Supporting information

Covalent Functionalization of GaP(110) Surfaces via a Staudinger-Type Reaction with Perfluorophenyl Azide

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Materials and DFT details

PFPA ($C_6F_5N_3$) was prepared according to published procedures¹. For the STM/STS experiments, we used p-type GaP wafers doped with Zn atoms at a concentration of 2 × 10¹⁸ cm⁻³. PFPA molecules were deposited from a UHV-sealed flask attached to the UHV-STM chamber through a precision leak valve. The PFPA was purified by multiple freeze/pump/thaw cycles before deposition and the purity checked by quadrupole mass spectrometry. To obtain the 1D PFPA phase, GaP(110) surfaces were exposed to 0.7L-1L of PFPA molecules (PFPA partial pressure = 1.5×10^{-8} Torr for 45 s) at room temperature. The 2D close-packed covalent phase was obtained by annealing the 1D phase at ~325 K for 10 minutes. This phase could also be obtained by directly depositing PFPA molecules onto a GaP(110) surface held at 320 K.

Simulated structural and electronic properties were calculated using density functional theory (DFT) implemented in the VASP code²⁻³. We employed the optB86bvdW functional⁴ (whose kernel accounts for the effects of van der Waals interactions) as well as projector augmented wave (PAW) pseudopotentials³ and a plane-wave cutoff of 400 eV. The final structures correspond to energies converged better than 10-5 eV and forces smaller than 0.01 eV/Å. The 2D phase was simulated using a 1x1 GaP(110) unit cell containing a 9-layer slab of the substrate with one PFPN molecule (30-atom cell). The intermediate 1D phase was simulated in a larger 4x2 unit cell containing two molecules (PFPA and PFPN) and a 9-layer slab resulting in a 172-atom cell. Binding energies were calculated using an isolated PFPA molecule and optimized substrate structure as reference, and then adding the energy of an isolated N₂ molecule. Van der Waals interaction strengths were estimated through static calculations using the

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converged structures for optB86b-vdW with semiempirical vdW implementation (PBE-D3)⁵, where the vdW contribution is independent of the self-consistent electron density and is simply determined by the relaxed structure.

Morphology of the GaP(110) surface after the PFPA deposition

PFPA deposition on GaP(110) at room temperature results in 1D chains of molecules on the surface that are a precursor to the 2D covalent phase that functionalizes the (110) surface. Figure S1a shows a large-scale STM image (135 x 135 nm²) of GaP(110) after 0.8 Langmuir exposure of PFPA at room temperature (and with no subsequent annealing). Short molecular chains are found along the surface with an angle of 54° with respect to the [001] direction (Fig. 1Sb). The molecular chains show a periodicity along the chains of 9.2 Å, as shown in Fig. S1b. The orientation of the chains and the observed periodicity along them match the commensurate lattice vector $\mathbf{A} = 2\mathbf{a} + \mathbf{b}$, with $\mathbf{a} = (1-10)$ and $\mathbf{b} = (001)$ being the surface unit cell vectors (as sketched in Fig. 1Sc). Note that the positions of the dots do not indicate the adsorption sites of the PFPA molecules.



Figure S1. a) STM image shows large-scale view of the GaP(110) surface after 0.8 L exposure of PFPA ($V_s = -2.6 \text{ V}$, $I_t = 50 \text{ pA}$, T = 7 K). b) Close-up STM image showing the periodicity (9.2 Å) and angle of the chains (54°) with respect to the [110] direction ($V_s = -2.8 \text{ V}$, $I_t = 30 \text{ pA}$, T = 7 K). c) Sketch showing experimental orientation and periodicity of the 1D molecular chains.

Apparent height of phenyl-based nanostructures on GaP(110)

The measured heights of the phenyl-based nanostructures for the intermediate (Fig. S2b) and product (Fig. S2b) states are 5.3 ± 0.2 Å and 3.8 ± 0.2 Å, respectively. Similar values are found for STM images at both polarities in both cases. Despite the fact that these values are *apparent* and cannot be strictly interpreted as actual heights, they qualitatively suggest that the molecules are adsorbed vertically on the GaP(110) surface with the plane of the phenyl rings perpendicular to the surface plane. To confirm this scenario, we deposited a sparse, sub-monolayer coverage of iodobenzene molecules (C₆H₅I) onto GaP(110) at 15 K. lodobenzene has a similar structure to PFPA and PFPN molecules, but it adsorbs nearly flat on GaP(110) according to our DFT calculations (the inset of Fig. S2d shows the relaxed structure). Figure S2d shows an STM image with three iodobenzene molecules adsorbed on the GaP(110) surface. The rounded shape of the molecules supports a flat-lying configuration on the surface, in good agreement with calculations. The apparent height of the iodobenzene is 1.3 ± 0.2 Å, significantly lower than the height measured for the PFPA and PFPN nanostructures (see Fig. S2a). This provides further evidence that PFPA/PFPN molecules are oriented vertically on the GaP(110) surface.



Figure S2. a) Height profiles of 1D PFPA/PFPN chains (black), 2D PFPN islands (blue) and isolated iodobenzene molecules (red). High-resolution STM images of b) 1D PFPA/PFPN chain on GaP(110) (size: 7.3 x 5.3 nm², V_s = -3.2 V, I_t = 100 pA). c) 2D PFPN island on GaP(110) (V_s = -2 .5 V, I_t = 40 pA, T = 7 K) and d) individual iodobenzene molecules on GaP(110) (V_s = +2 .3 V, I_t = 26 pA, T = 7 K). The left upper inset in d) shows a sketch of the iodobenzene molecule. The bottom right inset in d) shows the relaxed structure of the iodobenzene on GaP(110) calculated by DFT.

DFT model of the intermediate state

We performed DFT-vdW (optB86b) calculations to examine the energies of several possible adsorbate structures in order to determine the most probable structure of the 1D configuration. These calculations explored different combinations of PFPA and PFPN molecules on a 4x2 GaP(110) unit cell containing a 9-layer slab of the substrate. The most stable configuration observed contains a pair of adsorbed PFPA-PFPN molecules within each supercell (see Fig. S3a). Both molecules are attached to the substrate through N atoms. The PFPN molecule, covalently bonded to the substrate, is in a vertical position while the PFPA molecule, in a more weakly bonded physisorbed configuration, is tilted towards the surface. The periodicity (9.3 Å) and orientation of the relaxed structure sis 3.81 eV/supercell (which corresponds to an average adsorption energy of 1.91 eV/molecule). PFPN molecules arise from PFPA molecules that have released N₂ upon adsorption onto GaP(110).

Figures S3b-c show two calculated STM images from the relaxed 4x2 PFPA-PFPN/GaP(110) structure. For occupied states, the calculated image shows both molecules as protrusions that exhibit internal structure (Fig. S3b). The PFPN molecules are brighter than the PFPA molecules due to their vertical orientation. This reasonably matches the experimental STM images at this polarity (Fig. S3d), in which two sets of protrusions with internal structure are clearly observed along the same crystal direction (although the structure in the experiment is not as pronounced as that of the calculated images, possibly due to the finite width of the tip). For unoccupied states, the calculated STM images show the chains as independent parallel pairs of PFPA-PFPN molecules.

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Each molecule produces a single featureless protrusion, with the PFPN molecules brighter than the PFPA molecules (Fig. S3c). The experimental unoccupied state images also show featureless protrusions with the correct periodicity along the chains, but with only one protrusion per supercell rather than two as predicted by theory. This is likely due to the fact that the finite size of the STM tip gives an enhanced signal for the vertically aligned PFPN molecule compared to the flatter PFPA molecule.



Figure S3. a) Relaxed structure for a PFPA-PFPN chain on GaP(110). Calculated STM image of the PFPA-PFPN chains on GaP(110) are shown in c) for occupied states ($V_s = -3 V$) and d) for unoccupied states ($V_s = +3 V$). STM images of molecular chain at T = 7 K are shown for (d) occupied states ($V_s = -3.2 V$, It = 100 pA) and (e) unoccupied states ($V_s = +2.8 V$, It = 15 pA).

Evolution of the reaction from intermediate to product state



Figure S4. Evolution of the thermally-activated chemical reaction: a) intermediate state after PFPA deposition onto GaP(110) at room temperature (V_s = -2.7 V, I_t = 15 pA, T = 7K). b) Early stage of the reaction toward the final product after annealing the sample shown in a) at 50°C for 180 seconds (V_s = -2.6 V, I_t = 40 pA, T = 7K). c) Later stage of the reaction after further annealing the sample shown in b) at 50°C for another 420 s seconds (V_s = -2.7 V, I_t = 30 pA, T = 7K). 1D chains are seen to convert to 2D islands with increased annealing. (The total number of molecules is not constant between the images because each image was taken at a different spot on the surface, but the ratio of 1D chains to 2D island growth is representative of the larger surface).

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