Sequential formation of N-doped nanohelicenes, nanographenes and nanodomes by surface-assisted chemical (cyclo)dehydrogenation of heteroaromatics

Anna Lisa Pinardi ^a, José Ignacio Martínez ^a, Andrej Jančařík ^b, Irena G. Stará ^b, Ivo Starý ^b, María Francisca López ^a, Javier Méndez ^a and José Ángel Martín-Gago ^{*ac}

^a*Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), C/Sor Juana Inés de la cruz 3, Cantoblanco, 28049 Madrid, Spain*

^b*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic*

^c*Centro de Astrobiología (CSIC-INTA), Carretera de Torrejón a Ajalvir, km 4, Torrejón de Ardoz, 28850 Madrid, Spain*

** E-mail: gago@icmm.csic.es*

We report on the stepwise formation of N-doped nanohelicenes, nanographenes, nanodomes and graphenes from the same heteroaromatic precursor through subsequent dehydrogenations on Pt(111) upon thermal annealing. The combined experimental (UHV-STM) and computational (DFT) studies provide a full atomistic description of the intermediate reaction stages.

The use of appropriately functionalised molecular building blocks to form novel nanoarchitectures with tailored structure and electronic properties has recently been brought under the spotlight.¹ However, such bottom-up assembly has so far allowed achieving a relatively small variety of complex molecular structures on different substrates. Intrinsically, surface-assisted chemical reactions have been essential in creating two-dimensional hydrogen bonded metal–organic or covalent networks.^{2–8} To this end, transition metal surfaces have widely been demonstrated to exhibit excellent catalytic activity in different polymerisation reactions,^{2,3,6} which are usually preceded by either dehalogenation^{9,10} or dehydrogenation^{11–13} of large organic molecules, such as polycyclic aromatic hydrocarbons (PAH). On the other hand, on-surface synthesis has also been shown to be efficient in fabricating graphene derivatives, such as nanoribbons,⁹ nanographenes¹² or molecular domes.¹³ Importantly, the use of heteroaromatic molecular precursors as building blocks is an elegant way of introducing dopants in the final nanoarchitecture.^{1,14} Recently, Lafferentz *et al.*¹⁵ have made a leap forward in the field of on-surface polymerisation proposing a hierarchical growth of nanostructures from a precursor, which can be selectively and sequentially activated at specific sites. On this basis, some recent studies have reported the formation of new 2D polymeric architectures of covalently bound networks.^{2–7}

In this communication, we report on an effective way of exploiting on-surface chemistry to grow different nanostructures in sequential steps from the same molecular precursor. We have used different activation temperatures to control the on-surface C–H bond breaking and C–C bond making processes of the nonplanar

helically chiral pyridyl-disubstituted dibenzo[5]helicene **1**, (Fig. 1) deposited on Pt(111). This molecule experiences dehydrogenation from different groups at different temperatures (Fig. 1). At 440 K it cyclodehydrogenates, by cleaving some internal C–H bonds, which subsequently close to form additional carbocycles, giving rise to N-doped nanohelicenes **2**. Further annealing at 650 K cyclodehydrogenates the aza-aromatic groups to form N-doped nanographenes **3**, and finally, at 770 K rim-dehydrogenation leads to N-doped nanodomes **4** covalently bound to the metal surface. By combining the room temperature (RT) ultra-high vacuum scanning tunnelling microscopy (UHV-STM) technique with first-principles calculations based on density functional theory (DFT), the sequential development of the different resultant structures has been monitored. Importantly, we have found significant agreement between experimental and calculated STM images of key intermediates that allows a detailed mapping of the individual steps of this complex on-surface transformation.

Fig. 1 Helically chiral pyridyl-disubstituted dibenzo[5]helicene **1** and the distinguished monomolecular products formed on Pt(111) upon heating: helical diazanano[5]helicene **2**, planar 2,5-diazahexabenzocoronene **3** (N-doped nanographene) and the geodesic **4** (N-doped nanodome) fixed to the Pt surface by dehydrogenated peripheral atoms (only (M) enantiomers of **1** and **2** are shown).

[Fig. 2](#) shows STM images of the thermally induced changes experienced by **1** on Pt(111). Intriguingly, a series of well-distinguished structural transformations are observed. We checked that the changes do not significantly depend on the bias voltage (or the scan direction). At RT ([Fig. 2a](#)), **1** does not diffuse on this surface, hampering surface polymerization. The intramolecular structure consists of four bright

lobes.¹ After annealing at 450 K (Fig. 2b), the four bright lobes featured by 1 coalesce to only two lobes, one of them being significantly brighter. Further annealing to 650 K (Fig. 2c) results in the vanishing of the submolecular resolution in STM images and the appearance of rounded structures. Upon further heating the sample at 770 K (Fig. 2d), the STM images show that the individual molecules shrink in height and width, as can be seen from height-histograms (ESI,[†] Fig. S3). Finally, annealing above 900 K (see Fig. S5 in the ESI[†]) leads to the formation of a layer of N-doped graphene on the surface (Fig. 2e).¹ In this image the bumps correspond to the Moiré patterns. The obtained N-doped graphene layer grows in small domains whose size is directly related to the amount of molecules deposited on the surface.

Fig. 2 STM images showing the sequential thermal induced transformations of 1 on a Pt(111) surface (a) 1 on Pt(111) at RT ($10 \times 10 \text{ nm}^2$; $V_s = 2 \text{ V}$); (b) at 450 K, ($10 \times 10 \text{ nm}^2$; $V_s = 2 \text{ V}$); (c) at 650 K, ($10 \times 10 \text{ nm}^2$; $V_s = 2 \text{ V}$); (d) at 770 K ($10 \times 10 \text{ nm}^2$; $V_s = 2 \text{ V}$); (e) annealing step at more than 900 K triggers the formation of N-doped graphene ($5.6 \times 3.0 \text{ nm}^2$; $V_s = 0.01 \text{ V}$).

To unveil the chemical nature of the aforementioned different structures generated upon annealing, we have performed DFT calculations and simulated STM images (Fig. 3). All the stages of the transformation of 1 upon annealing on Pt(111) at different temperatures before turning into graphene are represented by calculated structures, theoretical and experimental STM images and the experimental apparent heights compared to the theoretically calculated ones. The stable structures correspond to the transformation from 1 to 4.

Fig. 3 Stages of the sequential transformation of **1** into *N*-doped nanohelicene **2**, nanographene **3** and nanodome **4** upon thermal activation on Pt(111). Topmost row: DFT optimised structures. Second row: calculated STM images. Third row: experimental STM images ($2 \times 2 \text{ nm}^2$). Fourth row: experimental apparent heights (colour-shaded regions) as compared to the theoretical ones (dashed black lines).

The DFT calculations include an effective van der Waals correction and the theoretical STM images have been simulated under constant-current scanning conditions in order to mimic the experiments (see ESI†). The calculations have resulted in the adsorbates

1, 2 and 3 all being located at an average distance from the platinum substrate of around 3.1 ± 0.1 Å (for a detailed description of the full dehydrogenation reaction energy path from 1 to 3 see [ref. 1](#)). The interaction between 1, 2, 3 and Pt(111) is electrostatic, strong enough to prevent diffusion of the molecules on the surface, but unable to disrupt the intramolecular structure.

The experimental STM image of 1 at RT features four bright lobes, fairly well-reproduced by the theoretical simulations. One brighter lobe corresponds to the terminal benzene ring that lifts up ([Fig. 1-1](#), left side, in bold), another to the two benzene rings ([Fig. 1-1](#), left-up side) and the other two to the 4-pyridyl groups of 1. These groups are slightly lifted (to a different extent) with respect to the main plane of the molecule and thus the STM image mainly reflects topography rather than electronic effects.

The width of the molecule and height of the brightest lobe of 1 are 1.70 and 0.28 nm, respectively, as indicated by the apparent height profiles. The dashed black line indicates the profile of the STM simulation and, remarkably, the shape, height and width are very similar to the experimentally determined ones.

The transformation of 1 into the stable planar 2,5-diazaheptabenzocoronene 3 (C₄₀H₁₆N₂, [Fig. 1](#)) is not pursued in a single step, rather it involves some intermediate phases described in [ref. 1](#). Upon thermal activation at 450 K, 1 undergoes a partial cyclodehydrogenation, in which six C–H bonds break and three new C–C bonds are formed to close three new aromatic rings. Among all the intermediates involved, nanohelicene 2 exhibits the highest agreement between the experimental and theoretical STM images, as shown in [Fig. 3](#), indicating that it is the only stable intermediate, and that the barrier to form partially dehydrogenated cycles is very small. 2 exhibits the highest adsorption energy on Pt(111), of around 1.8 eV with respect to the initial precursor. This justifies its preferential experimental observation among other formed intermediates along the whole annealing process. As far as the STM image of 2 is concerned, the four intramolecular maxima merged into two lobes. According to the apparent height profile, the experimental STM image reveals a brighter lobe (0.28 nm) and a dimmer lobe (0.23 nm). From these calculations we can infer that the most intense feature of 2 corresponds to the lifted terminal pyridine unit, which is now a part of the diazanano[5]helicene backbone. The dimmer lobe concurs with a rather planar central part of 2.

The full cyclodehydrogenation of 1 into 3 is not yet achieved, as the cleavage of the two remaining C–H bonds of the 4-pyridyl groups requires a higher activation temperature. The transformation of the twisted 2 into planar 3 at 650 K is evidenced in both experimental and theoretical STM images by the loss of intramolecular resolution (3 has attained a higher symmetry) and the decrease of the apparent height to 0.23 nm and width to 1.44 nm, respectively.

The complete dehydrogenation of the rim of 3 at 770 K to form the nanodome 4 is manifested in experimental and theoretical STM images by the absence of intramolecular structure and, more significantly, by a reduction in the width of the geodesic 4 (to 1.27 nm) with respect to the planar 3. Unexpectedly, a decrease in the apparent height of 4 (to 0.19 nm) in comparison with 3 is also observed. This seems surprising, as the central core of the nanodome 4 is elevated. However, the reason for such an apparent height reduction lies in the formation of covalent bonds between the edge C atoms and the surface platinum atoms, which brings 4 closer to the substrate.

Hence, even if 4 is three-dimensional and 3 is planar, the N-doped nanodome is, on average, closer to the Pt than the N-doped nanographene, whose edges are passivated by the H atoms and do not interact covalently with the surface. Other panoramic images of the four stages of dehydrogenation are reported in the ESI.[†]

The 4–Pt(111) complex features a significant covalent interaction between the lowest C atoms and the Pt surface. DFT-based molecular dynamics calculations reveal (see details in the ESI[†]) that the fully dehydrogenated molecule tends to resize its parallel effective area by pulling up its central part so that the external C atoms with the dangling bonds are able to sit on top of the Pt atoms and to bind covalently to the surface Pt atoms at an average distance of around 2.3 Å, and with an adsorption energy of 2.9 eV higher than the original precursor 1. The strong covalent bond between 4 and the platinum substrate hence enforces a pronounced distortion of the molecule to form a curved nanodome.

The agreement between all the experimental and theoretical images is remarkable. The energy needed to break the internal C–H bonds to undergo intramolecular cyclodehydrogenation is lower than that needed to cleave the rim C–H bonds. Moreover, the energy needed to form a benzene-like cycle is lower than that required to form an azabenzene cycle. Therefore, this methodology can be used to *sequentially* form different architectures by using different activation temperatures. Previous reports describe examples in which nanographene flakes similar to 3 (such as hexabenzocoronene C₄₂H₁₈) are transformed into nanodomes.⁸ The apparent height of the nanodome was reported to be about 0.20 nm, which is quite similar to that of 4 measured in this study. Coronene (C₂₄H₁₂) also served as a precursor for growing smaller nanodomes,¹⁶ giving further proof that the geometry of the pristine molecule is crucial to build the desired nanoarchitecture. In fact, these results suggest that the sequential dehydrogenation reactions of 1 described above are possible due to the suitable geometry of the molecular precursor, *i.e.*, steric effects of the cycles.

In summary, sequential cyclodehydrogenation and dehydrogenation of a specifically designed PAH can be exploited for the formation of different nanostructures. Thus, we have formed N-doped nanohelicenes, nanographenes and nanodomes with efficiencies of about 100% by controlling the annealing temperature. The energy needed to cleave internal C–H bonds to obtain intramolecular cyclodehydrogenation and form new cycles is lower than that needed to cleave the peripheral C–H bonds. The choice of an adequate precursor is of paramount importance to achieve tailored nano-architectures with the desired doping.

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