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SUPPLEMENTARY INFORMATION

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Submolecular control, spectroscopy and imaging of bond-selective chemistry in single functionalized molecules

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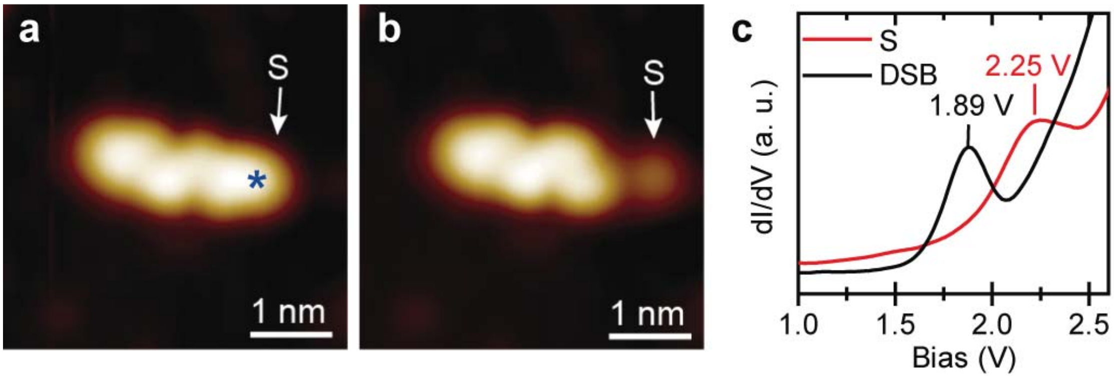

Figure S1 | Isolated sulfur atom on the NiAl(110) surface. a, STM topography of a DSB-2S (I) molecule. The asterisk indicates the location where the 2.5-eV tunneling electrons were injected. **b**, Topographic image showing that the sulfur atom was abstracted from the molecule and trapped on the surface. Set point for **a** and **b**: V=1.8 V, I=50 pA. **c**, dI/dV spectra taken on the "DSB" molecule and on the isolated sulfur atom. The spectra were taken at the set point (V=2.5 V, I=0.1 nA).

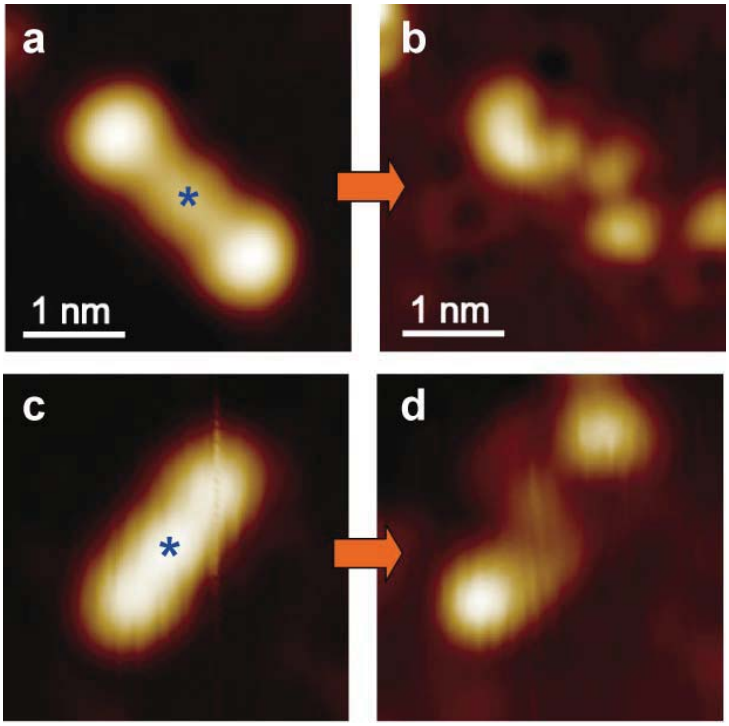

Figure S2 | Molecular decomposition under high-voltage pulses. a, STM topography of a DSB-2S-2Ac (I) molecule. **b**, The molecule decomposed after applying a 3.5-V voltage pulse. **c**, STM topography of a DSB-2S (I) molecule. **d**, The molecule decomposed after applying a 3.2-V voltage pulse. Imaging conditions: V=1.0 V, I=50 pA. The asterisks in a and b indicate the locations for injecting electrons by STM tip.

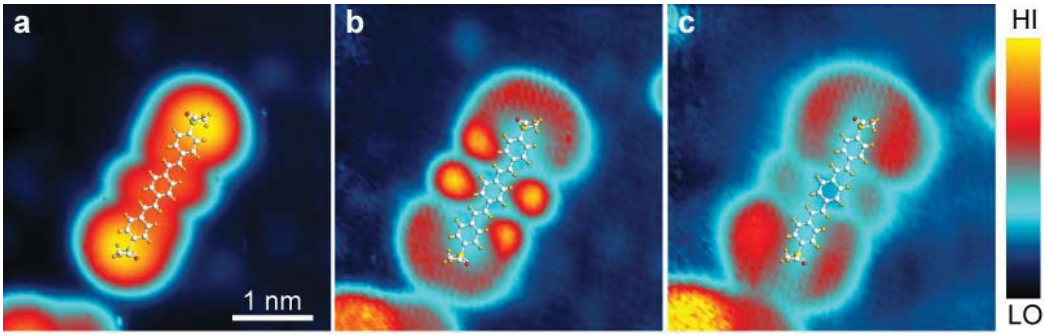

Figure S3 | dI/dV images of a DSB-2S-2Ac (I) molecule showing the spatial distributions of DSB-derived and Ac-derived states. a, STM topography of the DSB-2S-2Ac (I) molecule obtained at V=1.6 V, I=50 pA. **b** and **c**, dI/dV images acquired at the selected bias voltages corresponding to the DSB-derived and Ac-derived states, respectively. Imaging conditions: V=1.4 V, I=50 pA for **b**; V=1.75 V, I=50 pA for **c**. The properly scaled ball-and-stick molecular models are superimposed on the topographic and dI/dV images.

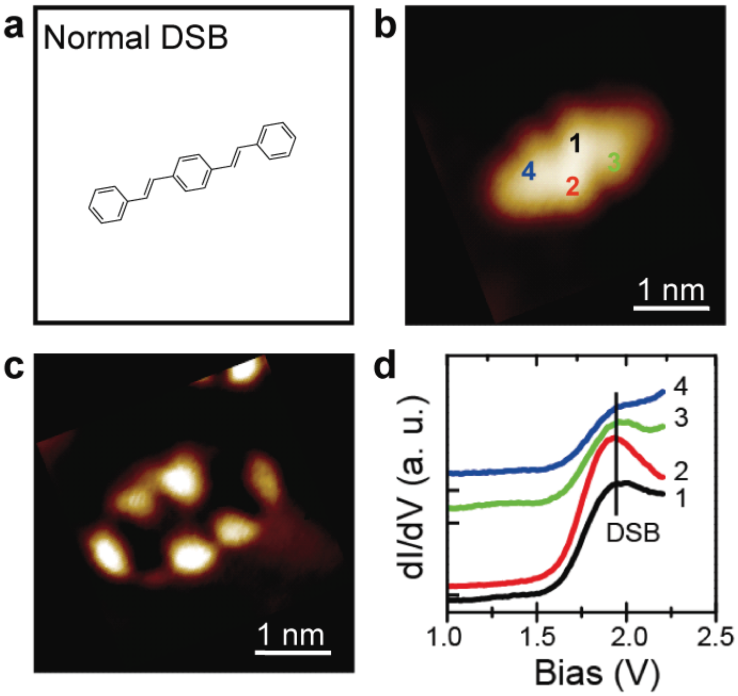

Figure S4 | Electronic structure of a normal DSB (I) molecule. a: Schematic, **b**: Topography, **c**: dI/dV image, and **d**: Spatially resolved dI/dV spectra. Imaging condition: V=1.8 V, I=0.1 nA. The spectra were taken at four locations (1, 2, 3, 4) on the molecules as noted in **b** and are offset for clarity. Set point: V=2.0 V, I=0.1 nA. The peak (1.95 V) in the spectra is highlighted by the vertical line, corresponding to the π-resonance of the DSB molecule. The resonance is broad and images were scanned at 1.8 V in order to decrease the contribution of the rising dI/dV signal from the substrate and thus increase the contrast.

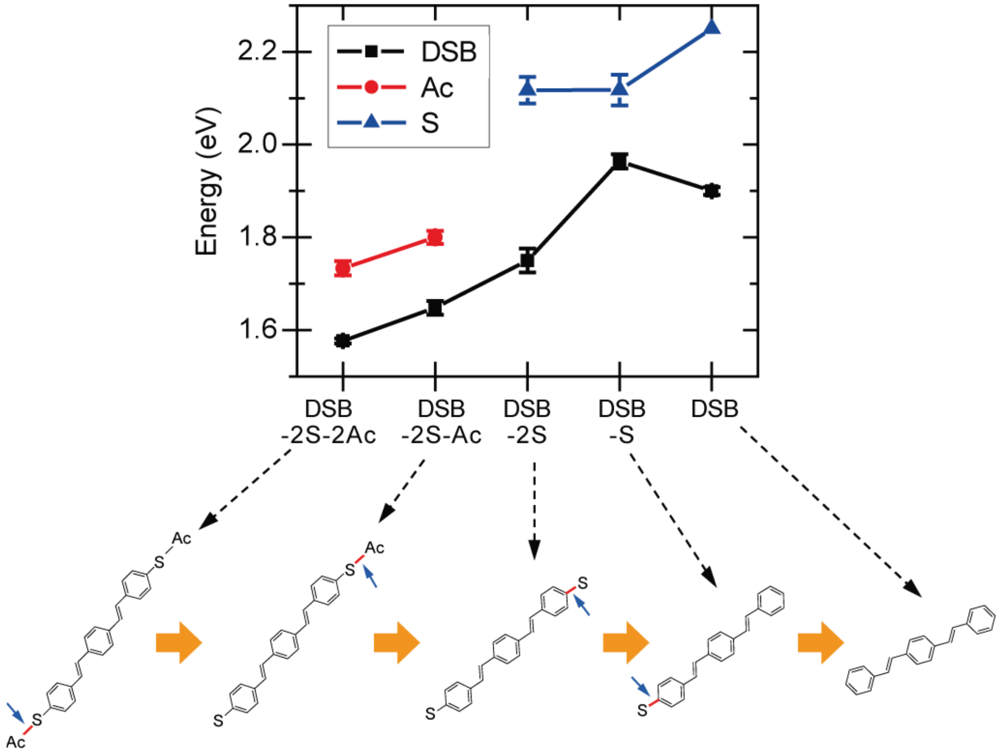

Figure S5 | Evolution of the DSB-, acetyl-, and sulfur-derived resonance energies along the dissociation sequence. The data points were summarized by analyzing over 50 different molecules. The error bars arise from the standard deviations of the statistical averages. The data point for “S” of “DSB” was acquired on the isolated S atoms as shown in Fig. S1b. Along with the selective abstraction of the different functional groups, the π-resonance is increasingly blue-shifted with the exception from DSB-S to DSB, probably because of the asymmetric bonding with the substrate at the ends of DSB-S. Although the functional groups give rise to states that are relatively localized at their bonding sites, they can affect the π-system throughout the whole molecule.

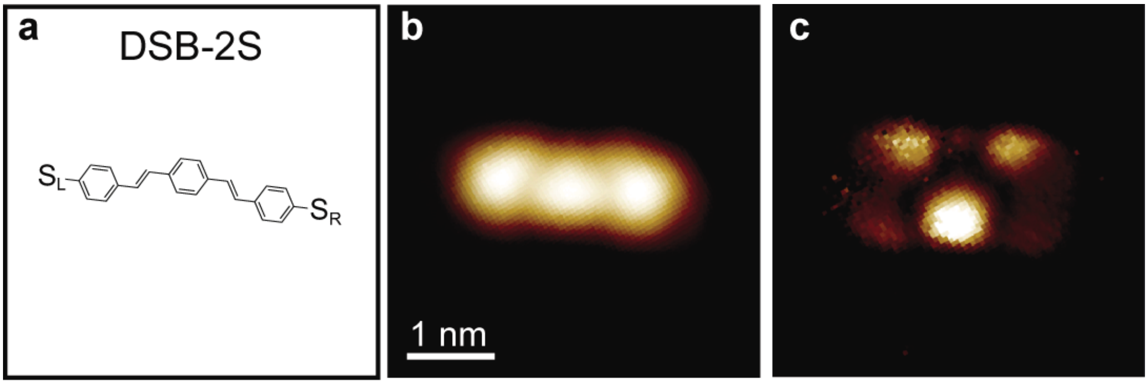

Figure S6 | Spatial distribution of the π-resonance of a DSB-2S (II) molecule. a: Schematic model, **b**: STM topography, and **c**: Simultaneously recorded dI/dV image. Imaging condition: V=1.6 V, I=50 pA.

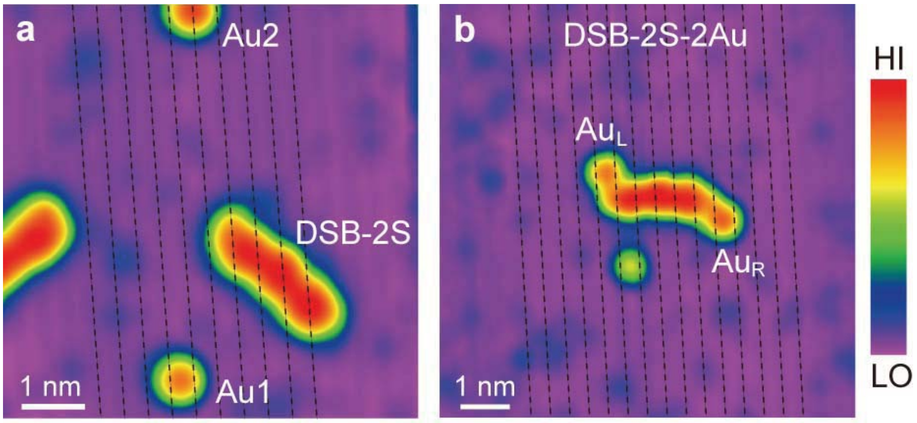

Figure S7 | The adsorption sites of Au atoms on the NiAl(110) surface. a, Atomically resolved STM topography showing two different adsorption sites of Au atoms on the NiAl(110) surface: Au1 at the bridge position between the protruding Al rows and Au2 on top of the Al rows. The resonance state of Au atom can be affected by the adsorption site on the NiAl(110) surface depending on which elements (Ni or Al) they are bonded with. The resonance energy of Aul is about 0.2 eV higher than that of Au2. **b**, Atomically resolved STM topography of DSB-2S-2Au complex discussed in Fig. 3 and 4, showing that both Au$_L$ and Au$_R$ adsorb at the bridge position between the Al rows. The black dash lines in **a** and **b** highlight the protruding Al rows on the NiAl(110) surface.

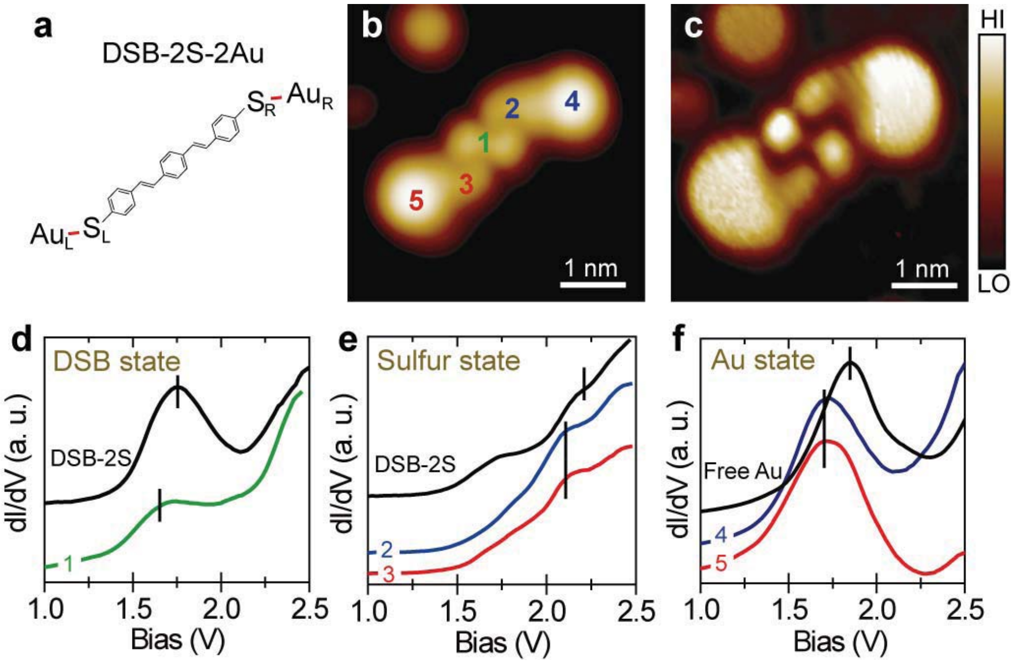

Figure S8 | Spectroscopy and imaging of the DSB-2S-2Au complex (isomer I). a, Schematic model of the DSB-2S-2Au complex. **b**, Topographic image of the DSB-2S-2Au complex. Set point: V=1.6 V, I=50 pA. **c**, dI/dV image of the DSB-2S-2Au complex, simultaneously acquired with **a**. **d-f**, dI/dV spectra taken at locations 1, 2, 3, 4, and 5 of the complex as indicated in **b**, showing states originated from DSB, sulfur, and Au. All the spectra were taken at the same set point (V=2.5 V, I=0.1 nA) and offset for clarity. The energetic positions of the molecular resonances in the dI/dV spectra are highlighted by the vertical lines. The spectra denoted by "DSB-2S" and "Free Au" were taken on the acetyl-free molecule and isolated gold atom. In contrast to the DSB-2S-2Au complex (isomer II) in Fig. 3 and 4, both Au atoms were adsorbed on top of the Al rows and formed covalent bonds with the S atoms.