Controlling selectivity of reactions is an ongoing quest in chemistry. In this work, we demonstrate reversible and selective bond formation and dissociation promoted by tip-induced reduction-oxidation reactions on a surface. Molecular rearrangements leading to different constitutional isomers are selected by the polarity and magnitude of applied voltage pulses from the tip of a combined scanning tunneling and atomic force microscope. Characterization of voltage dependence of the reactions and determination of reaction rates demonstrate selectivity in constitutional isomerization reactions and provide insight into the underlying mechanisms. With support of density functional theory calculations, we find that the energy landscape of the isomers in different charge states is important to rationalize the selectivity. Tip-induced selective single-molecule reactions increase our understanding of redox chemistry and could lead to novel molecular machines.
structures combining enyne and cumulene groups (3′) or two enynes (3′′) within the central 10-membered ring can also be considered. The transannular C–C bond formation between the radicals in structure 3′′ would lead to the formation of diyne 4, whereas the C–C bond formation between radicals in 3′ would afford the chrysene-based bisaryne 5.

First, we characterize on the NaCl surface the products 3, 4, and 5. The STM-measured maps of electronic resonances are shown in Fig. 3 and fig. S8, accompanied by density functional theory (DFT) calculations. We find that 4 and 5 are charge neutral, with the shape of the imaged frontier orbital densities, of the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO, respectively), in agreement with the DFT calculations (Fig. 3, A to K, and fig. S9). For 4, we did not observe the positive ion resonance (HOMO) for voltages up to −2 V (fig. S10). For 3, the experiment shows that the molecule is in its anionic charge state. This is consistently indicated by the scattering of interface-state electrons (fig. S11), Kelvin probe force spectroscopy (table S3), and STM maps of the electronic resonances (Fig. 3, B and C) and their comparison with theory (figs. S12 and S13). The identification of structure 3 as a radical anion agrees with the expected tendency of sigma radicals to be reduced, in contrast to closed-shell compounds 4 and 5.

Moreover, our measurements reveal that the anion of 3 undergoes a Jahn-Teller distortion that is also found by B3LYP-based DFT (Fig. 3P) and explains the symmetry breaking with respect to the long molecular axis that is observed for both electronic resonances (Fig. 3, B and C). Structurally, the Jahn-Teller distortion of the anion 3′′ features an inward bend on one long side of the 10-membered ring (Fig. 3P) and can be observed in high-resolution AFM images (Fig. 3M and fig. S4). The first electronic resonance at negative bias shows two lobes of increased orbital density on the side of the inward bend (Fig. 3, B and H, and fig. S12). Whereas the first electronic resonance at positive bias exhibits increased density on the side opposite to the inward bend (Fig. 3, C and I, and figs. S12 and S13), in excellent agreement of experiment and theory.

Next, we study tip-induced reactions between 3, 4, and 5. When we applied pulses of relatively large bias, $V > +2.5$ V with $I = 10$ pA, we could transform molecules between all of these three structures—with limited control of the outcome, however. A rearrangement after a bias pulse of $V = +2.5$ V mostly resulted in structure 5 (≈50% of the attempts) and less often in structures 4 or 3 (≈25% each). Structure 5 was stable for $|V| < 2$ V. However, voltage pulses of $|V| < 2$ V, when applied to 3 and 4, resulted in different reactions, depending on the applied voltage.

Histograms showing the outcome of voltage pulses with currents of 0.5 pA applied above 3 and 4 as different resonance structures are displayed. The intermediates 1a and 2a might be transiently charged. We also observed partly dehalogenated intermediates other than 2 (see fig. S3), indicating several pathways for the initial formation of 3, 4, and 5.

Fig. 2. AFM images of precursor, intermediate, and products. Constant-height, CO-tip AFM images of precursor 1 (A), intermediate 2 (B), and products 4 (C), 3 (D), and 5 (E) on NaCl. (A), (B), and (D) on 2-ML NaCl, and (C) and (E) on 1-ML NaCl. Scale bars, 0.5 nm. For images at different tip-height offsets and imaging parameters, see figs. S1, S2, and S4 to S6.
For the transitions between 3 and 4, we investigated the respective reaction rates (Fig. 4C). These were measured at $V = -1.3$ V for transitions $\alpha$ (from 3 to 4 at negative $V$) and $\beta$ (from 4 to 3 at negative $V$) and at $V = +1.1$ V for $\gamma$ (from 4 to 3 at positive $V$), as a function of current by using different tip heights. The slopes of the linear fits in the double logarithmic plot are $1.86 \pm 0.18$ for $\alpha$, $1.90 \pm 0.26$ for $\beta$, and $1.61 \pm 0.76$ for $\gamma$. This indicates that transitions $\alpha$ and $\beta$ are two-electron processes. For $\gamma$, the error is too large to differentiate between a one-electron and a two-electron process.

Figure 4D visualizes the transitions between 3 and 4. The transitions $\alpha$ and $\gamma$ coincide with the onset of ionic resonances of the initial structures, as probed by STM (Fig. 3, B and A, respectively), suggesting that these transitions involve (de)charging the initial structure. Note that at electronic resonance, the charge state...
is transiently changed by charge transfer between tip and molecule. After a typical lifetime on the order of a few picoseconds on 2-ML NaCl, the molecular charge ground state is restored by charge transfer between molecule and metal substrate (4). The structural relaxation that follows a charge transition can oscillate for several tens of picoseconds (26).

For Fig. 4D, we calculated on a NaCl surface the ground state energies of 3 and 4 in different charge states and the related relaxation energies \( \Delta \) (see SM (27)). The relatively large energy of the intermediate \( 3^\text{geo} \), for the transition from \( 3^{-1} \) is rationalized by the Jahn-Teller distortion of \( 3^1 \). The calculated energies for the charge transitions are in good agreement with the resonances measured by STM when assuming similar energies for \( 4^0 \) and \( 3^{-1} \). A partial voltage drop across NaCl of \(-20\%\) can be considered for this junction geometry (27).

The observed two-electron process for \( \alpha \) indicates that in addition to the charge transition, a second charge carrier is needed to provide additional energy in an inelastic electron tunneling (IET) process (28). In contrast, transition \( \beta \) involves no charging of the initial structure \( 4^3 \), but probably only by IET processes a transition to \( 4^3 \) occurs, which is subsequenly charged from the substrate to \( 3^{-1} \), the charge ground state of structure 3. In transition \( \gamma \), the LUMO of 4, shown in Fig. 3G, is transiently occupied. This orbital exhibits a nodal plane along the long axis of the molecule and therefore is an antibonding state in the neutral molecule and therefore is an antibonding state and therefore is an antibonding state nodal plane along the long axis of the molecule and therefore is an antibonding state.

The insights obtained in redox reactions studied by tip-induced electrochemistry will be useful to better understand redox reactions that are important in organic synthesis (32) and nature (33). For future artificial molecular machines (23), controlled, reversible, and selected switching between more than two different constitutional isomers, as demonstrated in our work, could enable novel functionalities. In addition, increased workload and operation at elevated temperatures could be facilitated by the relatively high energy barriers, on the order of 1 eV, involved in constitutional isomerization reactions.

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SUPPLEMENTARY MATERIALS

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Supplementary Text

Fig. S1 to S17

Tables S1 to S3

References (34–49)

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