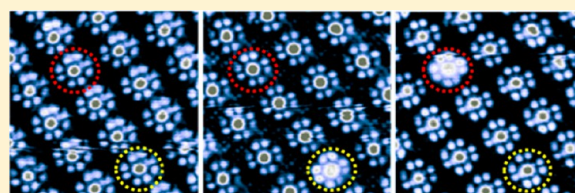


Reversible Switching of a Single-Dipole Molecule Imbedded in Two-Dimensional Hydrogen-Bonded Binary Molecular Networks

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S Supporting Information

ABSTRACT: Understanding the single-molecule switching mechanism in densely packed, rationally designed, and highly organized nanostructures is crucial for practical applications such as high-density data storage devices. In this article, we report an in situ low-temperature scanning tunneling microscopy (LT-STM) investigation of reversible switching of a single-dipole molecule (chloroaluminium phthalocyanine, ClAlPc) imbedded in two-dimensional (2D) hydrogen-bonded binary molecular networks on graphite. The single-molecule switching is highly localized and reversible and leaves the neighboring molecular network unaffected. The switching direction can be controlled by the polarity of the voltage pulse applied to the STM tip. On the basis of experimental results and theoretical calculations, the reversible switching is proposed to be caused by the “shuttling” of the Cl atom between two sides of the ClAlPc molecular plane.



1. INTRODUCTION

The concept of using single molecules as key building blocks for logic gates, diodes, transistors, and switches to perform the basis function of digital electronic devices was well established over the past decades.^{1–5} To achieve this it is crucial to control the electronic, magnetic, or optical properties of individual functional molecules on surfaces. Molecular switches, which can be interconverted between bistable^{6–31} or even multiple states^{32,33} by external stimuli like electric field,^{7,21} light,^{27,34} electrons,^{6,8–14,23,28,30,32,33} and temperature,³⁵ have attracted much attention. Single molecular switches can be operated by a variety of ways, for instance, conformational changes,^{7–12,19–22,24–27,32–36} examples are *cis*–*trans* isomerization of the azobenzene molecules,^{9,10,21,24,27,34,36} mechanically interlocked switches formed by catenanes and rotaxanes,²² flip flop of dipole molecules,²⁰ atom tunneling through a molecule plane,¹¹ and hydrogen tautomerization reaction in naphthalocyanine;^{8,33} other ways like controlling the charge states of single atoms or molecules,^{13–16,18,37} switching the chirality of the adsorbate on surfaces,^{28,35,38} manipulating the spin state of spin cross-over (SCO) complexes,^{29,30} modifying bond formation,¹⁷ and controlling the orbital sequence of a negatively charged copper(II)phthalocyanine molecule³¹ have also been realized.

Dipolar phthalocyanine molecules, which have been of great interest for controlling surface or interface properties in molecular electronic devices and tuning the energy level alignment at the interface for molecule-based devices,^{39–42} represent a very interesting example of a molecular switch. Its operating mechanism is based on a reversible dipole switching.

As the nonplanar dipolar molecule possesses an out-of-plane electric dipole moment it adopts two distinct configurations on a surface, namely, dipole up and dipole down. Reversible switching of a single-dipole molecule of chloroaluminium phthalocyanine (ClAlPc) in an ordered molecular array has been recently demonstrated.⁴³

However, most of the studies of these molecular switches were performed either individually or in a self-assembled single-component monolayer. Incorporation of these molecular switches into more complex and rationally designed nanoarchitectures is needed for practical applications. To achieve this, single-molecular switches should be interconnected with other molecules via intermolecular interactions to form desired long-range ordered nanostructures over a macroscopic area; at the same time, the molecular functionality responsible for molecular switching must remain intact during the self-assembly process. Self-assembly of binary molecular systems on an inert graphite surface via formation of multiple intermolecular hydrogen bonding represents a versatile approach to fabricating ordered and robust molecular nanostructure arrays.^{44–46} By varying the binary molecular ratio, the interdipole distance of the molecular dipole dot arrays and hence the dipole densities can be easily tuned with atomic precision.⁴⁷ Moreover, formation of multiple intermolecular hydrogen bonding can further enhance the structure stability of these molecular nanostructure arrays during device operation.

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By placing the STM tip above a molecule, the energy of inelastically tunneled electrons can be transferred into the molecule, which can induce excitation of molecular vibrations as well as various dynamical processes at surfaces, such as rotation or translation of molecules,^{48,49} molecular desorption,⁵⁰ dissociation,⁵¹ or bond breaking.⁵² Here, we use in situ low-temperature scanning tunneling microscopy (LT-STM) to demonstrate for the first time reversible switching of single-dipole molecule CIAIPc imbedded in two-dimensional (2D) hydrogen-bonded binary molecular networks formed by coassembly of CIAIPc and perfluoropentacene (PFP) on graphite. Molecular structures of these two molecules are shown in Figure 1. By controlling the polarity of the pulse

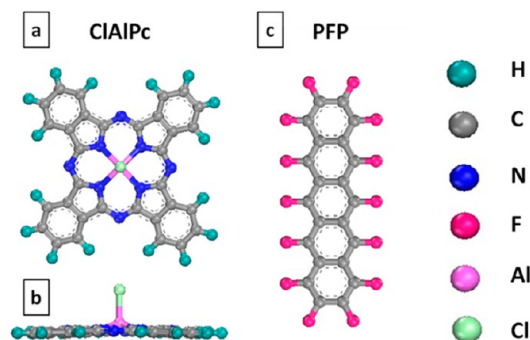


Figure 1. (a) Top view and (b) side view of CIAIPc molecular structure. (c) Molecular structure of PFP molecule.

voltage applied to the STM tip, CIAIPc molecules can be switched between dipole-up and dipole-down configurations without affecting the neighboring molecules. As corroborated by density functional theory (DFT) calculations, we propose that the switching is achieved by “shuttling” the Cl atom between two sides of the CIAIPc molecular plane.

2. METHODS AND THEORETICAL CALCULATIONS

Experiments were carried out in a multichamber ultra-high-vacuum (UHV) system housing an Omicron LT-STM with a base pressure of about 10^{-10} mbar.⁵³ Freshly cleaved highly ordered pyrolytic graphite

(HOPG) substrate was thoroughly degassed at around 800 K overnight before molecular deposition. CIAIPc and PFP molecules were thermally evaporated from separate Knudsen cells at 560 and 390 K onto HOPG kept at room temperature. Deposition rate was monitored by a quartz microbalance (QCM) and further calibrated by counting the adsorbed molecule coverage in large-scale STM images. Prior to deposition, molecular sources were purified by gradient vacuum sublimation. All STM images were recorded in constant-current mode with a chemically etched tungsten tip at liquid nitrogen temperature (77 K). All single-dipole molecule switching experiments were performed at 77 K with the bias voltage applied to the tip.

Theoretical calculations were performed using the Vienna ab initio Simulation Package (VASP) code based on DFT. Exchange-correlation effects were modeled using the Perdew–Burke–Ernzerhof (PBE) functional, and the projector-augmented wave (PAW) method was employed.^{54–58} When calculating the properties of a free molecule, a $20 \text{ \AA} \times 20 \text{ \AA} \times 15 \text{ \AA}$ supercell was used. The Brillouin zone is sampled by a $2 \times 2 \times 2$ Monkhorst–Pack k -point mesh. Atomic positions are relaxed until the total energy converged to 0.1 meV.

3. RESULTS AND DISCUSSION

Directional and selective intermolecular interactions, such as hydrogen bonding, have been widely used to fabricate single-component, binary, or multicomponent supramolecular assemblies on surfaces with a high degree of controllability and tunability.^{44–47,53,59–61} By carefully selecting the molecular building blocks, the molecules with desired functionalities can be isolated and immobilized in a repetitive and spatially ordered manner. Support surfaces also play a critical role during the single-molecule switching operation. For example, the strong interfacial coupling between the metal surface electrons and the molecule may cause the intrinsic switching properties of the molecules to disappear, or in other cases the lateral electron transport at metal surfaces may lead to nonlocal effects.⁶² To minimize the substrate effect, atomically flat and chemically inert substrates, such as graphite, are preferred for the single-molecule switching study. As shown in Figure 2a, a highly ordered hexagonal binary network was formed after coadsorption of PFP and CIAIPc with a PFP:CIAIPc ratio of 1:2 on HOPG followed by annealing at 370 K for 40 min. This hexagonal molecular array is proposed to be stabilized via

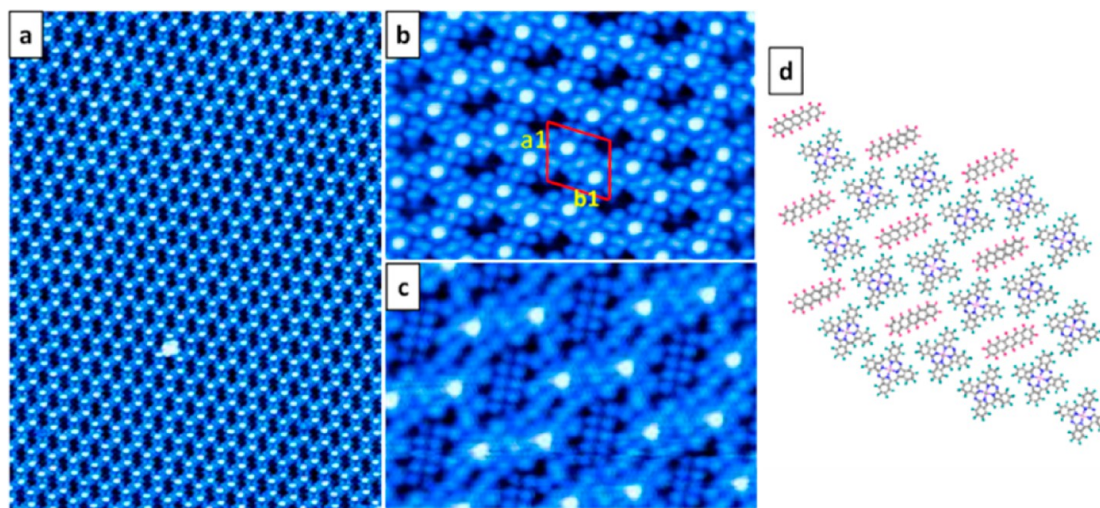


Figure 2. (a) STM image ($45 \times 60 \text{ nm}^2$, $V_{\text{tip}} = 2.2 \text{ V}$) of a long-range-ordered hexagonal binary molecular network formed by PFP and CIAIPc with a molecular ratio of 1:2 on HOPG. Corresponding high-resolution STM images of the hexagonal structure: (b) ($15 \times 10 \text{ nm}^2$, $V_{\text{tip}} = 1.9 \text{ V}$) and (c) ($9 \times 6 \text{ nm}^2$, $V_{\text{tip}} = 2.5 \text{ V}$). (d) Schematic packing structure for the hexagonal network.

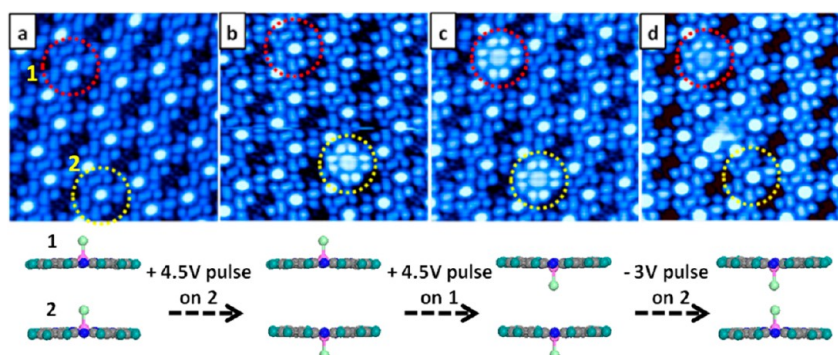


Figure 3. (a–d) Sequential STM images showing the reversible switching between the Cl-up and the Cl-down configurations ($10 \times 10 \text{ nm}^2$; $V_{\text{tip}} = 2.0 \text{ V}$, $I_{\text{set}} = 100 \text{ pA}$). Molecule indicated by the red circle (molecule 1) was switched from Cl-up (b) to Cl-down (c) by a positive voltage (+4.5 V, 5 ms), and molecule indicated by the yellow circle (molecule 2) was switched from the Cl-up configuration (a) to the Cl-down configuration (b) by a positive voltage pulse and back to the Cl-up configuration (d) by applying a negative pulse (−3 V, 5 ms). Corresponding schematics demonstrating the switching of molecules 1 and 2 are shown below each STM image.

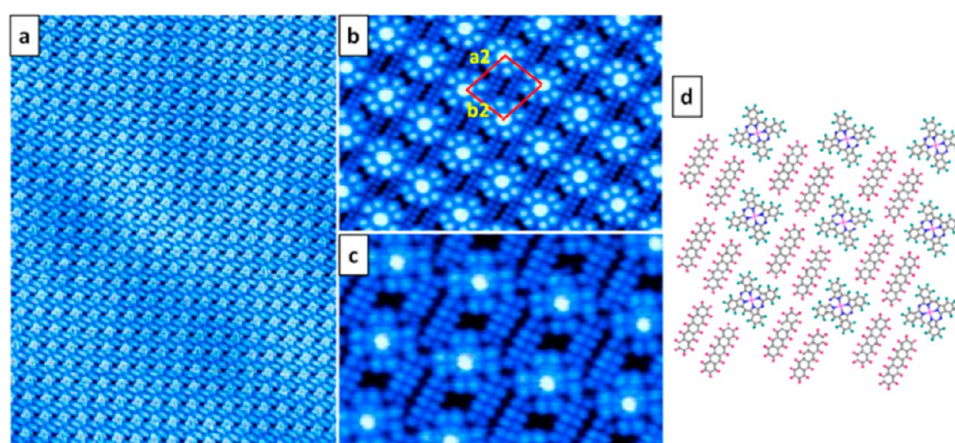


Figure 4. (a) STM image ($45 \times 60 \text{ nm}^2$, $V_{\text{tip}} = 2.0 \text{ V}$) of a long-range-ordered “square” binary molecular network formed by PFP and CIAIPc with a binary molecular ratio of 2:1 on HOPG. (b) High-resolution STM images of the “square” structure: ($15 \times 10 \text{ nm}^2$, $V_{\text{tip}} = 2.5 \text{ V}$) and (c) ($9 \times 6 \text{ nm}^2$, $V_{\text{tip}} = 2.5 \text{ V}$). (d) Schematic packing structure for the “square” network.

formation of multiple intermolecular C–H...F–C hydrogen bonding between the periphery F atom on PFP and the H atoms of neighboring CIAIPc molecules.^{44,47,63} Figure 2b and 2c displays the corresponding high-resolution STM images, where the rod-like feature represents a single PFP molecule and the four-lobe feature with a central protrusion represents a single CIAIPc. Careful inspection of the STM image reveals that two CIAIPc molecules are surrounded by four PFP molecules, forming an oblique unit cell with $a_1 = 2.50 \text{ nm}$, $b_1 = 2.80 \text{ nm}$ with an included angle $\alpha = 82^\circ$. The corresponding schematic molecular superstructure is given in Figure 2d with a dipole density of $2.86 \times 10^{13} \text{ dipoles/cm}^2$. Both PFP and CIAIPc lie flat on HOPG with their conjugated π plane oriented parallel to the HOPG surface due to interfacial π – π interactions. The bright central protrusion in individual CIAIPc can be assigned to the Cl atom residing on the flat-lying CIAIPc with a Cl-up configuration.^{43,47} As can be seen clearly in Figure 2, the directional interfacial π – π interactions can lead to almost all the CIAIPc molecules adopting the Cl-up configuration, consistent with previous reports.^{39,43,47}

Single-molecule switching can be realized in this binary network by positioning the STM tip above the target molecule and subsequently applying a voltage pulse. The image was then scanned subsequently to confirm the successful switch. By controlling the polarity of the voltage applied to the tip, we can

switch the CIAIPc molecule between Cl-up and Cl-down configurations reversibly. During the pulsing process, the tip was held at 2.0 V and 100 pA (with the feedback loop off) to fix the tip above the target molecule. CIAIPc molecules can be switched to the desired configurations as clearly shown by the sequential STM images in Figure 3a–d. The bistable states of the CIAIPc molecule can be discriminated from the molecularly resolved STM images, where the four-lobe feature with a central bright protrusion represents a CIAIPc molecule with Cl-up configuration and the four-lobe feature with a homogeneous brightness is attributed to a Cl-down configuration. Initially, the molecule in the Cl-up configuration (Figure 3a), as indicated by a yellow circle, was switched to a down configuration (Figure 3b) by applying a positive voltage pulse (4.5 V, 5 ms) to the tip. Subsequently, another molecule in the Cl-up configuration, now denoted by a red circle, was switched to the Cl-down configuration (Figure 3c) by applying the same positive voltage pulse. It is worth noting that only the CIAIPc molecule under the STM was switched with the neighboring CIAIPc molecules unaffected, revealing a true single-dipole molecule switching. In addition, the hydrogen-bonded binary molecular network remained unperturbed, confirming the good structural stability of the dipole molecules imbedded in the hydrogen-bonded molecular network. Such dipole molecule switching is highly reversible. The molecule, as denoted by a yellow circle, which

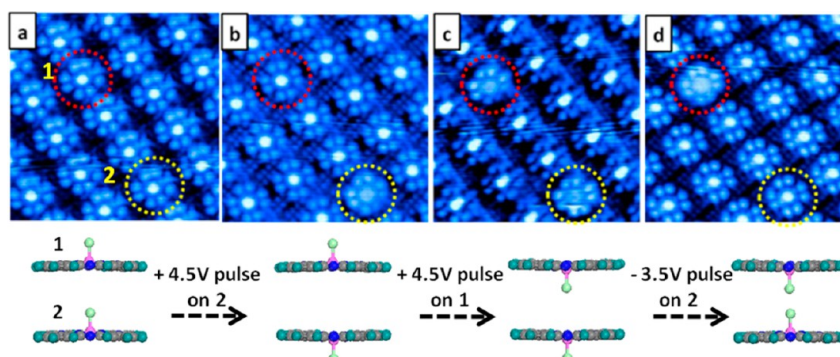


Figure 5. (a–d) Sequential STM images showing the reversible switching between the Cl-up and the Cl-down configurations ($10 \times 10 \text{ nm}^2$; $V_{\text{tip}} = 2.1, 2.0, 2.0, 2.2 \text{ V}$; $I_{\text{set}} = 100 \text{ pA}$). Molecule indicated by the red circle (molecule 1) was switched from Cl-up (b) to Cl-down (c) by a positive voltage ($+4.5 \text{ V}$, 5 ms), and molecule indicated by the yellow circle (molecule 2) was switched from the Cl-up configuration (a) to the Cl-down configuration (b) by a positive voltage pulse and back to the Cl-up configuration (d) by applying a negative pulse (-3.5 V , 5 ms). Corresponding schematics demonstrating the switching of molecules 1 and 2 are shown below each STM image.

was previously switched from the Cl-up to the Cl-down configuration (Figure 3a and 3b), can now be switched back to the Cl-up configuration again after applying a negative voltage pulse (-3 V , 5 ms), as evidenced in Figure 3d. Again, the negative voltage pulse did not affect the surrounding molecules and the molecular networks. Careful inspection of the STM image reveals that the in-plane orientation of the CIAIPc molecule also remains the same during the switching process.

In order to study the influence of the surrounding molecular frame on the single-molecule switches we construct a different binary molecular network by varying the relative molecular ratio. Increasing the molecular ratio of PFP:CIAIPc to 2:1 gave rise to formation of another intriguing binary molecular network. Figure 4a shows a highly ordered “square” network after deposition of PFP and CIAIPc on HOPG, followed by annealing at 370 K for 30 min . High-resolution STM images (Figure 4b and 4c) reveal that each PFP doublet is surrounded by four CIAIPc molecules, forming an oblique unit cell with $a_2 = 2.50 \text{ nm}$, $b_2 = 2.25 \text{ nm}$ with an included angle of 84° . Both CIAIPc and PFP lie flat on HOPG, and almost all the CIAIPc molecules are aligned in the Cl-up configuration. Now, all CIAIPc molecules are well separated by neighboring PFP molecules, which enables addressing them at the single-molecule scale. The schematic of the packing structure is illustrated in Figure 4d with the dipole density decreased to $1.78 \times 10^{13} \text{ dipoles/cm}^2$.

Switching between the Cl-up and the Cl-down configurations can also be realized in this “square” network, as shown in Figure 5a–d. The molecule indicated by the red circle can be switched from the initial Cl-up configuration (Figure 5a and 5b) to the Cl-down configuration (Figure 5c and 5d) by positioning the tip above the target molecule and applying a positive voltage pulse (4.5 V , 5 ms). The molecule indicated by the yellow circle shows a reversible switching from the Cl-up (Figure 5a) to the Cl-down configuration (Figure 5b and 5c) and then back to the Cl-up configuration (Figure 5d). The switching direction can be controlled by the polarity of the pulse voltage, with parameters of 4.5 V , 5 ms for Cl-up to Cl-down configurations and -3.5 V , 5 ms for Cl-down to Cl-up configurations, respectively. Similar to the case of PFP:CIAIPc with a ratio of 1:2, both the adjacent molecular network and the in-plane orientation of the switched molecule remain unchanged.

To understand the mechanism of the dipole switching of the CIAIPc molecule imbedded in these hydrogen-bonded binary

molecular networks, we statistically analyzed the dependence of the reaction yield on the voltage pulse. In our experiments, the reaction yield is defined as the number of switching events per injected electron. Figure 6 shows the reaction yield as a

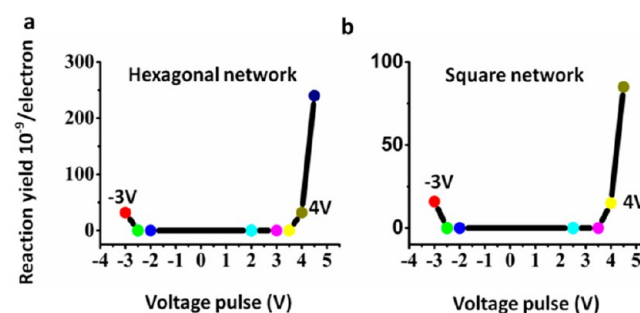


Figure 6. Reaction yield as a function of voltage pulse ($V_{\text{tip}} = 2.5 \text{ V}$, $I_{\text{set}} = 100 \text{ pA}$, feedback loop off). (a) Plot for the CIAIPc imbedded in the hexagonal network, and (b) “square” network. Threshold voltage for switching from the Cl-up to the Cl-down configuration (positive voltage pulse) or the Cl-down to the Cl-up configuration (negative voltage pulse) can be extracted from the plot.

function of voltage pulse for the hexagonal network (Figure 6a) and the “square” network (Figure 6b). Switching from the Cl-up to the Cl-down configuration was induced by positive voltage pulse, and we determined the threshold voltage for both the hexagonal and the “square” networks to be 4 V . For the reverse switching from the Cl-down to the Cl-up configuration, a negative voltage pulse is used and the corresponding energy onset is around -3 V for both systems. The arrangement of the CIAIPc molecule in these two networks results in a different number of intermolecular hydrogen bonds; however, the threshold voltage for both systems is the same. This suggests that during the switching process the whole molecular plane remains intact, and the only thing that can change is the location of the Cl atom.

On the basis of previous work for the dipole switching for CIAIPc⁴³ or other dipole phthalocyanine molecules,¹¹ two possible mechanisms can be proposed for the reversible switching of an individual CIAIPc molecule between two configurations, including flipping of the dipole molecule or the “shuttling” of the Cl atom between two sides of the CIAIPc molecular plane. In our experiment, the molecular networks are stabilized by the intermolecular $\text{C} \cdots \text{F} \cdots \text{H} - \text{C}$ hydrogen bonding

between PFP and CIAIPc. The reversible dipole switching observed for CIAIPc molecules exclusively affects the addressed molecule and leaves the neighboring molecular network and in-plane orientation of the switched molecule unaffected. Although the arrangement and hence the number of hydrogen bonds of CIAIPc imbedded in the hexagonal and “square” networks is different, the threshold voltage for these two systems are the same. All these observations suggest that the dipole switching process is unlikely to be caused by the molecular flipping. Very recently, Gopakumar et al. investigated a very similar dipole molecule of iron tetraphenylporphyrin chloride (FeTPPcI) adsorbed on Au(111) using LT-STM.⁶ They proposed that the two contrasts (bright central protrusion and the dimmed center in FeTPPcI) are due to the Cl atom transferred between the Fe center of a selected molecule and the STM tip.³⁵ In our experiments and a previous report we successfully demonstrated a consecutive switching of a number of CIAIPc molecules (>10 molecules) from the Cl-up to the Cl-down configurations, followed by the reversed switching from the Cl-down to the Cl-up configurations. If the CIAIPc is switched via the Cl atom transferring between the STM tip and the CIAIPc molecule, the STM tip has to be decorated with a few Cl atoms during this consecutive switching process and hence to greatly affect the following molecular switching process as well as the STM imaging contrast. In our experiments, we can achieve the consecutive switching of different CIAIPc molecules under the exact same switching condition. At the same time, we did not observe any distinct change in the STM imaging contrast during the consecutive molecular switching process. As such, we believe that the reversible CIAIPc switching in our experiments is not via the Cl-atom transfer mechanism.

On the basis of the experimental results we propose the “shuttling” of the Cl atom between two sides of the CIAIPc molecular plane with the phthalocyanine intact as a possible mechanism to explain how the reversible switching is induced. To reveal the reasonable pathway for Cl-atom shuttling between two sides of the CIAIPc molecular plane, we performed first-principles calculations based on DFT (see experimental methods), and the nudged elastic band (NEB) algorithm was employed to find the minimum-energy path of the Cl atom. Four possible paths were proposed by considering the symmetry of the CIAIPc molecule. As shown in Figure 7, PATHs 1, 2, and 3 sketch the paths of the Cl atom, where it first moves above the molecular plane along the Al–N1 direction, Al–H1 direction, or Al–N2 direction (N1 and N2 are the nearest and second nearest N atoms from the center Al atom, and H1 is the nearest H atom from the center), then bypasses the edge of the CIAIPc molecule, and finally bonds to

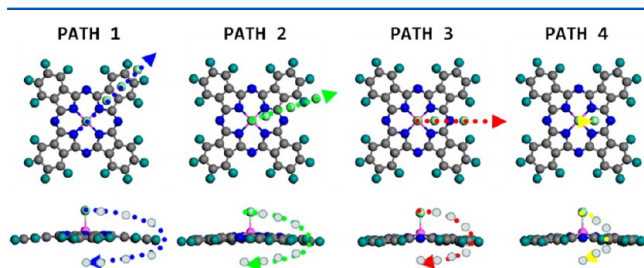


Figure 7. Schematic molecular models showing the possible pathways for Cl-atom shuttling from the upper side to the lower side of the CIAIPc molecular plane.

the Al atom from another side of the molecular plane, whereas PATH 4 describes the case that the Cl atom “tunnels” through the phthalocyanine core directly to another side of the molecular plane.

Figure 8 shows the calculated minimum-energy paths for these four channels. Along the *x* axis are 16 intermediate

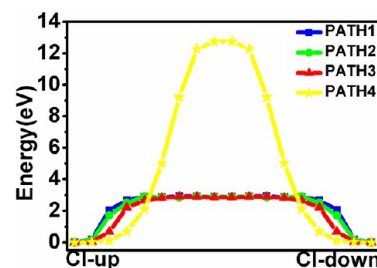


Figure 8. Calculated minimum-energy paths for Cl-atom shuttling between two sides of the molecular plane along PATH 1, PATH 2, PATH 3, and PATH 4.

configuration images of a NBE calculation process. The energy barriers for a single switching are found to be 2.93 (PATH 1), 2.92 (PATH 2), 2.89 (PATH 3), and 12.75 eV (PATH 4). By combining the experimentally observed threshold voltage (4 V for Cl-up to Cl-down switching or −3 V for the reversed case) and the calculated results we propose a possible pathway for Cl-atom shuttling between two sides: the inelastically tunneled electrons first induce partial breaking of the Cl–Al bond, the released Cl atom moves from the molecular center to the edge of the molecule following the minimum energy path, then switches to the other side of the molecular plane, and finally bonds with the Al atom. In addition, due to the lowest calculated energy barrier of PATH 3 and its smaller steric hindrance compared with other pathways, we suggest that the Cl atom moving along the Al–N2 direction is the most reasonable pathway. In the experiment, we apply a voltage of 4 V (−3 V) to the tip, which provides ample energy to overcome the energy barrier to move the Cl atom from the molecular center and push (pull) it to the other side. The different threshold voltage between the Cl-up to Cl-down switching and the reverse process may be caused by the asymmetry of the tip–CIAIPc–graphite system.

4. CONCLUSION

We demonstrated reversible switching of a single-dipole molecule imbedded in two different 2D hydrogen-bonded binary CIAIPc:PFP molecular networks on HOPG. The CIAIPc molecule can be reversibly switched between the Cl-up and the Cl-down configurations by controlling the polarity of the voltage pulse applied to the STM tip. On the basis of experimental results and density functional theory (DFT) calculations, we propose that the reversible switching between the Cl-up and the Cl-down configurations is induced by the “shuttling” of the Cl atom between two sides of the CIAIPc molecular plane. The switching is spatially confined to the addressed molecule, reversible, controllable, and leaves the neighboring binary molecular network unaffected, demonstrating great potential for applications in molecular high-density data storage devices.

■ ASSOCIATED CONTENT

■ Supporting Information

STM image and the corresponding height profile for the Cl-up and the Cl-down configurations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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