# Pathways to complex interfacial networks and 2D tesselations

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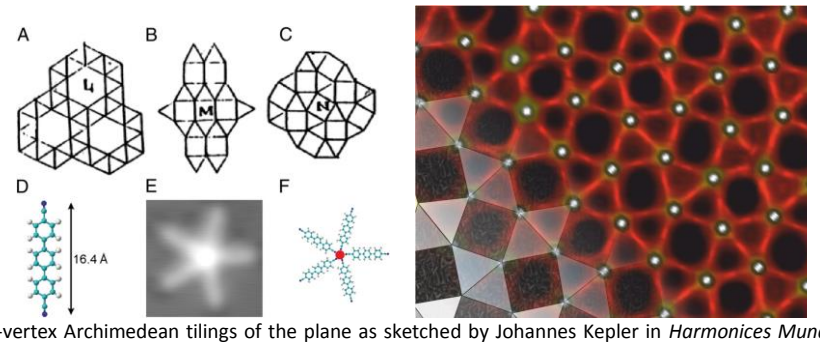
A major objective in modern surface and nanoscale science is the study of complex interfaces and the development of protocols for their control, both in the static and dynamic regime. Fascinating examples regarding self-assembled networks on solid surfaces include hierarchical assemblies, pentagon tilings, or glassy 2D architectures. Moreover, intricate chirality phenomena and glassy networks were recognized, and quasicrystalline order was observed in epitaxial and soft-matter self-assembled systems or polymers. Herein we report advances towards surface-confined complex networks using metal-directed assembly on surfaces. This approach constitutes a versatile route to design low-dimensional nanoarchitectures, frequently affording a favorable balance between robustness and spatial regularity. We convey the general strategy, give various examples and highlight networks and tesselations comprising (i) rare-earth metal centers and (ii) flexible molecular units, where intriguing ordering phenomena unfold.

Following the first approach, by taking advantage of lanthanide centers for the engineering of surface coordination nanostructures and layers, we achieved a 2-D pattern known as the "semiregular snub square tiling", representing a molecular-level demonstration of one of the canonical tessellation patterns Johannes Kepler described more than 400 years ago (cf. Fig. below). This becomes possible by fivefold Ce- (or Gd)-ligand CN-coordination motifs, which are planar and flexible, such that vertices connecting simultaneously trigonal and square polygons can be expressed. With the right concentration and stoichiometric ratio of rare-earth metal centers to ligands fully reticulated layers are expressed providing large domains of the prevailing snub square tiling. In addition, using Eu centers on Au(111), a random square-triangle tessellation with dodecagonal rotational symmetry evolves, associated with 2D random tiling quasicrystallinity. [1]




Left panel: (A–C) Five-vertex Archimedean tilings of the plane as sketched by Johannes Kepler in *Harmonices Mundi*. (A) Snub hexagonal tiling, (B) elongated triangular tiling, and (C) snub square tiling. (D–F) Fivefold coordination node of cerium and carbonitrile linkers on Ag(111). (D) Para-terphenyl-dicarbonitrile; C (H, N) atoms in green (white, blue). (E and F) STM image and model of isolated pentameric Ce–carbonitrile coordination unit. Central panel: Five-vertex Archimedean surface tessellation by fully reticulated rare-earth-organic networks. Right panel: STM overview data of quasicrystalline network following Eu-directed assembly of para-quaterphenyl-dicarbonitrile on Au(111) at a ~ 5:1 stoichiometric ratio.

Regarding (ii) we notably investigated a 1,3,5-tris(pyridin-4-ylethynyl)benzene linker with three pyridyl groups connected to a central aryl ring through ethynyl moieties. The molecule is specifically equipped with pyridyl functional groups to steer a simultaneous expression of lateral pyri-dyl–pyridyl interactions and Cu–pyridyl coordination bonds. Carefully developed assembly protocols yield a new class of porous open assemblies, the formation of which is driven by multiple interactions. We notably identified superlattice fromations interpreted in terms of 2D short-range disordered crystalline networks, i.e., sheet materials that displays a discrete diffraction diagram and present any of the following ordering characteristics: (1) the constituents are positioned following a crystalline lattice, but at the same time disordered with respect to their orientational or distortional degrees of freedom, or (2) the intermolecular links span a crystalline lattice, but the molecular building blocks present distortional or orientational short-range disorder. [2]

[1] D. Ecija et al., Proc. Nat. Acad. Sci. 110,6678 (2013); Urgel et al., subm..
[2] D. Ecija et al., ACS Nano. 6 (2012) 4258; Chem. Eur. J. 19 (2013) 14143.