

## Supporting Information:

### Direct Observation of the Geometric Isomer Selectivity of a Reaction Controlled via Adsorbed Bromine

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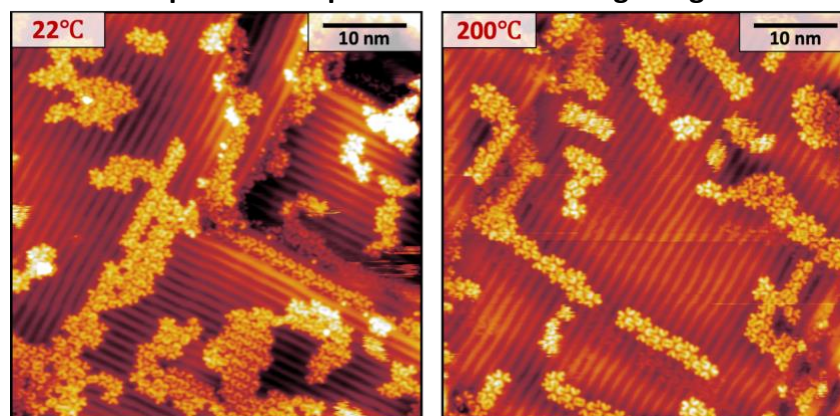
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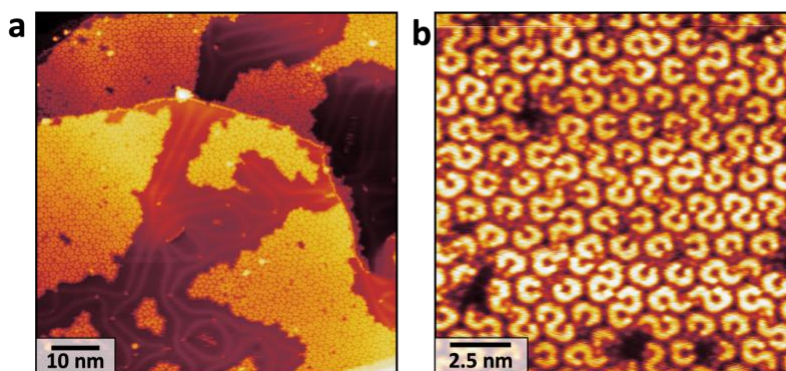
#### 1. Results of a Room Temperature Deposition and Following a Slight Anneal



**Figure S1.** STM images following a room temperature deposition and an anneal to 200°C. The DBPQ molecules are observed to remain intact with no dissociation of the C-Br bond and no bromine atoms visible on the surface.  $U = +1.0\text{ V}$ ,  $I = 100\text{ pA}$ .

The above STM images depict the results of a room temperature deposition of DBPQ on Au(100) and following an anneal to 200°C. These results closely match the STM image that appears in **Figure 1** of the main text. No long-range ordering is observed, but some clusters are evident as a result of hydrogen bonding between aromatic hydrogens and the oxygen atoms in the ketone functional groups. The STM image showing the results of the anneal to 200°C demonstrates the stability of the C-Br bond in the case of these molecules. This stability is further confirmed by the absence of any bromine atoms observed on the surface in STM imaging. A result consistent with previously published studies involving this class of reactions on Au(111).<sup>1</sup>

## 2. Results of a Thermal Anneal on Au(111)



**Figure S2.** STM images following an anneal to 375°C after the deposition of DBPQ onto a room temperature Au(111) substrate. (a) Zoomed-out image showing the absence of bromine on the surface.  $U = -1.0\text{ V}$ ,  $I = 100\text{ pA}$ . (b) Zoomed-in image illustrating the early termination of the reaction process, the most common products visible are cis dimers and S-shaped tetramers on this surface.  $U = -1.0\text{ V}$ ,  $I = 100\text{ pA}$ .

## References

1. L. Dong, P. N. Liu and N. Lin, *Acc. Chem. Res.*, 2015, **48**, 2765-2774.