Encapsulations of terpenes, aromatic and non-aromatic compound in metal-organic framework via the crystalline sponge method

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The crystalline sponge method[1],[2] allows the absolute structural determination of non-crystalline compounds such as powder, amorphous solid, liquid, volatile matter or oily state. In this method, metal-organic frameworks (MOFs) are used as 'crystalline sponges' which can absorb target sample (guest) molecules from their solution into the pores and allow them to arrange themselves in a regular pattern with the help of specific interactions between MOF pores and the guests, such as π-π, CH-π, and charge-transfer interactions. This technique was first introduced in 2013[1] and since then has grown rapidly and proved helpful in the structure elucidation of liquids and other volatile compounds.

In this work, the crystalline sponge [{$(ZnI_2)_3$(tris(4-pyridyl)-1,3,5- triazine)$_2$·x(solvent)$_n$] (**1**) was used to produce three novel encapsulation complexes of terpenes, such as geraniol-monoterpenoid, farnesol-sesquiterpenoid and β-damascone-tetraterpenoids.[3] Along with the structure determination of the terpenoids, non-bonding CH-π, π-π interactions were identified in the host-guest complexes shown in Figure 1, which were responsible for holding the guests in the specific position with respect to the framework. Since pores of sponge **1** were hydrophobic, no hydrogen bonding between host and guest was observed.

In addition, new crystalline sponges were explored {[Co2(bis-(3,5-dicarboxy-phenyl) terephthalamide)(H2O)3]·solventx}[4] (2) and [Cd7(4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid)(H2O)]·solvent x][5] (3). With sponge 2 two novel inclusion complexes with 3-Phenyl-1-propanol and 2-Phenylethanol were obtained. Sponge 2 has three coordinated water molecules indicating the hydrophilic nature, which was further observed in the inclusion complexes where the hydroxyl group of guest molecules were found to form hydrogen bonds with the framework of 2. Further, 3 shows great potential to act as a crystalline sponge because of larger pore size than 1 and the hydrophilic nature which will allow a wide range of guest molecule for encapsulation and their structure elucidation.

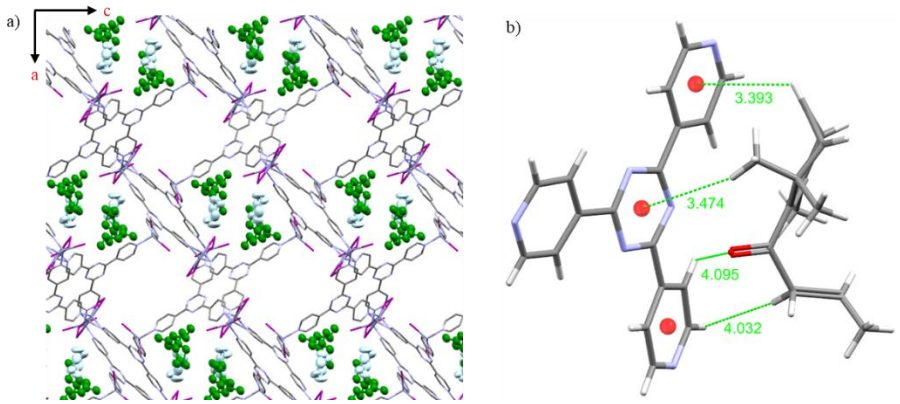

Figure 1 **a)** Packing diagram of β-damascone inclusion complex viewed down the b axis. Framework shown as capped stick model, β-damascone as ellipsoids shown in green colour, residual cyclohexane in light blue colour. Hydrogen atoms have been are omitted **b)** CH-π interaction between host framework and β-damascone.[3]

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