NANO LETTERS
Letter
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# Remotely Controlled Isomer Selective Molecular Switching

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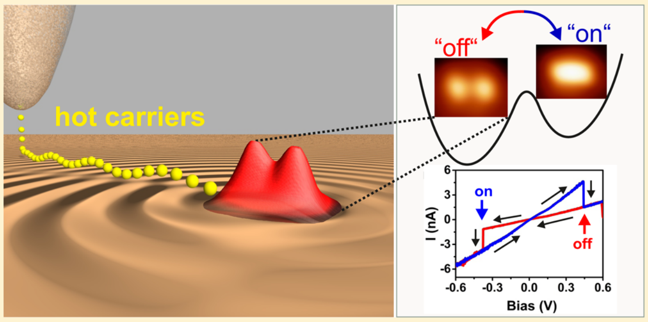
Ⓢ *Supporting Information*

**ABSTRACT:** Nonlocal addressing—the "remote control"—of molecular switches promises more efficient processing for information technology, where fast speed of switching is essential. The surface state of the (111) facets of noble metals, a confined two-dimensional electron gas, provides a medium that enables transport of signals over large distances and hence can be used to address an entire ensemble of molecules simultaneously with a single stimulus. In this study we employ this characteristic to trigger a conformational switch in anthradithiophene (ADT) molecules by injection of hot carriers from a scanning tunneling microscope (STM) tip into the surface state of Cu(111). The carriers propagate laterally and trigger the switch in molecules at distances as far as 100 nm from the tip location. The switching process is shown to be long-ranged, fully reversible, and isomer selective, discriminating between *cis* and *trans* diastereomers, enabling maximum control.



**KEYWORDS:** *Molecular switches, STM, surface state, nonlocal reactions, organic−metal interface*

Future electronic devices based in functionalities of single molecules are one route that is envisioned to revolutionize current technology.[1] Molecular switches represent such functional components that can be reversibly and repeatedly interconverted between two or more stable states. Switching of individual molecules[2−9] is by now well established; however, for rapid information processing, parallel addressing, which is effective over large distances, is desirable. One way to meet these requirements is to use surface state carriers present within the first few atomic layers of the (111) faces of noble metals which have a free electron-like character.[10−13] Hot carriers that are injected from an STM tip can travel laterally in the surface state to the molecule and induce reactions in a spatially extended area around the tip location. In this context, it has been shown that molecules can be dissociated in a certain radius around the tip, which however is an irreversible process.[14−17] For actual devices reversible processes are much more relevant. Therefore, we employ molecular switches which are "remotely" toggled by means of surface state carriers.

As a molecular switch, we use the anthradithiophene (ADT), which is a structural analog of pentacene. Individual ADT molecules adsorb on Cu(111) in a dumbbell-like appearance aligned along the close-packed directions (Figure 1a). The source material contains an equal mixture of two diastereomers, *cis* and *trans* (Figure 1b), which cannot be discriminated when imaged in constant current mode with a metallic tip (Figure 1c). Using a functionalized ADT tip, their orbital structure can be visualized enabling the distinction between the diastereomers[18,19] (Figure 1d). Local switching is conducted by positioning the tip apex on top of an individual molecule (Figure 2a,b). Sweeping the applied bias voltage from positive to negative and back reveals a hysteretic current−voltage ($I$−$V$) characteristics (Figure 2c). When ramping the voltage $V$ from positive to negative (red curve in Figure 2c), an abrupt increase in the current at negative bias indicates a change to a higher conductivity accompanied by a change in the topographic appearance of the molecule from a dumbbell-like to a rod-like structure (Figure 2a,b). When ramping the voltage in the opposite direction (blue curve in Figure 2c), the initial conformation is restored at a positive bias, apparent by a sudden drop of the current. In the following, the conformation showing the higher conductance at a fixed tip−sample distance is referred to as the "on" state, whereas the one with the lower conductance to as the "off" state. A similar switching behavior is observed for the *trans* isomer (Figure 2d,e), which however undergoes an additional rotation upon switching and for which the switching occurs at slightly higher voltages (Figure 2f) compared to the *cis* molecule (Figure 2c). The two isomers constitute voltage-controlled conductance switches whose switching characteristics differ solely in their threshold energies.

**Received:** July 28, 2015
**Revised:** November 25, 2015
**Published:** November 30, 2015

DOI: 10.1021/acs.nanolett.5b02974
*Nano Lett.* 2016, 16, 93−97

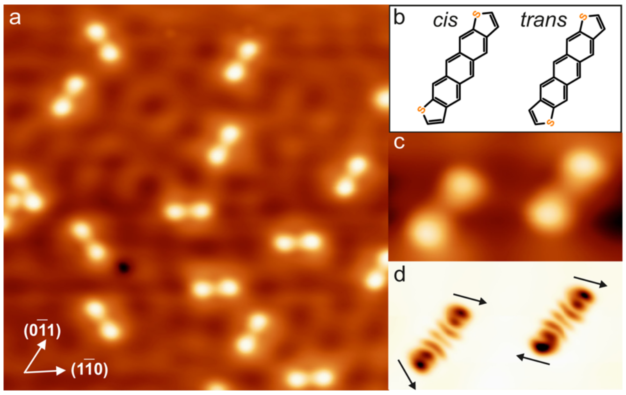


**Figure 1.** Definition of the system. (a) STM constant current image (16 nm × 16 nm, 10 mV, 100 pA) of ADT deposited on Cu(111). Molecules adsorb along the close-packed directions in a dumbbell-like configuration. (b) Chemical structures of the *cis* and *trans* ADT diastereomers. (c) Constant current images (4.5 nm × 2.4 nm, 10 mV, 100 pA) taken with a metal tip show no difference in appearance between *cis* and *trans* ADT molecules. (d) Constant height scan taken with a functionalized tip acquired at −10 mV shows the submolecular structure of the diastereomers. The patterns exhibit differences in the orientation of the outermost lobes, as indicated by the arrows, enabling discrimination between the two isomers.

The underlying switching mechanism can be attributed to a change of the molecule−substrate interaction accompanied by a conformational change of the molecule, which has been experimentally demonstrated for the ADT molecule[9] and theoretically predicted for benzene derivatives.[20] The ADT molecule possesses a bistable behavior between a strongly and a weakly bound state on a metal surface. A strong interaction arises at a small molecule−substrate separation leading to a substantial hybridization, whereas a weaker interaction is caused by an increased separation between molecule and substrate and the hybridization is reduced. In the former case the molecular orbitals are broadened and shifted in energy, while in the latter they remain mostly unaffected.

Constant height scans acquired at small bias voltages with a functionalized tip reveal that the orbital structures close to the Fermi energy ($E_{\mathrm{F}}$) resemble the LUMO (lowest unoccupied molecular orbital) in the "off" state and the HOMO (highest occupied molecular orbital) in the "on" state (see Supporting Information). As shown by Borca et al.[9] in the "off" state the molecular orbitals strongly hybridize with the Cu substrate, leading to a partial population of the LUMO accompanied by a shift of the LUMO to the Fermi energy. Conversely, in the "on" state we image the HOMO closer to $E_{\mathrm{F}}$, which corresponds more to the electronic configuration of the molecule in the gas phase, indicating a much weaker interaction.

To switch the molecule, which is achieved by the injection of holes, the LUMO is depopulated. This leads to a shift of the LUMO to higher energies restoring the HOMO−LUMO gap around $E_{\mathrm{F}}$. The molecule is switched back to its pristine configuration by injection of charge carriers at a voltage of about 0.4 V.

The necessity for charge carriers of different polarities to initialize the switching and back-switching gives rise to the directionality of the process.

The nonlocal switching process is induced by hot carriers injected from the STM tip into the Cu substrate. Applying a negative voltage pulse (pulse position indicated by the yellow

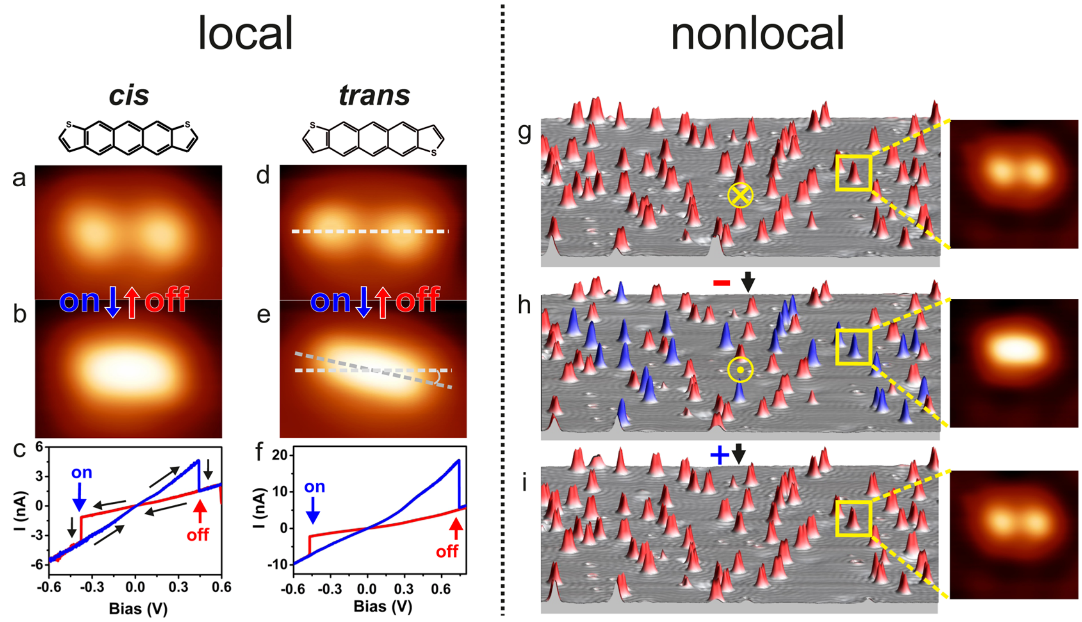


**Figure 2.** Local and Nonlocal switching: (a−f) local switching: (a, b, d, e) constant current scans (3 nm × 2.2 nm, 0.1 nA, 0.1 V) of the nonswitched (a, d) and switched (b, e) structures of the *cis* (a, b) and *trans* (d, e) isomers. (c, f) $I$−$V$ curves acquired on the *cis* (c) and *trans* (f) isomers. Switching from the "off" to the "on" state (blue arrow) occurs at negative bias concomitant with a change from a lower to a higher conductivity. Switching from "on" to "off" (red arrow) is triggered at positive voltages, indicated by an abrupt change from a high conducting to a low conducting state (at same tip−sample distance). (g−i) Nonlocal switching: (g) STM constant current image (80 nm × 80 nm, 0.1 nA and 0.1 V) showing all molecules in the "off" state. Applying a pulse (yellow cross) of −0.4 V for 16 s ($I = 2.2\ \mu$A) directly into the bare copper substrate enables switching of the molecules to the "on" state. (h) shows a topography recorded after applying the pulse; switched molecules are shown in blue. After applying a pulse with a positive polarity (0.4 V, 1.7 $\mu$A, yellow circle), all the molecules are switched back from the "on" to the "off" state (i). Panels on the right (3.5 nm × 3.5 nm, 0.1 nA, 0.1 V) show close-ups of the molecules in the "off" and "on" state.

DOI: 10.1021/acs.nanolett.5b02974
*Nano Lett.* 2016, 16, 93−97

cross in Figure 2g) activates switching of about 50% of the molecules to their "on" state within an area of 80 nm × 80 nm around the pulse position (Figure 2h, blue coded molecules). Applying the same pulse with opposite voltage polarity switches all molecules back to the "off" state (Figure 2i). These characteristics, switching from "off" to "on" by a negative voltage pulse and switching back from "on" to "off" by a positive pulse, demonstrate a direct analogy to the local switching process. Addressing the molecule locally and nonlocally results in the same "off" and "on" state, respectively (compare Figure 2a,b with insets in Figure 2g,h).

From isomer-resolving images obtained with a functionalized tip before (Figure 3a–c) and after (Figure 3d–f) applying a voltage pulse, we can deduce that the nonlocal switching process only addresses *cis* isomers, whereas *trans* isomers remain in their initial configuration. This is in contrast to the locally initiated switching process where both isomers were switchable. Therefore, the nonlocal process is found to be isomer selective and explains why only about 50% of the molecules can be addressed (Figure 2h).

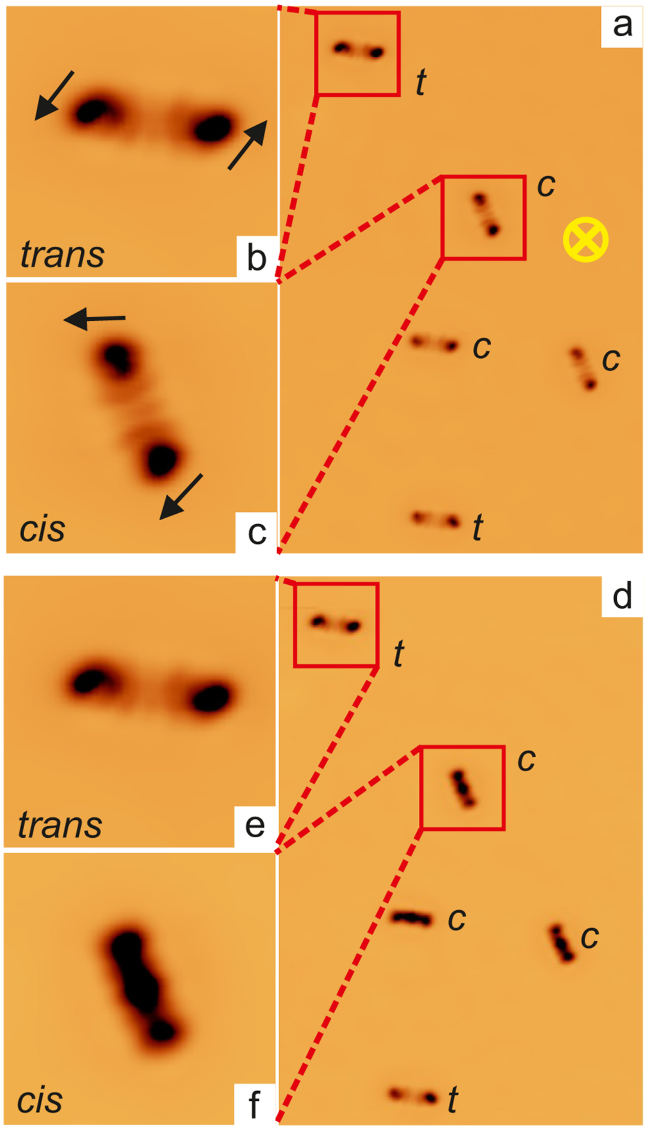


**Figure 3.** Isomer selection by means of surface state carrier-mediated switching. (a) Constant height scan (12 nm × 18 nm) acquired at 10 mV with a functionalized tip enables the distinction between the *cis* (c) and the *trans* (t) isomers; all molecules are in the "off" state. The yellow cross represents the position where a voltage pulse has been applied with −0.4 V ($I = 0.3\ \mu$A). (b, c) Close-up images (2.1 nm × 2.1 nm) of *trans* and *cis* isomers. (d) Constant height scan after pulsing reveals that only the *cis* isomers have switched. (e, f) Close-ups of the orbital structures of the *trans* and *cis* isomers after pulsing.

Exploring the nonlocal switching process for different negative bias values within an area of 80 nm × 80 nm (lower panel of Figure 4a) reveals that the switching probability from the "off" to the "on" state increases steadily from −0.2 to −0.5 V and then almost vanishes at −1 V. From this we can conclude that to trigger the switching process, a threshold energy of the charge carriers is required. Furthermore, the drop of the switching probability for more negative voltages indicates that the triggering is most effective for charge carriers in a specific energy window.[21,22] Thus, switching by means of an electric field effect can be ruled out, in which case the switching probability would be expected to increase with increasing bias instead of the observed decrease for bias voltages beyond −0.5 V. The voltage dependence for positive polarities (Figure 4a) shows a drastic increase of the probability for remote switching from the "on" to the "off" state exceeding a bias voltage of 0.35 V. Beyond this threshold voltage, the probability to switch the molecules back into their initial conformation is about 100%, indicating a highly efficient "back"-switching process.

All these characteristics strongly suggest that the remote switching is mediated by the surface state of the Cu(111) surface. The surface state has an onset energy of −0.44 eV,[10,12] which coincides with the voltage at which the maximum switching probability occurs at negative voltages (Figure 4a, upper panel). Holes propagating in the surface state can only possess energies up to the onset energy. Therefore, switching is only enabled if the threshold voltage for the switching process lies within the energy range of the surface state. Since slightly higher energies are required for the *trans* species, which lie beyond the onset of the surface state (Figure 2f), the switching process cannot be induced by charge carriers propagated through the surface state. To trigger the switching/back-switching process via the surface state, the energy window where the surface state is present must coincide with the excitation energy required to switch the molecule.

The decrease in the switching probability at negative bias voltages beyond −0.5 V is due to increased tunneling into the bulk states. The lower edge of the directional band gap in which the surface state exists is at −0.7 eV.[12] As charge carriers with all energies between the applied voltage and the Fermi energy contribute to the current, an increased tunneling of charge carriers from the tip into the bulk state at more negative bias voltages leads to a reduced switching probability.

Further evidence for the mechanism involving the surface state is provided by experiments performed near monatomic steps, which constitute a potential barrier for the surface state electrons,[23] but would not effect, e.g., the distance dependence expected for a mechanism due to electric field or charge carriers propagating in bulk states. Images acquired after applying a voltage pulse on one side of a step edge clearly show that the number of switched molecules is substantially larger on the same terrace on which the pulse has been applied than on an adjacent terrace, where the switching probability is significantly reduced (see Supporting Information). Hence, in the case of surface state—mediated switching the hot carriers that are injected from the tip into the substrate are "transported" by the surface state carriers to the molecules where they interact with the molecule thereby inducing the switch. In contrast, for local excitations the charge carriers from the tip directly trigger the molecule.

Most importantly, the switching characteristics that have been explored locally remain the same for the nonlocal excitation—only the way of addressing differs. If at all, the surface state plays only a negligible role for the local switching, as when triggering a molecule locally the surrounding molecules are not affected.

To extract quantitative information about the spatial dependence of the switching probability, we have studied the process at negative bias polarity at a voltage of −0.4 V for three different currents as a function of the radial distance with a bin size of 10 nm. The distance dependence is characterized by a saturation regime in the immediate vicinity of the pulse position, where all *cis* isomers are switched (Figure 4b, gray shaded area). For larger distances the probability decays in a characteristic manner, which is governed by a geometric $1/r$ behavior as well as by the coherence length $\lambda$ of the charge carriers. The $1/r$ dependence is distinctive for the decay of quasiparticles in a two-dimensional gas, in contrast to a bulk dominated process where the decay is governed by a $1/r^2$ behavior. The best fit is obtained for a $1/r$ dependence and treating the coherence length as a fit parameter yields about $\lambda$ = 23 nm at −0.4 V. In addition, the switching probability is reduced for a lower current (Figure 4b) and shorter injection times of the hot carriers (see Supporting Information).

The efficiency for surface state—mediated switching from "on" to "off" and vice versa is not identical. This asymmetry arises due to the different coherence lengths $\lambda$ for holes and electrons within the surface state. The coherence length sets the distance over which the charge carriers propagate without scattering while retaining their energy. The coherence length is directly related to the lifetime of the charge carriers $\tau$ and their group velocity $v_g$. It has been shown from calculations that the lifetime of holes is reduced compared to that of electrons due to interband scattering.[24−26] For voltages of 0.3 and −0.3 V, the lifetimes amount to 113 and 62 fs[25] with corresponding group velocities of $0.83 \times 10^6$ and $0.36 \times 10^6$ m/s, resulting in coherence lengths $\lambda$ of about 93 and 22 nm, respectively. Hence, surface state-mediated switching at positive polarity is substantially more efficient compared to the process at negative polarity.

In conclusion, we have demonstrated a surface state-mediated switching process that is effective over distances on the order of 100 nm. The local switching characteristics of single molecules directly translate into the nonlocal switching process. The interplay of the molecule's electronic states and the surface state of Cu(111) enables remote control, reversibility, directionality, and isomer selectivity at the same time. These features allow a precise control of the system and provide a new pathway toward rapid write/delete processes for future device elements.

**Methods.** *Sample Preparation.* Experiments were conducted in a home-built low-temperature scanning tunneling microscope operating in ultrahigh vacuum and at a base temperature of about 7 K. The Cu(111) single crystal was cleaned by repeated cycles of $Ar^+$ sputtering and annealing up to 800 K. ADT molecules were thermally evaporated using a quartz crucible at a temperature of 505−510 K for 15−18 min with the Cu substrate cooled down to 210 K. The crystalline powder was used as obtained from Sigma-Aldrich. The sample was transferred *in situ* into the STM chamber.

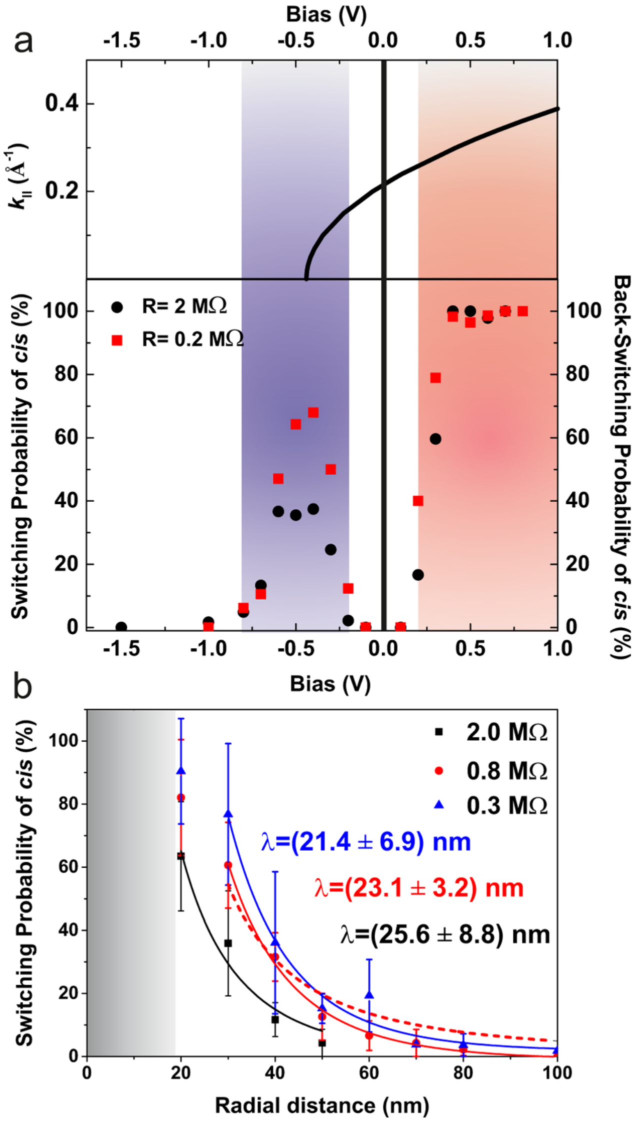


**Figure 4.** Bias dependence of the switching probability. (a) Upper panel: The dispersion of the surface state of Cu(111) is shown for comparison, with an onset energy of −0.4 V and an effective mass $m^* = 0.4m_e$. Lower panel: Probability of switching and back-switching the *cis* isomers remotely as a function of bias voltage, within an area of 80 nm × 80 nm. Data have been recorded with two different tunnel resistances, $R$ = 2 and 0.2 MΩ. The switching process is initiated at negative bias (blue shaded) and the back-switching at positive bias (red shaded). (b) Radial decay of the switching probability measured at a voltage of −0.4 V and different currents. The tail of the decay curve was fitted by an exponential function $1/r \exp(-r/\lambda)$, where $r$ denotes the radial distance and $\lambda$ the decay length. The region in close proximity to the location where the pulse was applied was ignored in the fit due to saturation. Red dotted line represents a decay governed by a $1/r^2$ dependence, which would be expected for a bulk-dependent process.

For determining the radial decay and switching probability, the pulses were applied in the middle of the scan frame. The tunneling set-point before deactivating the feedback loop was set to 1 nA and 100 mV. The pulse was subsequently applied by setting a constant voltage, and the tip was approached 200−300 pm toward the sample. The resulting current was on the order of 0.1 and 3 $\mu$A, respectively, and the pulse was maintained for 16 s. Scans were taken before and after the pulse in constant current mode with tunneling parameters of 100 mV and 100 pA.

*I*−*V* measurements acquired on top of the molecule were recorded as the sample voltage was ramped between 0.6 and −0.6 V and back for the *cis* and 0.7 and −0.6 V within 10 s for the *trans* molecule with a set point of 100 mV and 100 pA. Bias voltages are applied to the sample, with the tip at virtual ground.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02974.

> Orbital structure of the nonswitched and switched state and switching mechanism, ADT adsorption on Cu(111), switching at step edges, influence of pulse length and current on probability of remote switching, efficiency of remote back-switching process (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank A. Arnau and M. Ternes for discussions on the switching mechanism. We acknowledge funding by the Emmy-Noether-Program of the Deutsche Forschungsgemeinschaft, the SFB 767, and the Baden-Württemberg Stiftung.

## ■ REFERENCES

(1) Lörtscher, E. *Nat. Nanotechnol.* **2013**, *8*, 381−384.
(2) Liljeroth, P.; Repp, J.; Meyer, G. *Science* **2007**, *317*, 1203−1206.
(3) Wu, S. W.; Ogawa, N.; Nazin, G. V.; Ho, W. *J. Phys. Chem. C* **2008**, *112*, 5241−5244.
(4) Wu, S. W.; Ho, W. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 085444.
(5) Swart, I.; Sonnleitner, T.; Repp, J. *Nano Lett.* **2011**, *11*, 1580−1584.
(6) Weigelt, S.; Busse, C.; Petersen, L.; Rauls, E.; Hammer, B.; Gothelf, K. V.; Besenbacher, F.; Linderoth, T. R. *Nat. Mater.* **2006**, *5*, 112−117.
(7) Moresco, F.; Meyer, G.; Tang, H.; Joachim, C. *J. Electron Spectrosc. Relat. Phenom.* **2003**, *129*, 149−155.
(8) Mohn, F.; Repp, J.; Gross, L.; Meyer, G.; Dyer, M. S.; Persson, M. *Phys. Rev. Lett.* **2010**, *105*, 266102.
(9) Borca, B.; Schendel, V.; Petuya, R.; Pentegov, I.; Michnowicz, T.; Kraft, U.; Klauk, H.; Arnau, A.; Wahl, P.; Schlickum, U.; Kern, K. *ACS Nano* **2015**, DOI: 10.1021/ascnano.5b06000.
(10) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Nature* **1993**, *363*, 524−527.
(11) Manoharan, H. C.; Lutz, C. P.; Eigler, D. M. *Nature* **2000**, *403*, 512−515.
(12) Hörmandinger, G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 13897−13905.
(13) MacLeod, J. M.; Lipton-Duffin, J.; Fu, C.; Rosei, F. *ACS Nano* **2009**, *3*, 3347−3351.
(14) Maksymovych, P.; Dougherty, D.; Zhu, X.-Y.; Yates, J. *Phys. Rev. Lett.* **2007**, *99*, 016101.
(15) Chen, L.; Li, H.; Wee, A. T. S. *ACS Nano* **2009**, *3*, 3684−3690.
(16) Ladenthin, J. N.; Grill, L.; Gawinkowski, S.; Liu, S.; Waluk, J.; Kumagai, T. *ACS Nano* **2015**, *9*, 7287−7295.
(17) Sloan, P. A.; Sakulsermsuk, S.; Palmer, R. E. *Phys. Rev. Lett.* **2010**, *105*, 048301.
(18) Gross, L.; Moll, N.; Mohn, F.; Curioni, A.; Meyer, G.; Hanke, F.; Persson, M. *Phys. Rev. Lett.* **2011**, *107*, 086101.
(19) Repp, J.; Meyer, G.; Stojković, S. M.; Gourdon, A.; Joachim, C. *Phys. Rev. Lett.* **2005**, *94*, 026803.
(20) Liu, W.; Filimonov, S. N.; Carrasco, J.; Tkatchenko, A. *Nat. Commun.* **2013**, *4*, 2569.
(21) Zhu, X. *Annu. Rev. Phys. Chem.* **2002**, *53*, 221−247.
(22) Gadzuk, J. W. *Phys. Rev. Lett.* **1996**, *76*, 4234−4237.
(23) Avouris, P.; Lyo, I.-W.; Molinàs-Mata, P. *Chem. Phys. Lett.* **1995**, *240*, 423−428.
(24) Kliewer, J.; Berndt, R.; Chulkov, E. V.; Silkin, V. M.; Echenique, P. M.; Crampin, S. *Science* **2000**, *288*, 1399−1402.
(25) Echenique, P. M.; Osma, J.; Machado, M.; Silkin, V. M.; Chulkov, E. V.; Pitarke, J. M. *Prog. Surf. Sci.* **2001**, *67*, 271−283.
(26) Echenique, P. M.; Berndt, R.; Chulkov, E. V.; Fauster, T.; Goldmann, A.; Höfer, U. *Surf. Sci. Rep.* **2004**, *52*, 219−317.

# Supporting Information for: Remotely controlled isomer selective molecular switching

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## 1 Orbital structure of the non-switched and switched state and switching mechanism

STM constant current images of the non-switched ("off") and switched ("on") state show a dumbbell-like and rod-like topographic appearance (Fig. S1, top row). Imaging both states with an ADT-functionalized tip at small bias voltages (close to the Fermi energy $E_F$) in constant height mode reveals the orbital structure (Fig. S1, middle row). The molecular orbitals for the LUMO and HOMO were calculated in the gas phase by means of Hückel calculations and show a clear resemblance of the orbital structures obtained by the constant height scans. From this we conclude that in the "off" state the LUMO is located at $E_F$ and in the "on" state the HOMO is located at $E_F$. The appearance of the LUMO at $E_F$ suggests a strong hybridization with the metallic substrate accompanied by a charge transfer from the metal to the molecule. Upon switching to the "on" state, which is achieved by the injection of holes, the LUMO is depopulated and consequently is shifted to higher energies. Switching back to the "off" state is triggered by electrons resulting in the population of the LUMO.

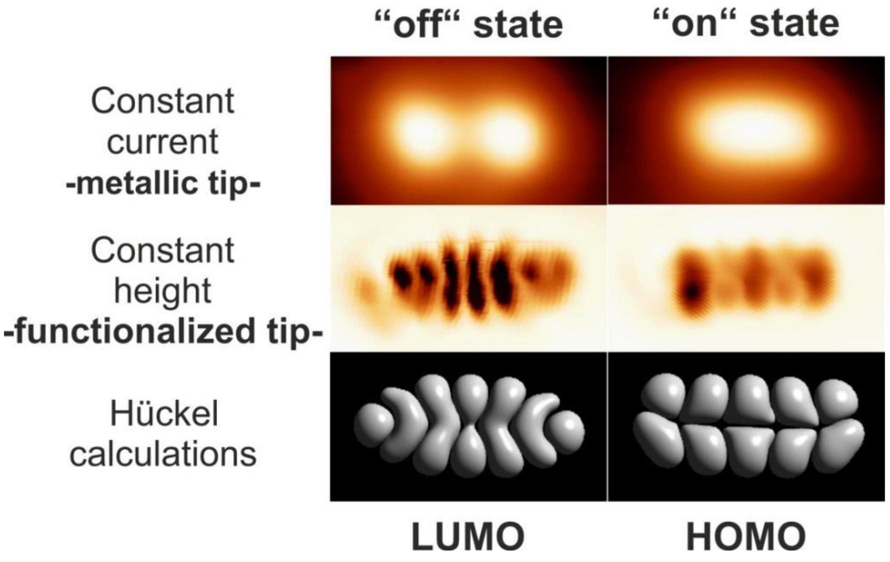

**Figure S1: Orbital structure of the "on" and "off" state: upper row**, STM constant current images (tunnel parameters: 0.1 V, 0.1 nA) of a *cis* ADT isomer in the "off" and "on" state. **middle row**, Constant height images acquired at 5 mV with a functionalized tip showing the molecular orbital structure of the ADT molecule in both states. **bottom row**, LUMO and HOMO calculated with the Hückel method for the free molecule.

## 2 ADT adsorption on Cu(111)

To obtain information about the switching, an understanding of the molecule's registry to the underlying Cu(111) substrate is required. Fig. S2a-c depicts a series of scans, where switching of a *cis* and a *trans* isomer was subsequently initiated. In panel (a), a *cis* (right) and a *trans* (left) molecule are in their non-switched configuration, aligned along the $[\bar{1}01]$-axis. In panel (b), the *cis* isomer is switched, and in panel (c) the *trans* molecule is switched. As indicated in (c), the switching of the *trans* isomer is accompanied by a rotation of about 11° away from the close-packed Cu rows. This rotation is a strong indication for different interactions of the molecule with the metal giving rise to two different adsorption conformations. As depicted in Fig. S2d-f, a simple sphere model for the substrate is used to illustrate the adsorption configuration of single *cis* and *trans* ADT isomers on Cu(111) in their switched and non-switched configurations. The approach that is taken is guided by the assumption that those moieties of the molecule which dominate the bonding to the substrate in the respective configuration, possess similar adsorption sites for both isomers.

In the "off" state, the center of the molecules (*cis* and *trans*) resides atop a hollow side of the substrate (d). This configuration is similar to the registry of pentacene on Cu(111), as reported by

Lagoute *et al.* (*Phys. Rev. B*, **2004**, 70 (245415)). As seen from the model, in this case the S atoms do not reside in the same sites of the substrate for both isomer species. For the *cis* isomer, both S atoms sit on top of a Cu atom, whereas for the *trans* isomer, one S atom is located on top of a Cu atom and the other one occupies a hollow site. Upon switching the *cis* isomer (e), the molecule remains aligned along the close-packed direction of the substrate. However, when switching the *trans* isomer (f) the rotation of the trans molecule by an angle of 11° can only be explained by assuming that the S atoms are required to reside on a top position of the substrate, which is similar to the registry of the *cis* species. Hence, from this adsorption scenario one can conclude that in the non-switched state the π-electron system of the backbone dominates the bonding to the substrate, whereas in the switched state the S containing groups dictate the registry to Cu(111). Consequently, as for the switched state the S atoms are required to reside in the same site on Cu(111) for both isomers, the rotation by 11° for the *trans* molecule is explained.

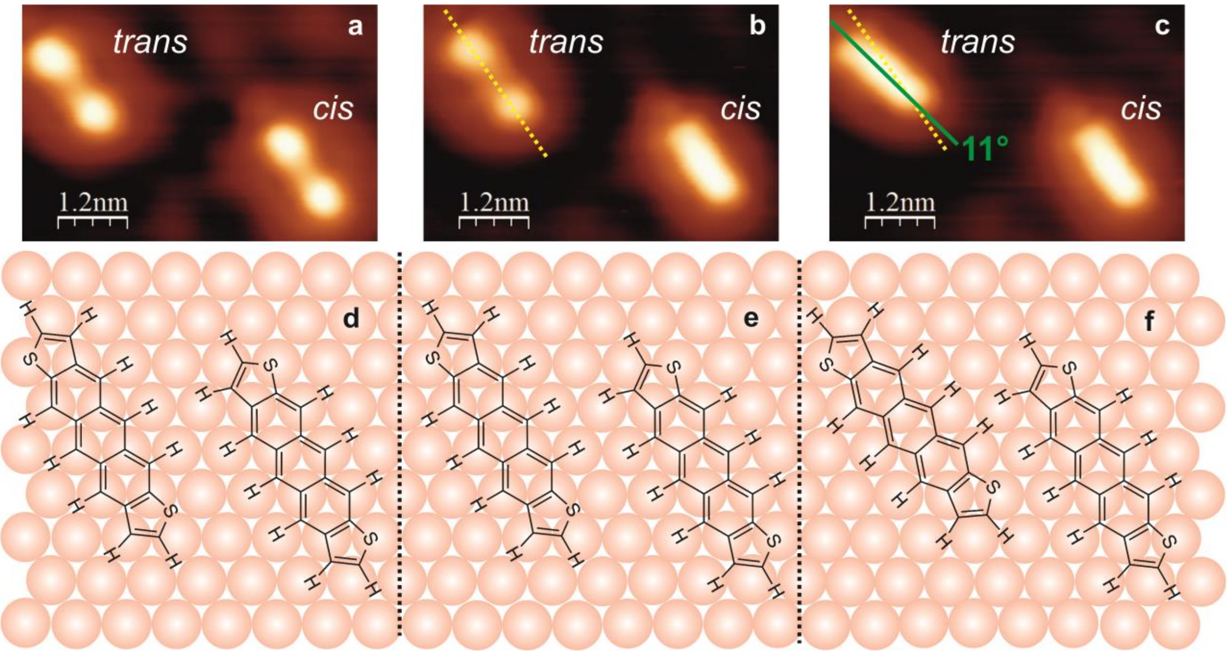

**Figure S2: ADT adsorption on Cu(111):** a, Constant current image (tunnel parameters: 0.1 V, 0.1 nA) of a *cis* (right) and a *trans* (left) isomer. b, Upon switching, the *cis* isomer remains aligned along the close-packed rows of Cu(111). c, Conversely, the *trans* ADT isomer tilts by an angle of 11° upon switching (c). d, Sphere model of the Cu(111) surface. The orange spheres indicate the top layer of the substrate. In the "off" state, the centers of both ADT molecules are located on top of a hollow site of the substrate aligned along the $[\bar{1}01]$-axis. e, Upon switching, the *cis* isomer remains aligned along the close-packed rows of the Cu substrate, whereas the switching of the *trans* species is accompanied by a rotation of about 11°. This leads to a registry where both S atoms reside in a hollow site similar to the registry of the *cis* species.

## 3 Switching at step edges

To further support our interpretation of the remote switching mechanism via surface state electrons, we have performed experiments near step edges. Surface state electrons are strongly scattered at step edges, therefore it is expected that the remote switching is suppressed across them. As depicted in Fig. S3a, a pulse was applied at the upper terraces near a step edge. Subsequent scanning shows that molecules are only switched on the upper terrace. In the opposite case, when applying the pulse at the lower terrace, molecules are preferentially switched on the lower terrace, as depicted in Fig. S3b.

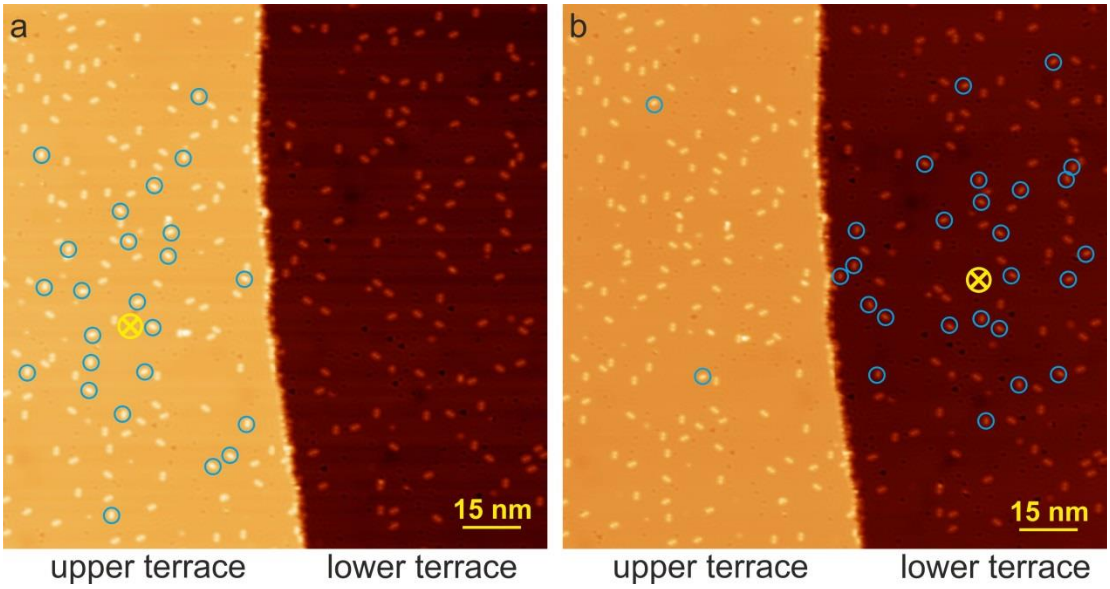

**Figure S3: Switching in the vicinity of a step edge:** a, A pulse of -0.4 V (16 s, *I*=1.5 µA) was applied at the *upper* terrace in the vicinity of a step edge. The location where the pulse was applied is indicated by the yellow cross. Switching occurs exclusively on the upper terrace. Switched molecules are encircled in blue. b, When injecting hot carriers in the *lower* terrace (yellow cross), molecules primarily get switched on the lower plateau. Pulsing parameters: -0.4 V, *I*=1.5 µA, 16 s. Constant current scans (150 x 150 nm) were acquired with 0.1 V and 0.1 nA.

## 4 Influence of pulse length and current on probability of remote switching

As discussed in section 1 of the Supporting Information, the switching mechanism is related to a depopulation of the LUMO. Therefore, the switching probability depends substantially on the number of injected charge carriers, which is determined by the pulse length and the applied current. Fig. S4a shows a constant current scan, where a pulse of 16 sec and *I*=0.54 µA has been applied in the middle of the scan frame (indicated by the yellow cross). In Fig. S4b, a pulse of roughly double the time and three times the current was applied (33 sec, *I*=1.8 µA), resulting in a significantly increased area in which molecules are switched.

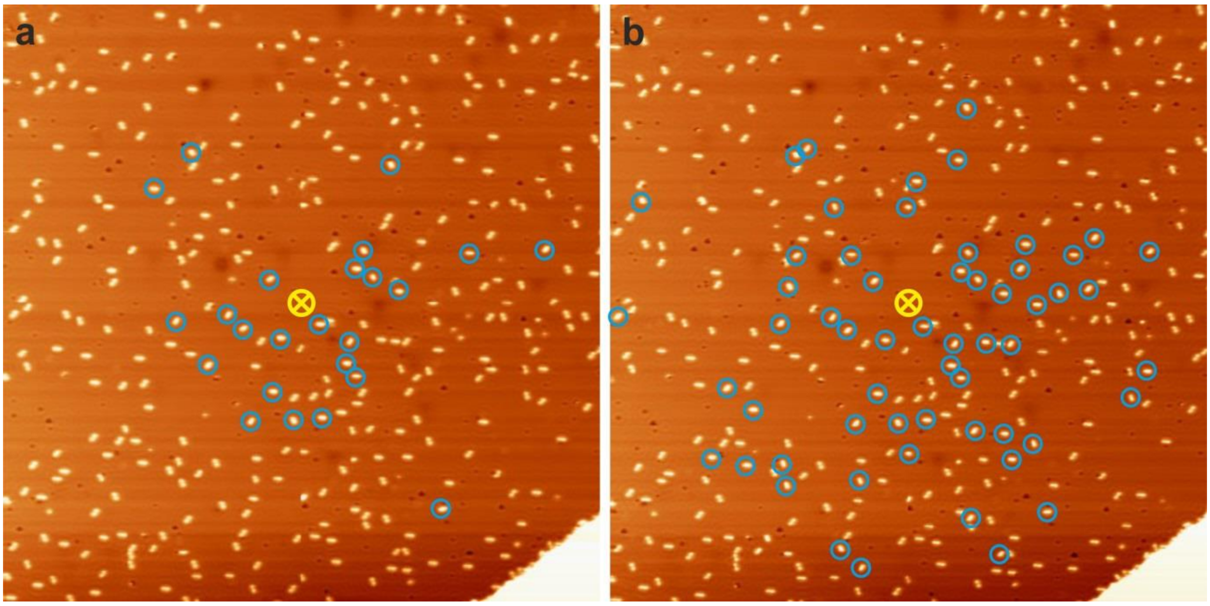

**Figure S4: Switching with different pulse length and current:** a, A pulse of -0.4 V (*I*=0.54 µA) was applied for 16 sec. b, A pulse of -0.4 V (*I*=1.8 µA) was applied for 33 sec. Switched molecules are encircled in blue and the location of hot carrier injection is labeled with a yellow cross. STM scans (150 nm x 150 nm) have been taken in constant current mode with tunnel parameters of 0.1 V and 0.1 nA.

## 5 Efficiency of remote back-switching process

To demonstrate the different efficiencies for the switching and back-switching processes, we show in Fig. S5a, b a constant current image (100 nm x 100 nm) where a negative current pulse was applied in the middle of the scan frame (pulse parameters: -0.4 V, 1.2 µA, 30 sec). The switched molecules are encircled in blue (panel b). The back-switching process was conducted with only 1/6 of the current that was used for the switching process (0.4 V, 200 nA, 30 sec), where almost all molecules were back-switched (Fig. S5c). This demonstrates the high effectiveness of surface state electrons compared to surface state holes, as the same area can be addressed with a substantially smaller current pulse.

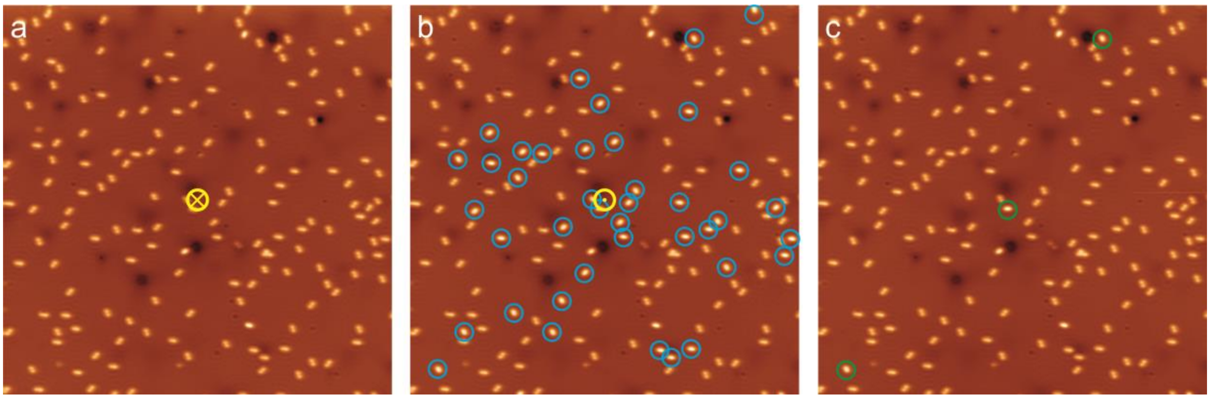

**Figure S5: Efficiency of remote back-switching process** a, A pulse of -0.4 V (*I*=1.2 µA) was applied for 30 sec within an area of 100 nm x 100 nm. b, Switched molecules are encircled in blue. To back-switch the molecules a pulse with only 1/6 of the current, that was used for the switching process, was applied (U=0.4V, *I*=200 nA, 30 sec). c, Almost all molecules were switched back to their initial configuration. Those molecules that remained switched are encircled in green. Constant current scans were acquired with 0.1 V and 0.1 nA.