

## Preparation of non-covalent organic frameworks using dodecasubstituted porphyrin

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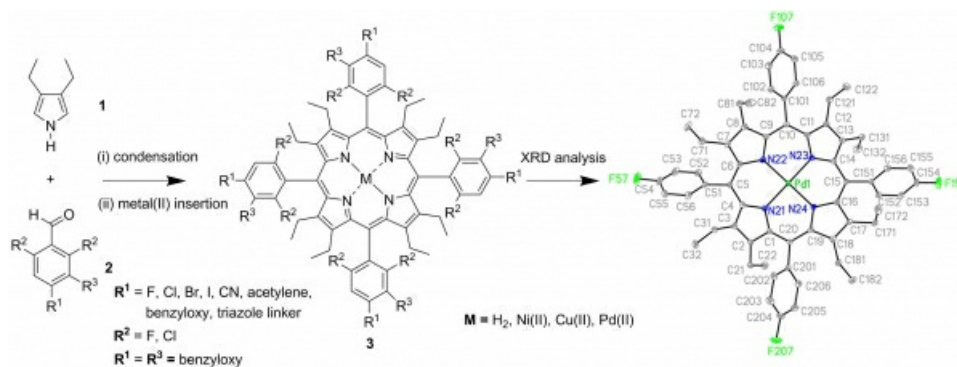
Nowadays the use of porphyrins to create highly porous, sponge-like frameworks is a well-studied field, established by the seminal work of Byrn et al. coining the phrase "porphyrin sponge" in 1991.[1] This initial study used a porphyrin host, trapping a variety of guests within the crystal lattice. Since then, many contributions have focused on the manipulation of planar porphyrins containing a variety of functional groups (namely carboxylic acids or halogens) to obtain directly linked porphyrin frameworks.[2] However, as of yet, there are no specific examples of the use of highly distorted porphyrins [3] being used to obtain such highly porous materials. In this work, we have synthesized a series of 5,10,15,20-tetraaryl-2,3,7,8,12,13,17,18-octaethylporphyrins with alternating halogen, alkyl and aryl substitution patterns to probe the effects of non-planarity on the formation of non-covalent organic frameworks.

The target porphyrins were synthesized according to a modified Lindsey condensation reaction followed by metal(II) insertion. To investigate substituent interactions, modified aldehydes were used. For halogen effects, a family of derivatives with F, Cl, Br or I in either the ortho- or para-position of the meso-aryl residues were selected. Hydrogen bonding interactions were examined by incorporating a nitrile group. Steric effects were examined through the incorporation of a benzyloxy group at either the meta- or para-positions. Finally, investigations were conducted into the use of arm-extended porphyrins using a triazole linker group to further extend their functionality. Solid-state structures were determined via small molecule X-ray crystallography to elucidate the major distortion modes and to characterize any non-covalent interactions. These were then compared to their planar derivatives to determine effects the substitution patterns may have on the formation of non-covalent organic frameworks.

[1] Byrn, M. P. et al. (1991). *J. Am. Chem. Soc.* 113, 6549–6557.

[2] Goldberg, I. (2008). *Cryst. Eng. Comm.* 10, 637–645.

[3] Senge, M. O. et al. (2015). *Chem. Commun.* 51, 17031–17063.



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