

Tunable Quantum Dots Arrays by Self-Assembled Metal-Organic Networks: Supporting Information

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EXPERIMENTAL DETAILS

The experiments were carried out in a vacuum apparatus with a base pressure of $\sim 3 \times 10^{-11}$ mbar, where a clean Ag(111) surface was prepared by repeated cycles of Ar⁺ sputtering and annealing to 740 K. Dicarbonitrile-quaterphenyl (NC-Ph₄-CN) and dicarbonitrile-sexiphenyl (NC-Ph₆-CN) molecules [1, 2] were sublimated from a quartz glass crucible inside a Knudsen cell, held at 483 K for NC-Ph₄-CN and at 572 K for NC-Ph₆-CN, onto the Ag substrate stabilized at room temperature (RT). The deposition time for a dense-packed monolayer [3] is approximately 10 mins. After the sublimation of the organic molecules, Co adatoms were dosed by e-beam evaporation while keeping the substrate at RT. Posteriorly, the sample was transferred into our home-made [4] beetle-type low-temperature STM where data were recorded at ≈ 8 K. The indicated bias values V_B refer to the sample voltage. Scanning tunneling spectroscopy (STS) was carried out by open-feedback loop dI/dV point spectra with set points as indicated, bias modulation with frequencies ~ 1400 Hz, an am-

plitude of 5 mV rms, and a lock-in time constant of 20 to 50 ms. The dI/dV maps were extracted from a set of 84 x 84 point spectra equally distributed over the area of interest. All spectra were normalized such that the average value of the intensity between -250 mV and -150 mV was 1. The spectroscopic maps are displayed as measured *without* convolution or high pass filtering. The automated procedure for taking a set of spectra takes 10 to 20 h, therefore maps are slightly distorted due to drift.

DESCRIPTION OF THE BOUNDARY ELEMENT METHOD

In the boundary element method (BEM), surface electrons are considered to evolve in a 2D potential that represents the effect of corrugations such as surface steps or adsorbed atoms and molecules. The surface state wavelength is generally large compared to the atomic spacing, so we can consider planar surfaces supporting surface states, and in particular Ag(111), as described by flat effective potentials. Setting the zero of energy at the bottom of the surface-state band, the evolution of the electron wave function $\phi(x, y)$ along the surface is governed by Schrödinger equation,

$$(\nabla^2 + k^2)\phi = 0, \quad (1)$$

where $k = \sqrt{2m_{\text{eff}}E}/\hbar$ is the electron wave vector, E is the energy, and m_{eff} is the effective mass [$0.42 m_e$] of electrons in the Ag(111) surface state. In the presence of a metal organic network, the electrons are subject to an effective potential V as described in Fig. 2 of the main paper, so that Eq. (1) has to be changed to

$$(\nabla^2 + k^2 - 2m_{\text{eff}}V/\hbar^2)\phi = 0. \quad (2)$$

We solve Eq. (2) by placing electron sources at the boundaries between different potential regions. These sources are propagated through each region j of potential V_j by means of the 2D Green function of Helmholtz equation

$$G_j(R) = (-im_{\text{eff}}/2\hbar^2)H_0^{(1)}(k_j R),$$

implicitly defined by the relation

$$(\nabla^2 + k_j^2)G_j(R) = (2m_{\text{eff}}/\hbar^2)\delta(\mathbf{R}),$$

where $\mathbf{R} = (x, y)$ and $k_j = \sqrt{2m_{\text{eff}}(E - V_j)}/\hbar$ is the wave vector inside region j . The sources σ_j defined on the boundary of region j contribute to the scattered wave function inside it as

$$\phi^{\text{scat}}(\mathbf{R}) = \int_{S_j} ds G_j(|\mathbf{R} - \mathbf{R}_s|) \sigma_j(s), \quad (3)$$

where the integral extends over points \mathbf{R}_s along the contour S_j defining region j . The total wave function is then imposed to be $\phi^{\text{source}} + \phi^{\text{scat}}$, where ϕ^{source} describes an external source (e.g., a point source, as considered below). The boundary sources are determined from the condition that both the total wave function and its derivatives are continuous across the boundaries, following similar procedures to those employed in the application of this method to the solution of Maxwell's equations for the electromagnetic problem [5].

We are in particular interested in calculating the local density of states (LDOS). The LDOS at a position \mathbf{R}_0 within a given region j can be derived by considering a point source at that position defined by $\phi^{\text{source}}(\mathbf{R}) = G_j(|\mathbf{R} - \mathbf{R}_0|)$. The LDOS is simply given by $m_{\text{eff}}/\pi\hbar^2 - (2/\pi)\text{Im}\{\phi^{\text{scat}}(\mathbf{R}_0)\}$, where the first term is the background LDOS of the unpatterned surface, the second term is computed using Eq. (3), and a factor of 2 accounting for electron spin has been included.

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EIGENSTATES OF CONFINED ELECTRONS

Table 1 shows the energies of the five lowest-lying eigenstates of a hexagonal box, i.e., a two-dimensional, infinitely strong confining potential surrounding a hexagonal area of zero potential. In the metal-organic network employing NC-Ph₆-CN linkers the distance D between parallel sides of the hexagons amounts to $D = 57.78 \text{ \AA}$. The assumed effective distance $D_{eff} = 60.75 \text{ \AA}$ results from fitting the theoretical values of the eigenstates $E_n(D_{eff})$ for $n = 1$ to 4 to the experimental energies $E_n(\text{Exp})$. The energy separation $E_{sep,n} = E_{n+1}(D_{eff}) - E_n(D_{eff})$ between the energies of Ψ_n and Ψ_{n+1} is smallest for $n = 3$.

TABLE I: For the five lowest-lying eigenstates of a hexagonal box the columns denote the number, the energy assuming a distance D , the energy assuming distance D_{eff} , the energy separation $E_{sep,n}$ and the experimental energy $E_n(\text{Exp})$.

Ψ_n	$E_n(D_{real})$	$E_n(D_{eff})$	$E_{sep,n}$	$E_n(\text{Exp})$
1	-6.7 meV	-12.2 meV	80.8 meV	-11 meV
2	82.7 meV	68.6 meV	105.6 meV	69 meV
3	199.5 meV	174.2 meV	37.2 meV	167 meV
4	240.5 meV	211.4 meV	74.7 meV	209 meV
5	323.1 meV	286.1 meV	36.9 meV	≈ 280 meV

TUNING OF EIGENSTATES

The eigenstate energies can be tuned by choosing the appropriate length of the linking molecule. The bias voltage $V_{Ph6,Exp}$ of the characteristic features ($n = 1$ to 4) of the c -spectrum in the network constructed with NC-Ph₆-CN is converted into energy and shifted by the surface state offset $E_0 = -65$ mV to give the energetic separation $E_{Ph6,Sep}$ from the surface state band minimum. The same conversion was used for the bias voltages $V_{Ph4,Exp}$ of the corresponding spectrum of the network employing NC-Ph₄-CN. The shorter linkers result in higher-lying resonance energies, $E_{Ph4,Sep}$, as expected for smaller confinement dimensions. Scaling $E_{Ph6,Sep}$ with the ratio of the unit cell areas of the two networks, $R = 1.83$, results in energies, $E_{Ph4,Scaled}$ slightly higher than observed in the experiment. The fact that the constant experimental ratio $R_{exp} = 1.75$, obtained by dividing $E_{Ph4,Sep}$ by $E_{Ph6,Sep}$, is slightly smaller than R is consistent with the attractive potential of the Co atoms, which enlarges the confining volume. The bias values of the scaled version of the c -spectrum in the NC-Ph₄-CN case (Fig. 4, red dashed line) were calculated using the formula:

$$E_{B,scaled} = ((E_B - E_0)/R_{exp}) + E_0.$$

TABLE II: For the four lowest-lying characteristic features, $n = 1$ to 4 , the columns denote the bias voltage $V_{Ph6,Exp}$, the energetic separation $E_{Ph6,Sep}$, the bias voltages $V_{Ph4,Exp}$, the energetic separation $E_{Ph4,Sep}$, the scaled energies $E_{Ph4,Scaled}$, and the experimental ratio R_{exp} .

n	$V_{Ph6,Exp}$	$E_{Ph6,Sep}$	$V_{Ph4,Exp}$	$E_{Ph4,Sep}$	$E_{Ph4,Scaled}$	R_{exp}
1	-13.7 mV	51.3 meV	23.5 mV	88.5 meV	93.9 meV	1.73
2	125.5 mV	190.5 meV	268.2 mV	333.2 meV	348.6 meV	1.75
3	210.9 mV	275.9 meV	414.6 mV	479.6 meV	504.9 meV	1.74
4	293.2 mV	358.2 meV	564.8 mV	629.8 meV	655.4 meV	1.76