Remotely Triggered Geometrical Isomerization of a Binuclear Complex

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S Supporting Information

ABSTRACT: Binuclear organometallic molecules are model systems for investigating intramolecular spin-coupling and charge-transfer processes. Using electrospray ionization, Fe(salten) dimers linked by dipyridyl disulfide are deposited on gold for probing with a low-temperature scanning tunneling microscope. Each monomer constitutes a multistable switch owing to its geometric isomerism. Controlled and reversible remote switching within a single dimer is demonstrated. The process is attributed to intramolecular electron transfer.

One approach to molecule-based functional devices relies on switches on surfaces. Switching in molecular layers has been achieved using stimuli like light, temperature, and electric fields.[1−8] Upon injecting current with a scanning tunneling microscope (STM), changes of molecular conformation, spin, and adsorption state have been observed.[9−15]

Usually the current-induced changes occur directly under the STM tip.[16] For molecule-based logic, however, a lateral energy transfer appears to be necessary. Few examples—controlled molecular hopping[17] and tautomerization propagating over an intervening molecule[18]—have been reported from custom-made molecular arrays. Implementing a pathway for energy transfer within a single molecule by chemical synthesis is a desirable alternative to on-surface preparation with a STM.

Here we demonstrate controlled and reversible remote switching within a single binuclear organometallic molecule. By injecting current to one subunit, a reversible isomerization of the other via a Bailar twist[19] is induced. The choice of the linker between the subunits is seen to be crucial for electron transfer comparing results from electron-rich disulfides and less conducting ethyl chains.

As a switch we synthesized the binuclear compound [Fe(salten)pyS]$_2$ (Figure 1a).[20] It is composed of two iron(III) bis(3-salicylideneaminopropyl)amine (Fe-salten) subunits that are coupled via a dipyridyl disulfide (pySSpy) linker. To enable single-molecule experiments in ultrahigh vacuum and at low temperature (∼5 K), we used electrospray ionization for deposition of molecules onto Au(111).[21]

The geometry of pseudo-octahedral [Fe(salten)L] complexes depends on the coligand L. Strong or bulky ligands, e.g., pyridine or pyridine derivatives, lead to a *trans* geometry
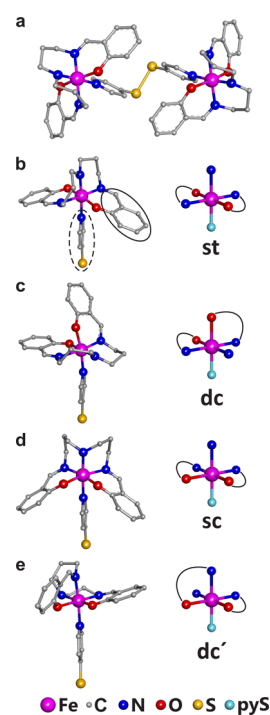

Figure 1. Structures of [Fe(salten)pyS]$_2$ dimer and monomers. H atoms are not shown. (a) Calculated structure of [Fe(salten)pyS]$_2$. (b−e) Geometrical isomers of the (thiopyridine)-Fe(salten) subunit: (b) symmetric *trans* (st), (c) dissymmetric *cis* (dc), (d) symmetric *cis* (sc), and (e) second dissymmetric *cis* (dc′). Solid and dotted ellipses indicate phenolate and the coligand L = pyridine thiolate, respectively. The molecular structures in the left panel are represented by simplified symbols of the quasi-octahedral cores on the right. Arches indicate the positions of phenolate rings.

(Figure 1b).[22] Weaker ligands favor a *cis* configuration (Figure 1c).[23] While the *cis* configuration is dissymmetric, the *trans* configuration exhibits a C_2 axis. Besides these geometries, which have been observed in crystals before,[22,23] two additional configurations are conceivable, namely a symmetric *cis* configuration with a mirror plane (Figure 1d), and a second dissymmetric configuration with both phenolate groups *cis* to

the axial ligand (Figure 1e). Below we use the naming scheme st, dc, sc, and dc′ introduced in Figure 1. The dimer of Figure 1a with two st subunits is accordingly denoted st-st. Our calculations (see Computational Methods in the Supporting Information for details) show that with L = pyridine thiolate, the st and dc isomers are most stable (see Table S1). The energies of dc′ and sc are higher by ∼0.5 and 0.9 eV, respectively, in agreement with the fact that dc and st are experimentally observed[22] whereas dc′ and sc are hypothetical.

After deposition of sub-monolayer amounts of [Fe(salten)-pyS]₂ onto Au(111), STM images reveal three closely related dimeric patterns (Figure 2). They may be divided in halves

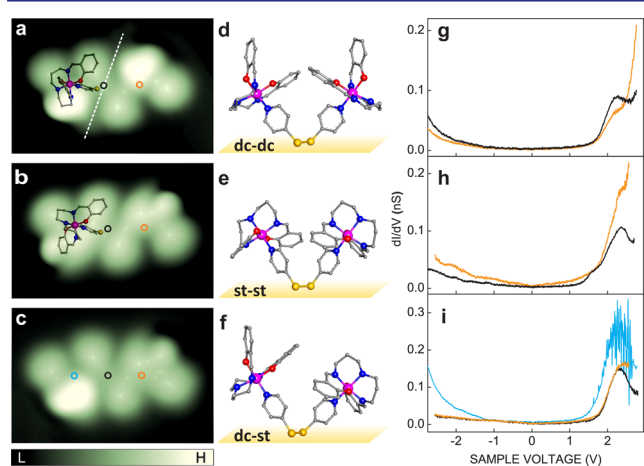**Figure 2.** (a−c) STM images (3.5 × 2.4 nm²) of three distinct structures of [Fe(salten)pyS]₂ on Au(111). The data are displayed in a pseudo-three-dimensional fashion with the color scale covering a range of 0.21 nm. Images (in all the figures) were acquired with sample voltages V = 0.20−0.25 V at constant currents I = 10−50 pA. A dotted line in (a) separates the two subunits of the binuclear molecule. Colored circles indicate the positions where dI/dV spectroscopy was performed. In (a) and (b), top views of models of dc and st monomers are overlaid over one half. (d−f) Side views of [Fe(salten)pyS]₂ comprising different isomers. (g−i) dI/dV spectra recorded at the positions indicated in a−c. Before opening the current feedback, the STM was operated at V = 2.7 V and I = 100 pA.

(dotted line in Figure 2a) that exhibit either three (Figure 2a) or three major and one minor (Figure 2b) lobes. Two patterns are composed of identical halves (Figure 2a,b), and the third one (Figure 2c) is a combination thereof. The submolecular contrasts may be understood on the basis of the structures of dimers (Figure 2d−f) comprising combinations of the isomers shown in Figure 1. The molecules are assumed to adsorb with the disulfide linker attached to the substrate. The molecule of Figure 2a is a symmetric dc-dc dimer. Its highest lobes appear to originate from the phenolate ligand. The pattern of Figure 2b is consistent with a st-st dimer (Figure 2e) where the phenolate ligands are located at heights similar to that Fe, with a propyl chain (C3 linkage) above one of them. The propyl chain is likely causing the extra lobe in the image. Finally, the asymmetric species of Figure 2c combines the dc and st subunits and is denoted dc-st. The abundances of st-st, dc-st, and dc-dc dimers determined from large-scale images (∼40%, 35%, and 25%, respectively) are consistent with the calculated sequence of energies (Table S1). A dc configuration of a subunit of the adsorbed [Fe(salten)pyS]₂ seems to be at conflict with the st configuration reported for bulk materials. However, infrared reflection absorption spectra indicate that on

Au(111) a dc configuration is also possible,[20] which is consistent with our STM observations.

Spectra of the differential conductance dI/dV of the three species (Figure 2g−i) were acquired at the positions marked in the STM images. With the tip above the disulfide moiety, all species show a prominent unoccupied electronic state at ∼2.35 V (black lines). Indication of this resonance is also discernible closer to the centers of the individual subunits (orange lines). The similarity of the spectra of all species lends support to the geometric interpretation of the STM images in Figure 2a−c.

dc-st molecules display a striking anomaly when the tip is placed over the center of the dc subunit (blue circle and line in Figure 2c,i). Fluctuations occur at sample voltages exceeding ∼1.5 V, which signal rapid changes of the tunneling junction. Figure 3b presents the result of current injection to the dc
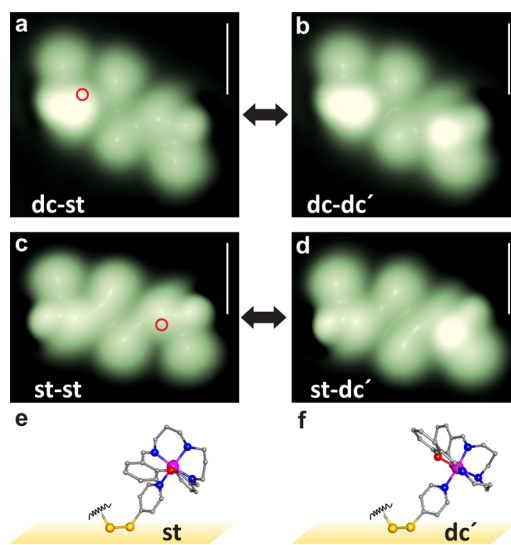

Figure 3. Reversible isomerization of dc-st and st-st molecules. STM images recorded (a,c) before and (b,d) after injecting current at 1.6 V at the positions marked by red circles in a and c. Scale bars correspond to 1 nm. (e,f) Side views of st and dc′ subunits, respectively.

subunit of the dc-st dimer shown in Figure 3a. The st subunit has switched to a new state with a bright protrusion at its center. We attribute it to the dc′ isomer of Figure 1e, where the phenolate ligand with its conjugated π system is located above the Fe center (Figure 3f).

The manipulated monomer is located ∼1 nm away from the point of current injection; i.e., the switching occurs remotely. The process is fully reversible. By injecting another current pulse on the dc side, the original dc-st state is restored. Remarkably, the dc unit itself does not switch to any other configuration so long as nondestructive currents and voltages are used.

On st-st dimers (Figure 3c) a transformation to st-dc′ was occasionally found (Figure 3d). However, the switching took place locally, i.e., at the st subunit to which the current was injected. st-dc dimers behaved similarly (reversible, local switching to dc′-dc).

We suggest that the isomerization between st and dc′ is effected by a Bailar twist,[19] whereby two opposite triangular faces of the octahedral coordination shell rotate by 120° with respect to each other. Figure 4 shows the transformation of a dc′ isomer to st via a twist of the upper triangle, while the lower one is fixed to the substrate. It involves only one flexible C3
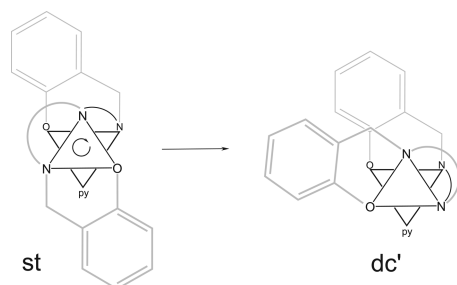
Figure 4. Isomerization of st to dc′ via a Bailar twist. Two opposite triangular faces of the octahedral coordination shell of [Fe(salten)pyS] are displayed with black lines. C3 linkages are indicated by arches, and C–N double bonds are omitted. In the Bailar twist transforming the st isomer to dc′, the upper triangle rotates clockwise by 120° with respect to the lower one, which is fixed to the substrate by the pyridine disulfide linker. Further rotation is sterically inhibited.

linkage, while all other metal–ligand bonds remain fixed. It may be reversed, but the ligands do not allow for further rotation. Consequently, the st subunit represents a two-state configurational switch. The absence of any switching from dc subunits can also be understood on the basis of this mechanism (see Figure S1). A twist from dc to dc′ would involve a propylene and an iminophenol bridge. The conjugated π system of the latter is more rigid and thus suppresses this twist. Another conceivable twist involving only a flexible C3 linkage leads to the unfavorable (*vide supra*) sc configuration. This explains why remote switching is found only when injecting electrons into the dc part of dc-st dimers (or the resulting dc-dc′ dimers) and not on st-st dimers. dc cannot be switched and thus serves as a relay to transfer the excitation energy to the other subunit, while st uses the energy itself to convert to dc′.

The mechanism of the remote switching is of particular interest. Remote switching on dc-st and only local switching on st-st are difficult to reconcile with a force-related mechanism. Moreover, the threshold voltage of ∼1.5 V, which is close to the onset of the unoccupied molecular resonance, and the absence of switching at reversed polarity favor an electron-induced process.

The different total energies of the dimers (Table S1) are essentially due to the different energies of their subunits rather than their mutual interaction. This means that a sufficient fraction of the excitation energy has to be transferred from the dc to the st subunit to achieve isomerization to dc′.

The injection of an electron to the dc subunit locally creates an electronically and possibly vibrationally excited state. To discriminate between vibrational and electronic energy-transfer mechanisms, a dimer linked by a less electron-rich dipyridylethane moiety was synthesized. Using deposition conditions similar to those used before, ∼60% st-st and ∼40% dc-st dimers were observed (see Figure S2a), which appear very similar to the disulfide-linked molecules. Switching experiments on dipyridylethane-linked dimers, however, led to strikingly different results. On the dc-st species, remote switching was never observed. Occasionally, we found local interconversion between st and dc′ when tunneling directly into these subunits (Figure S2b,c).

The results from the dipyridylethane-linked dimers allow for the following conclusions. First, through-space tunneling from the excited dc subunit to the st part is not relevant for switching. The absence of remote switching of sulfide-linked st-st molecules is also in line with this interpretation. Next,

vibrational energy transfer may tentatively be excluded. The energies of the S–S stretching and bending modes are lower than the energies of the modes of the Fe(salten) monomers. This, along with the bonding of the S atoms to Au, is expected to make vibrational energy transfer over the S–S linker rather inefficient. The fact that the dipyridylethane bridge does not enable remote switching despite its different vibrational modes does not favor vibrational energy transfer. This leaves electron transfer through the disulfide bridge, possibly involving the S–Au bonds, as the most likely scenario. Our calculations for sulfide-linked dimers indeed show that the lowest unoccupied molecular orbital exhibits a high electron density at the disulfide bridge and overlaps with the Fe(salten) subunits (see Figure S3). With a dipyridylethane bridge, this orbital is localized to the separate subunits and hardly overlaps via the ethyl chain (Figure S3).

In conclusion, a custom-made binuclear Fe(salten) complex on Au exhibits geometrical isomerism of the individual subunits. Reversible switching between two isomers has been achieved within single molecules. A disulfide bridge connecting the molecular subunits enables remote switching, whereas an ethyl link is inactive. It is conceivable that our approach may be extended to implement basic logic functions within a single molecule.

■ ASSOCIATED CONTENT

ⓈSupporting Information
Experimental details; computational methods; calculated total energy differences for [Fe(salten)pyS] and [Fe(salten)pyS]$_2$; Bailar twists not observed in the experiments; STM data from dipyridylethane-linked dimers; calculated orbital energies of [Fe(salten)pyS]$_2$ and [Fe(salten)pyCH$_2$]$_2$; oxidation state of Fe centers. 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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