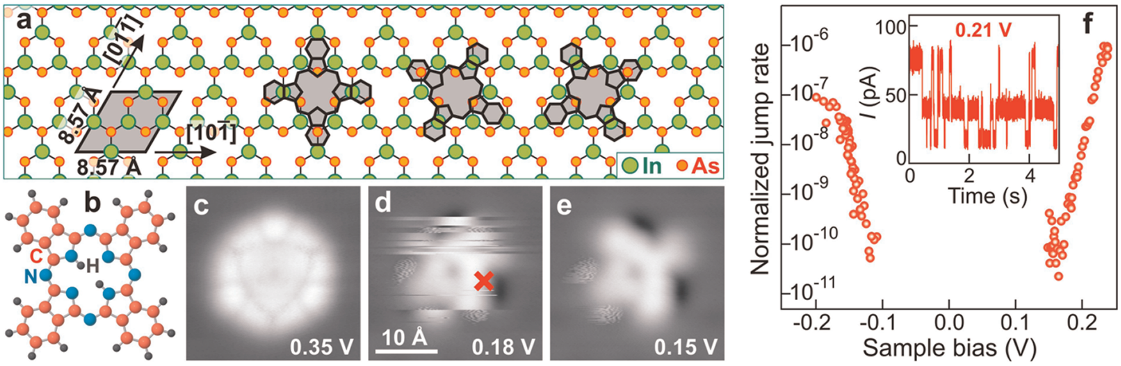

**Figure 1. Molecular rotation stimulated by STM tunnel current. (a) Three equivalent rotational orientations of a phthalocyanine molecule ($H_2Pc$, black) physisorbed on the InAs(111)A-(2×2) surface. (b) Structural model of the free $H_2Pc$ molecule as determined from DFT. (c–e) Rotational jumping triggered by STM tunnel current at different values of sample bias. Fast rotation at 0.35 V reveals the underlying 3-fold symmetry of the InAs substrate, while slower rotation at 0.18 V reveals discrete $H_2Pc$ orientational jumps. The rotation completely stops at 0.15 V. All images acquired at constant current $I$ = 50 pA. (f) Normalized jump rate $e/I\tau$ ($\tau$: residence time in a given orientation) *versus* sample bias, as determined from time-dependent current spectra acquired with the tip intentionally fixed away from the molecular center as marked in (d). Set point parameters: 50 pA, 0.18 V. Inset: representative time spectrum showing the three-level current signal.**

## RESULTS AND DISCUSSION

We performed cryogenic scanning tunneling microscopy experiments on the InAs(111)A surface combined with complementary density-functional theory calculations. The InAs(111)A surface (Figure 1a) is free of partially filled dangling bonds—and thus chemically nonreactive—due to its intrinsic (2×2) cation-vacancy reconstruction.[13] Here, we focus on free base phthalocyanine ($H_2Pc$, Figure 1b), which is a planar $\pi$-conjugated molecule with $D_{2h}$ symmetry.[14] $H_2Pc$ is known to undergo a tautomerization reaction in which the two inner hydrogens in the cavity switch their positions from one pair of opposite nitrogens to the other.[15]

After depositing $H_2Pc$ at low coverage ($\sim 1 \times 10^{12}$ molecules per cm$^2$) and substrate temperatures below 20 K we find a planar adsorption geometry with the molecule always centered above the In vacancy site of the reconstructed surface. Although $H_2Pc$ is of $D_{2h}$ symmetry, constant-current STM imaging of the adsorbed molecule at 0.35 V sample bias (Figure 1c) yields a uniform protrusion of 3-fold symmetry. Imaging at reduced bias reveals rotational fluctuations of the molecule within the tunnel junction (0.18 V, Figure 1d), which come to a halt at even lower bias (0.15 V, Figure 1e), eventually reflecting the expected cross-shaped appearance of the molecule. We find three equivalent adsorption states with the molecular lobes oriented parallel/perpendicular to any of the three ⟨110⟩ in-plane directions, as illustrated in Figure 1a.

The rotational jumps between the three in-plane molecular orientations give rise to a three-level signal in the tunnel current $I$ when the tip is placed at an off-center position above the molecule with a disabled feedback loop and at sufficiently large bias $U$. The inset in Figure 1f shows a corresponding current-*versus*-time spectrum recorded at 0.21 V with the tip held at the position indicated in Figure 1d. The bias-dependent normalized jump rate (the probability per tunneling electron to induce a single jump, $e/I\tau$, $\tau$: mean residence time in a given state) in Figure 1f shows a nearly symmetrical bipolar threshold behavior,[16] suggesting that an inelastic scattering of the tunneling electrons (inelastic electron tunneling, IET) is important for exciting the molecular rotation. IET-induced rotational excitations were previously reported for molecules adsorbed on metal surfaces.[17–20]

The IET-induced rotation observed here suggests the absence of the covalent molecule–surface bonds commonly formed between molecules and semiconductor surfaces with unsaturated dangling bonds.[7,8] We propose that van der Waals (vdW) interactions are the primary binding mechanism in the present system and that, for this reason, the barrier for in-plane rotation is sufficiently low to be overcome by IET at small bias voltages of ~0.1 V and above. The rotational fluctuation of the weakly coupled $H_2Pc$ molecule can be stabilized by applying STM-based atom and molecule manipulation techniques,[4,21] as demonstrated in Figure 2a,b: First, two native In adatoms ($In_{ad}$) are positioned on two adjacent next-nearest neighbor In vacancy sites along ⟨110⟩ (spacing $2a_0\sqrt{2}$ = 17.14 Å, $a_0$ = 6.06 Å: cubic InAs lattice constant) by vertical manipulation.[22] Next, an $H_2Pc$ molecule is moved along the surface by lateral manipulation[23] (red line in Figure 2a) and dragged in between of the two $In_{ad}$. The tunnel current response during lateral manipulation[21,24] indicates that the molecule is repositioned by means of short-range attractive force interaction with the STM tip. The resulting complex in Figure 2b shows a stable cross-shaped appearance of the incorporated $H_2Pc$ molecule, confirming that its rotation is sterically hindered by the two $In_{ad}$ atoms nearby.

Bias-dependent STM imaging reveals the existence of a left-handed and a right-handed conformer, as

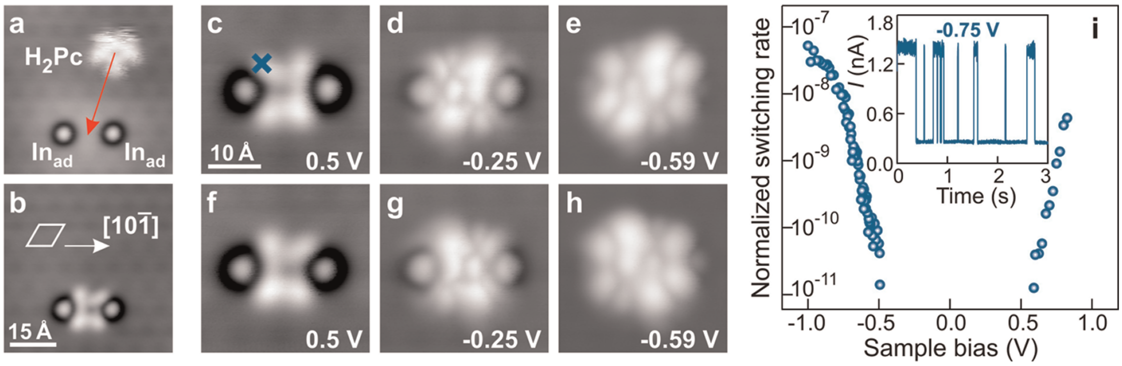

**Figure 2. Hydrogen atom switching within an $H_2Pc$ molecule pinned between two In adatoms. (a, b) STM images (75 pA, 0.25 V) of the intermediate and final configurations of an $H_2Pc$ molecule being positioned between two $In_{ad}$ atoms by lateral manipulation. (c–h) STM images (50 pA) of two rotationally inequivalent chiral conformations of the pinned $H_2Pc$; compare panels (c–e) with (f–h). (i) Normalized switching rate $e/I\tau$ between the two conformers *versus* sample bias, as determined from time-dependent current spectra acquired with the tip fixed at the position shown in (c). Set point parameters: 50 pA, 0.5 V. Inset: representative time spectrum showing the two-level current signal.**

evident from the images in panels c–e in comparison to those in panels f–h of Figure 2. It is possible to reversibly switch between the two enantiomers. This is achieved, for example, by placing the STM tip at the position indicated in Figure 2c and applying a bias of −0.75 V. The two-level current response (inset in Figure 2i) recorded with disabled feedback loop reflects a binary switching with a high to low current ratio on the order of 10 to 1. In addition, a bipolar threshold in the bias-dependent normalized switching rate is revealed that is nearly symmetrical with respect to the Fermi level at $U = 0$ (Figure 2i), albeit at significantly higher bias voltages than for the IET-induced rotation (Figure 1f). These observations suggest that the adatom-induced single-molecule pinning leaves the tautomerization switching largely undisturbed and that it can be triggered by the tunneling electrons.[25−27] For the unpinned molecule, on the other hand, read-out of the tautomerization switching is obscured by the excitation of low-energy rotational fluctuations.

For a direct comparison, we also studied Cu phthalocyanine (Cu*Pc*) molecules on InAs(111)A, *i.e.*, a *Pc* species of $D_{4h}$ symmetry[14] that does not exhibit a tautomerization-based bistability in the free molecular state. Similar to the case of free base *Pc* shown in Figure 1, the isolated CuPc molecule is excited by the tunnel current to perform rotational jumps, and the bias-dependent jump rate shows a bipolar threshold behavior symmetrical with respect to zero bias. On the other hand, when a Cu*Pc* molecule is pinned by two $In_{ad}$ nearby—analogous to the $H_2Pc$-related complex shown in Figure 2—no current switching or bistability of any sort is found. Figure 3 shows bias-dependent STM images of a Cu*Pc* molecule pinned in between two $In_{ad}$ located on next-nearest neighbor vacancy sites along ⟨110⟩, indicating an STM appearance with two mirror planes: one normal to, and the other coplanar with, the ⟨110⟩ direction connecting the $In_{ad}$ positions.

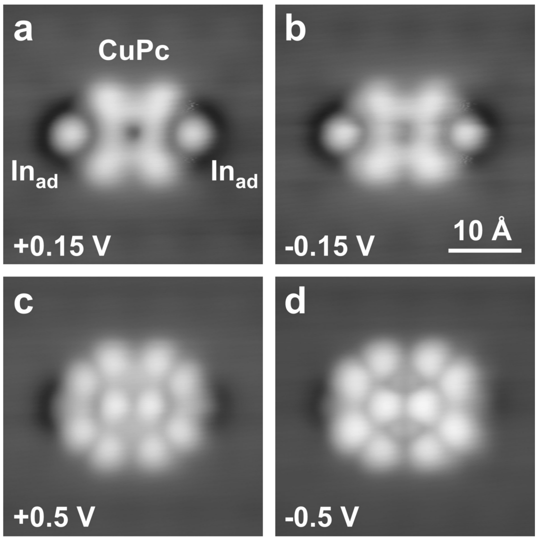

**Figure 3. (a–d) STM images of a Cu*Pc* molecule pinned by two $In_{ad}$ atoms located on nearest-neighbor vacancy sites along ⟨110⟩ recorded at bias voltages as indicated and a tunnel current of 0.1 nA. Different from the $H_2Pc$ case (Figure 2), the complex exists in one conformation only, characterized by an STM appearance with two mirror planes: one normal to, and the other coplanar with, the ⟨110⟩ direction connecting the $In_{ad}$ positions.**

We performed density-functional theory (DFT) calculations to support and explore three aspects of our experimental findings: the equilibrium physical geometry of $H_2Pc$ adsorbed between two $In_{ad}$ atoms on InAs(111)A; the constant-current STM topography of this system; and the reaction pathway and activation barrier for tautomerization switching between the two equivalent enantiomers of the adsorbed, pinned $H_2Pc$. Because the binding of the $H_2Pc$ molecule to the InAs surface is dominated by vdW interactions, total energies and forces were calculated within the DFT-D2 method of Grimme, in which vdW interactions are included through a semiempirical term added to the standard DFT total energy.[28]

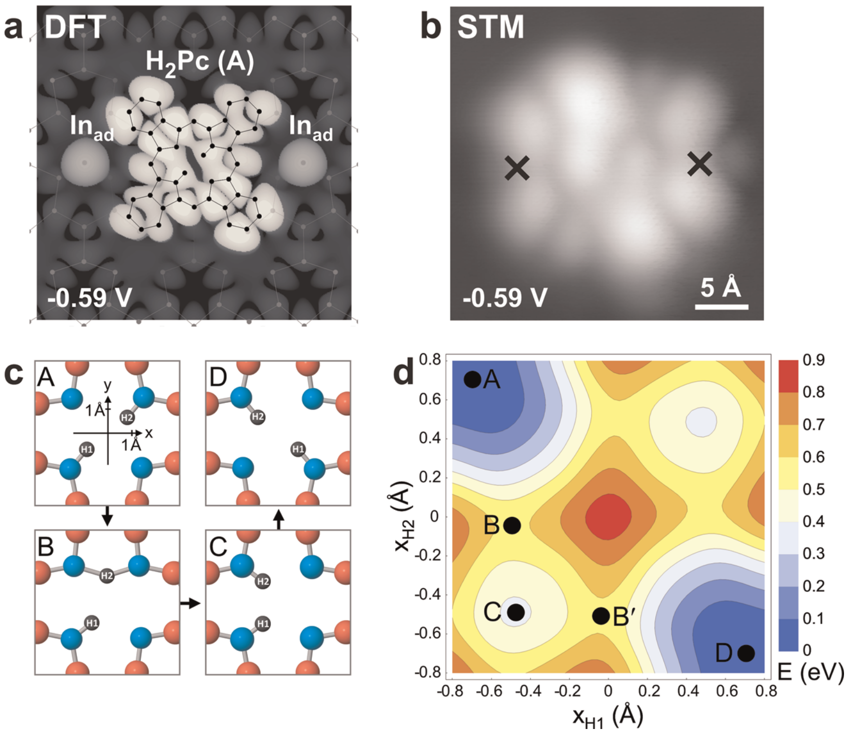

**Figure 4. Simulated STM imagery and theoretical energy landscape for hydrogen-atom switching. (a) Theoretically simulated STM image of one of the two equivalent ground-state conformations. (b) Close-up view of the STM image in Figure 2h for comparison; $In_{ad}$ positions are marked. (c, d) Potential-energy surface (PES) for hydrogen atom switching in an $H_2Pc$ molecule pinned between two $In_{ad}$ atoms on the InAs(111)A-(2×2) surface, as determined from DFT-D2 calculations. The two degrees of freedom are the *x* coordinates of the two H atoms; the *y* coordinates were fully relaxed, as were all other atomic coordinates describing the molecule and surface, at each point in the PES. Several critical points are illustrated in (c) and marked in (d): the two equivalent ground-state conformers (A and D), one of the transition states connecting them (B, nearly degenerate with B′), and a metastable intermediate state (C). The minimum-energy pathway connecting the two conformations is A→B→C→B′→D.**

We describe first the equilibrium position and orientation of $H_2Pc$ on clean InAs(111)A-(2×2). Starting with gas-phase molecular coordinates we systematically varied the position, height, and orientation of the molecule to locate the minimum-energy adsorption site. In agreement with STM observations, the center of the molecule is located at an In-vacancy site with the molecular lobes oriented parallel/perpendicular to a ⟨110⟩ in-plane direction, as illustrated in Figure 1a. At this site the internal molecular geometry and surface structure were then fully relaxed within DFT-D2. Only negligible distortions occur within the molecule and at the nearby surface. The equilibrium adsorption height is 3.1 Å above the InAs surface plane; without vdW interactions the molecule sits approximately 1 Å higher, demonstrating the importance of including this term in the total energy.

The two In adatoms were then added to the surface, and full structural relaxation of the entire system was repeated. Relative to the initial gas-phase geometry, the final molecular relaxation was small, less than 0.1 Å. Figure 4a shows a filled-state STM image, simulated using the method of Tersoff and Hamann,[29] for one of the two equivalent enantiomers. Experimental STM imaging does not unambiguously resolve all the details of the simulated nodal structure, primarily because the simulations lead (for technical reasons) to apparent heights that are significantly closer to the physical surface (typically less than 5 Å) than the experimental tip height (close to ∼10 Å). In addition, finite-size effects of the tip apex, which are not taken into account in the simulations, may further reduce the STM contrast. Nonetheless, we can associate the overall appearance of the simulated enantiomer in Figure 4a with that of the experimental image in Figure 2h, reproduced in a close-up view in Figure 4b for direct comparison.

Finally, we analyzed tautomerization in the adsorbed and pinned $H_2Pc$ molecule by computing the DFT-D2 potential-energy surface for hydrogen switching. The *x* coordinates of the two H atoms provide two convenient degrees of freedom for the PES, as illustrated in Figure 4c. At every point in the $x_{H1}-x_{H2}$ plane all other degrees of freedom (the *y* coordinates of the H atoms, as well as all other atomic positions) were fully relaxed. The resulting PES (Figure 4d) reveals that the minimum-energy pathway connecting the two equivalent conformers (states A and D) proceeds via the metastable intermediate *cis* conformation (state C). This result is very similar to ones previously reported for gas-phase $H_2Pc$.[30] The transition state (B) has an activation barrier of 0.58 eV, which is consistent with the measured bias thresholds of the switching rate in Figure 2i. The metastable state C is 0.40 eV above the ground state A. These critical points and barriers—and indeed the entire PES—are qualitatively and nearly quantitatively indistinguishable from those of the isolated $H_2Pc$ molecule. This establishes that the InAs surface and the two pinning In adatoms, both of which are important for enabling and controlling molecular function, also leave unperturbed the desirable characteristics of hydrogen tautomerization within the $H_2Pc$ molecule.

## CONCLUSIONS

To summarize, we find that switchable organic molecules adsorbed on a III−V semiconductor surface are only weakly coupled to the template. This is manifested by their high sensitivity to IET-induced excitations and the feasibility to reposition them with the STM tip at atomic-scale precision. Molecule−adatom complexes were assembled by STM-based manipulation to stabilize the weakly bound molecule, allowing us to trigger and probe its intrinsic bistability (here a hydrogen transfer reaction) by the tunnel current. First-principles total-energy calculations elucidate the reaction pathway and reveal that the energetics of the switching process is negligibly affected by the substrate and the stabilizing adatoms. Our results thus demonstrate that individual switchable molecules can be pinned into place on a semiconductor platform in a manner that leaves their switching characteristics undisturbed, fulfilling two prerequisites for the realization of nanoscale circuitry.

## METHODS

**Experimental Section.** The experiments were carried out with an STM operated at 5 K and in ultrahigh vacuum (UHV) at a base pressure in the lower $10^{-9}$ Pa range. We used electrochemically etched tungsten tips that were cleaned in UHV by Ne ion sputtering and electron beam heating. STM images were recorded in constant-current mode; bias voltages refer to the sample with respect to the STM tip. InAs(111)-(2×2) samples were prepared in a molecular beam epitaxy (MBE) system by desorbing the native oxide from the surface of an InAs wafer (purchased from Wafer Technology Ltd.) exposed to an arsenic flux at a substrate temperature of 753 K. To facilitate a sample transfer between the MBE and STM system under ambient conditions, the surface was capped with arsenic at a sample temperature below 273 K immediately after the preparation by MBE. The As capping layer was desorbed in the UHV chamber of the STM system by annealing at 630 K, and the sample transferred into the microscope cooled to 5 K. InAs(111)A samples prepared in this way showed the same surface features as MBE-grown and *in situ* investigated samples.[22,31−33] $H_2Pc$ (purchased from Aldrich) was purified in UHV by repeated cycles of degassing. Low coverages ($\sim 1 \times 10^{12}$ molecules per $cm^2$) of $H_2Pc$ were deposited directly into the microscope at sample temperatures < 20 K by sublimation from a tantalum crucible heated to 628 K.

**Theoretical.** Total energies and forces were calculated within the DFT-D2 method of Grimme, in which a semiempirical term representing vdW interactions is added to the standard DFT total energy.[28] This method provides a computationally efficient and numerically accurate description of the binding between the molecule and surface. For the DFT contribution we used the generalized-gradient approximation of Perdew, Burke, and Ernzerhof and projector-augmented-wave potentials as implemented in VASP.[34] The InAs surface was represented by a four-layer passivated slab, the topmost three layers of which were allowed to relax, with a vacuum region of 15 Å. The adsorption of individual $H_2Pc$ molecules was simulated using a large (6×6) supercell of the InAs(111) surface unit cell. The surface Brillouin zone for this supercell was sampled with a 2×2 $\Gamma$-centered grid, and the plane-wave cutoff was 280 eV.

*Conflict of Interest:* The authors declare no competing financial interest.

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## REFERENCES AND NOTES

1. Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
2. Heath, J. R. Molecular Electronics. *Annu. Rev. Mater. Res.* **2009**, *39*, 1–23.
3. Nitzan, A.; Ratner, M. A. Electron Transport in Molecular Wire Junctions. *Science* **2003**, *303*, 1384–1389.
4. Stroscio, J. A.; Eigler, D. M. Atomic and Molecular Manipulation in a Scanning Tunneling Microscope. *Science* **1991**, *254*, 1319–1326.
5. Avouris, Ph. Manipulation of Matter at the Atomic and Molecular Levels. *Acc. Chem. Res.* **1995**, *28*, 95–102.
6. Meyer, G.; Zöphel, S.; Rieder, K. H. Scanning Tunneling Microscopy Manipulation of Native Substrate Atoms: A New Way to Obtain Registry Information on Foreign Adsorbates. *Phys. Rev. Lett.* **1996**, *77*, 2113–2116.
7. Wolkow, R. A. Controlled Molecular Adsorption on Silicon: Laying a Foundation for Molecular Electronics. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413–441.
8. Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N., Jr. Cycloaddition Chemistry of Organic Molecules with Semiconductor Surfaces. *Acc. Chem. Res.* **2000**, *33*, 617–624.
9. Lin, R.; Galili, M.; Quaade, U. J.; Brandbyge, M.; Bjørnholm, T.; Esposti, A. D.; Biscarini, F.; Stokbro, K. Spontaneous Dissociation of a Conjugated Molecule on the Si(100) Surface. *J. Chem. Phys.* **2002**, *117*, 321–330.
10. Lastapis, M.; Martin, M.; Riedel, D.; Hellner, L.; Comtet, G.; Dujardin, G. Picometer-Scale Electronic Control of Molecular Dynamics Inside a Single Molecule. *Science* **2005**, *308*, 1000–1003.
11. Pitters, J. L.; Wolkow, R. A. Detailed Studies of Molecular Conductance Using Atomic Resolution Scanning Tunneling Microscopy. *Nano Lett.* **2006**, *6*, 390–397.
12. Nacci, C.; Lagoute, J.; Liu, X.; Fölsch, S. Conformational Switching of Single 1,5-Cyclooctadiene Molecules on Si(001) Induced by Inelastic Electron Tunneling. *Phys. Rev. B* **2008**, *77*, 121405(R)–1/4.
13. Tong, Y.; Xu, G.; Mei, W. N. Vacancy-Buckling Model for the (2×2) GaAs(111) Surface. *Phys. Rev. Lett.* **1984**, *52*, 1693–1696.
14. Day, P. N.; Wang, Z.; Pachter, R. Calculation of the Structure and Absorption Spectra of Phthalocyanines in the Gas-Phase and in Solution. *THEOCHEM* **1998**, *455*, 33–50.
15. Völker, S.; van der Waals, H. J. Laser-Induced Photochemical Isomerization of Free Base Porphyrin in an *n*-Octane Crystal at 4.2 K. *Mol. Phys.* **1976**, *32*, 1703–1718.
16. Stroscio, J. A.; Celotta, R. J. Controlling the Dynamics of a Single Atom in Lateral Atom Manipulation. *Science* **2004**, *306*, 242–247.

17. Stipe, B. C.; Rezaei, M. A.; Ho, W. Inducing and Viewing the Rotational Motion of a Single Molecule. *Science* **1998**, *279*, 1907–1909.
18. Matsumoto, C.; Kim, Y.; Okawa, T.; Sainoo, Y.; Kawai, M. Low-Temperature STM Investigation of Acetylene on Pd(1 1 1). *Surf. Sci.* **2005**, *587*, 19–24.
19. Wang, W.; Shi, X.; Jin, M.; Minot, C.; Van Hove, M. A.; Collin, J.-P.; Lin, N. Electron Stimulation of Internal Torsion of a Surface-Mounted Molecular Rotor. *ACS Nano* **2010**, *4*, 4929–4935.
20. Tierney, H. L.; Murphy, C. J.; Jewell, A. D.; Baber, A. E.; Iski, E. V.; Khodaverdian, H. Y.; McGuire, A. F.; Klebanov, N.; Sykes, E. C. H. Experimental Demonstration of a Single-Molecule Electric Motor. *Nat. Nanotechnol.* **2011**, *6*, 625–629.
21. Bartels, L.; Meyer, G.; Rieder, K. H. Basic Steps of Lateral Manipulation of Single Atoms and Diatomic Clusters with a Scanning Tunneling Microscope Tip. *Phys. Rev. Lett.* **1997**, *79*, 697–700.
22. Fölsch, S.; Yang, J.; Nacci, C.; Kanisawa, K. Atom-By-Atom Quantum State Control in Adatom Chains on a Semiconductor. *Phys. Rev. Lett.* **2009**, *103*, 096104–1/4.
23. Set point parameters of typically 6 nA and 0.1 V were used for lateral manipulation at constant current.
24. Lagoute, J.; Kanisawa, K.; Fölsch, S. Manipulation and Adsorption-Site Mapping of Single Pentacene Molecules on Cu(111). *Phys. Rev. B* **2004**, *70*, 245415–1/6.
25. Liljeroth, P.; Repp, J.; Meyer, G. Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules. *Science* **2007**, *317*, 1203–1206.
26. Sperl, A.; Kröger, J.; Berndt, R. Controlled Metalation of a Single Adsorbed Phthalocyanine. *Angew. Chem., Int. Ed.* **2011**, *50*, 5294–5297.
27. Auwärter, W.; Seufert, K.; Bischoff, F.; Ecija, D.; Vijayaraghavan, S.; Joshi, S.; Klappenberger, F.; Samudrala, N.; Barth, J. V. A Surface-Anchored Molecular Four-Level Conductance Switch Based on Single Proton Transfer. *Nat. Nanotechnol.* **2011**, *7*, 41–46.
28. Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
29. Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B* **1985**, *31*, 805–813.
30. Cortina, H.; Senent, M. L.; Smeyers, Y. G. Ab Initio Comparative Study of the Structure and Properties of $H_2$-Porphin and $H_2$-Phthalocyanine. The Electronic Absorption Spectra. *J. Phys. Chem.* **2003**, *107*, 8968–8974.
31. Yang, J.; Erwin, S. C.; Kanisawa, K.; Nacci, C.; Fölsch, S. Emergent Multistability in Assembled Nanostructures. *Nano Lett.* **2011**, *11*, 2486–2489.
32. Taguchi, A.; Kanisawa, K. Stable Reconstruction and Adsorbates of InAs(1 1 1)A Surface. *Appl. Surf. Sci.* **2006**, *252*, 5263–5266.
33. Kanisawa, K.; Butcher, M. J.; Yamaguchi, H.; Hirayama, Y. Imaging of Friedel Oscillation Patterns of Two-Dimensionally Accumulated Electrons at Epitaxially Grown InAs(111)A Surfaces. *Phys. Rev. Lett.* **2001**, *86*, 3384–3387.
34. Kresse, G.; Hafner, J. *Ab Initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561.