

# The growth of porphyrin-based two-dimensional covalent organic frameworks (2D-COFs) via the Schiff base reaction

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## Abstract

Two-dimensional covalent organic frameworks (2D-COFs) are an emerging area of materials chemistry, prompted by the exceptional properties of graphene. However, the growth of 2D-COFs using a 'bottom-up' approach offers several advantages, most notably a wide library of constituent monomer building blocks and tunable structures and properties [1].

In this work, we present our findings on the growth of porphyrin-based 2D-COFs using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The Schiff base condensation reaction was chosen to link the building blocks together due its reversible nature which allows for the formation of thermodynamically stable, highly ordered structures [2, 3]. By optimizing the conditions for a solid-vapour interface reaction between 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) and benzene-1,2-dicarboxaldehyde (BDCA), highly ordered and large scale (>100nm<sup>2</sup>) 2D-COF structures were produced as determined by STM. Further XPS studies were carried out to probe the chemical nature of the 2D-COF and provided evidence that the covalent linkages between the porphyrin building blocks consist of both imine and hemiaminal groups, a non-conjugated intermediate in the Schiff-base condensation reaction.

With the development of a reliable synthetic procedure of high quality 2D-COFs, the possibility of more complex architectures and post-synthetic functionalization of the structures can then be explored. In addition, these results have important implications regarding the electronic properties of these materials and poses further questions as to how the environmental conditions during Schiff-base 2D-COF growth influences chemical composition.

## References

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## Figures

