We present a new strategy for nanostructuring organic molecules in order to create either molecular chains or organic nanodots. The method is based on the use of patterned surfaces as templates for nucleation of the organic molecules. As the patterned substrate we use iron-island arrays grown on Au(111). These metallic arrays are formed spontaneously on the gold reconstructed surface via strain-relief nucleation. We show that deposited 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecules anchor at the iron islands forming new structures that are not observed for PTCDA adsorption on clean gold. Namely, PTCDA forms either chains of molecules connecting contiguous iron clusters, or aggregates surrounding the metallic core. The resulting arrangement of organic dots exhibits a different density of states than the two-dimensional self-assembled molecular monolayer. Scanning tunneling spectroscopy (STS) studies indicate that the main modifications are the absence of the gold surface state and the appearance of an iron state induced in the PTCDA highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap.

Organic molecules are one of the most promising candidates to substitute inorganic materials in nanoscale devices. Up to now, these organic materials have found several optoelectronic applications such as organic light-emitting devices, organic transistors, organic lasers, organic rectifiers, and organic memories. Most of these devices take advantage of the confinement properties due to the nanostructuring of the organic molecules in 2D thin films or 1D nanowires. Naturally, organic 0D nanostructures are envisioned as systems with potential applications. Among the strategies for nanostructuring organic materials, landing of molecules or tip-induced manipulation have been successfully used for single-molecule set-ups. More extended assemblies can be achieved by self-organization of molecules, by choosing the appropriate chemistry of the molecules, or by using metallic atoms as linkers to form molecular networks.

Small amounts of iron—as well as cobalt, nickel, and palladium—deposited on the strain relief (22 × √3) gold reconstruction lead to the formation of islands at the edges of the so called herringbone reconstruction. Figure 1 shows an array of iron islands nucleated on Au(111) after deposition of 0.08 ML (ML: monolayer) at room temperature. Iron atoms have nucleated forming clusters at the edges of the gold reconstruction. These iron atoms are arranged in a close-packed face-centered cubic phase, leading to the formation of triangular shapes observed in Figure 1b. The average size of the iron islands, determined from the distribution shown in Figure 1c, is close to 4 nm × 4 nm for this particular coverage. Similar metallic arrays have been obtained on strain-relief patterns, where dislocations repel diffusing adatoms. These patterns are obtained spontaneously when one or two monolayers of a material are deposited on a substrate with a different lattice constant. In our case, it is the Au(111) reconstruction itself that provides the dislocation network, the elbows of the reconstruction acting as nucleation centers for diffusing adatoms.

On the other hand, it is also known that PTCDA molecules deposited on clean Au(111) form highly ordered 2D films. The weak molecule–substrate interaction allows the organic molecules to diffuse at a high rate at room temperature without being altered by (or altering) the gold reconstruction. Molecules establish intermolecular interactions with their neighbors, linking the O atoms of one molecule with the H atoms of the next one, to form the characteristic herringbone and square phases. In both cases, PTCDA molecules are arranged perpendicular to each other.

Deposition of PTCDA organic molecules on a Au(111) surface tailored by iron cluster 2D arrays results in a completely different growth mode. Figure 2a shows several organic aggregates pinned to the iron islands. We observe several molecular structural arrangements that are never formed for PTCDA deposition on clean noble-metal substrates. Such small aggregates are not stable at room temperature without the presence of nucleation centers (as step edges or contaminants). Moreover, for this low PTCDA coverage (just 0.04 ML) the PTCDA characteristic structures are not observed. First, let us consider the distribution of these new aggregates. Most of the iron clusters in Figure 2a are unaltered (without nucleated molecules) and only a few of them have one or two molecules attached. PTCDA nucleation is preferred at iron clusters where other molecules are already nucleated. This irregular
distribution suggests that the iron-mediated PTCDA–PTCDA interaction is energetically more favorable than the interaction between PTCDA and the iron cluster itself.

Second, let us observe the structure of the aggregates. For instance, Figure 2b corresponds to chains of PTCDA molecules pinned to iron clusters. The molecules are placed with the longer axis parallel to the chain axis; therefore, the oxygen terminations of two consecutive molecules face each other. We suggest that this unusual structure is stabilized by iron placed between the molecules in a similar way to the supramolecular noncovalent interactions described by Lehn,[28] or the reported metallo-organic networks steadied by iron atoms.[15,16] In our case, the anhydride groups of the PTCDA are already saturated, and therefore an oxidation reaction with iron atoms is not possible.[29] Ab-initio calculations currently in progress[30] point out that the linkage between consecutive PTCDA molecules is constituted of two iron atoms interacting with the carboxylic groups of the PTCDA. The model for this linkage is shown in Figure 2c, where two PTCDA molecules are connected by two iron atoms.

We have also found other PTCDA structures induced by iron, such as the ladderlike structures observed in Figure 2d. For these kinds of aggregates, perpendicular PTCDA molecules connect two parallel chains, and three PTCDA molecules are attached by the same iron linkage.

Annealing the substrate up to 370 K after deposition favors molecular-chain formation, leading to longer PTCDA chains (molecular wires) connecting several iron islands, mainly along the [112] crystallographic direction. Further annealing to higher temperatures (420 K) breaks up the PTCDA–iron link, allowing iron atoms to diffuse to the step edges and the PTCDA molecules to form islands with the “herringbone” phase characteristic of PTCDA on Au(111). The interaction between PTCDA and the iron is therefore reversible upon annealing. The lack of OH groups in the PTCDA molecules is also in concordance with the observed reversibility for the iron–PTCDA linkage in the present metallo-organic aggregates.[29]

In analogy to standard crystal growth modes,[31] one may expect the organic aggregates either to grow in concentric circles around a nucleation point for high substrate temperatures, or to form dendrite chains for low temperatures. However, we experimentally observe the opposite behavior: formation of chains at higher temperature and rounded structures at lower temperature. Assuming that the diffusion of PTCDA mole-

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Figure 1. Iron island array on Au(111). a) Scanning tunneling microscopy (STM) image (145 nm × 145 nm) of Au(111) substrate after evaporation of 0.08 ML of iron. The iron nucleates forming islands at the gold reconstruction edges [17]. b) Derivative image (24 nm × 24 nm) showing iron islands at the edges of the reconstruction. c) Island distribution plot of the image in (a) with an average size of the islands around 4 nm × 4 nm.

Figure 2. Pinning of PTCDA molecules at the iron islands. a) STM image (120 nm × 120 nm) after evaporation of 0.04 ML of PTCDA molecules on an iron array (iron coverage, $\theta_{Fe} \sim 0.08$ ML). The organic molecules form aggregates pinned by the iron. The observed arrangements, such as molecular chains or ladderlike structures, are never observed for PTCDA on clean gold. Iron atoms in between the organic molecules stabilize these arrangements. b) Chains of PTCDA molecules pinned at two iron clusters (brighter features) (18 nm × 16 nm). c) Model for the chain structure with two iron atoms as linkage between two consecutive PTCDA molecules. d) Ladderlike structure. (13 nm × 11 nm).
molecules is high enough in the temperature range accessible in these experiments, the promoted formation of molecular wires for higher temperature suggests that the crucial parameter is the amount of free iron adatoms diffusing on the gold substrate. For higher temperature, the number of diffusing iron adatoms increases, being enough to couple to the carboxylic groups and to form chains where iron atoms link two consecutive molecules. On the contrary, cooling the substrate after iron deposition, or reducing the iron coverage, means that most of the iron atoms are nucleated at the reconstruction corners and leads to the formation of organic aggregates exhibiting a more circular shape (see Fig. 3), which we have named organic nanodots (ODs).

![Image 1](https://example.com/image1)

**Figure 3.** Organic nanodots. STM image (40 nm × 40 nm) where PTCDA molecules have grown around small iron islands nucleated at the gold substrate reconstruction’s elbows. The reconstruction lines of the gold substrate are clearly observed in the background. The organic nanodots are 4–6 nm in diameter. The arrows point to the iron seeds in two nanodots. The coverages are \( \theta_{FE} \approx 0.01 \) ML and \( \theta_{PTCDA} \approx 0.15 \) ML.

Therefore, by tuning the experimental growth conditions (temperature and iron coverage) we can switch from the formation of molecular chains connecting consecutive iron clusters to organic (unconnected) aggregates sited at the gold reconstruction corners.

In Figure 3 we present an STM image with several organic nanodots. These are grown around small iron clusters of a few tens of atoms (the iron coverage was lower than 0.01 ML). In some organic aggregates a bright feature inside, related to the iron-cluster seed, is observed. In others, the presence of iron is supported by the different intermolecular assembling of the PTCDA molecules. As is shown below, a different electronic behavior is also observed. In the image of Figure 3 the gold reconstruction lines are clearly resolved. The organic dots are pinned to the reconstruction elbows, as these are nucleation centers for the iron. The average diameter of these dots is about 4–6 nm and they follow the network of the iron clusters, presenting, therefore, a high degree of ordering. Nanostructured dot formation occurs in a narrow range of experimental parameters. Indeed, it is a compromise between the amount of free diffusing iron that favors molecular wires versus organic nanodots, and a minimum amount of deposited iron that forms an extended iron network at every reconstruction elbow. Again, increasing the temperature leads to the separation of the phases: ordered PTCDA phases and iron nucleation at the steps.

In order to explore the electronic properties of the organic nanodots, we have performed STS measurements for different situations. Previously, we have recorded STS curves on clean Au(111) and on the PTCDA monolayer grown with a herringbone structure.[26] These plots are used here as a reference, checking that the tungsten tip is “in good condition”, that is, free of contaminants or absorbed molecules.

Spectroscopic conductance plots on the Fe–Au(111) system show the different electronic behavior between the iron clusters and the gold substrate. In Figure 4, the \( dI/dV \) plot obtained for the gold substrate (dashed line) shows the gold surface state feature around –0.6 V is the only observed feature.

![Image 2](https://example.com/image2)

**Figure 4.** Tunneling spectroscopy on the iron clusters. STS spectroscopic plot \( dI/dV \) obtained over an iron island (continuous line) in comparison with a plot obtained on the gold terrace (dashed line). On the gold, the characteristic surface state peak is obtained, while on the iron cluster a bump close to –0.6 V is the only observed feature.
Figure 5. Spectroscopic images of the organic nanodots. a) Topographic STM image (40 nm × 40 nm) for 0.9 ML PTCDA covering the Fe–Au(111) surface. The marked areas correspond to: A, PTCDA molecules on the gold terrace; B, PTCDA molecules close to the iron cluster; and C, the iron clusters. b–d) Conductivity maps (d(I)/d(V)) extracted from CITS corresponding to bias voltages labeled F, G, and H, in Figure 6. b) At F, the organic dot appears brighter, corresponding to the iron state. c) At G, the molecules at the boundaries appear brighter due to the contribution from both peaks. d) At H, the PTCDA molecules away from the organic dot appear brighter, corresponding to the gold surface state observed through the molecules [26]. Notice that the darker area is smoother than the structural shape of the dot.

Figure 6. Spectroscopy on the organic nanodots. STS spectroscopic plots (d(I)/d(V)) measured for the different areas shown in Figure 5. For A, characteristic PTCDA HOMO–LUMO peaks at –1.8 and +1.0 V, and the Au(111) Shockley type surface state at ~0.4 eV are observed [26]. For B, a peak at ~0.7 V is induced in the organic molecules. This peak is also observed for the iron core C.

(C) and surrounded by PTCDA molecules (B) in a less-ordered disposition than the molecules in (A).

Figure 6 shows STS curves obtained by averaging I–V plots recorded on different areas. These curves are presented as the derivative d(I)/d(V) for voltages between –2 and +2 V. For PTCDA areas with the well-ordered herringbone structure, as the region marked A, we have obtained curves similar to those previously observed for the PTCDA monolayer on gold [20]. Curve A is characterized by the presence of a peak at ~0.4 eV, corresponding to the Shockley surface state of Au(111), visible through the PTCDA layer. [20] Curve C, recorded on the iron core, exhibits an electronic feature at ~0.7 eV, which resembles the one observed on iron clusters, and therefore can be assigned to an iron electronic state [21]. The conductance curve for PTCDA areas surrounding the iron core, plot B, shows a peak at ~0.7 eV corresponding to the iron, while the Au(111) surface state at ~0.4 eV is not observed. The PTCDA molecules of the organic nanodot, modified by the iron, have a different electronic structure than the molecules in a single monolayer. The main difference concerns the transparency of the molecules to the gold surface state. In contrast to a charge-transfer process [23] where a shift in the STS plot would be expected, we assume here that there is an iron-induced state in the surrounding PTCDA molecules. Furthermore, as a consequence of the induced state, the HOMO–LUMO gap value of the PTCDA opens for the molecules close to the iron core. The position of these peaks varies slightly with the tip and for different organic dots, but we reproducibly observe that the feature obtained over the iron persists in the surrounding PTCDA molecules and that these molecules present a different spectroscopic behavior. We can not exclude the possibility that the observed iron feature at the organic nanodots originates from iron atoms situated between the PTCDA molecules in the dot, but the lack of the gold feature is a clear evidence of the change in the electronic character in the organic nanodot.

Conductivity (d(I)/d(V)) maps, extracted from current imaging tunneling spectroscopy (CITS), [34] are presented in Figure 5b–d. These images are measured simultaneously with the topography in Figure 5a and correspond to bias voltages labeled as F, G, and H in Figure 6, respectively. At F, the nanodot-related electronic state is the main contribution to the total current (Fig. 5b). At H, the main peak is the gold surface state; therefore, the molecules exhibiting this state appear brighter in the spectroscopic image, while the nanodot appears dark (Fig. 5d). In between, at G, molecules at the boundaries of the organic nanodot are the brightest as they receive contribution from both peaks (Fig. 5c). Notice that the perimeter of the dark area (Fig. 5d) is smoother than the tip of the iron cluster (Fig. 5a), that is, the electronic effect is also extended to nearby molecules with the herringbone phase. The extension of this dark area strongly depends on the voltage. For low negative voltages the area corresponds to the size of the dot. When the voltage decreases towards negative values the effect that the iron cluster in the PTCDA molecule has decayed, which results in a shrinking of the dark area.

The iron cluster induces an electronic state inside the gap of the surrounding molecules (similar to a metal-induced gap...
state\(^{30}\) at \(-0.7\) eV. As we move away from the iron core, the contribution of this state to the PTCDA molecules decays, until we reach the 1 ML regime for molecules in A. The inclusion of this electronic state in the organic molecules slightly opens the HOMO–LUMO gap, as observed in the STS curves. It is also remarkable that the gold reconstruction is not observed through the PTCDA molecules of the nanodot surrounding the iron clusters (see Fig. 5a), while it is clearly visible through the PTCDA layer far from the dot. This fact again indicates that the iron modifies locally the electronic structure of the molecular nanodot, opening the gap and changing the transparency of the organic layer to the gold states.

In summary, we conclude that by controlling the amount of iron deposited on a gold surface, we are able to switch from PTCDA organic chains to organic nanodots. These nanostructures possess a local density of states different from that obtained in a molecular monolayer.

This method, to fabricate controlled shaped nanoscopic molecular objects, could be used to guide molecular chains towards contacts to experimentally determine conduction through a single molecule, or to form arrays of nanoscale organic aggregates with potential application in optoelectronic devices.

**Experimental**

Experiments were performed in an ultrahigh-vacuum chamber with commercial Omicron STM using Nanotec’s electronics and software. The base pressure of the chamber was \(1 \times 10^{-10}\) mbar (1 bar = 1000000 Pa). A gold single crystal was prepared by sputtering-annealing cycles. Iron was evaporated by means of electron bombardment until we reach the 1 ML regime for molecules in A. The evaporation rate was kept below \(0.3 \) Å min\(^{-1}\). STM tips were made of electrochemically etched tungsten. PTCDA molecules were sublimated from a cell at a rate of \(2\) Å min\(^{-1}\) from a cell at a rate of \(0.3 \) Å min\(^{-1}\). STM tips were made of electrochemically etched tungsten. Tips were cleaned and resharpened in situ by annealing at high temperature until stable field emission was obtained. Tunneling spectroscopy was measured by local \(J-V\) plots and using a CITS technique. All the results were checked by observing the characteristic Shockley state for the clean gold prior to and after performing the spectroscopic measurements.

Received: October 5, 2005
Final version: April 1, 2006

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