Molecule-by-molecule positioning using template-guided self-assembly

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Achieving precise control of molecular self-assembly to form designed three-dimensional (3D) structures is a major goal in nanoscale science and technology. Using scanning tunnelling microscopy and density functional theory calculations, we have investigated the use of a single-atom-thick 2D covalent organic framework (COF-1) to template solution processed guest molecules.[1] This versatile approach can be used to trap and organize molecules at the solution/solid interface and in the subsequently obtained dried films. The molecular adsorption geometries depend on the solvent used for processing, and through the use of different solvents different (pseudo)polymorphs can be obtained. These template films can grow vertically, transition from two-dimensional to three-dimensional, which indicates that these nanoscale COF-1 templates may enable novel packing geometries suitable for device applications.[2] Furthermore, the relatively weak guidance provided by the templates allows flexibility in packing geometries, which can foster the formation of mesophases.[3] The approach can also be used to pattern molecules that have intrinsic barriers to forming periodic lattices, such as molecules with five-fold symmetry.[4] This suggests that monolayer templates may allow molecules designed specifically for function, rather than for crystallization into regular lattices, to be used in applications where crystallinity is desirable.

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[2] Cui, D., Ebrahimi, M., Rosei, F., & Macleod, J. M. (2017). Control of fullerene crystallization from 2D to 3D through combined solvent and template effects. *Journal of the American Chemical Society*, 139(46), 16732-16740.

[3] Cui, D., MacLeod, J.M. & Rosei, F. (2019) Planar Anchoring of C70 Liquid Crystals Using a Covalent Organic Framework Template. *Small*. https://doi.org/10.1002/smll.201903294

[4] Cui, D., Ebrahimi, M., Macleod, J. M., & Rosei, F. (2018). Template-driven dense packing of pentagonal molecules in monolayer films. *Nano Letters*, 18, 7570-7575.