Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supporting information file for:

‘Supramolecular templating of hierarchically porous metal-organic frameworks’

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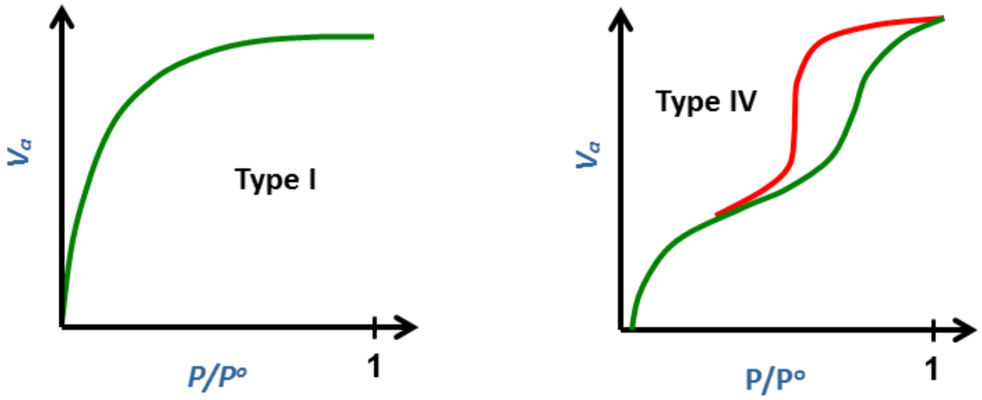

Figure S1. Representative isotherm shapes for the characterisation of porous materials (V_a = volume of gas adsorbed and p/p^0 = relative pressure of gas).[S1] Type I or Langmuir isotherms (left) are typical for microporous materials where the pore sizes are < 2 nm. Most MOFs display a type I isotherm with very steep uptake in the low relative pressure region owing to their very high degree of microporosity. MOFs reported as mesoporous which contain large mesoscale cages separated by small windows will still display type I isotherms as the pore size is not > 2 nm along its length. Type IV isotherms are observed for pure mesoporous materials (pore size 2 – 50 nm), with a rise at higher relative pressures and characterised by a hysteresis loop (red line) during desorption. The hierarchical structures described in this review will display intermediate type I/IV isotherms arising from the two different pore size regimes, which may be more complex if the mesopore walls also have textural porosity (see figure S2b).

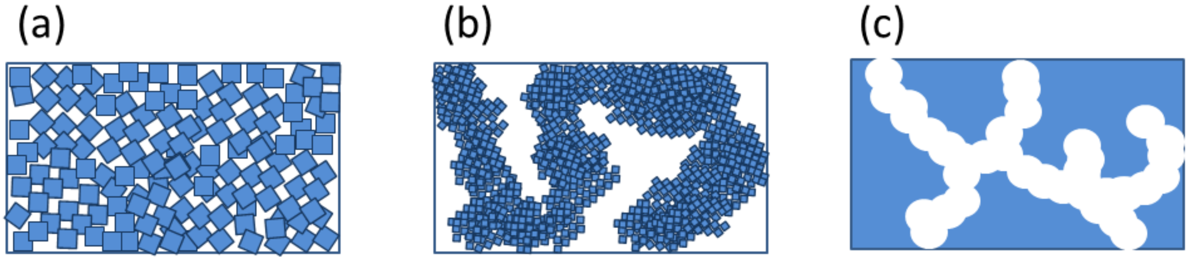

Figure S2. Origin of hierarchical (mesoscale) porosity in MOFs. (a) Mesoporosity (white) in MOFs commonly arises from the interstices between MOF nanoparticles (blue). In this case the nanoparticles are typically 50 – 100 nm in size, where the gaps arising from inefficient crystal packing fall into the mesoporous regime.[S2] (b) Mesoporosity (white) can also occur via template-guided aggregation of very small ultrafine crystallites (blue) via interaction with the surface groups or charges of a supramolecular assembly of amphiphilic molecules that is the subject of this review. The walls between the mesopores are composed of aggregates of very small microporous MOF particles (typically ≤ 20 nm) which assemble to form the observed mesoporous MOF crystals, which are poly- rather than single crystalline materials. Depending on the size of the crystallites within the aggregates, the walls that delineate the mesopores may display further levels of textural porosity which could contribute to the adsorption response. A recent report by Yue et al[S3], demonstrates the template-free synthesis of mesoporous MOF particles as shown in (b) which is proposed to occur via solvent etching of the initially deposited aggregates of MOF nanoparticles. This method is likely to be very system dependent and thus hard to predict *a priori*, so will be limited as a strategy for more general mesoporous MOF formation. (c) Mesoporosity (white) can also arise due to the presence of specific defects or channels within MOF (single) crystals and can be induced via chemical etching of crystals or space-filling effects from long-chain molecules during crystal growth as described in the manuscript (ref 15). Chemical etching of pre-formed MOF crystals remains relatively unexplored, but has recently been shown to enhance the liquid phase separation of aromatic molecules when these hierarchically porous crystals are used as a stationary phase in HPLC. (manuscript ref 49)

S3 – Further comment regarding mesoMOF synthesis

Control of the pH is often very important to ensure successful template assembly; for example, if the template aggregate is only stable under acidic conditions but the framework synthesis requires addition of a large excess of a strongly basic ligand, the concomitant increase in pH necessary for framework formation will cause the mesoscale template to break up. Such pH changes may also alter the type/strength of interactions between the SDA and precursors: as reaction progresses into the cross-linking phase, ligands are deprotonated and protons released.

Most syntheses of mesoporous silica are carried out in strongly acidic or basic aqueous media, sometimes under hydrothermal conditions, where hydrolysis, condensation and assembly readily occur. (Manuscript ref 13 provides an extensive discussion of these) These parameters with respect to template co-assembly are now generally well understood for silica, but for the vast majority of MOFs, synthesis under analogous conditions is not possible given their sensitivity to moisture and comparative fragility to extremes of pH. So the question remains about the nature of the mesophase under MOF compatible synthesis conditions.

Successful templating is largely dependent on the critical micelle temperature (CMT) and the cloud point (CP) of the surfactants: these are, respectively, the minimum temperature at which they form micelles and the temperature when they are no longer soluble in the reaction medium, and are determined by the nature of the amphiphile: *e.g* cationic surfactants tend to have low CMTs, whereas both CMT and CP are high for block co-polymers. Reaction temperature thus needs to be somewhere between the two at an appropriate surfactant concentration (*viz*. above the critical micelle concentration, itself a temperature-dependent parameter).

Both CMT and CP will be strongly affected by the polarity of the solvent, and for MOF synthesis this is typically non-aqueous. Ideally, weakly polar solvents should be avoided as the amphiphilic SDAs will lose the distinction between the hydrophilic/-phobic components thus hindering the overall assembly process. Non-aqueous highly polar solvents on the other hand could also influence the strength of interactions between the SDAs and the building blocks. This could be disruptive by screening charges where electrostatic interactions dominate, but could equally be reinforcing via metal-binding and hydrogen-bonding

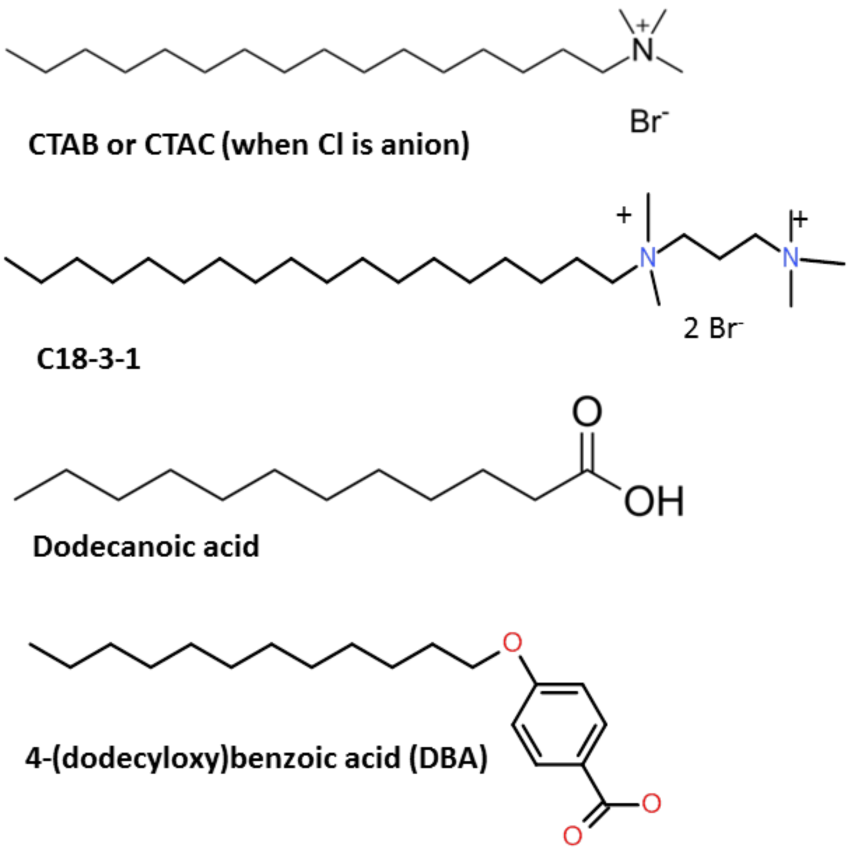

Figure S4. Surfactants employed as structure-directing agents for mesoMOFs that are referred to in this article.

Additional References

S1. IUPAC *Pure & Appl. Chem.*, 1994, **66**, 1739.

S2. For examples please see: (a) Y. Pan, Y. Liu, G. Zeng, L. Zhao, Z. Lai, *Chem. Commun*. 2011, **47**, 2071; (b) J. Huo, M. Brightwell, S. El Hankari, A. Garai and D. Bradshaw, *J. Mater. Chem. A*, 2013, **1**, 15220; (c) Z. Xin, J. Bai, Y. Shen and Y. Pan, *Crys. Grow. & Des.*, 2010, **10**, 2451.

S3. Y. Yue, Z.-A. Qiao, P. F. Fulvio, A. J. Binder, C. Tian, J. Chen, K. M. Nelson, X. Zhu, and S. Dai, *J. Am. Chem. Soc.* 2013, **135**, 9572.