

Tunable energy and mass renormalization from homothetic Quantum dot arrays

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Over the last decades, the concepts of supramolecular chemistry [1] have been successfully transferred to construct long-range ordered, regular and robust two-dimensional self-assembled nanoporous networks [2-5]. Such regular structures stand out as excellent playgrounds to investigate scattering properties of surface electrons, and hence potential testing platforms of quantum device concepts. Indeed, organic nanoporous networks are also referred to as quantum dot arrays since they can confine surface state electrons [5-8], providing a vast playground for studying and engineering the electronic properties of new and exotic 2D materials [6-8].

Organic nanoporous networks grown on (111) noble metal surfaces are highly successful model systems to study the modulation of the simple free-electron like Shockley states. On such surfaces, robust 2D molecular scaffolds have been achieved, commonly exhibiting weak perturbations in the form of an upward energy shift of the Shockley state and the formation of shallow bands, which results from the repulsive scattering at the molecular walls and partial quantum confinement within each nanodot [5-8].

In this work, we present experimental evidence of a tunable downward energy shift (away from the Fermi energy) through scalable metal-organic nanoporous networks [5,9] grown on Au(111) (see Figure 1). The electronic structure is determined by two state-of-the-art, highly complementary techniques (STM and ARPES), and supported by first principles and model calculation. Notably, the *counterintuitive* downshift is gradual with decreasing pore size and increasing adatom density, something that cannot be explained through standard quantum confinement in the molecular cavity. Therefore we assign the origin of this effect to metal-

organic overlayer-substrate interactions in the form of adatom-surface state hybridizations. This local coupling keeps the Shockley state nature, but renormalizes it, thereby changing its fundamental energy and effective mass. The absence to date of the experimental band structure resulting from single adatom metal-coordinated nanoporous networks has precluded the observation of the significant surface state renormalization we have observed.

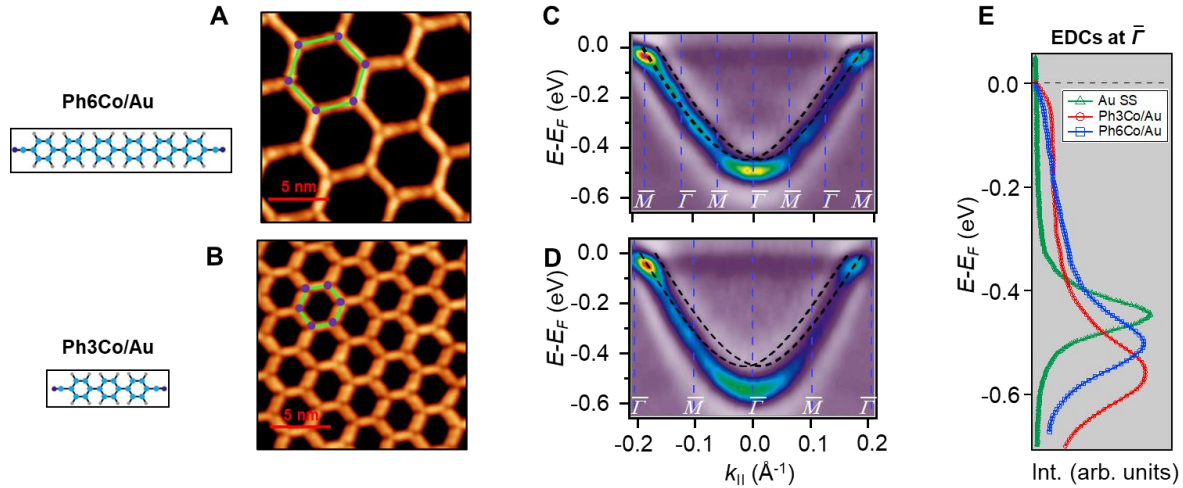


Figure 1: STM topographies of the single domain Co-coordinated hexagonal QD arrays using (A, C) dicyanitrile-sexypheny (Ph6) and (B, D) dicyanitrile-terphenyl (Ph3). (C, D) Second derivative of the spectral density obtained by ARPES at 150 K for the two nanoporous networks compared to the pristine Au(111) Shockley state (black dotted lines). (E) Energy distribution curves at normal emission for pristine Au(111) (green), Ph6Co (blue) and Ph3Co (red). A gradual downshift of the fundamental energy as the pore size is reduced is found concomitant with gap openings at the superstructure symmetry points.

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