Growth of N-Heterocyclic Carbene Assemblies on Cu(100) and Cu(111): From Single Molecules to Magic-Number Islands

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1. Experimental Procedures

1,3-Bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium-2-carboxylate (IPr . CO2):

1.3-bis(2,6-diisopropylphenyl)imidazolium-2-carboxylate was prepared according to a procedure by van Ausdall et al.\(^\text{[1]}\) in a glovebox. 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-tetrafluoroborate (476.4 mg, 1.00 mmol, 1.00 eq) and KO\(_\text{Bu}\) (112.2 mg, 1.00 mmol, 1.00 eq.) were added to a schlenk flask. Dry toluene (30 mL, 0.03 M) was added under argon and the suspension was stirred for two hours. The suspension was filtered under argon through a celite pad into a flame dried schlenk flask and dry carbon dioxide (dried with conc. sulfuric acid) was bubbled through the solution for 1 hour. During this time a white solid precipitated. The white solid was filtered off and washed with dry diethyl ether (3 x 10 mL) and dried in high vacuum (339 mg, 0.78 mmol, 78%). Analytical data is in accordance with the literature.\(^\text{[2]}\)

The Cu-surfaces were prepared in a UHV chamber with a background pressure < 5 \times 10^{-10} \text{ mbar} and equipped with e-beam annealing, a sputter gun and an evaporator containing three Knudsen cells. Cu(111) and Cu(100) surfaces were prepared combining Ar\(^+\) bombardment cycles at 1 kV for 30 min and annealing steps at 950 K for 5 min. Once the substrate cools down to 310 K, it is positioned in front of the molecular evaporator, in which IPr-NHC precursors are heated in a quartz crucible at 343 K. This procedure results in the evaporation of IPr-NHC molecules with a deposition rate of 0.05 monolayers(ML)/min. The sample is then transferred into a low-temperature STM operating at 5 K and a pressure < 2 \times 10^{-10} \text{ mbar}. The transfer of the sample into the STM stage takes around 15 min without thermal contact with the cryogenic bath. Once the sample is in the STM stage, it takes more than 1 h to thermalize. All STM images were taken in constant-current mode using a PtIr tip. \(V_s\) denotes the bias voltage at the sample, while \(I_t\) refers to the tunneling current.

2. Computational Methods

The adsorption of IPr-NHC is simulated on 5 layers-thick slab models of Cu(111) and Cu(100), adopting 10x10 supercells. All calculations were done with the Vienna ab initio simulation package.\(^\text{[3]}\) The Perdew-Burke-Ernzerhof functional\(^\text{[4]}\) was adopted for the exchange-correlation potential adding the long-range dispersion by the D2' approach.\(^\text{[5]}\) The sampling of the reciprocal space is reduced to the \(\Gamma\) point. Local minima are identified by means of static relaxation using a conjugated-gradient algorithm. Diffusion barriers are estimated recurring to nudged elastic band (NEB) calculations considering two images along the diffusion path.
3. IPr-NHC on Cu(100) and Cu(111) at High Coverage

In order to analyze the arrangement of IPr-NHC on the studied copper surfaces, large-scale STM images like the ones shown in Figure S1 were taken. The fast Fourier transforms (FFT) obtained from these images are discussed in the main text (Figure 2c and Figure 3c) and facilitate the elaboration of a model of the molecular lattice. The FFT in Figure S1b is quite blurry compared to that of Figure S1d, indicating a lower degree of order on Cu(100) than on Cu(111). The lines crossing the lattice spots in Figure S1d come from the trenches appearing in the STM image of Figure S1c.

Figure S1. Arrangement of 0.75 ML IPr-NHC. On Cu(100), a) STM, 6 nm × 96 nm, Vs = +1.5 V, It = 50 pA and b) corresponding FFT. On Cu(111), c) STM, 96 nm × 96 nm, Vs = +1.5 V, It = 50 pA and d) corresponding FFT.
4. Pair Correlation Function of Closed-Packed Phases

IPr-NHC molecules form closed-packed patches at a coverage of 0.75 ML on Cu(100). The nearest neighbour distance between molecules appearing in these patches is 12 Å. This distance can be deduced from the corresponding pair correlation function, that is, the probability of finding a molecule at certain distances from a selected molecule, represented by the blue curve of Figure S2. Interestingly, the same nearest neighbor distance is found in the arrangement of IPr-NHC on Cu(111) at different coverages. The pink curve of Figure S2 was calculated in the nanoislands appearing on Cu(111) covered with 0.25 ML of IPr-NHC.

Figure S2. Pair correlation function showing the probability of finding a molecule at a given distance from another molecule. Blue data refer to the closed-packed patches found on Cu(100) with 0.75 ML of IPr-NHC. Pink data refer to the nanoislands found on Cu(111) with 0.25 ML of IPr-NHC. In both cases, a nearest neighbour distance of 12.0 Å can be clearly distinguished.
5. Apparent Height of IPr-NHC on Cu(100) and Cu(111)

The height profiles taken on numerous STM images reveal a larger apparent height for IPr-NHC molecules on Cu(111) in comparison to Cu(100), as shown in Figure S3. This observation is in agreement with DFT calculations, which predict a larger uplift of the Cu atom bound to the IPr-NHC molecule on Cu(111) as compared to Cu(100).

Figure S3. Height profile of IPr-NHC on Cu(100) (blue) and Cu(111) (red) for a coverage of 0.25 ML. STM image on Cu(100): 20 nm × 20 nm, Vs = 1.5 V, It = 50 pA. STM image on Cu(111): 20 nm × 20 nm, Vs = 1.5 V, It = 50 pA.
6. Strain-Related Effects on the Aggregation of IPr-NHC on Cu(111) and Cu(100).

Figure S4. Free-standing ballbot layer. Relaxed two-dimensional lattice of IPr-NHC molecules bound to Cu atoms and coincidence to Cu(111) and Cu(100) lattices. The a- and b-axes discussed in Table 2 of the main text are indicated.

By means of DFT, lattice parameters and internal coordinates of a ballbot two-dimensional arrangement have been relaxed by keeping fixed the Cu fractional coordinates in order to avoid spurious clustering of the molecules during the relaxation and maintain the two-dimensional arrangement, mimicking what happens on the Cu surfaces. At the same time, atomic positions of the IPr-NHC molecules are relaxed, as well as the lattice parameters. This permits finding the optimal molecule-molecule distance and molecular structure. The mismatch of the free-standing molecular lattice with respect to the underlying support induces a strain affecting the molecular arrangement. The larger the strain, the worse the match to the underlying lattice of adsorption sites on the closed-pack Cu surfaces. It is worth noting (Table 2 in the main text) that the situation on Cu(111) and Cu(100) is very different. On Cu(100), the strain is large on both directions (8% compressive and 4% tensile), envisaging unfavourable conditions for the formation of extended layers. To this end, it is also relevant the bad match between the optimal molecule-molecule distance and the Cu-Cu distance separating top sites on Cu(100). On Cu(111), the match along one direction is almost perfect, while on the other we observe a remarkable compressive strain (4%). This uniaxial strain explains the growth of ribbons on Cu(111) and may also explain the formation of discrete islands, where beneficial intermolecular interactions are established in the inner part, while the strain is released at the borders.

We tried to experimentally find lattice distortions for both molecular ribbons and molecular islands on Cu(111). In the case of the molecular ribbons, we analysed more than 75 topography profiles from STM images like that shown in Figure S5a along three main directions (A,B,C). Representative STM profiles taken along the coloured arrows in Figure S5a are shown in Figure S5b. Through this method, we obtained the average molecule-molecule distance along A, B and C directions (Table S1). It is difficult to conclude the existence of some kind of distortion due to a possible uniaxial strain, since the deviation for these values (8 - 9 %) is higher than the strain predicted by DFT (-4.4 %). It is also worth mentioning that the obtained values are in agreement with the value reported in the main text (1.2 ± 0.1 nm).

In the case of the molecular islands, we analysed more than 60 topography profiles from STM images like the one shown in Figure S5c. Figure S5d shows the STM profiles taken along the coloured arrows from Figure S5c. The molecule-molecule distances are almost the same for the three directions, as collected in Table S1, although they tend to be slightly shorter along the A direction. It is also interesting to note that the molecule-molecule distance tends to be smaller in the magic-number islands than in the ribbons.

The precision of the molecule-molecule distance measurements is not limited by our instrument, which allows typical lateral distance measurements with error below ± 10 pm [6], but by the nature of the molecular assemblies. It can be seen in STM images and profiles that the molecules have a certain degree of freedom choosing a location inside the lattice, giving rise to an intrinsic dispersion for the molecule-molecule distance. In addition, we observe some elongated molecular shapes. This leads to non-symmetric arrangements, but without presenting a systematic behaviour with respect to the molecular orientation.
Figure S5. Analyzing the molecule-molecule distance along different directions. a) 0.75 ML of IPr-NHC on Cu(111), 15.4 nm × 15.4 nm, V_s = +2.0 V, I_t = 70 pA. b) Profiles taken along A (blue), B (red) and C (green) arrows from panel a). c) 0.25 ML of IPr-NHC on Cu(111), 21.7 nm × 21.7 nm, V_s = +1.0 V, I_t = 20 pA. d) Profiles taken along A (blue), B (red) and C (green) arrows from panel c). White arrows in panels a) and c) indicate the high symmetry directions of Cu(111). Position of the molecules marked with grey lines.

Table S1. Collected molecule-molecule distances along the directions A, B and C, indicated in Figure S5, for molecular ribbons and islands.

|          | A (nm) | B (nm) | C (nm) |
|----------|--------|--------|--------|
| Ribbons  | 1.1 ± 0.1 | 1.3 ± 0.1 | 1.2 ± 0.1 |
| Islands  | 1.0 ± 0.1 | 1.1 ± 0.1 | 1.1 ± 0.1 |
7. Coverage-Dependent Structure Evolution of IPr-NHC on Cu(111)

The resulting molecular structures evolve as the coverage of IPr-NHC on Cu(111) increases, ranging from nanoislands with selectivity in shape and size to molecular ribbons. The shape of the structures is mainly governed by the island edge tension generated by the intermolecular interactions and the uniaxial strain of the molecular lattice. The intermolecular interactions favor compact structures exhibiting the hexagonal symmetry of the molecular layer. As the amount of molecules increases, the uniaxial strain becomes a driving factor, leading to the formation of elongated structures (Figure S6).

Figure S6. Structure evolution of IPr-NHC on Cu(111) according to different coverages. a) 0.05 ML, b) 0.15 ML, c) 0.25 ML, d) 0.35 ML, e) 0.50 ML, f) 0.75 ML. 50 nm × 50 nm, Vs = +1.5 V, It = 20 pA for all STM images. Insets show the FFT of the corresponding STM images.
8. Molecular Clusters and Magic Islands

Molecular clusters appear on Cu(100) and Cu(111) for low coverages of IPr-NHC. While on Cu(100) the molecules do not adopt a well-defined arrangement, on Cu(111) the formation of well-defined nanoislands takes place. These nanoislands present preferential sizes and shapes, as discussed in the main text and shown in Figure S8.

Figure S7. IPr-NHC molecular nanoclusters on Cu surfaces. a) 0.25 ML on Cu(100), 100 nm × 100 nm, Vs = 1.5 V, It = 20 pA. b) 0.25 ML on Cu(111), 100 nm × 100 nm, Vs = 1.5 V, It = 20 pA. c) 0.05 ML on Cu(111), 100 nm × 100 nm, Vs = -1.0 V, It = 15 pA. On Cu(111), a selectivity for islands with sizes of 3, 7 and 12 molecules can be observed, as discussed in the main text.

Figure S8. Histograms representing the different sizes of the molecular nanoislands appearing on Cu(111) for a) 0.05 ML and b) 0.25 ML depositions. The formation of magic islands composed of 3, 7 and 12 molecules can be observed. Data obtained from STM images like those shown in Figures S6b and S6c.
9. Surface State Effects and Magic-Number Molecular Islands

Since we can not exclude the formation of ballbot assemblies (IPr-NHC bound to a Cu adatom), one possibility would be that the ballbots behave like Cu single atoms on Cu(111). In addition, the formation of large-scale superlattices has been observed to be produced by the interaction of adatoms with surface state electrons. In order to address this hypothesis, we can consider the surface where the 12-magic-number island predominate (0.25 ML IPr-NHC on Cu(111)). Figure S9a is the corresponding FFT taken from Figure S6b, where features from the molecular lattice and three concentric rings can be observed. These rings are related to different parameters of the molecular islands. The smallest and most intense ring, marked in black, corresponds to the distance between islands and it is represented in real space in Figure S9b. We obtain an average distance between islands of 7.8 ± 0.2 nm. This value does not match with the Friedel oscillations observed for Cu single atoms on Cu(111). The distance between molecules is on the other hand 1.2 nm, which is close to the first minimum of the potential energy produced by the surface state electrons. However, the same distance between molecules is observed on Cu(100), where no surface state exists, as shown in the pair correlation functions of Figure S2. The ring marked in red in Figure S9a is related to the distances between island edges, as can be seen in real space in Figure S9c. Finally, the green ring from Figure S9a originates from the distance between the center and the edge of the islands, with an average value of 2 ± 1 nm.

Figure S9. Relevant features from magic-number islands. a) FFT from Figure S6b, related to 0.25 ML IPr-NHC on Cu(111). Features coming from the two rotational domains of the molecular lattice (orange) and three concentric rings (black, red and green) are marked. Signal in real space for the b) black, c) red and d) green rings in (a). STM parameters: 100 nm × 100 nm, Vs = 1.5 V, It = 20 pA.
10. Mobility of IPr-NHC on Cu(111) during STM Measurements.

While on Cu(100) no mobility at all is observed, on Cu(111) the STM tip can induce, depending on scanning conditions and on tip configuration, the motion of some of the molecules during scanning. Figure S10 shows a series of consecutive STM images exhibiting different events. However, we would like to point out that for the discussion in the entire manuscript, only STM images of unperturbed molecules have been considered.

It is interesting to note that sometimes, even under mild STM tunnelling conditions, an increase in the disorder of the surface is observed, contributing to the decomposition of the islands. This indicates that the island arrangement is driven by relative weak interactions. Therefore, the formation of magic-number islands only takes place when these interactions are dominant against other external contributions.

Figure S10. Mobility of IPr-NHC on Cu(111). Red circles indicate one of the events in each STM image. The consecutive images are taken each 90 s. 21.7 nm × 12.0 nm, Vs = +1.5 V, It = 20 pA for all STM images.
11. Thermal Stability of IPr-NHC on Cu(111) and Evolution of The Magic-Number Islands.

In order to assess the thermal stability of the molecular layer on Cu(111), 0.75 ML IPr-NHC were deposited on Cu(111) resulting in the arrangement of Figure S11a. We took this sample out of the STM, heated it to 473 K for 1 min in a different chamber and brought it back into the STM. Figure S11b shows the resulting surface. The straight empty trenches observed in the as prepared surface become curved trenches, which can be related to the creation of new defects in the molecular layer due to the annealing step. These defects may be related to the fragmentation of some molecules at the annealing temperatures. The overall order of the molecular lattice does not get distorted, as confirmed by the FFT in the inset. On the other hand, the signal coming from the trenches is not visible in the FFT. The molecule-molecule distance is 1.2 ± 0.1 nm, as in the as-prepared surface. After heating the sample at 523 K for 1 min, only some ordered islands surrounded by different molecular products generated during annealing can be distinguished (Figure S11c). Consecutive annealing of the sample at 573 K for 1 min results in a disordered organic layer where no IPr-NHC can be identified by means of STM (Figure S11d).

In order to study the thermal stability of the magic-number islands, we prepared 0.25 ML of IPr-NHC on Cu(111) and studied the behaviour of the surface after successive annealing steps. The as-prepared sample, shown in Figure S12a, reproduces the formation of magic-number islands, being the 12-membered island the most favoured one as discussed in the main text. We took the sample out of the STM stage, and annealed it at 373 K for 1 min. The resulting surface (Figure S12b) exhibits the same type of magic-number islands and, additionally, some individual adsorbates with lower apparent height. These new adsorbates could be generated due to fragmentation of the IPr-NHC species during annealing. After the 423 K and 473 K annealing steps (Figure S12c and S12d, respectively) the 12-membered islands can be still observed, although, as discussed below, its relative amount seems to be lower compared to the as-prepared surface. The molecule-molecule distance remains constant inside the islands independently of the employed annealing treatment.
The evolution of the size distribution of the molecular islands after annealing was also studied (Figure S13). There is a change in the shape of the size distribution as the annealing temperature increases. This behaviour is a result of the desorption by some of the molecules during the annealing. The coverage decreases during the annealing steps until reaching 0.20 ML at 473 K. Another important reason that could explain this behavior is the minor fragmentation of the molecules at these temperatures, which may be promoted by the copper substrate. The generation of defects is driving the observed changes in the size distribution of the islands by inserting defects in the molecular lattice. In any event, the 12-membered number-magic islands are also observed after the 473 K annealing step, indicating that they are most likely not related to a kinetically trapped state.
12. STM Measurements of IPr-NHC on Cu(111) at Different Temperatures.

In order to analyze the cooling down process, we took STM images of 0.25 ML IPr-NHC on Cu(111) at additional temperatures, namely: RT and 78 K and compared to the results obtained to those measured at 5 K (Figure S14). The mobility at RT is so high, that we cannot distinguish any molecule on the surface. At 78 K some molecules can be observed around defects and at the steps. However, the mobility is still high, and these structures change continuously with consecutive scans. Therefore, for temperatures higher than 78 K, the molecules have enough thermal energy to diffuse. Only at 5 K it is possible to observe the total amount of molecules deposited on the surface. The formation of the number-magic islands sets in at the cool down process in the low temperature region between 78 K and 5 K.

![STM images](image)

**Figure S14.** STM images of 0.25 ML IPr-NHC on Cu(111) taken at different temperatures. a) RT (65 nm × 40 nm, Vs = +1.5 V, It = 15 pA), b) 78 K (65 nm × 40 nm, Vs = +1.5 V, It = 15 pA), c) 5 K (65 nm × 40 nm, Vs = +1.5 V, It = 20 pA).
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Author Contributions

STM measurements and data analysis were conducted by J. J. N. and F. L.. M. D. and M. K. performed the synthesis and chemical analysis of the IPr-NHC precursors. S. T. and G. P. carried out the theoretical calculations and contributed to the elaboration of the manuscript. B. R. C. contributed to the writing of the manuscript. J. J. N., M. H. and F. G. planed the experiments and wrote the manuscript with contributions from all authors.