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NANO LETTERS

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Vol. xx, No. x

Dichotomous Array of Chiral Quantum Corrals by a Self-Assembled Nanoporous Kagomé Network

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12 Received May 29, 2009

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ABSTRACT

The confinement of surface-state electrons by a complex supramolecular network is studied using low-temperature scanning tunneling microscopy and rationalized by electronic structure calculations using a boundary element method. We focus on the self-assembly of dicarbonitrile sexiphenyl molecules on Ag(111) creating an open kagomé topology tessellating the surface into pores with different size and symmetry. This superlattice imposes a distinct surface electronic structure modulation, as observed by tunneling spectroscopy and thus acts as a dichotomous array of quantum corrals. The inhomogenous lateral electronic density distribution in the chiral cavities is reproduced by an effective pseudopotential model. Our results demonstrate the engineering of ensembles of elaborate quantum resonance states by molecular selfassembly at surfaces.

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The manipulation of individual atoms by scanning tunneling 22microscopy (STM) made it possible to build nanoscale 2324 structures for electron confinement, the so-called quantum corrals.¹ The corresponding scanning tunneling spectroscopy 25(STS) measurements allowed visualizing the resulting reso-26nance states of the originally nearly free two-dimensional 27electron gas supplied by the surface-state electrons of the 2829 employed Cu(111) surface. This work inspired several impressive demonstrations of exquisite control over elec-30 tronic quantum states,^{2,3} including the quantum mirage effect 31 projecting the Kondo signature of a magnetic adatom to a 32 remote location.⁴ More recently, the coherent scattering 33 34 present in such structures was employed for quantum holographic encoding.⁵ Sophisticated theories for the inter-35 pretation of these experiments have been developed,⁶⁻⁸ and 36 based thereupon, systematic quantum corral wave function 37 engineering was proposed.9 38

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An alternate route to design architectures for the surface 39 state quantum laboratory is provided by self-assembly of 40 adsorbate superlattices.^{10–13} This approach provides inherent 41 advantages regarding ease of fabrication and parallel pro-42 cessing and could be furthermore expanded to steer the 43arrangement of individual atoms in quantum resonators.^{14,15} 44 However, to date mainly rather simple confinement geom-45 etries, such as one-dimensional trenches have been investi-46 gated. Here we explore the supramolecular engineering of 47 complex quantum corrals. We employ surface-confined 48 supramolecular self-assembly¹⁶ to achieve an intricate tes-49 sellation of the Ag(111) surface.¹⁷ Our STS observations 50 reveal how the presence of the deployed nanoporous chiral 51 kagomé network with regular cavities induces confinement 52 of the quasi-two-dimensional surface-state electron gas 53creating an ensemble of quantum corrals. We have repro-54 duced the characteristics of the pertaining spectral electron 55 eigenstate densities by electronic structure calculations using 56a boundary element method. 57

In our vacuum apparatus (base pressure $\sim 3 \times 10^{-11}$) a 58 clean Ag(111) surface was prepared by repeated cycles of 59 Ar⁺ sputtering and annealing to 470 °C. Dicarbonitrile-60 sexiphenyl (NC-Ph₆-CN) molecules were synthesized as 61 described in ref 18 and sublimated from a quartz glass 62

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Figure 1. (a) Topograph of large-area domains of a porous, chiral kagomé network self-assembled by evaporating ~ 0.4 ML of NC-Ph₆-CN onto the Ag(111) surface. (Tunneling current $I_T = 0.14$ nA, bias voltage $V_B = 1.25$ V.) (b) High-resolution image of the kagomé structure with superimposed ball-and-stick models of the molecules. ($I_T = 0.1$ nA, $V_B = -0.5$ V.) The network divides the surface into a regular arrangement of two different types of pores (hexagons and triangles). Chirality originates form the counterclockwise rotating nodes. (c) Constant-current dI/dV map (rainbow color coded) simultaneously taken while scanning the topography (displayed in black, $V_B = 320$ mV). The local density of states is periodically modulated by the presence of the organic network. The dichotomous confinement with quasi-hexagonal and triangular-terminated areas imposes a distinct electronic structure in each type of pore. The two white dotted hexagons highlight the rotation of the electronic mode inside the quasi-hexagon with respect to the kagomé lattice caused by the chirality of the network.

crucible inside a Knudsen cell held at 572 K onto the Ag 63 substrate at room temperature (RT). For the organic layers, 64 a deposition time of 10 min resulted in a molecular coverage 65 of approximately 0.4 monolayers (ML), with one monolayer 66 defined as a saturated layer of dense-packed molecules. The 67 samples were transferred into a homemade¹⁹ beetle-type low-68 temperature STM, in which data were recorded at 7 K. STS 69 was accomplished in an open-feedback loop operation mode 70 with set points as given in the corresponding figure captions 7172and modulation frequencies between 1600 and 1800 Hz with 73 an amplitude of 5 mV rms. The lock-in time constant was 100 ms. The dI/dV maps of Figure 4 were extracted from a 74 set (84×84) of such point spectra, with a reduced number 75of bias points that were equally distributed over the area of 76 77 the topographic image. All spectra were normalized so that 78 the differential conductance averaged over the energy range between -180 and -130 mV equals unity. The constant-79 current dI/dV map of Figure 1 was simultaneously measured 80 while recording the corresponding topograph with both the 81 feedback loop time constant and the scan time per pixel much 82 longer than the period of the bias modulation. 83

An earlier study¹⁷ on dicarbonitrile-polyphenyl molecules 84 $(NC-Ph_r-CN)$ demonstrated that this class of ditopic 85 organic molecules assemble in networks with different 86 87 symmetry and complexity depending on the length of the polyphenyl backbone. For the case of x = 5, a complex, 88 chiral kagomé network formed domains with lateral dimen-89 sions reaching the micrometer range. Here, we evaporated 90 approximately 0.4 ML of NC-Ph₆-CN onto the Ag(111) 91 92 surface and found a similar chiral kagomé topology (Figure 1a), presenting larger pores due to the increased number of 93 phenyl moieties. This supramolecular arrangement again 94 features a micrometer domain size with a low defect density. 95 Some of the pores contain additional molecules as guests. 96 97 A high-resolution image (Figure 1b) highlights that the kagomé structure divides the surface into two types of 98 nanopores. Six molecules (white protrusions) form a larger, 99 quasi-hexagonal-shaped pore, which is surrounded by six 100

triangular-shaped cavities, each of them formed by three 101 molecules. Chirality originates from the supramolecular 102 organization of the achiral molecules mediated by weak 103 lateral interaction. As can be seen from the superimposed 104 ball-and-stick models of the molecules, the end groups of 105 four molecules come together at each node. Hereby, they 106 are not pointing to the node center but are laterally offset, 107 forming a chiral rotor motif (red arrow) turning counter-108 clockwise. A constant-current dI/dV map (Figure 1c, rainbow 109 color coded, bias voltage $V_{\rm b} = 0.32$ V) demonstrates the 110 pertaining periodic pattern of the local differential conduc-111 tance which is, within the Tersoff-Harmann approxima-112tion,²⁰ directly proportional to the local density of states 113 (LDOS).²¹ Thus, the self-assembled organic network imposes 114 a novel, complex electronic structure to the underlying metal 115 substrate, not only locally but over macroscopic extent. The 116 superimposed, inverted topograph of the same measurement 117(molecules in black) highlights the different electronic 118 structure in the two different types of cavities, i.e., the 119 dichotomous confinement character. The chirality of the 120 network is reflected in the chirality of the imposed electronic 121 structure. The outline of the green area of the mode inside 122 the quasi-hexagonal-shaped pore (inner white dotted line in 123Figure 1c) defines a hexagon rotated clockwise against the 124hexagon made up by the centers of the surrounding nodes 125(outer white dotted line). 126

To quantify the novel electronic structure of the substrate, 127 we have performed spectroscopic measurements at the points 128 indicated in Figure 2a. The reference spectrum (Figure 2b, 129 F2 gray curve) taken on the clean substrate shows the steplike 130 onset and the nearly constant LDOS connected with the 131 surface band starting at an offset energy near to -65132 meV.^{22,23} The spectra acquired over the supramolecular 133 assembly exhibit prominent position-dependent modulations 134 of the differential conductance. At the center of the large 135 pore (black curve), two dominant peaks occur at bias voltages 136 $V_{\rm B} = -20$ mV and $V_{\rm B} = 280$ mV. Halfway between the 137 center and the border of the quasi-hexagon (red curve), a 138

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Figure 2. (a) Topograph of the purely organic kagomé network. The symbols depict the positions at which the dI/dV spectra of (b) were taken. (b) Experimental dI/dV spectra demonstrating a strong position-dependent modulation of the LDOS. The nearly constant LDOS of the pristine surface (gray dashed line) is shown for comparison. (c) Theoretical spectra simulated with the boundary element method at the same positions as in (b) (see symbols in (a)).

third resonance appears at $V_{\rm B} = 80$ mV in between the two 139 previous ones. The spectrum taken above the backbone of a 140 molecule (blue curve) exhibits the strongest reduction of the 141 surface state LDOS. In the center of the smaller, triangular 142 pore the lowest-lying peak appears at $V_{\rm B} = 60 \text{ mV}$ bias 143 voltage, thus at a remarkably higher energy than that of the 144 first resonance in the larger pore. We attribute the LDOS 145modulation to quantum mechanical confinement of the 146 surface-state band by the nanoporous network. This inter-147 pretation is strongly supported by the good agreement 148 between experimental (Figure 2b) and simulated spectra 149 (Figure 2c), which will be discussed in detail later on. 150

To better understand the spectral distribution of the 151 different resonant states, a series of dI/dV spectra (Figure 1523b) was taken along a line connecting two nodes of opposing 153triangles (Figure 3a). The measurement presented in Figure 1543 was conducted on a domain featuring the opposite chirality 155 (clockwise rotating nodes) than the one displayed in Figure 156 1b. Several of these line spectra have been obtained on both 157 enantiomers of the kagomé structure resulting in consistent 158 spectral distributions. In the central, quasi-hexagonal pore, 159 the first resonance displaying one maximum (no node) at 160 the center of the hexagon is visible around $V_{\rm B} = -10$ mV. 161 With increasing energy the resonance is displaced by a 162 distinct two-peak structure between $V_{\rm B} = 50 \text{ mV}$ and $V_{\rm B} =$ 163200 mV. For even higher energies a state with three antinodes 164

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Figure 3. (a) STM topograph showing the line along which the dI/dV spectra of (b) were taken. (b) Plot of the differential conductance in the -120 to 400 mV bias range. A linear grayscale is used for the spectral intensity.

appears ($V_{\rm B} \sim 250$ mV). In the triangular pores the first 165 resonance is centered around $V_{\rm B} = 75$ mV and extends over 166 an energy range ($-50 \text{ mV} < V_B < 200 \text{ mV}$) roughly 2.5 times 167 wider than the first resonance in the larger pore. The spectra 168 in the vicinity of points 1 and 2 reveal slightly different 169 behavior that reflects the asymmetry of the triangles with 170 respect to the scan-line center (end-triangles pointing up and 171 down). In pore 2, the single maximum resonance turns into 172two maxima at voltages exceeding 300 mV. In contrast, in 173 pore 1 no second maximum can be observed. The whole set 174 of spectra clearly indicates that the kagomé network divides 175 the surface into a regular array of two types of pores with 176 different electronic structure. The distinct resonances appear 177with a varying spatial distribution and energy width reflecting 178the effects of both elastic and inelastic scattering due to 179 coupling of surface-state electrons with projected bulk bands 180 and electron-electron interactions, respectively. 181

Next, to fully characterize the spatial extent of the different 182 resonances and the pertaining electron density distribution, 183we constructed differential conductance maps (Figure 4) at 184 **F**4 bias voltages corresponding to the different peaks in the point 185 spectra. At $V_{\rm B} = 0$ mV, a bright domelike structure dominates 186 in the center of the hexagonal pore, while underneath the 187 molecules the electronic density is strongly reduced (cf. parts 188 a and b of Figure 4). Upon increase of $V_{\rm B}$ to 125 mV, the 189 intensity distribution in the quasi-hexagon exhibits a mini-190 mum in the center, whereas the triangular pores exhibit even 191 brighter intensity than the large pores (Figure 4c). For both 192



Figure 4. The kagomé network (topograph in (a)) induces standing wave patterns (b–e) in the otherwise uniform measured LDOS. (f) The model structure used for the BEM calculations. Black and white areas correspond to V = 0 and V = 500 meV, respectively. At all bias voltages, there is excellent agreement between experimental maps (b–e), which were retrieved from open-feedback loop point spectra, and calculated LDOS distributions (g–j).

bias voltage (cf. parts b and c of Figure 4), the envelope of 193 the quasi-hexagon mode reflects the chirality of the network 194 195 by its ratched wheel border, i.e., nearly hexagonal, but with an asymmetric dent at each corner. At higher energies ($V_{\rm B}$ 196 = 300 mV, Figure 4d) a sombrero-shaped pattern is visible; 197 i.e., a central maximum is surrounded by a circular depres-198 sion, which is in turn surrounded by a ring of bright intensity 199 200 near the hexagon borders. The ring is modulated such that 201 the strongest intensity is near the asymmetric corners. Furthermore, a three-winged propeller-shape distribution of 202the LDOS is visible in the triangular pores. Each propeller 203evolves into a set of three bright lobes at the highest bias 204

values ($V_{\rm B} = 400$ mV, Figure 4e), whereby inside the 205 hexagonal pores the central maximum has almost disappeared 206 with the modulation of the outer ring persisting. The maps 207 taken at high bias values emphasize how the chiral arrangement of the molecules introduces chiral electronic properties 209 to the underlying Ag surface. 210

We have gained further insight into the electron confine-211 ment properties of the network through model simulations 212 using a scalar version of the electromagnetic boundary 213element method (BEM) described in ref 24. In our BEM, 214 the Schrödinger equation is solved for a planar patterned 215 surface, which is modeled through homogeneous regions of 216 constant potential describing the kagomé motif. The bound-217 aries between these regions are considered to be abrupt, and 218the solution for the wave function is expressed in terms of 219 auxiliary electron boundary sources, which are propagated 220 throughout each homogeneous region via the electron 221 Green's function of the corresponding infinite, homogeneous 222surface. This involves integration of the sources over the 223boundary contours. The auxiliary sources are then determined 224 from the continuity of both the wave function and its 225gradient, thus setting up a system of integral equations that 226 we solve upon discretization using standard numerical linear-227 algebra techniques. A total of 1296 boundary discretization 228points have been required to achieve convergence in our 229 model structure. Here, we obtain the LDOS at a given spatial 230location from the imaginary part of the reflected wave 231 function produced by an electron point source placed at that 232location. 233

We have defined the effective scattering potential land-234 scape as depicted in Figure 4f, in which the molecules are 235described by rectangles (white) with the length (2.9 nm) and 236 the width (0.25 nm, carbon-carbon distance perpendicular 237 to the long molecular axis) given by the molecules and with 238an effective scattering potential value of $V_{\rm mol} = 500 \text{ meV}$ 239 with respect to the remaining area (black). For the surface-240 state electron band, we have assumed an effective electron 241 mass $m^* = 0.42m_e$, where m_e is the free electron mass, 242 consistent with the measured band of the unpatterned 243Ag(111) surface, an onset energy of -65 meV,^{22,25} and an 244 energy-independent broadening (25 meV) of all electronic 245states. The latter represents a single phenomenological value 246 taking into account both of the two above-mentioned elastic 247 and inelastic contributions to the energy width of the surface-248state resonances. 249

Using the BEM, we have calculated the energy-dependent 250LDOS(E) at different positions and compared it to the 251measured dI/dV spectra. Despite the simplicity of the model 252and the fact that only one fitting parameter, namely, $V_{\rm mol}$, 253has been used, the simulated spectra (Figure 2c) agree very 254well with the measured point spectra (Figure 2b) regarding 255both peak positions and peak intensities. More precisely, two 256clear maxima (-5 and 293 meV) are present in the center 257of the quasi-hexagon (black, plus symbols) and an intermedi-258ate peak shows up at 81 meV at a halfway position (red, 259crosses). In the smaller triangular pore (green, triangles), the 260lowest-lying resonance is upshifted to 127 meV. Right on 261 top of a molecule (blue, squares), the first maximum appears 262 263 at a similar energy as in the triangular pore, but with a 264 reduced height.

In general, the measured spectroscopic features have 265similar broadening as the simulated ones. We attribute the 266 sources of lifetime broadening to both inelastic (electron-267electron, electron-phonon) and elastic (coupling to projected 268 bulk bands at the same energy) scattering, as well as to the 269 finite transmission through the potential barriers. The two 270 peaks of the experimental spectrum taken in the center of 271the quasi-hexagon have widths of 56 and 153 mV at the 272 273differential conductance value of the reference curve. The time taken by surface-state electrons of the corresponding 274 k-vectors to travel the distance between two parallel mol-275 ecules of a hexagon boundary is ~ 15 and ~ 6 fs. The 276 broadening connected with such times amounts to 45 and 277 105 meV, respectively, indicating that interaction takes place 278mainly at the boundaries. We suggest, that inelastic and 279 elastic broadening dominate for the electron energy $E \ll V_{\rm mol}$, 280 while finite transmission constitutes the more the nearer E281 gets to $V_{\rm mol}$. In the theoretical curves, inelastic scattering 282 processes are included only phenomenologically via a 283 Lorentzian width (25 meV) of the electron states in the BEM 284 simulation. The widths of the peaks in the calculated spectra 285of the center of the quasi-hexagon pore (55 and 160 meV, 286 287 taken at the state density of the reference curve, cf. Figure 2c) outrange the Lorentzian width by far and are in good 288 agreement with the experimental values. This demonstrates 289 that the sole effect of the scattering barriers already leads to 290 spectral features of finite width and supports our description 291 of the barrier potential. 292

Conductance maps (LDOS(x,y)) were calculated at the 293 relevant energies where the maxima in the point spectra 294 indicate the existence of a resonance. To facilitate quantita-295 tive comparison between different maps, all simulations are 296 297 displayed using an identical color scale in Figure 4. The same is true for the experimental maps. An inspection of the 298measured maps demonstrates that the simulated standing-299 wave patterns reproduce the experimental data in great detail. 300 A central bright dome-shaped resonance, surrounded by 301 triangles of much weaker intensity for the lowest energy map 302 (Figure 4g), is clearly discernible against the bright intensity 303 in the triangles, combined with a ratchet-wheel wave pattern 304of weaker intensity for the second map (Figure 4h). For the 305 next higher energy (293 meV, Figure 4i), the sombrero 306 pattern with the modulated outer rim in the quasi-hexagon 307 and the propeller pattern inside the triangles resemble closely 308 the experiment. With an increase in the wave vector of the 309 310 surface-state electrons, their de Broglie wavelength becomes shorter. Accordingly, in the 415 meV map (Figure 4j) the 311 features exhibit the shortest lateral dimensions of the whole 312 series, namely, three small protrusions in each triangle 313 surrounding a central depression. In the larger pore the central 314315 protrusion appears with reduced brightness compared to Figure 4i. Both of these features are similarly reflected in 316 the measured data. 317

The remarkable agreement between theory and experiment is clear indication that the physically relevant properties regarding confinement and scattering are well described by our simple model of rectangular areas featuring a constant 321 effective potential. In additional calculated maps, we tested 322 the influence on the LDOS due to interaction between 323neighboring pores by defining triangles having one, two, or 324 three neighboring triangles. We found that only minor 325 differences are visible in the conduction maps. We conclude, 326 that transmission through the cavity boundaries is weak and 327 interaction between cavities is therefore small and does not 328 play a major role in the formation of the standing wave 329 patterns. Accordingly, in a simple one-dimensional quantum 330 mechanical calculation of the reflection of an electron wave 331 under perpendicular incidence scattered by a barrier with the 332 thickness and potential height as used in the BEM simulation, 333 we obtained a reflectivity $\rho_{\text{Kag}} = 0.7$ at E_{F} . This compares 334 to reflectivity values of $\rho_{desc} = 0.85$ and $\rho_{asc} = 0.5$ for a 335 descending and an ascending step on the pristine Ag(111) 336 surface, respectively.²⁵ It has already been shown¹² that rows 337 of organic methionine molecules on Ag(111) can lead to 338 reflection ($\rho_{\text{meth}} = 0.85$) of similar strength as in the 339 descending step case. Gross et al. have studied the scattering 340 of Cu(111) surface-state electrons by so-called Lander 341 molecules, which contain an extended aromatic backbone 342 and di-tert-butylphenyl spacers.²⁶ They demonstrated that the 343 aromatic backbone dominates the scattering properties of the 344 molecules, although only the butyl spacers were in direct 345 contact with the substrate. Their assumption that the π system 346 is responsible for the interaction with the surface-state 347 electrons is confirmed by our study. In a semiempirical 348 calculation within the PM1 framework²⁷ of NC-Ph₆-CN 349 in the gas phase, the frontier orbitals HOMO-2 to LUMO+2 350 feature π -orbitals conjugated over the entire molecule, 351 including sexiphenyl backbone and carbonitrile groups. The 352geometry of these orbitals tentatively explains why our 353 simple rectangular model for the scattering properties of the 354 molecules works so well. A monolayer of sexiphenyl on 355 Au(111) has been reported²⁸ to produce a substantial shift 356 of the work function (0.73 eV) that was attributed to a surface 357 dipole. The corresponding surface potential variation pro-358 duces electron scattering, and therefore, we attribute the 359 origin of the surface-state confinement to such a dipolar 360 interaction. 361

In conclusion, we have demonstrated that molecular self-362 assembly provides an intrinsically parallel method to impose 363 novel electronic properties on entire surfaces. In our study, 364 the simple Ag(111) surface is tessellated with a chiral 365 kagomé topology of NC-Ph₆-CN molecules representing 366 a dichotomous network with two symmetrically different 367 types of chiral pores. The purely organic adlayer confines 368 the surface-state electrons and thus represents a supramo-369 lecularly engineered nanoarchitecture of complex quantum 370 corrals creating a rich electronic structure in the cavities. 371The nontrivial geometry of the system prevents from an 372analytic theoretical description and rather calls for a numeric 373 approach. The presented BEM simulations allow a thorough 374analysis of the electron scattering properties evidenced by 375the detailed reproduction of the experimental findings. We 376 expect our work to open new avenues toward large-scale 377

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nanopatterning of complex electronic states and their un-378 derstanding through reliable model calculations. 379

Acknowledgment. This work has been supported by the 380 European Science Foundation Collaborative Research Pro-381 382 gramme FunSMARTs, the TUM Institute of Advanced Studies, the DFG Cluster of Excellence Munich Center for 383 Advanced Photonics, the Spanish MICINN (MAT2007-384 66050), the EU (NMP4-SL-2008-213660-ENSEMBLE), the 385 Basque Departamento de Educación, UPV/EHU (Grant No. 386 387 IT-366-07), and the Spanish Ministerio de Ciencia e Inno-

vación (Grant No. FIS2007-6671-C02-01). 388

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