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Adsorbate-Induced Modification of the Confining Barriers in a Quantum Box Array

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Supporting Information

ABSTRACT: Quantum devices depend on addressable elements, which can be modified separately and in their mutual interaction. Self-assembly at surfaces, for example, formation of a porous (metal-) organic network, provides an ideal way to manufacture arrays of identical quantum boxes, arising in this case from the confinement of the electronic (Shockley) surface state within the pores. We show that the electronic quantum box state as well as the interbox coupling can be modified locally to a varying extent by a selective choice of adsorbates, here C₆₀, interacting with the barrier. In view of the wealth of differently acting adsorbates, this approach allows for engineering quantum states in on-surface network architectures.

KEYWORDS: quantum box, electronic coupling, on-surface self-assembled network, surface state, adsorption

Configurable quantum states are indispensable for the development of optoelectronic devices, including quantum-dot photovoltaics and light emitting devices.^{1–3} Being able to locally govern the coupling between addressable quantum states, for example, arranged in an array,

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Figure 1. Quantum box array formed by deposition of Zn(II) porphyrin 1 on Ag(111). (a) Molecular structure of Zn(II) porphyrin 1. (b) STM image (100 nm × 100 nm) of two terraces covered by enantiomeric domains of a porous network of 1. Each domain consists of a single conformational enantiomer: “L” on the upper terrace and “R” on the lower terrace; for high-resolution STM images see Figure S1. (c) LEED data of the porous network of 1 on Ag(111) taken at room temperature (RT). The pattern of the porous network of 1 was recorded at a beam energy of 5 eV, that of the Ag(111) substrate at 50 eV (lower inset). The reciprocal unit cell vectors b_{1L}^* (b_{1R}^*) and b_{2L}^* (b_{2R}^*) of “L” (“R”) domains are indicated by violet (coral) arrows. The reciprocal unit cell vectors a_1^* and a_2^* of the Ag(111) substrate are indicated by green arrows (lines). The sets of spots for the “L” or “R” domains draw an angle of $\pm 10^\circ$ with the principle Ag(111) directions. The simulated LEED pattern is shown in the upper inset (cf. Figure S3).

provides the next level of control, which is desired for the further advancement of quantum technologies.⁴ Toward higher level integration of quantum circuitry, that is, for performing operations between different quantum states, the reliable manufacturing of identical quantum units at large numbers and the reproducible control of their interaction is of utmost importance.

Individual adsorbates on metallic surfaces exhibiting a Shockley surface state are known to scatter this electronic state.^{5–7} Thus, with the help of artificially fabricated on-surface structures, the surface state can be confined, and thereby, quantum units can be generated.^{8–23} A practical way to fabricate arrays consisting of hundreds of quantum units is provided by on-surface self-assembly, ultimately assuring high precision concerning the individual quantum unit, the periodicity of the array, and the coupling with the surrounding units.^{8,23} Importantly, the coupling strength depends on the properties of the confining barrier, especially on its interaction with the surface. This dependence has been demonstrated, for example, by the comparison of the confinement strength in quantum systems featuring the same arrangement but being constructed from slightly different building blocks (*i.e.*, metal free *vs* metalated porphyrin).¹¹

Periodic 2D arrays of quantum units are best probed by two complementary techniques: spatially resolved and momentum-averaging scanning tunneling spectroscopy (STS) as well as spatially averaging and momentum-resolved angle-resolved photoemission spectroscopy (ARPES). STS accesses the local electronic structure of the quantum units and the barriers between them, whereas ARPES reveals how the overlap of the electronic wave functions of such units, that is, the coupling, gives rise to a well-defined band dispersing in energy and momentum. The dispersion of the bottom or top of a band can be approximated with a certain effective mass, thus giving information about the carrier velocity. These properties determine the carrier mobility and are, ultimately, of fundamental interest for quantum devices as well as their architectures. It is worthy to note that ARPES has been

successfully used to probe quantum confinement in different materials^{24,25} and can even give an accurate description of many-body interactions.^{24,26}

Here, we use the self-assembly of a porphyrin derivative on a Ag(111) surface to fabricate a 2D periodic array of coupled quantum units, and we demonstrate that the transmission probability of the confining barrier, hence the interunit coupling, can be modified by deposition of adsorbates. As a result, a perfect system is demonstrated to test various fundamental concepts related to quantum confinement and its use in quantum devices.

RESULTS AND DISCUSSION

The Design of the Building Block. To fabricate a 2D periodic array of quantum units, we designed a porphyrin building block 1 to self-assemble into a porous network *via* C–H...F–C interactions, which have been reported for 3D crystals^{27–31} as well as 2D assemblies on surfaces.^{32–36} Specifically, 2',3',4',5',6'-pentafluorobiphenyl-4-yl and 3,5-dimethoxybiphenyl-4-yl substituents have been employed (Figure 1a, for the synthesis see the Supporting Information synthesis file) on the basis of earlier reports regarding 2D interactions between arenes and fluoroarenes^{32–36} and the experience that functionalized porphyrins with two different, oppositely positioned binding groups are ideal building blocks for porous networks on crystal surfaces having (111) orientation, as reported for example, for cyanophenyl,³⁷ alkoxyphenyl³⁸ and pyridine-derived³⁹ substituents.

Structure of the Porous Porphyrin Network. Zn(II) porphyrin 1 self-assembles in an extended hexagonal porous network on Ag(111) and is characterized by the presence of two mirror-image domains creating a $(14 \times 14)R \pm 10^\circ$ overlayer structure as evidenced by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) (Figure 1). High-resolution STM images reveal that each domain is homochiral, *i.e.*, it exclusively consists of a single one out of two conformational enantiomers, labeled as either “L” or “R”, which occur upon adsorption of Zn(II) porphyrin 1

Figure 2. The dI/dV characterization of the barrier regions between the quantum boxes. (First row) STM image ($11\text{ nm} \times 11\text{ nm}$) and corresponding molecular model showing the arrangement of the individual molecules. The barriers between three different arrangements of the quantum boxes were investigated, namely between: (a) two *small* boxes, (b) two *big* boxes, and (c) a *small* and a *big* box. (Second row) For each barrier region, dI/dV data were taken along a line through a porphyrin macrocycle as indicated by the yellow and black arrows superimposed on the STM image and the molecular model, respectively (the arrows illustrate the starting and the final points of each dI/dV line). (Third row) Selected dI/dV spectra taken at the positions marked by colored dots in the STM image, the molecular model, and in the spatially resolved dI/dV spectra. The green and orange numbers indicate the value of the QBS peak shift toward higher BE at the position of the porphyrin macrocycle and the pentafluorophenyl substituents, respectively. The close-up dI/dV spectra of the QBS peak regions are shown in Figure S5. Please note that the asymmetry between the starting and ending point of the dI/dV line acquired across the porphyrin macrocycle in (b) is caused by the fact that the former was acquired closer to the pore center, which is dominated by the state at -5 meV , whereas the latter is closer to the rim of the pore dominated by the state at -80 meV (cf. Figure S4). For the dI/dV data taken along a line through pentafluorophenyl substituents see Figure S6.

on the Ag(111) substrate and which are characterized by opposite torsion angles around the bond connecting the porphyrin macrocycle and the 3,5-dimethoxybiphenyl-4-yl substituents (Figure S1). As intended, the network is held together primarily by C–H $\cdots$ F–C interactions (Figure 2 and Figure S1), although other interactions may also play a role. Noteworthy is the absence of any phenyl-pentafluorophenyl stacking interactions, which are observed in the 3D crystal structure of **1** (cf. Section 3.2 in the Synthesis Supporting Information file) and typically in crystals of molecules with aryl and perfluoroaryl subunits.^{40–44} The on-surface 2D network is mainly comprised of regular pores enclosed by six Zn(II) porphyrin molecules **1** (Figure 2 and Figure S1), denoted hereafter as *small*. Between supra-molecular islands, a domain boundary in the form of a linear array of larger pores enclosed by eight molecules (Figure 2) is observed (cf. Figure S2). The latter pores are hereafter referred to as *big*.

Quantum Confinement in the Pores of the Network.

On Ag(111) the Shockley surface state disperses across the Fermi level with its energy maximum just below the Fermi level, that is, at the binding energy (BE) of 65 meV .⁴⁵ In the presence of the porous network, the surface state is shifted above the Fermi level, due to the confinement of the surface state electrons by the pores of the network, as evidenced by the characteristic peaks in our dI/dV spectra (Figure 2). Thus, each pore constitutes a quantum box (QB) embedded in a quantum array. The *small* pore features a quantum box state (QBS) peak at BE of -40 meV (Figure 2a, red spectrum), whereas the *big* pore exhibits two peaks: one at -5 meV (Figure 2b, violet spectrum), dominating in the center of the pore, and the second one at -80 meV (Figure 2c, violet spectrum), located at the rim of the pore (the exact spatial distribution of those QBSs is shown in Figure S4).

Figure 3. Synchrotron-based ARPES measurements of a 2D periodic array of quantum units formed by a Zn(II) porphyrin **1** porous network on Ag(111). (a) ARPES spectrum for a Ag(111) surface partially covered with the Zn(II) porphyrin **1** network: Two electronic states are revealed, the Ag(111) Shockley surface state dispersing across the Fermi level and the quantum box state dispersing above the Fermi level. The bottom of both states is fitted by two parabolic dispersions (black lines), and an effective mass is extracted (the fitted points with error bars are marked in red). The parabolas marked by dotted lines indicate the expected periodicity of the QBS. (b) Intensity profile (red curve) obtained by integrating the spectra in (a) over the momentum range illustrated by the red area. The black line and arrows serve as guides for the eyes. (c) The EDCs at various k values of the data presented in (a). (d) The reference ARPES data for clean Ag(111) surface. The ARPES measurements were carried out at RT and at a photon energy of 21 eV. The data were normalized with a Fermi function with a constant offset added to increase the visibility of the state above the Fermi level (see the [Materials and Methods](#) section for details about the ARPES data analysis including fitting of EDCs and extracting effective mass). STM data acquired at RT for an analogue sample are presented in [Figure S8](#).

Electronic Interpore Coupling. To modify the transmission probability of the molecular barrier, first the properties of the unmodified barrier have to be understood. For this purpose, spatially resolved dI/dV measurements were performed across the network backbone ([Figure 2](#)). Specifically, the barrier regions of three different pore arrangements were investigated, that is, between two *small* pores, between two *big* pores, and between a *small* and a *big* pore. The barrier between two *small* pores is characterized by the presence of a QBS peak, which is shifted toward higher BE by either ~ 5 meV at the position of the porphyrin macrocycle or by ~ 15 meV at the position of the pentafluorophenyl substituents ([Figure 2a](#) and [Figure S5](#)). At the barrier between two *big* pores, the shift amounts to ~ 5 meV at the position of both the porphyrin macrocycle and the pentafluorophenyl substituents ([Figure 2b](#) and [Figure S5](#)).

It is worth mentioning that the QBS shifts in the barriers of electronically coupled quantum systems toward higher BE are in accordance with the observations reported by Seufert *et al.*¹¹ for two coupled quantum wells. The authors demonstrated that in such a system the bonding component Ψ_n of the quantum state dominates in the barrier region over the antibonding component Ψ_n^* . Therefore, the former mainly contributes to the dI/dV signal measured above the barrier, causing the overall shift of the quantum state toward higher BE.

Importantly, first-principle density functional theory (DFT) calculations of a Zn(II) porphyrin **1** molecule adsorbed on Ag(111) reveal that there is a HOMO–LUMO gap centered around the Fermi level and that the charge distribution of Ag(111), especially in the first atomic layer, is significantly affected by the adsorption of Zn(II) porphyrin **1** ([Figure S7](#)). Thus, the features close to the Fermi level detected in the dI/dV spectra taken at the barriers are QBSs related. The penetration into the barrier, and hence also the electronic interaction of the neighboring pores, is critically dependent on the interaction of the components of the barrier with the confined surface state. In our example, both the porphyrin macrocycle and the pentafluorophenyl substituents affect the confined surface state, and thus, both influence the lateral coupling between neighboring quantum states.

At the barrier connecting a *small* pore with a *big* pore, the quantum states of these pores are both detected with a very low intensity and without a measurable energy shift ([Figure 2c](#) and [Figure S5](#)). That means that they both penetrate the barrier. This demonstrates the lack of electronic coupling between these pores due to the energy level misalignment.

The partial confinement of the Shockley surface state in the pores of the Zn(II) porphyrin **1** network on the Ag(111) surface is also suggested in ARPES data. In [Figure 3a](#) ARPES data collected for a sample partially covered with the network domains is shown. The electronic structure of this system is characterized by two states: (1) the Ag(111) Shockley state ([Figure 3d](#)), originating from the bare surface, which crosses the Fermi level and reaches its maximum dispersion at BE ~ 65 meV, and (2) a state dispersing above the Fermi level, originating from the network, which we attribute to the partially confined state, resulting from the coupling between the electronic states of the QBs embedded in the array⁸ (for better visualization, the ARPES spectrum was integrated over a small k -range around the band center [Figure 3b](#), and the energy distribution curves (EDCs) have been extracted [Figure 3c](#)). Since the band maximum of the QBS is well above the Fermi level, it is only occupied by the small tail of the thermally broadened Fermi–Dirac distribution reaching above the Fermi level (note that the ARPES data have been collected at RT). This makes the photoemission intensity of the QBS in this system much weaker than that of the Ag(111) Shockley state. One would expect the $(14 \times 14)R \pm 10^\circ$ overlayer superstructure to give rise to a reduced Brillouin zone with boundaries at $k = \pm 0.08 \text{ \AA}^{-1}$, but since the QBS energy at that k value amounts to ~ 200 meV above the Fermi level, the thermal occupancy of the band results in such a low photoemission intensity that the presence or absence of this periodicity cannot be confirmed in the presented ARPES data.

Another feature of the network, which also has to be taken into account, is that the vast majority of the pores are *small*, as the *big* pores are observed only at the domain boundaries (*cf.* [Figure S2](#)), meaning that mainly the QBS of the former will contribute to the spatially averaged ARPES signal. The QBS, however, is detected slightly further away from the Fermi level as by STS (*cf.* [Figure 2a](#) and [Figure 3](#)). This difference

Figure 4. Modification of barrier regions between the quantum boxes by adsorbates – STM/STS studies. (a) A barrier with two Xe atoms; (b) a barrier with a single C_{60} molecule; and (c) a barrier with two C_{60} molecules. (First row) Molecular models. (Second row) Corresponding STM images (10 nm $\times$ 8 nm). (Third row) Spatially resolved dI/dV traces acquired along the yellow lines superimposed on the STM images. (Fourth row) Selected dI/dV spectra taken at the positions indicated by the colored dots in the STM images and in the dI/dV traces. The molecular models overlaid on the STM pictures are presented in Figures S9b and S11, whereas the simulated STM images for cases (a) and (b) in Figure S12.

presumably arises from the temperature dependence of the energy of the QBS: the higher the temperature, the more the confined state shifts toward lower BE,⁴⁶ and the Shockley surface state shifts likewise⁴⁷ (note that the STS data were acquired at 4.2 K, whereas the ARPES data at RT). Additionally an uncertainty in Fermi level determination of ± 10 meV needs to be taken into account.

In order to extract the effective mass (m^*) of the system, we have fitted the bottom of both ARPES spectra of Figure 3a with parabolas (for details see the Materials and Methods section) and extracted $m^* = 0.40 \pm 0.08 m_e$ for the Ag(111) Shockley surface state in agreement with literature,⁴⁵ and $m^* = 0.38 \pm 0.11 m_e$ for the QBS. Thus, we have no evidence for a significant change of the effective mass of the surface state upon the network formation. This is in agreement with ref 48 in which the effective mass of the surface state upon metal–organic network formation on Cu(111) changed from $m^* = 0.43 \pm 0.01 m_e$ to $m^* = 0.57 \pm 0.02 m_e$ (state below the Fermi

level). In our study, due to the intrinsically reduced intensity above the Fermi level, the uncertainty in determining m^* is significantly higher ($\pm 0.11 m_e$), therefore we cannot exclude a small change in m^* for our QBS, that is, comparable to the one reported in ref 48.

Modification of the Interpore Coupling by Adsorbates. Next we investigated the possibility of a modification of the barriers *via* their interaction with adsorbates. For that purpose we chose two adsorbates exhibiting characteristically different electronic properties: a closed-shell noble gas, Xe, and a strong electron acceptor, fullerene C_{60} .

STM images acquired after Xe exposure revealed that two Xe atoms can adsorb on top of one porphyrin macrocycle (Figure 4a). Besides, single Xe atoms adsorb: (i) on the porphyrin macrocycle, (ii) between three pentafluorophenyl substituents, and (iii) between methoxy, pentafluorophenyl, and phenyl groups (Figure S9). Significantly increased Xe exposure resulted in the decoration of the network backbone and

Figure 5. Modification of the electronic properties of the confining barrier by adsorbates – DFT calculations. (a) A barrier with two Xe atoms; and (b) a barrier with a single C₆₀. (First row) Optimized structures and (second row) and (third row) 2D charge difference cuts taken along planes 1 (red) and 2 (blue), respectively, as marked in the optimized structures. The values are given in [$e \text{ \AA}^{-3}$]. The charge difference was calculated in the following way: $\Delta\rho_q = \rho_q[\text{adsorbate} + \text{Zn(II) porphyrin 1} + \text{Ag(111)}] - \rho_q[\text{Zn(II) porphyrin 1} + \text{Ag(111)}] - \rho_q[\text{adsorbate}]$ (where adsorbate stands either for two Xe atoms or for one C₆₀). In this way, the charge redistribution induced by porphyrin adsorption on Ag(111) is included, and the visible changes are only representing the influence of adsorbates.

adsorption at the rim of the pores. No Xe was found to be adsorbed at the center of the pores (Figure S10) pointing at the significantly lower interaction between Xe and the QBS (having its maximum at the center of the pore), similar to the case of Xe adsorbed in the pores of the Cu-coordinated 3deh-DPDI network on Cu(111).⁴⁹ As revealed by dI/dV measurements (Figure 4a), the two Xe atoms adsorbed on the porphyrin macrocycle have almost no influence on the transmission probability of the barrier (red and green dI/dV spectra in Figure 4a vs red and green dI/dV spectra in Figure 2a).

In contrast, a single C₆₀ molecule adsorbed in the pore between two Zn(II) porphyrin molecules 1 (Figure 4b) reduces the barrier transmission probability (blue dI/dV spectrum in Figure 4b, spatially resolved dI/dV traces in Figure 4b vs in Figure 2a, second row). An even larger reduction of the

transmission probability is caused by two C₆₀ molecules adsorbed in the pore close to the phenyl groups of three Zn(II) porphyrin molecules 1 (orange dI/dV spectrum in Figure 4c vs blue dI/dV spectrum in Figure 4b).

The presence of C₆₀ molecule(s) in a pore additionally shifts the QBS to lower BE: to ~ -55 meV in case of a single C₆₀ and to ~ -65 meV in case of two C₆₀ molecules. Importantly, the reduction of the coupling between the pores is not caused by energy level misalignment, as there is still an overlap between the quantum states of an empty pore and a pore filled with one C₆₀ or two C₆₀ molecules. Furthermore, C₆₀ molecules do not locally destroy the QBS on the rim of the pore and thus the inter pore coupling, as evidenced by the presence of the modified QBS in the blue dI/dV spectrum in Figure 4b and the magenta dI/dV spectrum in Figure S13. Thus, our results

Figure 6. Electronic landscape modification upon deposition of C_{60} . (a) STM image of a pore with a single C_{60} molecule adsorbed and (b) the corresponding work function map (size: 6 nm $\times$ 6 nm). The pyrrole unit and the substituents closest to the adsorbed C_{60} are more electropositive (green arrow) than the corresponding groups of a Zn(II) porphyrin 1 surrounding an empty pore (yellow arrows). The reference work function map setting the $\Phi = 0$ on Ag(111) is presented in Figure S17. (c) Top view of 3D charge difference plot; the red isosurface denotes a positive charge density, whereas the blue isosurface denotes a negative charge density (isosurface value $\pm 1.0 \times 10^{-4} \text{ e } \text{\AA}^{-3}$).

demonstrate that the adsorption of C_{60} causes both the modification of the barrier transmission probability and changes in the quantum box state.

Interestingly, the QBS peak is detected at the same energy at the position of the Zn(II) porphyrin 1 macrocycle for all three adsorbate cases (cf. gray dashed line and green dI/dV spectra in Figure 4), as for the reference case (cf. green dI/dV spectra Figure 2a). This point will be discussed in the following section.

Modification of the Confining Barrier by Adsorbates – DFT Insights. In order to understand the effect of the adsorbates on the confining barriers, we have analyzed the interactions between the Zn(II) porphyrin 1 adsorbed on Ag(111) and Xe/ C_{60} using DFT. While the reproduction of the entire pore structure is computationally prohibitive, this approach captures the essence of physics governing the interactions between the confining barriers and the adsorbates.

Our calculations have shown that two Xe atoms can bind on top of the N atoms of the Zn(II) porphyrin 1 macrocycle, as observed experimentally (cf. Figure 4a). In this case, the calculated adsorption energy amounts to only -0.18 eV , and no chemical bond is formed (cf. Figure S14a,c), suggesting the presence of weak van der Waals interactions. Notably, the two Xe atoms induce an almost negligible and very localized charge redistribution in Zn(II) porphyrin 1 ($<0.01 \text{ e}$ per Xe atom), while the Ag(111) substrate stays unaffected (Figure 5a and Figure S15a). Thus, the confining barrier remains almost unchanged, which explains why its transmission probability is not detectably modified.

In agreement with the experiment (cf. Figure 4b), single C_{60} favors the adsorption on Ag(111) close to the Zn(II) porphyrin 1 substituents, while no chemical bond is directly formed between C_{60} and Zn(II) porphyrin 1 (Figure S14b,d). The presence of C_{60} induces a significant charge redistribution in the Zn(II) porphyrin 1 substituents and in the pyrrole unit closest to C_{60} , whereas the center of the molecule remains almost unaffected (Figure 5, Figure 6c, Figures S15b–16, and Movie S1). Reversely, the presence of the Zn(II) porphyrin 1 results in an energy gain of 0.65 eV for C_{60} , when compared to the case of isolated C_{60} on Ag(111). Furthermore, in this configuration the charge redistribution under the C_{60} and under the substituents and the pyrrole is distributed across a larger area of the Ag(111) substrate compared to the case of one isolated C_{60} adsorbed on Ag(111) and also compared to the case of one isolated Zn(II) porphyrin 1 on Ag(111) (cf. Figure S16 and Movie S1). Significant modifications of the

confining barrier, in contrast to the case of the Xe adsorption, are in line with the changes of transmission probability observed experimentally in the case of C_{60} adsorption.

Notably, the DFT results are in agreement with the experimentally obtained work function map displayed in Figure 6b. It shows that the adsorption of a single C_{60} near the Zn(II) porphyrin 1 results in the pyrrole unit and the substituents close to the adsorbed C_{60} being more electropositive (green arrow) than the corresponding groups of a Zn(II) porphyrin 1 surrounding an empty pore (yellow arrows). Furthermore, the fact that the macrocycle center of Zn(II) porphyrin 1, as well as the Ag(111) underneath it, is scarcely affected by the adsorption of either two Xe atoms or by the adsorption of a single C_{60} (Figure 5) agrees well with the observation of the QBS peak at the same energy (Figure 4a,b, green spectra) as in the reference case (Figure 2a, green spectra). On the basis of Figure S16c, which displays the charge difference plots for single C_{60} adsorbed near a phenyl of one Zn(II) porphyrin 1, we assume that this is also the case for the adsorption of two C_{60} near phenyl groups of three Zn(II) porphyrin 1 molecules (cf. Figure 4c).

CONCLUSION

In summary, we created an on-surface 2D array of coupled quantum boxes by careful design of the molecular building block. Upon adsorption of Zn(II) porphyrin 1 on Ag(111), an extended porous molecular network is formed. The pores confine the Ag(111) surface state, and, in particular, the surface state-derived quantum box state is shifted above the Fermi level. The quantum boxes are electronically coupled, and, importantly, adsorbates, that is, Xe and C_{60} , show a distinct influence on the transmission probability of the barrier; while Xe does not detectably affect it, C_{60} reduces it significantly. This is confirmed by state-of-the-art DFT calculations, which revealed that Xe has almost no influence on the electronic structure of the confining barrier, whereas C_{60} induces a strong charge redistribution within the barrier.

Our results suggest that a wide range of quantum arrays formed from functional molecular building blocks can be fabricated and, in combination with different adsorbates, provide a rich playground for the modification of the quantum box properties. Thus, the quantum states embedded in on-surface structures can be engineered for exploring physical phenomena, which could be implemented into future quantum devices.

MATERIALS AND METHODS

Synthesis of Zn(II) Porphyrin 1. The synthesis of Zn(II) porphyrin **1** is described in detail in the [Supporting Information](#) synthesis file.

Sample Preparation for STM/STS Measurements. The Ag(111) substrate was prepared by cycles of Ar⁺ sputtering at $E = 1000$ eV followed by annealing at 800 K. The Zn(II) porphyrin molecules **1** were deposited with the use of a 9-cell evaporator (Kentax GmbH, Germany) on the Ag(111) substrate held at RT. The glass crucible with the Zn(II) porphyrin **1** inside was heated up to the sublimation temperature (~ 320 °C). The rate was controlled prior to sublimation with a quartz crystal microbalance (QCM). In order to obtain a porous network, the molecular rate was lower than 0.4 Å/min. Otherwise, the formation of a close-packed assembly took place. The C₆₀ molecules (sublimation temperature ~ 350 °C) were deposited onto the sample with the porous network held at RT. Xe of purity 99.99% was dosed onto the sample placed in the STM operating at 4.2 K (Omicron Nanotechnology GmbH with Nanonis SPM control system) with the cryoshields open and the leak valve being in line-of-sight with the sample. The STM/STS measurements were performed after cooling the sample back to 4.2 K. In the main text and [Figures S1, S2, S4, S6, S9, S11, S13, and S17](#), the STM/STS data for a sample after 102 Langmuir (1.3×10^{-7} mbar for 100 s) of Xe exposure are shown. [Figure S10](#) presents the STM data taken after 100 Langmuir of Xe exposure, in which case the dosing time was increased 10 times by maintaining the same pressure as in the previous case. Both exposures resulted in an increase of the sample temperature to 8 K due to opening the cryoshield.

Note that all STM/STS data were acquired at 4.2 K, apart from [Figure S8](#) in which case the STM was operated at RT.

STM/STS Measurements and Their Analysis. For the STM measurements, the bias voltage is applied to the tip. The bias voltages in the manuscript and the [Supporting Information](#) data file refer to a grounded tip, such that the voltage axis in the dI/dV data can be related to the BE of the ARPES data.

STM measurements were performed in constant current mode with Pt–Ir tips (90% Pt, 10% Ir), prepared by mechanical cutting, followed by sputtering and controlled indentation in the bare Ag(111) substrate. The majority of STM images were acquired with a single Xe atom functionalized tip (*cf.* [Table S1](#)), which increases the spatial resolution. The exact tunneling parameters for the STM images presented in the main text and [Supporting Information](#) data file are displayed in [Table S1](#). The STM data were processed with the WSxM software.⁵⁰ For better comparability of the data, the color histograms of the STM images were adjusted. Low-pass filtering was used for noise reduction.

All dI/dV spectra were recorded with open-feedback loop and with Xe-functionalized tips. Control spectra were acquired with a metallic tip, and no difference was observed in accordance with *ref* [S1](#). The lock-in parameters were 513 Hz (frequency) and 8 mV (zero-to-peak amplitude).

The dI/dV data presented in [Figure 2](#), [Figure 4](#), [Figure S4](#), and [Figure S6](#) were acquired along the line indicated in the corresponding STM images and are displayed in form of spatially resolved dI/dV traces. The amount of measurement points for the traces was adjusted in dependence on the measured barrier (from 40 to 80 points per line). The initial tip conditions when taking dI/dV spectra amounted to 200 mV/150 pA, with the exception of the dI/dV data shown [Figure 4a](#), in which case 200 mV/50 pA was used. The reason for more delicate initial tip conditions when investigating Xe atoms adsorbed on a Zn(II) porphyrin **1** macrocycle is the relatively weak interaction strength, which led to desorption when harsher dI/dV parameters were applied. The dI/dV maps presented in [Figure S4](#) were extracted from a grid spectroscopy measurement, in which an area of $6 \text{ nm} \times 5 \text{ nm}$ was mapped with a resolution of 30 points $\times$ 25 points. At each point, a dI/dV spectrum was measured (initial tip conditions 200 mV/150 pA). As described in detail in *ref* [S2](#), the value of the initial voltage was chosen such that no quantum box state or network backbone-related contribution was present (*cf.* [Figure S7a](#)). Owing to this, a

normalization procedure could be performed by setting the same dI/dV value at the set point energy for all of the dI/dV spectra. In this way, artifacts originating from local work function variations are eliminated.

$I(z)$ Measurements and Their Analysis. The work function maps presented in [Figure 6](#) and [Figure S17](#) were obtained with the use of methods developed by Vitali *et al.*⁵³ The maps were extracted from a grid spectroscopy measurement, in which at each point $I(z)$ curves were measured. From an exponential fit of the average of three $I(z)$ curves, the work function was extracted for each point.

LEED Measurements and Their Analysis. The LEED measurements were performed with the use of a V. G. Electrovac LTD 474 unit. The LEED data were taken at energies between 5 and 60 eV. For simulating the experimentally obtained patterns, the software LEEDpat 2.1 (K. Hermann, M. A. van Hove, LEED pattern simulator LEEDpat version 2.1, 2006) was used (*cf.* [Figure 1c](#), [Figure S3](#)).

ARPES Measurements and Their Analysis. ARPES data were acquired at the beamline I3 of the synchrotron radiation source of MAX-III (Lund, Sweden). The Ag(111) crystal was prepared by consecutive cycles of Ar⁺ sputtering and annealing, similarly to the preparation used for the STM/STS measurements. The Zn(II) porphyrin molecules **1** were deposited with the use of a homemade evaporator. The rate prior to deposition was checked by QCM.

It is worth mentioning that collecting ARPES data from organic materials is a challenging task,⁸ as organic molecules can be destroyed by the incident UV light (beam damage). A way to overcome this problem is to use a defocused light source and low photon energies for the experiment. Therefore, beamline undulator was detuned in order to reduce the intensity of the photon beam, hence avoiding any radiation damage to the sample. The slits were set such that a light spot of 0.5 mm on the sample was obtained. Such a large light spot minimizes flux (and hence beam-damage), but causes a reduction in the angular resolution (and hence momentum resolution) of the ARPES measurement, estimated to be 0.04 1/Å for the measurements presented in [Figure 3](#) of the main text. A photon energy of 21 eV was sufficient to keep the molecules intact over the whole acquisition time amounting to ~ 1 h. Moreover, no signs of degradation in the ARPES data were observed, even after several hours of experimental time, demonstrating the full viability of this approach for studying the particular system presented here.

The ARPES measurements were carried out at normal emission and at RT. The choice of the temperature is extremely important, since it induces a broadening of the Fermi–Dirac distribution, resulting in a promotion of thermal electrons from states below to states above the Fermi level. This allows the detection of electronic states even at energies above the Fermi level. However, the spectral intensity of such states is so weak that it is barely detectable by eye. In order to enhance the intensity of these states with respect to the intensities below the Fermi level, we normalized the data by a Fermi function at RT. In addition, since the Fermi function goes exponentially to zero for low BE values, in order to avoid numerical issues in dividing the spectral intensity by ‘zero’, we added a small constant to the Fermi function (*i.e.*, 0.03). While the normalization allows an exceptionally good enhancement of the spectral features above the Fermi level, it artificially moves the center of mass of the spectral intensity toward the Fermi level, resulting in an apparent small energy shift of the band minimum. [Figure S18](#) displays the raw data, the raw data with amplified intensity, and the normalized data of a Ag(111) surface partially covered with the Zn(II) porphyrin **1** network. In [Figure S19](#) raw and normalized ARPES data of bare Ag(111) are shown. In the such treated data, there is no additional state, which demonstrates the validity of the used normalization procedure.

From the ARPES data presented in [Figure 3a](#), EDCs have been extracted at different values of momentum k , and each individual EDC has been fitted by a Lorentzian component convoluted with a Gaussian component, to account for the energy resolution of the instrument. From the fits, the peak positions are readily extracted, together with their corresponding uncertainties (red points and error bars in [Figure 3a](#)). Those peak positions have been fitted with parabolas ([Figure 3a](#)), from the curvature of which the effective masses were extracted.

DFT Calculations. First-principle DFT calculations were performed using the Vienna *ab initio* simulation code (VASP)^{54–57} with the generalized gradient approximation (GGA) and the projector augmented wave (PAW) method.^{58,59} The plane-wave cutoff energy was set to 400 eV. The adsorption of Zn(II) porphyrin 1, C₆₀, Xe, and their co-adsorption on the three layer FCC slabs of Ag (111) was modeled using 10 × 10 supercell. The vacuum layer thickness was about 17 Å. Atoms of the bottom layer of the Ag slab were kept fixed. All the other atoms were fully relaxed until the residual forces became <0.02 eV/Å. The structural optimization was performed using the Γ *k*-point. Gaussian smearing was applied to improve convergence. Additional calculations using a larger supercell (the systems containing up to 800 atoms) showed that the adsorption energies of Zn(II) porphyrin 1 and C₆₀, as well as the charge redistribution, are almost unaffected by the size of the simulation cell. Our preliminary calculations showed that the dispersion interactions play very important role when considering the adsorption of Zn(II) porphyrin 1 on Ag(111). For this reason we included dispersion interactions using the semiempirical model by Grimme (PBE+D2)^{60,61} for all the systems analyzed here. Compared to GGA-PBE, which gave Ag lattice constant of 4.145 Å, PBE+D2 approach gave 4.121 Å, which better agrees with the experimental value (4.079 Å). The charge analysis was carried out using the Bader algorithm⁶² on a charge density grid by Henkelman *et al.*⁶³

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b07989.

Detailed description of synthesis and characterization of Zn(II) porphyrin 1 (single crystal XRD (1), spectroscopic data (1) and synthetic intermediates)) (PDF) CCDC-1455039 (1) contain the supporting crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif (PDF, CIF)

All Supporting Figures referred to in the main text are assembled in this file (Figures S1–S19, Table S1) (PDF) Volume slice through the charge difference volumetric data of single C₆₀ adsorbed at Ag(111) and C₆₀ adsorbed close to Zn(II) porphyrin 1 on Ag(111) (MPG)

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Notes

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