

Supporting Information

On-Surface Synthesis with Atomic Hydrogen

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TBPDT molecules

Figure S1a shows bond-resolved frequency shift nc-AFM image of a diagonal linking between two S-doped 5-AGNRs. The image shows that the interconnection is formed by faulty stacking between the neighboring segments. In effect instead of two C-C bonds formed usually between two precursors only one C-C bond is formed. Subsequently a second C-C bond is formed when one precursor attaches the second one through the debrominated site. In Figure S1b we show the schematic image of the structure. As shown in the main text it seems that a significant fraction of defects within the S-doped 5-AGNRs originates from such a faulty stacking.

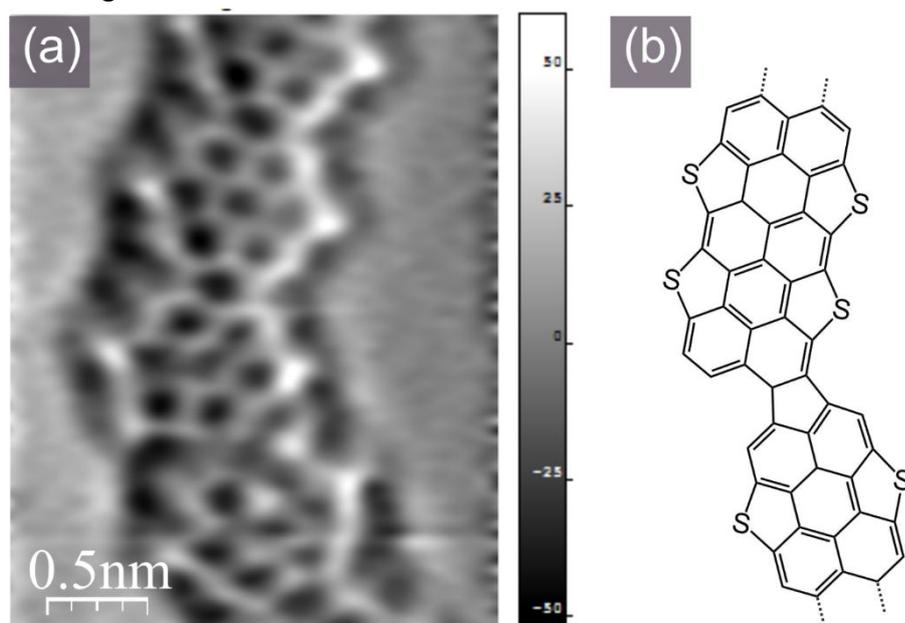
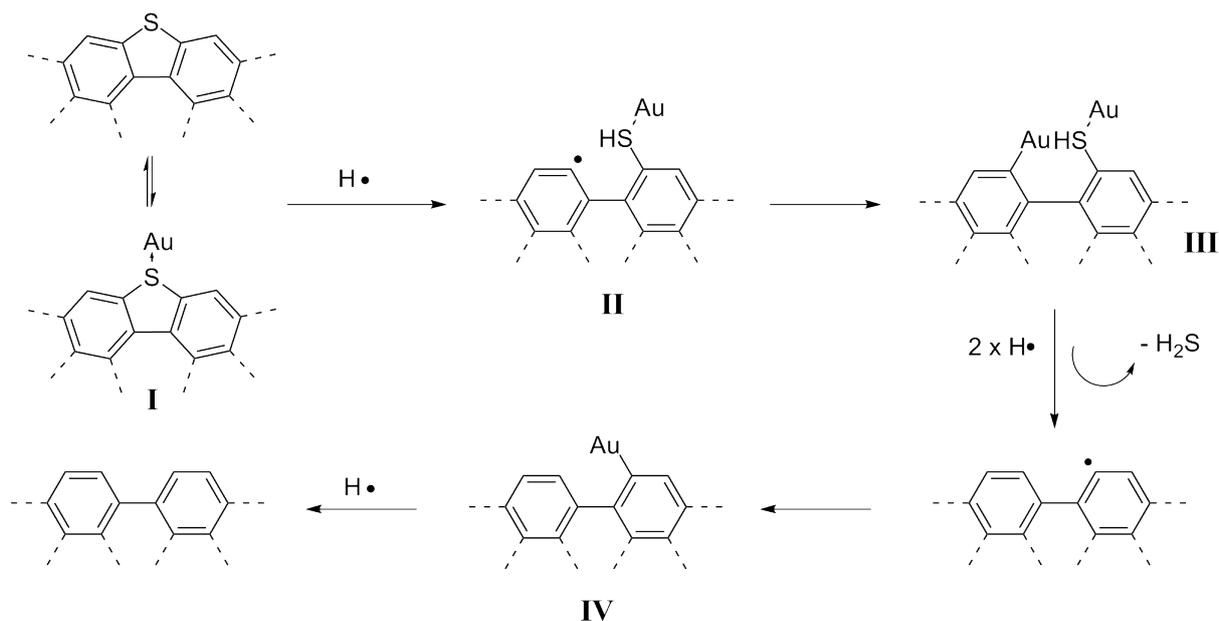


Figure S1. (a) Bond-resolved nc-AFM image of two interconnected S-doped 5-AGNRs created by annealing of TBPDT precursors at 350 °C; (b) structural model of molecular motif shown in (a).

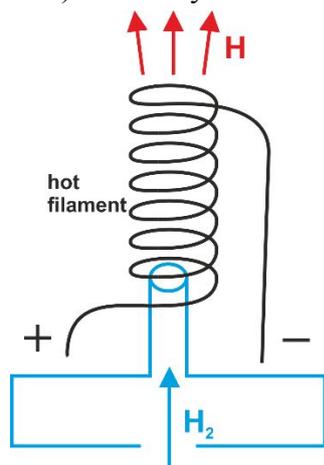
Proposed mechanism for the desulfurization on gold surface with atomic hydrogen

We propose a plausible mechanism for desulfurization on gold surface with atomic hydrogen similar to radical desulfurization by Raney nickel. In the first step, the sulfide coordinated to the metallic substrate I is cleaved with atomic hydrogen and the formed radical intermediate on metallic substrate II is transformed to organometallic specie III. In the next step, the thiol group is cleaved by another atom hydrogen releasing hydrogen sulfide. The final radical intermediate is bonded to the metal surface IV and in the last step this organometallic is cleaved with atomic hydrogen to form the product.



Hydrogen cracker

We are using home-built thermal hydrogen cracker with hot tungsten filament (scheme below) cooled by water:



The filament is heated by the current flow ($P=56\text{W}$). The estimated temperature of the filament during operation is $\sim 2200\text{ }^\circ\text{C}$. Molecular hydrogen flux is going directly through the hot tungsten helix and is being cracked to atomic hydrogen with the estimated efficiency of $\sim 5\%$. The tungsten filament is mounted inside the cooling tube (the tube is cooled by water). Cooling of the cracker is essential to keep the outer parts of the cracker not too hot to prevent from vacuum level lowering. For our cracker we have found the optimal parameters by checking the quality of the hydrogen passivation of the Ge(001) surface in previous experiments.¹⁻³ The optimal hydrogen pressure in our case has been found in the range of 1×10^{-7} mbar and the cracker operation power of 56W.

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