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Electronic Supplementary Information

Retention of chirality in electron-induced reaction

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1. Experiment details

Experiments were performed in a low temperature ultra-high vacuum ($\leq 3.0 \times 10^{-11}$ mbar) STM (Omicron) system. The Cu(110) single crystal was cleaned by repeated cycles of Ar^+ sputtering (0.6 keV, 7 μA) followed by annealing at 800 K till less than 1 % of contaminants could be detected by STM. Commercially available m-iodopyridine, IPy, (Sigma Aldrich, 98%) was purified by multiple freeze-pump-thaw cycles, and then dosed from a capillary tube directed towards the Cu(110) surface. The copper crystal reached a maximum temperature of 8.6 K during dosing. STM images were taken in the constant current mode with the bias voltage applied to the sample at 4.6 K. Dissociation of IPy was electron-induced by placing the STM tip over the middle of the IPy feature and maintaining a constant bias voltage in the range of 1.35 to 1.60 V, with the feedback loop disabled for up to 1s.

2. Computational details

All density functional theory (DFT) calculations, including the energies of the physisorbed IPy, the products, the image simulations and the molecular dynamics (MD) trajectories, were carried out using the generalized-gradient approximation (GGA) for exchange-correlation potentials,[1] the projector-augmented wave (PAW) method,[2,3] and a plane-wave basis set as implemented in the Vienna ab-initio simulation package (VASP),[4,5] installed at the SciNet supercomputer.[6] The revised Perdew-Burke-Ernzerhof (RPBE)[7] functional with the second version of Grimme's dispersion corrections[8] was employed for structure relaxation and MD calculations. The energy cut-off for plane-wave basis was set to 400 eV for all configurations. A supercell (5×7) consisting of 175 copper atoms in 5 layers was employed to model the Cu-surface. The vacuum gap of the copper slab was kept to a minimum of 15 Å. The surface Brillouin zones of the system were sampled using the gamma point only. All atoms except those for the bottom two Cu layers were fully relaxed until the residual force per atom was less than 0.02 eV/Å.

The molecular dynamics were obtained by solving the equations of motion while conserving the total energy, the number of atoms and the volume of the system, for a time-step of 0.5 fs at 4.6 K. The excited-state potential-energy surface (pes*) was represented by the ionic pseudo-potential[3,9,10] as employed in the Impulsive Two-State model,[11-16] formulated in previous work by this group. The model was used to compute the momenta, after a time t*, obtained from the transition of the equilibrium ground pes configuration to the pes*. The pes* satisfactorily simulated the added electron charge by removing a part of an electron from the I-atom and N-atom and placing them in their valence shells to give the following pseudo ionic configuration, [Kr]$4d^{9.2}5s^{2}5p^{5.8}$ for the I-atom and [He]$2s^{1.8}2p^{3.2}$ for the N-atom. The system was returned to the ground pes after t*, the minimum time required for the reactive event to occur. The second part of the model was employed to calculate the final state following ~ 3 ps on the ground employing the momenta and atomic positions gained from the pes*. The calculated geometries were visualised using the VMD software.[17]

3. Molecular adsorption of IPy on Cu(110) at 4.6 K

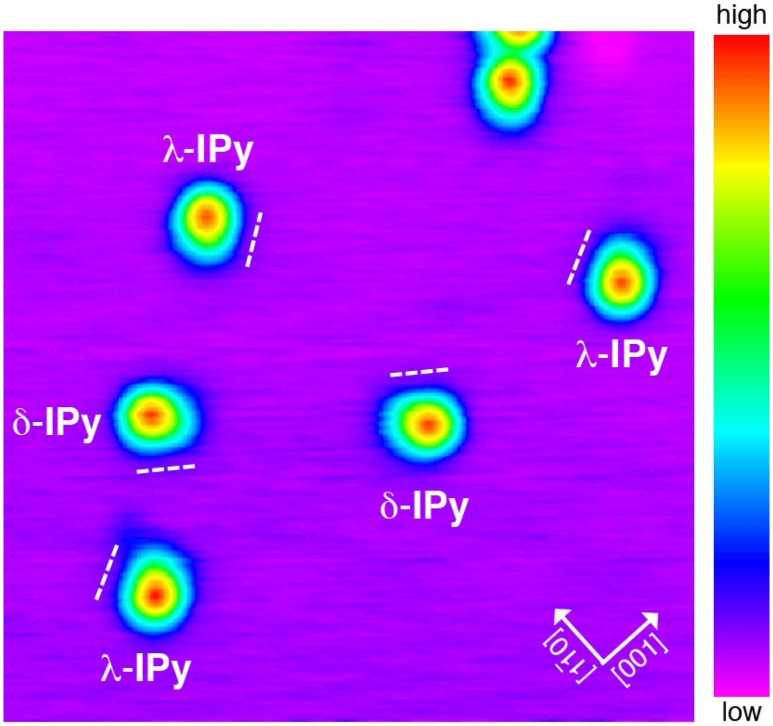

Fig. S1 STM image of the two enantiomers, λ- and δ-IPy, adsorbed on Cu(110). The white dashed line indicated the flattening of the feature at the location of the N-atom in the C5 ring. (STM image: 12 × 12 nm^2; 0.5 nA; – 0.3 V).

4. Threshold of the electron-induced reaction

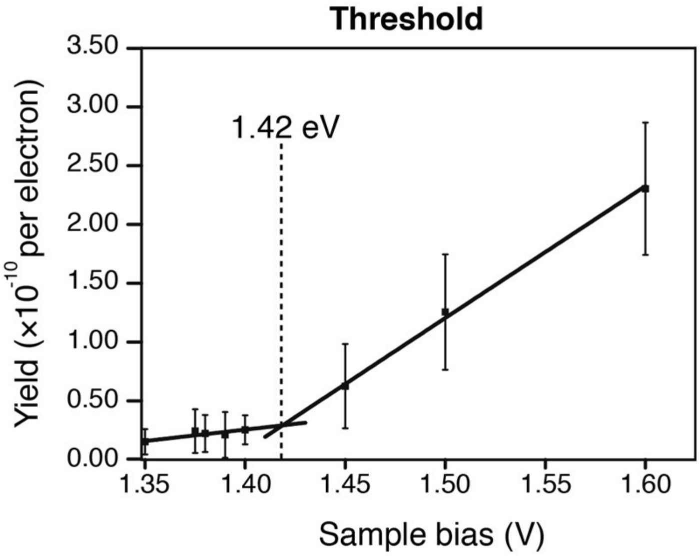

Fig. S2 The experimentally-measured reaction yield as a function of the bias voltage. The threshold is measured to be 1.42 eV, assuming a linear threshold law. The error bars give the standard deviation.

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