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Scanning tunnelling spectroscopy and manipulation of double-decker phthalocyanine molecules on a semiconductor surface

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Abstract

A scanning tunnelling microscope (STM) operated at 5 K was used to study dysprosium biphthalocyanine ($DyPc_2$) molecules adsorbed on the inert III–V semiconductor surface InAs(1 1 1)A. Orbital imaging and scanning tunnelling spectroscopy measurements reveal that the molecular electronic structure remains largely unperturbed, indicating a weak molecule-surface binding. The molecule adsorbs at the In vacancy site of the (2×2)-reconstructed surface and is highly sensitive to current-induced excitations leading to random rotational fluctuations. Owing to the weak surface binding, individual molecules can be precisely repositioned and arranged by the STM tip via attractive tip-molecule interaction. In this way, $DyPc_2$ dimers of well-defined internal structure can be assembled which exist in two conformations of equivalent appearance. A binary switching between these two conformers can be induced by injecting electrons into one of the two molecules. The conformational change of the dimer proceeds via a concerted molecular rotation and minor lateral displacement. The synchronised switching observed here is attributed to steric interactions between the two molecules constituting the dimer.

Keywords: scanning tunneling microscopy, semiconductor surfaces, III–V semiconductors, STM manipulations of single atoms and molecules

(Some figures may appear in colour only in the online journal)

1. Introduction

Lanthanide biphthalocyanine complexes ($LnPc_2$)—often referred to as phthalocyanine double-deckers—have gained increasing attention since the discovery of their single-molecule magnet behaviour [1]. The lanthanide cation sandwiched between two phthalocyanine (Pc) rings carries a large magnetic moment deriving from its 4*f* states. Besides a broad range of other experimental and theoretical efforts, this has triggered a number of scanning tunnelling microscopy (STM) studies to locally explore the magnetic and electronic properties of surface-supported $LnPc_2$ molecules [2–10]. Conformational effects involving the azimuthal orientation of the two Pc rings were found to induce reversible switching behaviour [7] as well as modifications of the magnetic and electronic properties [4, 11]. So far, adsorbed $LnPc_2$ molecules were studied by STM on surfaces of metals [2–4, 6–9], graphite [5, 12], and elemental semiconductors like silicon [10]. A strong interaction and bond formation between molecule and surface was observed in the latter case, owing to the chemical reactivity of the Si(1 0 0) surface [13–15].

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Here, we explore the case of Pc double-deckers supported by a III–V semiconductor surface that provides an exceptionally weak molecule-surface binding. Our cryogenic STM study shows that individual dysprosium biphthalocyanine ($DyPc_2$) molecules adsorbed on InAs(1 1 1)A are largely unperturbed regarding their frontier orbital structure and highly sensitive to tunnel current-induced excitations leading to random rotational fluctuations. As a further consequence of the weak binding, the molecule can be readily repositioned by the STM tip with atomic precision. This enables one to create $DyPc_2$ dimers of well-defined structure existing in two equivalent conformations. In the dimer, the random fluctuations are quenched due to steric interactions [16] between the $DyPc_2$ constituents. Instead, a bistable switching between the two equivalent conformations can be excited by transient electron attachment (tunnelling into empty molecular states). It is shown that the conformational switching proceeds via a concerted rotation and minor lateral displacement of both molecules.

2. Experimental details

The experiments were carried out with a cryogenic STM operated in ultrahigh vacuum (UHV). We used electrochemically etched tungsten tips cleaned in UHV by Ne ion bombardment and electron beam heating. STM images were recorded in constant-current mode; bias voltages refer to the sample with respect to the STM tip. Scanning tunnelling spectroscopy (STS) measurements of the differential tunnelling conductance dI/dV were carried out with lock-in technique (modulation frequency 675 Hz at a peak-to-peak modulation of 10 mV) to probe the local density of electronic states at constant tip height. Undoped 20 nm-thick InAs layers were grown by molecular beam epitaxy (MBE) on an InAs(1 1 1)A wafer (purchased from Wafer Technology Ltd) to prepare the In-terminated InAs(1 1 1)A-(2 × 2) surface. To allow for 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, followed by sample transfer into the microscope cooled to 5 K. Dysprosium biphthalocyanine was synthesised as described in the literature [17], loaded into a tantalum crucible and thoroughly degassed in UHV. Low coverages (roughly 1×10^{11} molecules per cm^2) were dosed directly into the microscope at a sample temperature <20 K by sublimation at a crucible temperature of 700 K.

3. Results and discussion

We used the InAs(1 1 1)A surface (figure 1(a)) as a substrate which is free of partially filled dangling bonds due to its intrinsic (2 × 2) cation-vacancy reconstruction [18, 19]. This reconstruction renders the surface chemically unreactive, leading to a weak binding of adsorbed Pc molecules [20]. Moreover, InAs(1 1 1)A is weakly metallic due to the presence of native surface donors, +1 ionized indium adatoms (In_{ad}), pinning the Fermi level E_F about 0.2 eV above the conduction band minimum [21, 22]. After depositing $DyPc_2$ as described above we observe a planar adsorption geometry with the molecule essentially centred at an In vacancy site, similar to the behaviour previously found for bare Pc molecules on InAs(1 1 1)A [20, 23, 24]. The STM topography image of a single $DyPc_2$ molecule in figure 1(b) (sample bias −1 V) reveals the fourfold ligand structure of the upper Pc ring and resembles the known eight-lobe appearance of adsorbed $LnPc_2$ when probing the filled states of the molecule [2–4, 6–10]. Calculations confirmed that the eight-lobe appearance is consistent with the filled-states orbital structure of the free $LnPc_2$ molecule [2, 4, 11].

As marked by the white bars in figure 1(b), the ligands of the upper ring are rotated by ±45° relative to the in-plane [1 0 $\bar{1}$] direction. Owing to the staggered molecular structure of Pc double-deckers [11], the ligands of the lower ring—which is not accessible by STM imaging [4]—are deduced to be parallel and perpendicular to the [1 0 $\bar{1}$] direction. This in-plane orientation of the lower ring is the same as that observed for bare Pc on InAs(1 1 1)A [20, 24]. The weakly bound $DyPc_2$ molecule performs random rotational jumps between different symmetry-equivalent orientations during the line-by-line scanning as evident from the images in figures 1(c)–(e). By analysing a large set of STM images we identified the three equivalent in-plane orientations depicted in figure 1(f), where the upper (lower) ring is shown in dark (light) colour. These three orientations occur in the STM images in figures 1(b)–(e) as indicated by the numbering defined in figure 1(f). Moreover, our analysis shows that the molecule is shifted away from the vacancy site by ~1.2 Å, namely along [$\bar{1}$ 2 $\bar{1}$] (orientation 1), [$\bar{1}$ $\bar{1}$ 2] (orientation 2), and [2 $\bar{1}$ $\bar{1}$] (orientation 3), respectively. Conformational switching from one orientation to another thus involves a rotation accompanied by a slight lateral displacement of the molecule. It is noted that the molecule is most sensitive to the tunnel current at positive bias polarity, causing rapid rotational fluctuations. This makes it impossible to image the internal molecular structure at positive bias, even at currents as low as 1 pA.

We find that $DyPc_2$ on InAs(1 1 1)A is negatively charged, implying electronic charge transfer from the substrate to the molecule. Due to the reduced electrostatic screening in a semiconductor, the effect of a local surface charge can be directly observed in STM images. A negative charge locally decreases the number of conduction band states available for tunnelling, resulting in a decreased apparent height in constant-current imaging at positive bias [25]. This effect is evident from the STM image in figure 1(g), displayed at enhanced grey-scale, revealing a faint depression around the $DyPc_2$ molecule (the inverted effect is observed around the two In adatoms which are +1 ionized [26]). Free $LnPc_2$ in its neutral state is known to have an open-shell π electronic system, owing to the trivalent character of the lanthanide ion and an even number of electrons associated with each Pc ring [27, 28].The unpaired π electron was found to be delocalized over both rings [27]. Formation of an $[LnPc_2]^-$ anion, on the other hand, saturates the Pc moieties and leads to a closed-shell system [27, 28].

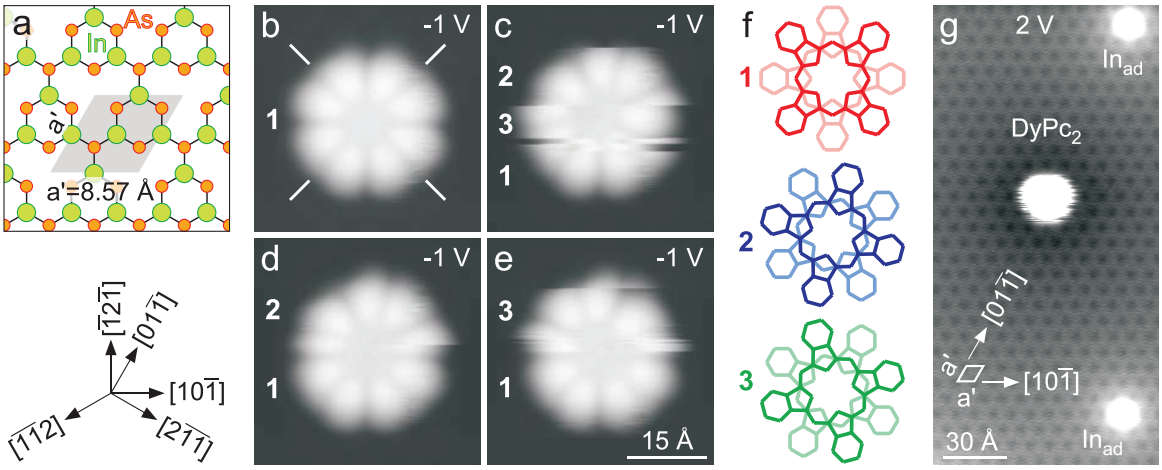


Figure 1. (a) Structure model of the InAs(1 1 1)A surface with In surface atoms (larger green spheres) in the top layer and As atoms (smaller orange spheres) in the second layer, the unit cell of the (2 × 2)-reconstructed surface is shown in grey. (b) Constant-current STM image (−1 V, 20 pA) of a discrete $DyPc_2$ molecule, white bars indicate the orientation of the ligands. (c)–(e) Same as (b) but taken at 50 pA, revealing rotational fluctuations induced by the tunnel current. (f) Scheme of the three equivalent azimuthal orientations occurring in the STM images in (b)–(e); the upper (lower) Pc ring is shown in dark (light) colour. (g) STM image (2 V, 20 pA) at enhanced grey scale revealing a faint depression around the molecule indicative for a negative charge state; positively charged In adatoms (In_{ad}) are located at the upper and lower right.

Obviously, this process is the driving force for the charge transfer observed here, analogous to the behaviour reported previously for $TbPc_2$ adsorbed on metal surfaces [2, 4, 6].

The weak surface binding is also reflected by fluctuations in the tunnel current when fixing the STM tip above a molecule and recording current-versus-bias voltage [$I(V)$] curves. Figure 2(a) shows an $I(V)$ curve obtained with the tip placed above the Pc ligands. A conductance gap of about 1.5 V is observed along with current fluctuations in the conducting regime. The discontinuity at positive bias (marked by an arrow) indicates a rotational jump of the molecule induced by the tunnelling electrons. This discontinuity is also evident from the corresponding dI/dV spectrum in figure 2(b). Spectra without any such discontinuities in the empty states were not acquirable, showing again that the molecule is highly sensitive to excitation via electron attachment.

The dI/dV spectrum in figure 2(b) reveals three spectral features deriving from filled (denoted A and B) and empty ligand-centred molecular orbitals (denoted C). We propose that the filled states A and B at −0.82 V and −0.59 V arise from the bonding and antibonding combination of the highest-occupied-molecular-orbital (HOMO) wave functions of the two Pc moieties, as previously predicted by density functional theory (DFT) calculations of the free $[LnPc_2]^-$ anion [11]. This correspondence to the free molecular state apparently results from the weak molecule-surface binding, leaving the lower Pc ring in contact with the InAs(1 1 1)A surface largely unperturbed. In principle, a bonding-antibonding splitting is expected to occur also for the empty states deriving from the lowest-unoccupied-molecular-orbital (LUMO) wave functions of the Pc moieties [11]. In the present case, such a splitting was not observable due to the current-induced fluctuations at positive sample bias. Nevertheless, the spectrum in figure 2(b) reveals an onset of the empty ligand states at a bias of about 1 V.

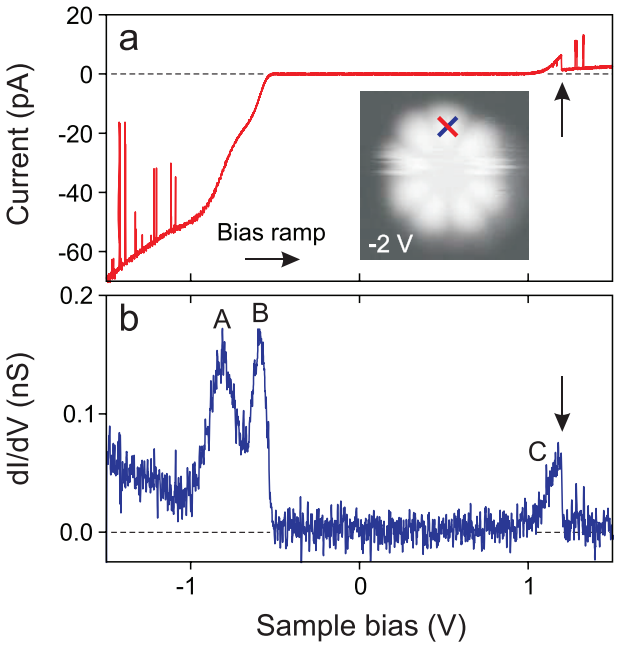


Figure 2. (a) $I(V)$ curve recorded with the tip probing the ligand-centred states of the $DyPc_2$ molecule (see inset) indicating a conductance gap of about 1.5 V and fluctuations in the tunnel current; the discontinuity at positive bias (arrow) is due to a rotational jump of the molecule. (b) Corresponding dI/dV spectrum revealing two filled states (denoted A and B) and the onset of an empty state (denoted C).

We also attempted to probe Dy-related states by STS. Previous DFT calculations showed that the Tb 4f states of $TbPc_2$ are located within the conductance gap, and complementary STS measurements suggested that these states give rise to only minor spectral features in the dI/dV signal of $TbPc_2$ adsorbed on Cu(1 1 1) [2]. Similarly, no spectroscopic evidence for f states was found in STS studies of $DyPc_2$ on

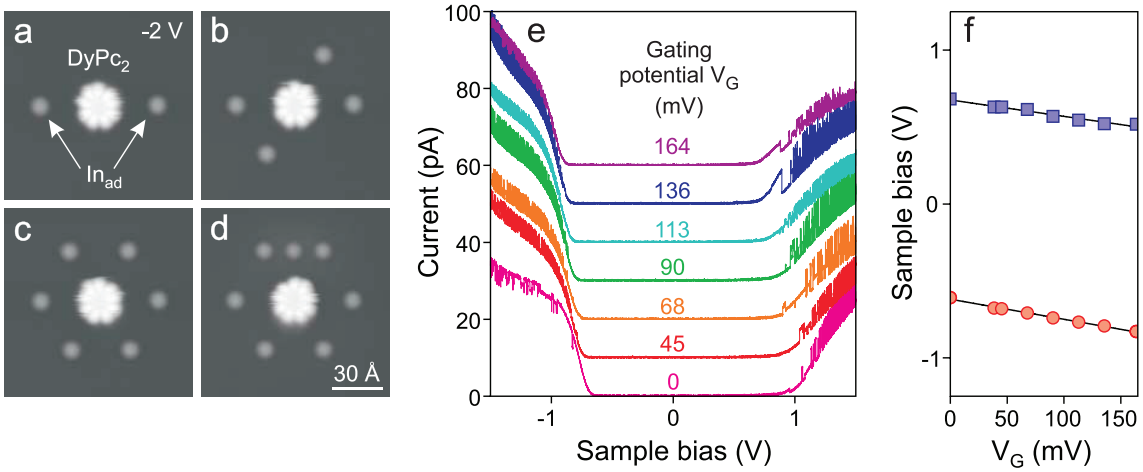


Figure 3. (a)–(d) STM images (−2 V, 10 pA) of a discrete $DyPc_2$ molecule and +1 ionized In adatoms (In_{ad}) placed around it one atom at a time. (e) $I(V)$ curves (showing the current magnitude) recorded with the tip centred above an $DyPc_2$ at different gating potential V_G induced by the In_{ad} nearby; for clarity, the curves are vertically offset. (f) V_G-dependent onsets of the filled (red dots) and empty states (blue squares) extracted from the data shown in (e), the uniform shift of the conductance gap edges indicates a pure electrostatic shift of the filled ($V < 0$) and empty molecular states ($V > 0$), respectively.

Au(1 1 1) [9]. Also here, we find no indication for Dy-related states in the gap region. This is consistent with the picture that the *f* states of the late lanthanides, such as Tb and Dy, are strongly localized, so that they are hardly accessible by STS probing of $TbPc_2$ and $DyPc_2$ molecules. For $LnPc_2$ containing early lanthanides such as Nd, on the other hand, it was reported that the Nd *f* states hybridise with the molecular π-electron system [8].

In our previous work, we found that the tunnel conductance of single H_2Pc and CuPc molecules on InAs(1 1 1)A can be understood as charge transport via a single level within a double-barrier tunnel junction (DBTJ) [24]. This simple picture relies on a molecule weakly coupled to the tip and surface, respectively, and an empty level close to E_F. In this situation, the level can enter the energy window between the tip and sample Fermi levels at both bias polarities, leading to bipolar sequential tunnelling through the DBTJ [29–31]. In contrast to the DBTJ scenario found for H_2Pc and CuPc, we verified that this is actually not the case for $DyPc_2$ on InAs(1 1 1)A. To prove this, the local electrostatic potential V_G[4] experienced by the $DyPc_2$ molecule was tuned by arranging +1 ionized In adatoms nearby as visualized by the STM images in figures 3(a)–(d). The positive potential lowers the energy of the molecular levels, similar to applying an electrostatic gating potential to a quantum dot connected to leads[5].

Figure 3(e) collects $I(V)$ curves (here showing the absolute current magnitude) obtained at different V_G values and recorded with the tip centred above the molecule. The current fluctuations in the conducting regime reflect current-induced excitations, similar to the spectra discussed in figure 2. Most importantly, the $I(V)$ curves show a uniform shift of the current onset both at positive and negative bias V, indicating a uniform electrostatic shift of the filled ($V < 0$) and empty molecular states ($V > 0$). For bipolar tunnelling via a single level, on the other hand, a varying conductance gap would be expected as V_G is changed [24]. Figure 3(f) shows the current onset at positive (blue squares) and negative bias (red dots) with V_G as the *x* axis and the sample bias V as the *y* axis. The slopes of the black lines marking the current onsets are essentially the same at $V < 0$ and $V > 0$ and amount to $\Delta V/\Delta V_G \cong 1.2$, corroborating that the nearby In adatoms exert a total potential on the molecule that is in good agreement with the potential value determined from the voltage offset in $I(V)$ curves recorded next to the +1 ionized adatoms [24, 26].

Similar to the procedure applied to bare Pc molecules on InAs(1 1 1)A [20, 23, 24], $DyPc_2$ can be repositioned with atomic precision via attractive tip-molecule interaction. Using this lateral manipulation technique, we joined molecules to form dimers as depicted in figure 4. These dimers exhibit a number of interesting properties: (i) they show a well-defined structure and arrangement with respect to the surface lattice, (ii) current-induced fluctuations inherent to the discrete molecule are quenched, and (iii) they exist in two conformations of equivalent appearance labelled #1 and #2, respectively. Figures 4(a)–(d) show the two dimer conformers imaged in the filled [(a) and (c)] and empty states [(b) and (d)]. Again, white bars mark the ligand orientations of the upper Pc ring, which are now rotated by about ±10° relative to those of discrete $DyPc_2$ on InAs(1 1 1)A. The molecules are located at two In vacancy sites adjacent along an in-plane ⟨1 1 2⟩ direction and show a lateral offset of ~2 Å relative to each respective vacancy. The molecular centres are separated by ~14 Å which is close to typical values of the intermolecular separation reported for $LnPc_2$ monolayers on metal surfaces [32]. We note that—upon formation of the dimer—the relative azimuthal orientation of the Pc rings may deviate from the staggered ground state of the free molecule [11], as it has been

[4] V_G refers to the total electrostatic potential at the location of the molecule resulting from all nearby In_{ad}. The single-atom potential was determined from the voltage offset of $I(V)$ curves sampled by the STM tip at constant height (roughly 10 Å) along a straight line containing the In_{ad} position [24, 26].
[5] Within the picture of a three-terminal device, the leads of the $DyPc_2$ molecule are the tip and the surface, respectively.

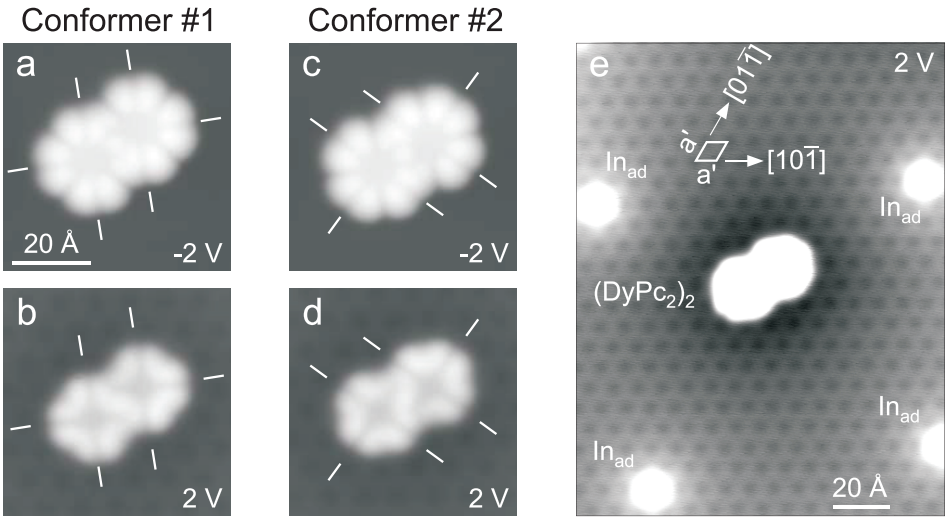


Figure 4. (a) and (b) STM images (20 pA) of a $DyPc_2$ dimer assembled by lateral manipulation and recorded in the filled (−2 V, (a)) and empty states (2 V, (b)), white bars mark the ligand orientations of the upper Pc rings. (c) and (d) Same as (a) and (b) but for the other conformer; the transition from the conformer in (a) and (b) to that in (c) and (d) involves a concerted rotation and displacement of both molecules. (e) STM image (2 V, 20 pA) at enhanced grey scale confirming that the negative molecular charge state is maintained in the dimer.

observed in $LnPc_2$ monolayers [32]. This, however, cannot be verified on the basis of our data since only the upper ring is accessible by STM imaging.

Steric effects in the dimer allow for a stable molecular imaging also in the empty states at positive bias, revealing the nodal planes of the ligand-centred wave function which are oriented along the ligands of the upper ring [11], see figures 4(b) and (d). Similar to the case of the discrete molecule discussed in figure 1(g), the STM image in figure 4(e) shows a depression around the dimer, indicating that the negative molecular charge state is maintained when joining two $DyPc_2$ molecules to form a dimer.

It is possible to reversibly switch between the two dimer conformations. The switching takes place in a concerted manner, i.e. injecting electrons into one of the two molecules leads to a synchronised switching of both molecules. The STM images in figures 5(a), (c) and (e) show the two conformations and the dots mark the vacancy sites of the underlying surface, visualizing that the switching involves a concerted rotation and minor lateral displacement of the molecules. For the dimer shown in figure 5 we recorded $I(t)$ time traces of the tunnel current at constant tip height to probe the switching process in detail. Injecting electrons into conformer #1 (sample bias 2 V) at the location indicated by the red mark in figure 5(a) results in the two-level noise signal shown in figure 5(b). The time trace starts at high current I_{H1} and ends at low current I_{L1}. Consequently, the resulting dimer state in figure 5(c) corresponds to the other conformer #2. Exciting the latter by placing the tip at the equivalent position marked blue in figure 5(c) yields a three-level current signal (figure 5(d)) with two lower levels of comparable current, I_{L21} and I_{L22}, and a level of significantly higher current, I_{H2}. After recording the time trace in figure 5(d) the dimer is switched back to conformation #1 (figure 5(e)), and the latter is associated with the lower current level I_{L22}. We attribute the switching between the lower current levels I_{L21} and I_{L22} to an additional degree of freedom of the dimer, whereas the switching between high current I_{H2} and any of the lower levels reflects the concerted rotation and displacement.

At this point, the unexpected result is that injecting electrons into conformers of equivalent appearance and at equivalent tip positions leads to qualitatively different behaviour, namely two-level switching in figure 5(b) versus three-level switching in figure 5(d). This difference proved to be fully reproducible when measuring several $I(t)$ spectra at varying initial tip height (i.e. different mean currents) with the tip placed at the two positions indicated in figures 5(a) and (c). We interpret this circumstance as an indication that the two experimentally observed conformers are actually not equivalent in a strict sense. This inequivalence may be due to conformational details of the lower Pc rings which are not directly accessible by STM imaging. It is also possible that the state associated with the lowest current I_{L21} is only of metastable nature and stabilized in the presence of the STM tip. Given P_{21} the probability of this state and P_{22} the probability of the other low-current state, we find $P_{21}/P_{22} \cong 0.075$ on the basis of a large set of $I(t)$ spectra.

The switching rate R depending on the mean current $\langle I \rangle$ is displayed as a double-logarithmic plot in figure 5(f). The rate of the concerted rotation for #1 (red dots) and #2 (blue squares) as the initial conformer as well as the $I_{L21} \leftrightarrow I_{L22}$ switching (green diamonds) can be described by a power law dependence $R \propto \langle I \rangle^{\alpha}$ with α values of 4.1, 3.8, and 3.2, respectively, revealing a highly nonlinear rate increase with increasing mean current. Similar behaviour was reported before for cases in which multi-electron processes govern the excitation of single-molecule rotation [33], conformational change [34], tautomerization [35], and bond breaking [36]. These reported cases involved the stepwise vibrational

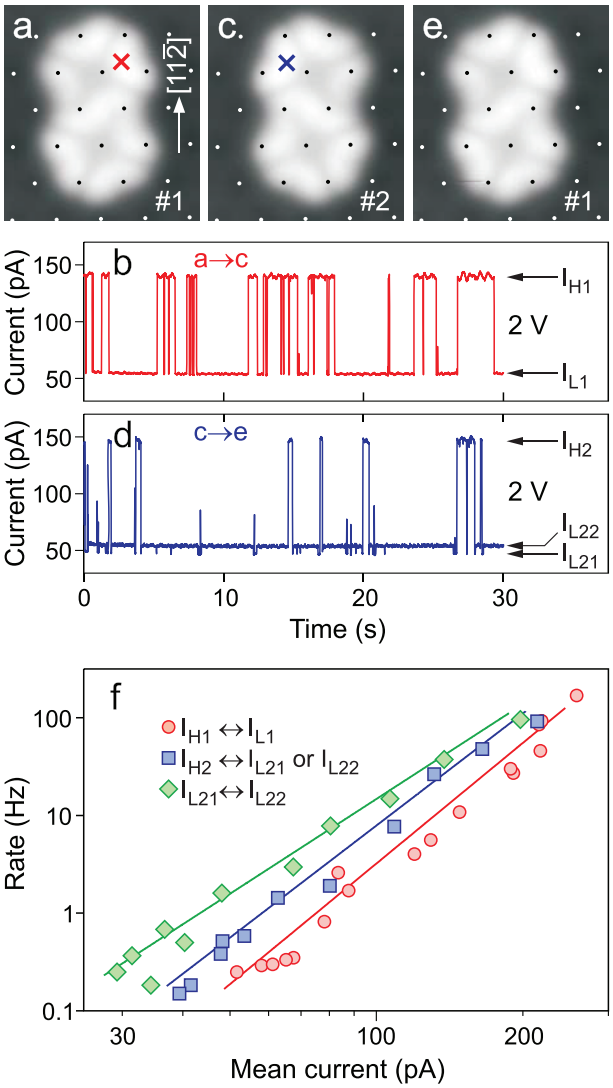


Figure 5. (a) STM image (2 V, 15 pA) of a $DyPc_2$ dimer in its initial conformer #1, the dots mark the vacancy sites of the underlying surface. (b) Tunnel current trace recorded at 2 V after fixing the tip at the position marked red in (a) and reducing the tip height by 0.7 Å, the two-level current signal reflects the switching between the two conformers. (c) STM image (2 V, 15 pA) showing the resulting conformer #2 associated with the low current level I_{L1} in (b). (d) Same as (b) but now exciting conformer #2 at the tip position marked blue in (c). Apart from the high-current level I_{H2}, two low-current levels (I_{L21} and I_{L22}) of comparable magnitude are observed. (e) STM image (2 V, 15 pA) showing the final conformer #1 associated with the low-current level I_{L22} in (d). (f) Double-logarithmic plot of the switching rate R versus mean current $\langle I \rangle$ for the concerted rotations #1 → #2 (red dots) and #2 → #1 (blue squares) as well as the $I_{L21} \leftrightarrow I_{L22}$ switching (green diamonds), revealing a highly nonlinear rate increase with increasing mean current.

excitation [37] of a given degree of freedom via inelastic electron tunnelling (IET). While IET is likely to be at work also in our case, the analogy to a stepwise excitation of a given vibrational degree of freedom seems limited because here a comparably high bias voltage was required to induce a concerted rotation. This can potentially give rise to a simultaneous excitation of various different internal degrees of freedom and a crosstalk between those. Furthermore, it cannot be ruled out that the tip-induced electric field [38] has a stabilizing or destabilizing effect on specific conformational states of the dimer.

Finally, we found that the bias-dependent normalized rate of the concerted rotation (the probability per tunnelling electron to induce a single switch, $eR/\langle I \rangle$) steadily increases from 1×10^{-9} at 1.2 V to 1×10^{-7} at 1.6 V and saturates at this value up to 2 V, the maximum bias probed in the experiment. Since the dimer—as well as the discrete molecule as such—is most sensitive to current-induced excitation at positive bias, the process is apparently driven by transient electron attachment via tunnelling into empty molecular states [39]. As a result of the steric interaction [16] between the two molecules that constitute the dimer, the switching proceeds by means of a concerted rotation and displacement.

4. Conclusions and prospects

Our results show that the Pc double-decker $DyPc_2$ is weakly bound to the InAs(1 1 1)A surface, leaving the molecular orbitals largely unperturbed and allowing one to precisely reposition the adsorbed molecule by lateral manipulation with the STM tip. Consistent with previously reported work [2, 9], no indications of STM tunnelling involving the lanthanide 4*f* states or inelastic excitations of the Dy-related spin system were observed. Furthermore, we found that the adsorbed $DyPc_2$ molecule is negatively charged, suggesting a closed-shell configuration and thus the absence of unpaired π-electron spins. This raises the interesting question, whether the molecule can be tuned into the neutral state by arranging negatively charged point defects[6] nearby to suppress charge donation from the substrate, thereby establishing an unpaired π-electron spin configuration [4, 27, 28] via electrostatic gating [24].

The artificial $DyPc_2$ dimer on InAs(1 1 1)A created here shows a bistable concerted switching behaviour, in contrast to the current-induced random fluctuations inherent to the discrete molecule. We propose that the observed synchronisation in rotational and translational molecular motion is a consequence of steric interactions between the two molecules constituting the dimer. It will be interesting to explore if the observed behaviour can be extended to a collective molecular switching [40–43] in $DyPc_2$ trimers or even larger structures assembled by STM manipulation.

Acknowledgments

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[6] We find that point defects of charge state −1 can be reversibly created on the InAs(1 1 1)A surface by extracting a single surface In atom with the STM tip at a sample bias of 1 V and tunnel currents of typically 1 μA.

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