## Title:

## Hydrogen-bonding in bi-component supramolecular nanoporous networks

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## Abstract:

We study the formation of four supramolecular bi-component networks based on four linear modules (linkers) bridging melamine via triple hydrogen-bonds. Scanning tunnelling microscopy (STM) experiments together with densityfunctional theory (DFT) calculations were used to explore the polymorphism and phase segregation, which rule the generation of highly crystalline nanoporous networks at the solid-liquid interface. The investigated linkers include two systems exposing diuracil groups in the α and œâ position, naphtalene tetracarboxylic diimide and pyromellitic diimide. In situ STM investigations revealed that, when blended with melamine, the first three systems are able to form two-dimensional porous architectures. Two of the linkers, exhibit highly ordered hexagonal structures while the third one gives a polymorph structure consisting of a variety of polygons. However, the fourth pyromellitic linker, diimide, assembles only into one-dimensional supramolecular arrays. DFT calculations of the hydrogen-bond energies for the different systems were able to show that the distribution of polygons depends on the backbone flexibility of the linkers. These comparative studies offer new insights into strategies towards the bottom-up fabrication of highly ordered tunable nano patterning at interfaces mediated by hydrogen bonds.