Enantioselective covalent coupling reactions on the chiral PdGa{111} surfaces

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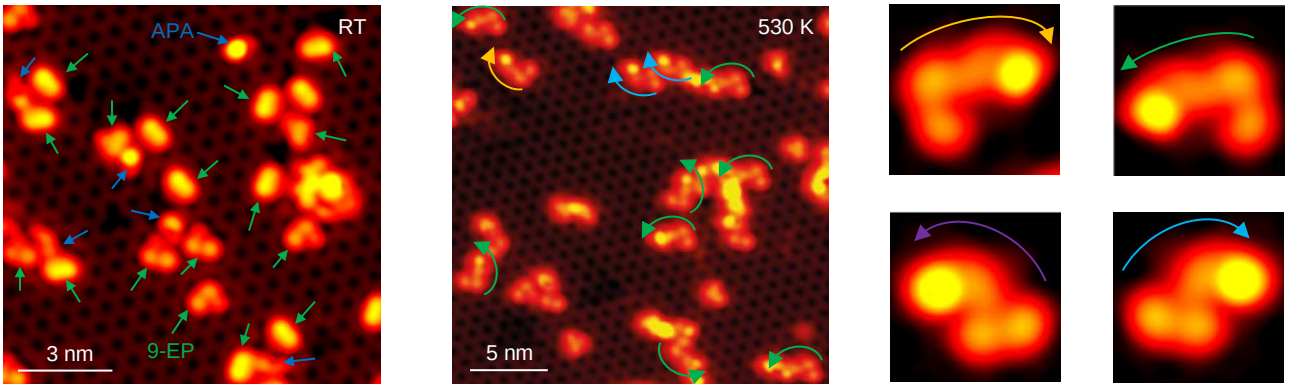
Owing to its non-centrosymmetric $P2_13$ space group PdGa exists in two enantiomeric crystal forms A and B and all surfaces of this intermetallic compound are chiral. This circumstance, together with the possibility to prepare atomically flat, well-ordered surfaces in ultra-high vacuum (UHV), enables detailed investigation of asymmetric chemical surface reactions on this system.

In the [111]-direction exhibits four non-equivalent atomic planes, resulting in structurally different (111) and (-1-1-1) surface terminations for the same crystal. Specifically, one is terminated by single, isolated Pd atoms, accordingly denoted as Pd_1, while the other reveals isolated Pd trimers as the top-most layer, referred to as Pd_3 [1]. The chiral selectivity of Pd_1 and Pd_3 was probed by adsorption of the prochiral 9-Ethynylphenanthrene (9-EP) molecule. On Pd_1 a massive enantiomeric excess (ee) of 94-98% is found at room temperature (RT) [2], while for the same conditions a racemic mixture is observed on Pd_3. Post-annealing at 500 K then results in the formation of propeller-like 9-EP trimers with a homochirality of 99% on Pd_3.

These results pave the way towards highly enantioselective covalent coupling reactions. In view of the d-band model proposed by Nørskov *et al* [3] and the copper-like d-band structure of PdGa, a classically copper-catalyzed Azide-Alkine Huisgen Cycloaddition, already demonstrated on Cu(111) under UHV conditions [4], was chosen as model reaction.

Indeed, RT co-adsorption of 9-EP and 3-(4-Azidophenyl)propionic acid (APA) (left figure) and subsequent post-annealing at 530 K leads to covalently coupled reaction products on Pd_1 which are marked in the central figure and shown in detail in the four figures on the right. The catalyzed reaction is regioselective as it is on Cu(111), but on Pd_1 an ee of up to 65% is found.

On the other hand, on Pd_3, the d-band model fails due to the big impact of the ensemble effect [5] on the reactivity for his particular reaction.



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