Supporting Information

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SI Materials and Methods

The supramolecular networks based on Ce–ligand coordination motifs described in the manuscript were fabricated in a two-step process, in which care was taken to calibrate properly both the molecule and the cerium evaporators:

(*i*) In a first step, the molecular linkers NC–Ph_3–CN (NC–Ph_4–CN) were deposited by organic molecular beam epitaxy from a quartz crucible held at T = 478 K (503 K) onto a clean Ag (111) crystal held at ∼300 K. The molecular coverage was estimated by inspecting the sample with scanning tunneling microscopes. The coverage was kept always below the monolayer. We use the term monolayer for the maximum coverage of molecules directly adsorbed on the metal surface.

(*ii*) Taking into account the molecular coverage and looking forward to the desired stoichiometry (linker/Ce), in a second step Ce atoms were evaporated from a home-made water-cooled cell by resistively heating a W filament enclosing a Ce ball of high purity (99.9999%; MaTecK) onto the sample held at ∼300 K. The scanning tunneling microscopy (STM) inspection reveals whether the deposition of Ce on the surface was adequate or, on the contrary, lower or higher than expected.

As a result of the protocol of growth, it is possible to locally achieve ratios of linker-to-cerium stoichiometry ranging from 4:1 (dodecameric phase) to 5:2 (Archimedean snub square tiling). Fig. S1 shows a region with such an intermediate stoichiometric ratio, in which a transition of phase from the dodecameric phase to the Archimedean snub square tiling is observed, resulting in the formation of supramolecules involving more than three Ce centers.

Details of the Density Functional Theory Calculations

We used the QuickStep module (1) of the CP2K program package (2), using a Gaussian basis set for the Kohn–Sham orbitals, a plane wave basis for the density, and the revised Perdew–Burke–Ernzerhof exchange-correlation functional (3) together with the empirical correction for the van der Waals forces (4). Goedecker–Teter–Hutter-type pseudopotentials (5) replaced the action of the core electrons on the (pseudo) valence states. The basis sets of double-zeta valence polarised (DZVP) level generated with the molecular-optimised (MOLOPT) type (6) were used for hydrogen, carbon, nitrogen, and silver, and a specific 5433-basis set for cerium (7). The slab consisted laterally of 217 metal atoms per layer and four layers of which two of the topmost ones were allowed to relax. A distance of 12.7 Å of vacuum separated the highest atoms from the periodic replicas of the lowest atoms in the substrate. The width of the Fermi–Dirac broadening of the occupation number of the Kohn–Sham orbitals corresponded to 300 K. Only the Γ point was used to sample the first surface Brillouin zone.

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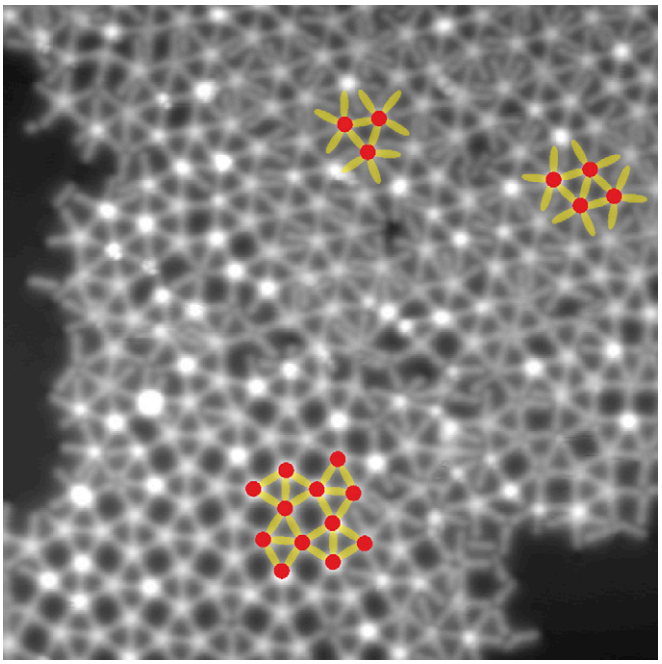

Fig. S1. STM image of the phase transition from a dodecameric phase to an Archimedean snub square tiling obtained by depositing NC–Ph4–CN and cerium on Ag(111) with an stoichiometric ratio (linker/Ce) close to 5:2, which is not enough to produce a regular Archimedean snub square tiling. The red dots represent the cerium centers, whereas the yellow lines depict the linear molecules underneath. Image size: 465 Å × 465 Å. Tunneling parameters: $I = 0.06$ nA, $V_{bias} = 0.2$ V.

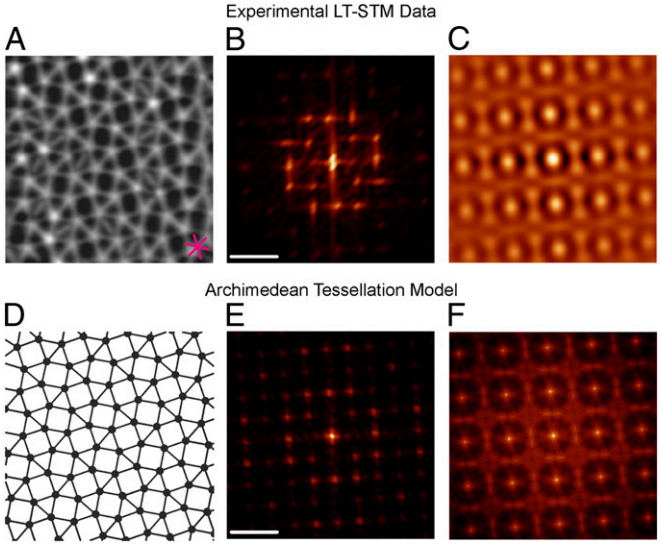

Fig. S2. Spatial periodicity of the molecular Archimedean snub square tessellation of Ag(111) reported in the manuscript. (*A*) High-resolution STM image of a snub square tiling domain, achieved by depositing NC–Ph_4–CN and cerium on Ag(111) under a stoichiometry (linker/Ce) of 5:2. Violet star marks high-symmetry substrate directions; (*B*) fast Fourier transform of *A*; (*C*) autocorrelation plot of *A*; (*D*) model network of *A*, representing a perfectly periodic snub square tiling of the plane; (*E*) fast Fourier transform of *D*; (*F*) autocorrelation plot of *D*. The agreement between the real image and the model is excellent, which reflects the high degree of spatial periodicity of the snub square tessellation domains presented in the manuscript. (The white scale bar represents 0.04 $Å^{-1}$.) Image size = 231 Å × 231 Å for *A*, *C*, *D*, and *F*. Tunneling parameters of *A*: $I = 0.08$ nA, $V_{bias} = 0.2$ V.