

2D covalent organic frameworks with built-in functional groups by sub-stoichiometric topological design

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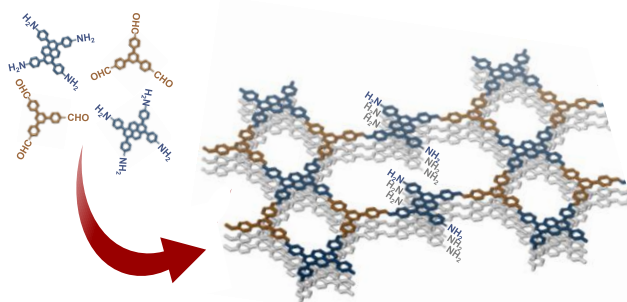
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Covalent organic frameworks (COFs) represent an intriguing class of crystalline porous materials where appropriately functionalized organic molecules are linked with an atomic level precision to give extended periodic structures.[1] COFs have shown great potential for applications in diverse fields including sensing, storage, (photo)catalysis, ion conduction and optoelectronics.[2] Such materials are typically designed by breaking down the desired network into feasible building blocks, which can be either simple and highly symmetric, or more convoluted and thus less symmetric. The linking molecules are chosen complementary to each other such that an extended, fully condensed network structure can form.[3] We show not only an exception, but a new design principle that allows breaking free of such design rules.[4] We show that triangular and tetratopic linkers can be combined to form crystalline and porous imine-linked [4+3] 2D-COFs with periodic uncondensed amine functional groups. These amine groups in the ‘sub-stoichiometric COFs’ featuring an unexpected **bex** net topology, enhance CO₂ adsorption of the framework, can be derivatized in a subsequent reaction, and can also act as catalysts in organic transformations. We further extend this class of nets by including a ditopic linker to form highly crystalline [4+3+2] COFs. The results open up possibilities towards an entirely new class of sub-valent COF structures with unprecedented structural, topological and compositional complexities for diverse applications.



References

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