On-Surface Reductive Coupling of Aldehydes on Au(111)

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1 Methods

STM

Experiments were performed in a commercial UHV low temperature STM/AFM (Omicron Nanotechnology GmbH) at a base pressure of 1×10^{-10} mbar, operated at T \approx 78 K. Such setup maintains the sample grounded while the tip is under a defined potential. The Au(111) single crystal (Mateck GmbH) was cleaned by repeated cycles of Argon sputtering and subsequent thermal annealing. The **DTA** compound was sublimated to the substrate under UHV conditions, from a quartz crucible at 90 °C during 5 minutes in every deposition experiment, to ensure a similar coverage of the surface. The substrate temperature was monitored with an IR thermometer (Optris GmbH, model 3ML) during the deposition of the reactants and the annealing processes. It should be noted that for such a device $T_{object} > T_{measured} + 25$ °C. All the temperatures reported in this work correspond to $T_{measured}$.

XPS

Photoemission experiments were carried out under UHV conditions at a base pressure of 2×10^{-10} mbar. The XPS system is directly connected to the STM chamber, which allows *in situ* sample transfer. The experiments were performed with a monochromated Al K_{α} X-ray source. Photoelectron detection was conducted in normal emission with a SPECS PHOIBOS 100 hemispherical analyzer and a 2D delayline detector. The binding energies were calibrated with the hydrocarbon C 1s peak at 285.0 eV.

DFT

Density Functional Theory calculations were performed using the VASP code in version 5.3.^[1] We used the oPBE-vdW functional^[2] in conjunction with the PAW method. The plane-wave cutoff for the wave functions was 400 eV throughout. The reactants were modeled with shorter aliphatic chains to facilitate the calculations. The Au(111) surface was modeled as a non-reconstructed three layer slab of a (6×8) supercell with the two upmost layers free to relax. K-point sampling was limited to the Γ -point only, and Gaussian broadening of 0.1 eV was used to determine occupation numbers. Molecules are adsorbed on one side of the slab and dipole corrections to the energy are carried out accordingly. Ionic relaxation for all stable structures was carried out until all forces were smaller than 10 meV/Å. Transition states were found with the climbing image nudged elastic band method^[3] and the Dimer method,^[4] and converged to forces smaller than 20 meV/Å on all images.

2 Synthesis of the 2,5-Dihexylterephthalaldehyde monomers

General Methods

All reactions involving air -or moisture- sensitive reagents or intermediates were carried out in heatgun-dried glassware under an argon atmosphere and were performed using standard Schlenk techniques. All solvents for extraction and flash chromatography (FC) were distilled before use. All chemicals were purchased from Sigma Aldrich, Acros Organics, ABCR, Alfa Aesar, TCI or Fluka and were used as received. Gas chromatography (GC) was performed on an Agilent 7890A chromatograph equipped with a HP-5 column ($30 \text{ m} \times 0.32 \text{ mm}$, film thickness $0.25 \mu \text{m}$) using H₂ ($\approx 1 \text{ bar}$) as carrier gas. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker DPX-300 (300 Mhz) or a Bruker AV 400 (400 Mhz). Chemical shifts δ in ppm are referenced to the solvent residual peak (CDCl₃: ¹H, δ = 7.26; ¹³C, δ = (77.0) as an internal standard. Peak multiplicities are given as follows: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS ESI (m/z) spectra were recorded on a Bruker MicroTof or an Orbitrap LTQ XL (Nanospray) from Thermo Scientific. Melting points (MP) were determined on a Stuart SMP10 and are uncorrected. IR spectra were recorded on a Digilab Varian 3100 FT-IR Excalibur Series. IR signals are described as w (weak), m (middle), s (strong), br (broad) in cm⁻¹. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F254 plates; detection with UV light or by dipping into a solution of KMnO₄ (1.5 g) and NaHCO₃ (5.0 g) in H₂O (0.40 L) followed by heating. FC was carried out on Merck silica gel 60 (40 -63 μ m) with an argon excess pressure of about 0.5 bar.

1,4-Dihexylbenzene (3)



In a three-neck flask equipped with a condenser magnesium (3.65 g, 150 mmol, 2.20 eq) was covered with dry Et₂O (5 mL) under an atmosphere of argon. A few drops of 1-bromohexane were added carefully. After the boiling began the mixture was diluted with Et₂O (45 mL) and 1-bromohexane (21.0 mL, 150 mmol, 2.20 eq) dissolved in Et₂O (50 mL) was added dropwise over a period of 30 min. The resulting mixture was then heated at reflux for 2 h.

Under an atmosphere of argon 1,4-dichlorobenzene (10 g, 68 mmol, 1.0 eq) was dissolved in Et₂O (50 mL). Then NiCl₂·dppp (111 mg, 204 μ mol, 0.30 mol%), followed by the freshly prepared 1-hexylmagnesium bromide solution were added and the resulting mixture was heated at reflux for 15 h. Afterwards the mixture was given into an ice/HCl-solution (aq. 1M, 100 mL), followed by a phase separation. The aqueous layer was extracted with Et₂O (3 × 100 mL) and the combined organic layers were washed with brine (300 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by distillation ($T = 121 \,^{\circ}$ C, $p = 3 \times 10^{-1}$ bar) yielded the 1,4-dihexylbenzene (**3**) (13.9 g, 56.4 mmol, 83%) as a colorless liquid.

¹**H-NMR** (300 MHz, CDCl₃): $\delta = 7.09$ (s, 4H, aryl-H), 2.57 (t, J = 7.8 Hz, 4H, 2 × aryl-CH₂), 1.66 - 1.53 (m, 4H, 2 × CH₂), 1.42 - 1.24 (m, 12H, 6 × CH₂), 0.88 (t, J = 6.6 Hz, 6H, 2 × CH₃).

The analytical data is in accordance with the data reported in literature.^[5]

1,4-Dihexyl-2,5-diiodobenzene (4)



1,4-Dihexylbenzene (3) (10.0 g, 40.6 mmol, 1.00 eq) was dissolved in a solvent mixture consisting of water (25 mL), CCl₄ (50 mL) and acetic acid (230 mL). To this solution H_5IO_6 (4.62 g, 20.3 mmol, 0.500 eq), iodine (10.3 g, 40.6 mmol, 1.00 eq) and concentrated sulfuric acid (6.9 mL, 0.13 mol, 3.2 eq) were added and the resulting mixture was heated at reflux for 24 h. After cooling to room temperature, water (300 mL) was added and the organic layer was separated. Then the aqueous layer was extracted with pentane (3 × 200 mL). The combined organic layers were sequentially washed with saturated Na₂S₂O₃-solution (aq.,

150 mL), saturated Na₂CO₃-solution (aq., 150 mL) and saturated Na₂SO₄-solution (aq., 150 mL) before being dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography using pentane as an eluent, which yielded diiodobenzene **4** (17.5 g, 35.1 mmol, 86%) as a colorless solid.

¹**H-NMR** (300 MHz, CDCl₃): $\delta = 7.59$ (s, 2H, aryl-H), 2.59 (t, J = 7.7 Hz, 4H, 2 × aryl-CH₂), 1.67 - 1.46 (m, 4H, 2 × CH₂), 1.44 - 1.26 (m, 12H, 6 × CH₂), 0.88 (t, J = 6.6 Hz, 6H, 2 × CH₃). The analytical data is in accordance with the data reported in literature.^[5]

2,5-Dihexylterephthalaldehyde (1)



Under an atmosphere of argon diiodobenzene 4 (2.0 g, 4.0 mmol, 1.0 eq) was dissolved in dry THF (20 mL) and cooled down to -78 °C. A solution of *tert*-butyllithium (1.6 M in pentane, 10.5 mL, 16.8 mmol, 4.20 eq) was added dropwise and the resulting reaction mixture was stirred at -78 °C for 2 h. DMF (3.1 mL, 40 mmol, 10 eq) was added slowly and the mixture was stirred for 20 h at room temperature. After addition of saturated NH₄Cl-solution (aq., 30 mL) the organic layer was separated and the aqueous phase was extracted with Et₂O (3 × 40 mL). The com-

bined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et₂O; 50:1) afforded the dicarbaldehyde **1** (380 mg, 1.26 mmol, 32%) as a pale-yellow solid.

Mp.: 44 - 46 °C. **IR** (neat): 3345*w*, 3151*w*, 3037*w*, 2920*m*, 2849*w*, 1678*s*, 1609*w*, 1565*w*, 1488*w*, 1400*w*, 1375*w*, 1352*w*, 1313*m*, 1280*w*, 1265*w*, 1241*w*, 1223*w*, 1160*s*, 1115*w*, 911*m*, 886*m*, 860*m*, 796*w*, 777*w*, 717*s*, 620*m*, 530*m*, 472*w* cm⁻¹. ¹**H-NMR** (400 MHz, CDCl₃): $\delta = 10.35$ (*s*, 2H, CHO), 7.72 (*s*, 2H, aryl-H), 3.12 - 2.93 (*m*, 4H, 2 × aryl-CH₂), 1.66 - 1.57 (*m*, 4H, 2 × aryl-CH₂CH₂), 1.43 - 1.24 (*m*, 12H, 6 × CH₂), 0.92 - 0.84 (*m*, 6H, 2 × CH₃) ppm. ¹³**C-NMR** (100 MHz, CDCl₃): $\delta = 191.8$ (C), 143.5 (C), 136.9 (C), 133.2 (CH), 32.4 (CH₂), 32.0 (CH₂), 31.7 (CH₂), 29.3 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm. **Ms** (ESI): m/z: 325 [M+Na]⁺, 357 [M+MeOH+Na]⁺, 691 [2M+Na]⁺. **HRMS** (ESI): m/z: calculated for [M+Na]⁺: 325.2138; found: 325.2136. **EA** in % calculated for C₂₀H₃₀O₂: C: 79.42, H: 10.00; found: C: 79.24, H: 10.02.

NMR spectra

2,5-Dihexylterephthalaldehyde (1)



3 Annealing treatment of the self-assembly of DTA monomers on Au(111)

As a consecutive step towards the targeted on-surface reaction, the DTA-SAM was annealed at temperatures ranging from 100 °C to 250 °C. Annealing at 100 °C and 150 °C for 15 minutes, respectively, did not change the self-assembled arrangement of the **DTA** reactants on the Au(111) substrate. When the annealing was conducted at 200 °C, STM experiments revealed the desorption of **DTA** monomers from large areas of the surface (Figure ESI-1a). However, we also observed large areas of intact DTA-SAM, and more interestingly, a phase indicating an initial step of oligomerization (Figure ESI-1a,b). On the other hand, imaging after the annealing performed at T = 250 °C for 15 minutes (Figure ESI-1c) and 30 minutes (Figure ESI-1d) revealed that disordered oligomers were produced and all the remaining **DTA** monomers desorbed from the substrate.



Figure ESI-1: STM images recorded after the annealing treatment of the self-assembly of **DTA** monomers on the Au(111) surface. All images were acquired at $T \approx 78$ K. **a**, Annealing at 200°C for 15 minutes results in areas where the reactants extensively desorbed from the substrate (200×200 nm²; U = -1.50 V; I = 0.35 nA). **b**, Annealing at 200°C for 15 minutes also results in areas where the reactants remained self-assembled on the surface, avoiding the desorption (200×200 nm²; U = -1.50 V; I = 0.3 nA). **c**, Annealing at 250°C for 15 minutes (300×300 nm²; U = 650 mV; I = 0.1 nA). **d**, Annealing at 250°C for 30 minutes (100×100 nm²; U = 650 mV; I = 0.25 nA).

It is important to note that on-surface oligomerization indicates that a possible activation of the aldehyde moiety occurred when the substrate was heated to this temperature. However, the oligomers produced by the annealing of the **DTA** self-assembly on Au(111) cannot be unambiguously identified as the targeted *p***-PPV** products, in contrast with those obtained when the reactants were deposited onto the Au(111) kept at 250 °C.

4 On-surface reaction yield assessment

Generally, the yield of a chemical reaction is determined by the ratio between the amount of products obtained and the amount of products that should be produced in a perfectly efficient reaction. However, to quantitatively estimate the yield by which the observed on-surface reaction of monomers 1 on Au(111) produce the targeted p-PPV products, it should be noted the extensive desorption the reactants undergo when they are deposited onto the pre-heated substrate, leading to a complete absence of isolated monomers on the surface (similar to the annealing treatment at the same temperature, Figure ESI-1). Therefore, a direct comparison between how many reacted and unreacted molecules are on the substrate after the on-surface reaction is not viable for this purpose. In contrast, a feasible alternative to estimate the yield is to compare the amount of those that were clearly observed to have formed oligomers 4 on the Au(111) surface (from the reacted state). To circumvent the desorption liability, we performed both depositions with the same parameters (base pressure, sublimation temperature and exposure time) which allows to assume a similar amount of monomers reaching the surface per unit of area and time.

The sublimation at 90 °C of **DTA** monomers onto the Au(111) at room temperature during 5 minutes was carefully checked by STM and observed to produce a complete self-assembled monolayer of reactants on the substrate. Based on this information, we estimated the amount of monomers per nm² available

for an ideal perfectly efficient on-surface reaction and found it to be 1.11 unreacted monomers/nm². Similarly, STM inspection of the products 4 obtained on the Au(111) surface after the deposition of reactants onto the pre-heated substrate allowed us to determine a total of 0.07 reacted monomers/nm². The comparison between these two values shows that about 6% of the **DTA** molecules reaching the Au(111) surface reacted to form p-**PPV** oligomers.

5 Experiments on Au(001) and Au(788) substrates

The p-PPV oligomers obtained after the on-surface reaction of the **DTA** monomers on Au(111) do not follow the surface herringbone reconstruction. Furthermore, according to our DFT calculations, the implication of reactive sites on the surface play an important role in the proposed reaction mechanism. However, the reaction yield and selectivity of the products remained relatively low on this substrate. Therefore, we also investigated the reactivity of the **DTA** monomers on other Au substrates with a different surface reconstruction, *e.g.*, Au(001) and Au(788), using the same experimental conditions as on Au(111). The different reconstructions and nano-facetting of these surfaces could provide additional constraints to gain more control on the spatial order of the products and potentially a higher selectivity for the reaction.

After depositing the molecules onto the Au(001) substrate, a self-assembled structure was found (Figure ESI-2a). It is straightforward to note that the molecules self-assembly on this substrate is different than on Au(111). The monomers adsorb on the top of every second row of the surface reconstruction (blue arrows). However, the aliphatic chains on the reactants adsorbed in those rows are not aligned along the [110] direction. Therefore, likely steric effects prevent additional reactants from adsorbing in the intermediate rows (highlighted with green arrows) following the same configuration. However, the width of the intermediate stripes in the surface reconstruction is enough for a single reactant to adsorb along the stripes direction. Therefore, two additional monomers can adsorb in this fashion, completing the "flower"-like **DTA** self-assembled monolayer (DTA-SAM) on Au(001).

Similar as on the Au(111) substrate, to further anneal the self-assembled structure on Au(001) results in a complete desorption of the reactants. Therefore, to directly compare the output with the experiments presented in the manuscript, the reactants were sublimated onto the preheated substrate at 250 °C. Figure ESI-2a shows an STM image of the deposition results: extensive areas of the surface are now uncovered while only small disordered oligomers are visible. Furthermore, the absence of **DTA** monomers likely indicates their desorption from the preheated surface, as in the experiments on Au(111). It is important to note that structures resembling the *p*-**PPV** products were not obtained. Possibly the more complicated adsorption mechanism of the monomers on the Au(001) is also affecting their diffusion and reactivity on this substrate.

Evidently, to use the Au(001) substrate as a template does not lead to more control on the onsurface reductive coupling of aldehydes. Therefore, the reaction was also investigated on a Au(788) substrate. Such a substrate is conformed by terraces of 16 atomic rows forming planes in the (111) direction, making the terraces approximately 3.83 nm wide. Such a width is considerably larger than for the reconstruction of the Au(001) surface, and enough for a single monomer to adsorb flat and along the terrace, with the aldehyde moieties facing each other. STM imaging of the DTA-SAM on Au(788)



Figure ESI-2: Experiments on (a) Au(001) and (b) Au(788). *Before*: As deposited onto the substrates at room temperature. *After*: After deposition onto the substrates preheated at $250 \,^{\circ}$ C.

resembled the adsorption on the Au(111) substrate (Figure ESI-2b). Also in this case, the subsequent annealing treatment of the sample resulted in the complete desorption of the monomers. Therefore, after depositing the reactants onto the Au(788) surface kept at 250 °C, the complete absence of reactants is not surprising. When compared with the experiments on Au(001), a significant increase of the amount of disordered oligomers on the substrate is evident. However, the successful formation of the *p*-**PPV** products was not observed in this case either.

In conclusion, the fact that the **DTA** reactants weakly adsorb on Au surfaces in general, and that such behavior is not an exception on the Au(111) surface is demonstrated. A similar monomer desorption was observed on the three substrates studied. Furthermore, an improvement of the on-surface reaction leading to PPV derivatives was not observed after its investigation on different gold surfaces with different levels of substrate confinement due to their characteristic atomic reconstructions.

6 Controlled STM tip manipulation of an oligomer

To demonstrate the strength of the oligomers 4 coupling and to assess their interaction with the Au substrate, controlled STM tip manipulations were carried out. An area of the surface where several p-**PPV** oligomers can be identified was chosen (Figure ESI-3a). The targeted oligomer to be manipulated is enclosed by a dashed square box. The white dashed ellipses mark a reference area on the surface throughout the manipulation experiment. The initial manipulation (Figure ESI-3b) was conducted along the vector represented by the white arrow. This resulted in the manipulated oligomer displaced about 7 nm from its initial position in the direction of the manipulation vector, as it can be observed in a consecutively recorded image (Figure ESI-3c). Subsequently, an additional manipulation was conducted, displacing the oligomer in the opposite direction (Figure ESI-3d).



Figure ESI-3: Consecutive STM tip manipulation experiments of a p-PPV oligomer. The dashed ellipses enclose a reference area on the surface. All manipulations were conducted along the white arrows with U = 5 mV and $0.1 \text{ nA} \leq I \leq 3 \text{ nA}$. a) STM image $(23 \times 23 \text{ nm}^2; U = 700 \text{ mV}; I = 10 \text{ pA})$ recorded before the manipulations. The dashed square box encloses the oligomer to be manipulated. b) STM image $(8 \times 8 \text{ nm}^2; U = 700 \text{ mV}; I = 8 \text{ pA})$ recorded before the initial manipulation. c) STM image $(15 \times 15 \text{ nm}^2; U = 800 \text{ mV}; I = 5 \text{ pA})$ showing the oligomer displaced intact about 7 nm with respect to its initial position. A subsequent manipulation was conducted here. d) STM image $(15 \times 15 \text{ nm}^2; U = 800 \text{ mV}; I = 5 \text{ pA})$ recorded after the second manipulation.

The manipulated oligomer remained intact after the manipulations. These experiments showed that the p-PPV products possess high mechanical stability, a typical feature of covalently bound chemical structures. Furthermore, the displacement of the intact oligomer over several nanometers strongly suggests a weak (non covalent) interaction with the metal substrate. Consequently, the reason why the p-PPV products do not desorb from the surface cannot be ascribed to a covalent interaction between the substrate and the oligomers. Alternatively, this behavior could be ascribed to the large molecular mass of the products as compared to the reactants.

7 Adsorption geometry of DTA monomers on Au(111)

We performed DFT calculations to complement the XPS results and to further rule out the possibility that the observed self-assembly of **DTA** monomers after deposition onto the Au(111) surface is driven by

the formation of a vicinal diolate intermediate. To facilitate the calculations, a simplified **DTA** monomer (Figure ESI-4a) was considered instead of the complete molecules. For this particular compound, the aliphatic chains are truncated, since their role in the interaction between the aldehyde moiety and the gold substrate can be neglected.



Figure ESI-4: Adsorption of a simplified **DTA** monomer on Au(111). The large distance between the oxygen of the aldehyde moiety and the nearest Au atom of the substrate is not consistent with the covalent bonding between these species. a) Top view. b) Side view.

After full relaxation on the Au(111) surface, the oxygen atom of the aldehyde moiety did not bend downwards but rather remained at a distance of 3.4 Å over the substrate (Figure ESI-4b). If there would be a metal coordination bond with the substrate as a possible intermediate towards formation of a diolate intermediate, considerably smaller intermolecular distances of 2.1 Å were calculated for this system. Therefore, our DFT calculations indicate only a weak physisorption of **DTA** monomers after being deposited onto the Au(111) surface kept at room temperature.

8 Additional information for the reaction mechanism

In the following, detailed information about the theoretical investigations for a feasible reaction mechanism dominating the on-surface coupling of terminal aldehydes to produce a p-PPV derivative on a Au(111) surface is presented. We describe our DFT simulations leading to the proposed reaction mechanism, which is described in the main paper (Figure 4). It should be noted that all energies presented here are given with respect to the configuration at 0 eV. In the following subsections, the C-H activation of the aldehyde moieties is thoroughly discussed, as this is the common initial reaction step for all considered possibilities described afterwards. Alternatives to the proposed mechanism explained in the main manuscript were explored, by considering the absence of any reactive sites on the substrate, the formation of an α -hydroxy enol intermediate and the direct coupling of hydroxycarbenes. All these results are summarized in Figures ESI-6 and ESI-7, while the most feasible (proposed) mechanism is also shown for comparison. Following that point, our investigation regarding the interaction between dissociated oxygen atoms during the reaction and active sites of the Au(111) surface is quantitatively assessed. Finally, the calculations to estimate the free energy variation in the system due to desorption of molecular species at our experimental conditions are presented.

8.1 Initial activation of a carbonyl hydrogen

As mentioned in the manuscript, due to the large dissociation energy for the aldehyde oxygen^[6], we investigated instead the activation of the carbonyl hydrogen. We found that the C-H activation of the aldehyde moiety on the Au(111) surface and subsequent reaction with the second aldehyde leads to the formation of an α -benzoyloxy benzyl radical (Figure ESI-5; *config.* 2) intermediate, which is stable at 0.84 eV. However, although this pathway is energetically favored (1.13 eV transition state energy), it is not the only possible outcome of this chemical process. The hydrogen atom can also be transferred directly to the oxygen atom of the counter reactant (Figure ESI-5; *config.* 2'), resulting in a low energy state of 0.85 eV with transition state energy of 1.49 eV. Furthermore, a 1,3-biradical intermediate (Figure ESI-5; *config.* 3) is formed after the α -benzoyloxy benzyl radical moiety recombines with the dissociated



Figure ESI-5: C-H activation of the aldehyde moiety. Stable state energies are given in black and the transition state energies connecting two stable states are given in blue. The energies corresponding to the energetically favored pathway are highlighted in green.

hydrogen atom, with a transition state energy of 1.27 eV and increasing the total energy slightly to 0.90 eV. Additionally, this configuration could dissociate with a transition state energy of 1.11 eV to form a hydroxycarbene and starting aldehyde (Figure ESI-5; *config.* 3'), with the system now at a total energy of 1.01 eV. Subsequent hydrogen donation to the substrate is also possible (Figure ESI-5; *config.* 2"), with a transition state energy of 1.37 eV and the total energy remaining at 1.01 eV. A direct transition $1 \rightarrow 2$ " was investigated, but it converged to configuration 2.

8.2 Reaction on a flat unreconstructed Au(111) surface

In the manuscript, reactive sites on the Au(111) substrate were considered in the proposed reaction mechanism to explain the observed coupling of terminal aldehydes to produce a PPV derivative on this surface. However, to assess their role in a more quantitative way, it is necessary to compare that system with another without active sites, *i.e.*, a flat and unreconstructed Au(111) surface. Therefore, following from the enol intermediate (Figure ESI-6b; config. 5), the reaction was investigated without considering any active site on the substrate. The next step of the reaction is calculated in a system where an extra Au atom is not introduced, and the oxygen atom is already removed from the surface (Figure ESI-6b; config. 6), increasing the total energy to 1.64 eV and decreasing the free energy at the experimental conditions to 0.36 eV accordingly. From that point on, we found that a single reaction step is required to dissociate the remaining hydroxyl oxygen from the enol, with a transition state energy of $4.16\,\mathrm{eV}$ (Figure ESI-6b and ESI-9). This step significantly increases the system's energies by an additional 1.19 eV, bringing the total energy to 2.83 eV and the free energy to 1.55 eV (Figure ESI-6b; config. 7). The final step involves the assumption that the dissociated oxygen from the hydroxyl moiety also desorbs from the substrate at this point (Figure ESI-6b; config. 8), increasing the total energy of the system up to 3.22 eV. At the same time, the free energy of this configuration is reduced by 2.55 eV due to oxygen desorption to the gas phase, with the final product configuration now at an energy of 0.67 eV at the experimental conditions. Thus, the removal of the last oxygen atom from the hydroxyl group in the enol must overcome the largest energy barrier of 2.52 eV (rate-limiting step). When compared with the rate-limiting step of the mechanism proposed in the manuscript, which considers reactive sites on the surface (Figure ESI-6a), we found this alternative to be disfavored by 1.15 eV. Therefore, to neglect the many reactive sites of the Au(111) surface is not a viable alternative to explain the on-surface reductive



Figure ESI-6: Energy diagrams for the investigated reaction mechanisms. The rate-limiting steps appear highlighted in red. a) As presented in the main manuscript. b) Flat unreconstructed Au(111) surface as template. c) Alternative formation of an α -hydroxy enol intermediate should not dominate the coupling reaction due to a higher transition state barrier than to form an hydroxyoxirane (a,b; config. 4). d) Alternative formation of an α -hydroxy enol intermediate after direct coupling of hydroxycarbenes. In this case, the energy barrier is considerably larger than in a) and c).



Figure ESI-7: Configurations for the investigated reaction mechanisms. Herein only the total energies are presented. a) As presented in the main manuscript. b) Flat unreconstructed Au(111) surface as template. c) Alternative formation of an α -hydroxy enol intermediate after the formation of the 1,3-biradical (a,b; config. 3). d) Alternative formation of an α -hydroxy enol intermediate after direct coupling of hydroxycarbenes.

coupling of aldehydes on this surface at our experimental conditions.

8.3 Pathway involving an α -hydroxy enol intermediate

As discussed before, the C-H activation of the aldehyde moiety (Figure ESI-6a; config. 1) induces the sequential formation of an α -benzoyloxy benzyl radical (Figures ESI-5, ESI-6a; config. 2) and 1,3-biradical (Figures ESI-5, ESI-6a; config. 3) intermediates between the reactants at relatively low transition state energies. Following this configuration, an α -hydroxy enol intermediate can be formed in a three-step process: (i) carbon-carbon coupling between the reactants occurs (Figure ESI-6c; config. 4). This process occurs with a transition state energy of 2.52 eV, leaving the system at a total energy of 1.31 eV; (ii) this hydrogen atom is transferred to the substrate with a low transition state of $1.32 \,\mathrm{eV}$, with the system stabilized at a total energy of 0.99 eV (Figure ESI-6c; config.5); (iii) the adsorbed hydrogen recombines with the system to form the α -hydroxy enol intermediate (Figure ESI-6c; *config.6*) that is fairly stable at $0.19 \,\mathrm{eV}$ after overcoming a transition state energy barrier of $1.30 \,\mathrm{eV}$. From this point on, the reaction could proceed via oxygen dissociation from the hydroxyl moieties, a two step process similar to the final step of the main pathway for the reaction. However, it should be noted that the formation of the intermediate in configuration 4 (Figure ESI-6c) must overcome an energy barrier of $1.62 \,\mathrm{eV}$ (ratelimiting step). When compared with the rate-limiting step of the mechanism proposed in the manuscript (Figure ESI-6a), we found this alternative to be disfavored by 0.25 eV. Therefore, this pathway should not dominate the whole reaction mechanism, but it cannot be excluded as a viable alternative to explain the observed coupling of aldehydes on the Au(111) surface.

8.4 Direct coupling of hydroxycarbenes

Although not energetically favored due to disfavored rate-limiting step (Figure ESI-6c), the formation of an α -hydroxy enol intermediate could still be a viable alternative to explain the coupling of **DTA** monomers on Au(111). Therefore, we investigated the possibility of direct C-C coupling of hydroxycarbenes to form the α -hydroxy enol intermediate and compared it with the hydroxyoxirane intermediate alternative (Figure ESI-6a,b; configs. 1-4). After the initial C-H activation of one of the aldehyde moieties (Figure ESI-6d; config. 1) involved in the reaction, the donation of the dissociated hydrogen atom to the oxygen atom of the counter reactant is feasible after overcoming a transition state energy of 1.49 eV, with the system now at a total energy of 0.85 eV (Figure ESI-6d; config. 2). From that point, a hydrogen donation from the unactivated carbon atom to the oxygen atom of the activated monomer forms two carbene-type moieties, each bound to the substrate (Figure ESI-6d; config. 3) and stable at 2.57 eV, with a transition state energy of 2.82 eV. Subsequent C-C coupling to form the α -hydroxy enol intermediate (Figure ESI-6d; config. 4) must overcome a transition state energy of 3.72 eV with the system now at a total energy of 0.19 eV. However, it should be noted that the formation of the intermediate in configuration 3 (Figure ESI-6d) must overcome an energy barrier of 1.97 eV (rate-limiting step). When compared with the rate-limiting steps of the mechanisms proposed in the manuscript (Figure ESI-6a) and in the



Figure ESI-8: Alternative pathway to form the α -hydroxy enol intermediate after direct C-C coupling of hydroxycarbene moieties. This alternative has to overcome energy barriers considerably higher than the ones required to form the α -hydroxy enol intermediate from the 1,3-biradical configuration.

previous subsection (Figure ESI-6c), we found this alternative to be disfavored by 0.6 eV and 0.35 eV, respectively. Therefore, this alternative should not be involved in the reaction mechanism.

8.5 Alternative deoxygenation of the hydroxyl moiety in the enol intermediate

It was shown in Figure ESI-6b that the system must overcome a relatively large transition state energy barrier (4.16 eV) to directly dissociate the last oxygen atom from the hydroxyl moiety. Therefore, we investigated an alternative configuration to assess its energetic feasibility. We found that the hydrogen atom can be transferred from the hydroxyl oxygen to the neighboring carbon atom following a two step process: (i) the hydrogen atom is donated to the substrate bringing the total energy to 2.77 eV, *i.e.*, increasing the energy by 1.13 eV. The system hereby becomes an α -carbonyl radical (Figure ESI-9a); (ii) the hydrogen atom is picked up by the neighboring carbon atom to generate a ketone, with the system now at a total energy of 1.51 eV (Figure ESI-9b). It was not possible to estimate a transition state energy for the oxygen scission from the ketone at this point, which can be ascribed to a large dissociation energy. Therefore, the removal of the hydroxyl oxygen with subsequent hydrogen donation to the vicinal carbon atom remains as the only feasible alternative to reach the final product of the reaction, according to our calculations.



Figure ESI-9: Alternative configurations of the hydrogen transfer during the last step of the reaction mechanism in Figure ESI-6b. a) Dehydrogenation of the hydroxyl moiety with the hydrogen atom adsorbed on the substrate. The former hydroxyl moiety is now an α -carbonyl radical. b) The dissociated hydrogen atom is transferred to the neighbouring carbon forming a ketone, but subsequent oxygen scission at this point is not possible due to the large energies required to dissociate the ketone oxygen atom.

8.6 Preferential order for the deoxygenation of the 1,3-biradical intermediate



Figure ESI-10: Alternative configuration for the dissociation of the hydroxyl oxygen in the 1,3-biradical intermediate; this state is much higher in energy (2.14 eV) than the hydroxyoxirane configuration (Figure ESI-6a,b; config. 4) and therefore disfavored at this point of the reaction. As a result, the oxygen atom from the oxirane ring dissociates before the hydroxyl oxygen atom.

8.7 Interaction of the dissociated oxygen with the extra Au atom introduced on the surface

The proposed reaction mechanism (Figure ESI-6a) considers the introduction of a single extra Au atom to resemble the more realistic case where an active site of the surface is involved in the reaction. Although atomic oxygen has been shown to desorb from Au surfaces at our experimental conditions^[7], in this particular case its interaction with the single Au atom might be stronger and therefore, the evolution of the system without oxygen desorption was studied in more detail. Thus, the oxygen desorption was not considered to occur at this step of the reaction (Figure ESI-6a; *config.* 6). The results suggest that dissociation of the hydroxyl hydrogen results in its recombination with the surface-adsorbed oxygen atom and the formation of an α -carbonyl radical (Figure ESI-11; *config.* 6). This process must overcome a relatively low energy barrier of 0.91 eV, leaving the system at a total energy of 0.86 eV. The insertion of a single extra Au atom into such stable configuration results in the formation of a Au-enolate, leaving the system at a total energy of 0.40 eV with the activated oxygen coordinated to the extra Au atom (Figure ESI-11; *config.* 7). Following from this configuration, we found that an aurated oxirane can form after overcoming a transition state energy barrier of 2.07 eV leaving the system in configuration 8 at a total energy of 1.16 eV. Subsequent H recombination from the adsorbed OH with the aurated oxirane



Figure ESI-11: Energetics(top) and configurations (bottom) for an alternative coupling mechanism without considering oxygen desorption before the introduction of the extra Au atom. The rate-limiting step appears highlighted in red. This pathway is overall also not energetically favored, given that the ratelimiting step seats on 2.56 eV vs. 2.22 eV in the proposed mechanism (Figure ESI-6a).

can induce the formation of an oxirane, after overcoming an energy barrier of $2.56 \,\text{eV}$ with the system in configuration 9 now at a total energy of $1.64 \,\text{eV}$. It should be noted that in this configuration, the remaining oxygen atom is adsorbed on the surface and not bound to the extra Au atom. This strongly indicates that single dissociated oxygen atoms interact weakly with reactive sites on the surface.

After this point, the desorption of the adsorbed oxygen and the removal of the extra Au atom lead to the formation of the reaction product. The removal of those chemical species increases the total energy of the system up to $2.34 \,\mathrm{eV}$, but at the same time reduces its free energy to $1.06 \,\mathrm{eV}$ (Figure ESI-11; config. 10). Subsequent oxygen dissociation from the oxirane results in the formation of the PPV product, with the dissociated oxygen adsorbed on the substrate (Figure ESI-11; config. 11). This state is now at a total energy of 2.83 eV (free energy 1.55 eV) after overcoming a transition state energy of 3.28 eV (2.00 eV taking into consideration the free energy reduction). Given that our XPS experiments show the absence of oxygenated species on the surface after the on-surface reaction, it is safe to assume that oxygen desorption also occurs in configuration 11. To remove the oxygen from the surface results in the final product adsorbed on the substrate (Figure ESI-11; config. 12) with a total energy increase up to $3.22 \,\mathrm{eV}$, but meanwhile the free energy of the system is reduced to $0.67 \,\mathrm{eV}$. It should be noted that the formation of the intermediate in configuration 8 (Figure ESI-11) must overcome an energy barrier of 1.67 eV (rate-limiting step). When compared with the rate-limiting step of the mechanism proposed in the manuscript (Figure ESI-6a), we found this alternative to be disfavored by 0.3 eV. Therefore, this pathway should not dominate a reaction mechanism that explains the observed coupling of aldehydes on the Au(111) surface, which together with the poor interaction of the dissociated oxygen with the extra Au atom and its fleeting presence on the substrate (Figure ESI-11; config. 9), validates the assumption made in Figure ESI-6a; config. 6.

8.8 Free energy calculation

Unless stated otherwise, all energies are given as relative energies E_{rel} to the initial state energy E_{ini} :

$$E_{rel} = E - E_{ini} \tag{1}$$

In cases where n oxygen atoms were removed from the system, the energies are references to O_2 in the gas phase:

$$E_{rel} = E - E_{ini} + \left(\frac{n}{2}\right) \cdot E_{O_2} \tag{2}$$

To estimate the thermodynamic stability at elevated temperatures, not only total energies should be considered but also entropic effects. This is especially valid in ultrahigh vacuum conditions, where molecular desorption significantly decreases the system's free energy:^[8]

$$F = E - T \cdot S \tag{3}$$

The entropy variation due to O_2 desorption is given by:

$$S = S_0 - k \cdot \ln(p/p_0) \tag{4}$$

with S_0 being the standard entropy of O_2 at a pressure $p_0 = 1$ bar and a temperature of T = 523 K ($S_0 = 2.302 \text{ meV/K}$).^[9] For our experimental conditions (T=523 K, $p=10^{-10}$ mbar) we obtain a value for $T \cdot S$ of 2.55 eV per O_2 molecule. This energy amount (or one half) is subtracted from the total energies of the configurations were oxygen atoms were removed, to estimate the systems free energy at the experimental conditions (Figures ESI-6,ESI-11 and Manuscript Figure 4). It should be noted that in this discussion, as in the discussion of the total energies, changes in zero-point energies of molecular vibrational modes are neglected.

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