Interplay of weak interactions in the atom-by-atom condensation of xenon within quantum boxes

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Condensation processes are of key importance in nature and play a fundamental role in chemistry and physics. Owing to size effects at the nanoscale, it is conceptually desired to experimentally probe the dependence of condensate structure on the number of constituents one by one. Here we present an approach to study a condensation process atom-by-atom with the scanning tunnelling microscope, which provides a direct real-space access with atomic precision to the aggregates formed in atomically defined 'quantum boxes'. Our analysis reveals the subtle interplay of competing directional and nondirectional interactions in the emergence of structure and provides unprecedented input for the structural comparison with quantum mechanical models. This approach focuses on—but is not limited to—the model case of xenon condensation and goes significantly beyond the well-established statistical size analysis of clusters in atomic or molecular beams by mass spectrometry.
Condensation is a fundamental process, and the interactions involved in the aggregation of atoms or molecules govern the structure of condensates. Moreover, at the nanoscale level the properties of a condensate depend on its size, structure and bonding between the atoms or molecules. Although the analysis of noble gas condensates of different sizes, interacting by isotropic van der Waals forces, has provided valuable insight into the mechanisms of particle clustering, the condensation in a real environment usually proceeds under the competing influence of weak forces.

In order to take an interplay of such forces into account in a model condensation process, we chose a nanopatterned vacuum/solid interface, which not only provides the competition between interparticle forces and interactions with a surface but may also give rise to a more complex interplay of forces, which, as we observe, governs the emergence of structural patterns. We demonstrate how the atom-by-atom condensation of noble gas atoms proceeds under the influence of competing interactions. This is conveniently probed within the atomically defined cavities of a supramolecular network, generated on the metal substrate. This approach is based on the ability of such on-surface networks to trap different adsorbates and thus to create host–guest systems.

Results

Design of the host–guest system. We employ a highly ordered Cu-coordinated, triply dehydrogenated 4,9-diaminoperylene quinone-3,10-diimine (3deh-DPDI) porous network grown on Cu(111)21,22 as a template. The electronic Shockley surface state of the underlying substrate is confined in the pores23, resulting in a single quantum well state per pore with the spatial |Ψ|<sup>2</sup> maximum in its centre (Fig. 1a–c) and thus in a specific electronic environment in each pore. As a model condensate we choose Xe atoms, which provide an ideal probe of the weak interactions because of their closed-shell electronic configuration.

Repositioning sequences of single Xe atoms. Upon deposition of Xe unto the structured surface, the pores of the network were found to host different numbers of Xe atoms, as revealed in the scanning tunnelling microscopy (STM) image shown in Fig. 1d. Notably, no single Xe atom was observed to adsorb spontaneously in the centre of a pore. To investigate whether it was possible to place a single Xe atom at this position, we performed repositioning sequences as displayed in Fig. 1e–g. In each sequence the tip was first decorated with a single Xe atom and then placed above the pore centre where its deposition was performed.

Despite numerous attempts to place the Xe atom in the pore centre, none was successful. Each attempt resulted in the diffusion of the Xe atom to the border of the pore (Fig. 1f) or even in its displacement to a neighbouring pore (Fig. 1g). We assign this behaviour to the Pauli repulsion between the Xe atoms and the quantum well ground state of the pore. This contrasts with the observation made for open-shell Fe atoms and the π-acceptor CO molecules adsorbed in the pores of supramolecular networks grown on Cu(111), which experienced an attractive interaction with the quantum well state24,25.

Spontaneously occurring Xe condensates. The spontaneously occurring occupancies ranging from 0 to 12 Xe atoms (denoted hereafter as occ-0—occ-12) were found across the pores of the network. Figure 2 presents the various spatial arrangements of Xe atoms, with two different forms of aggregation being observed for occ-2, occ-5 and occ-7. The histogram of pore occupancy (Fig. 2) reveals the presence of favoured occupancies, which may be related to particularly stable condensates. The most favoured occupancies are occ-1 and occ-12, whereas condensates with greater occupancies (occ-6—occ-11) were less frequently observed. We note that occ-3 and occ-4 occur more frequently than occ-2, and that there is a slight preference for occ-8, indicating an increased stability of multiples of a tetrameric arrangement. In contrast, the occupancy of Fe adatoms inside pores of an organic on-surface network mentioned above was found to correspond to a Poisson distribution, further accentuating the fundamental differences between (open shell) metal atom condensation and noble gas condensation in somewhat related porous confinements, both of which exhibit a quantum well state (cf. Supplementary Fig. 2).

Discussion

For an analysis of the self-assembled patterns of Xe atoms within the pores, a closer inspection of the metal–organic surface structure is essential. Each pore of the network possesses threefold symmetry because of the inequivalence of its nodes. The node labelled A in the schematic representation of an occ-12 pore (Fig. 2) is centred above a hollow surface site, whereas the node B is centred above an on-top site of a surface atom. Three different adsorption sites of Xe are identified: one in the inner pore (which is only occupied for occ-7) and two at the pore boundary either near the organic network molecule or in the vicinity of node A. The sites next to node B are never occupied in the occ-12 condensates, and therefore the Xe
adsorption reflects the threefold rotational symmetry of the pores as indicated by the three yellow lines in the schematic occ-12 model in Fig. 2. In agreement with this, each occ-12 condensate consists of three tetramers, with Xe atoms adsorbed on-top sites of the Cu(111) atomic lattice in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure, in accordance with previous studies of Xe on Cu(111)\textsuperscript{26,27}.

For the classification of the structural arrangements of the occ-n inside the pores, we initially focus on two aspects: first, whether a certain n-mer exhibits a subset of the adsorption sites observed for the occ-12, meaning that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, exhibited by each tetramer of occ-12, is preserved, and second, whether the considered occ-n can be described either as occ-(n-1) with one additional Xe atom, or as superstition of condensate structures observed for lower occupancies. Focusing on the first aspect, we find that only condensates occ-2b, occ-5a, occ-7a, occ-8, occ-10 and occ-11 are always congruent with the registry of the occ-12. The other condensates (partially) violate the registry of the dodecamer (Figs 2 and 3, Table 1), implying that the interaction of a single Xe atom with the backbone of the organic network is sufficient to cause the Xe atom to occupy a slightly less favourable adsorption site. Moreover, the modified quantum well state may also have an impact on the favourability of the adsorption sites of Xe atoms. Furthermore, the observed registry violations retain or decrease the Xe–Xe distance, indicating an equal or increased Xe–Xe condensation energy as compared with the corresponding positions identified for occ-12 (Figs 2 and 3).

Figure 2 | Atom-by-atom self-assembly of Xe within quantum boxes influenced by the interplay of directional weak interactions. Pores with different numbers of adsorbed Xe atoms are indicated by the numbers placed in the left upper corner of each STM image (2.4 nm × 2.4 nm); letters are used to denominate condensates with the same number of Xe atoms but having different arrangements. As a guide to the eye, a colour code that defines the adsorption position and the number of nearest neighbours is used and is defined in the legend. In the bottom left corner, the histogram of the occupancy of the pores obtained from one sample exposed to 120 L of Xe at 9 K, resulting in a coverage $\Theta = 0.178$ (cf. Supplementary Note 1), is displayed (2,067 pores have been analysed).
With the second aspect brought into focus, namely the relationship between occ-n and its predecessors in the hierarchy, our analysis shows that only condensates occ-2, occ-5a, occ-9, occ-11 and occ-12 feature the same arrangement of adsorption sites as their corresponding occ-(n-1) condensates. In fact, they derive from their predecessor by having one additional adsorption site occupied. Only condensates occ-2a, occ-4 and occ-7a can be described by a superposition of condensates observed at lower occupancies. Moreover, all observed condensates were found to be stable with the exception of occ-5b in which five Xe atoms are sharing 12 adsorption sites along the rim of the pore and exhibit rapid site exchange (Fig. 2; the number of Xe atoms in this condensate was identified from Xe-repositioning sequences). In summary, the atom-by-atom condensation of Xe in the pores of the Cu-coordinated 3deh-DPDI network results in a wide range of occupancies (occ-1—occ-12), which do not follow a single set of ‘hierarchic filling rules’25, but adapt their structures in the different regimes. This work demonstrates that the confinement of adsorbates in the pores of a metal–organic on-surface network provides the opportunity to study condensation under the influence of the subtle interplay of weak forces with single-atom precision. The experimental resolution providing the real-space structure of atomic condensates adsorbed on an atomically defined patterned surface provides the unique opportunity to compare experimental data and theoretical models. We note that our approach can benefit from the comparison of the condensation behaviour in differently sized pores, as owing to that, the interference of weak interactions involved can be tuned, which is expected to be stronger/weaker with decreasing/increasing pore size.

**Methods**

**Sample preparation.** The samples were prepared and investigated in an ultrahigh vacuum system with a base pressure of $5 \times 10^{-11}$ mbar. The Cu(111) crystal (MaTecK GmbH) was prepared by cycles of Ar$^+$ sputtering at $E = 1,000$ eV performed at room temperature followed by annealing at 800 K. The DPDI molecules were deposited with the use of nine-cell commercial evaporator (Kentax, GmbH, Germany) on the Cu(111) by sublimation at $\approx 240$ °C. The rate was controlled before deposition by a quartz crystal microbalance. After deposition, the sample was annealed to 300 °C in order to convert DPDI into 3deh-DPDI, which creates the Cu-coordinated network21. Xe of purity 99.99% was dosed to the sample placed in the STM (Omicron Nanotechnology GmbH) operated at 4.2 K, with the cryoshields open and the leak valve being in line-of-sight with the sample. Supplementary Fig. 2 presents STM data acquired after exposure of the Cu-coordinated 3deh-DPDI network to 20 L of Xe performed at a pressure equal to 7 mbar for 200 s causing the increase in the sample temperature to 8 K. Xe was found to be adsorbed in the pores as well as in the nodes of the network. Figure 1d and the histogram in Fig. 2 present data after a 120-L exposure at the same pressure for 1,200 s resulting in the increase in the sample temperature to 9 K. Only Xe adsorbed in the pores was found.

**Repositioning sequences of single Xe atoms.** All the self-assembled condensates, except of occ-2b, were reproduced with the use of repositioning...
sequences, by taking away Xe atoms from the 12-fold occupied pore as these are represented in Fig. 2. The difficulty in reproducing occ-2b can be connected with increased stability of the rare gases. J. Chem. Phys. 23, 482–486 (1944).

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Author contributions
S.N., A.W., S.K., T.I., J.N., S.F., C.W. and T.N conducted the STM measurements and analysed the data under the supervision of T.A.J., L.H.G., M.S. and E.M.; J.B. and T.I. provided theoretical models; S.N., T.A.J. and L.H.G. wrote the manuscript.

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