CLAIMS

1. A method for synthesis of hierarchically ordered crystalline microporous material having a high-degree of long-range mesoporous ordering by dissolution/incision of parent crystalline microporous material into oligomeric components, and reorganization into hierarchically ordered mesostructures including mesopore periodicity repeating over a length of greater than 50 nm, the method comprising:

mixing a parent crystalline microporous material having an underlying microporous structure, an alkaline reagent selected from the group consisting of ammonia, ammonium hydroxide or urea provided at a concentration in the aqueous suspension of 0.1-5 wt%, and a supramolecular template to form an aqueous suspension, in which the supramolecular templates are bulky surfactants having one or more dimensions larger than dimensions of micropores of the crystalline microporous material to constrain diffusion into micropores of the crystalline microporous material, in which the dimensions relate to a head group of a surfactant, a tail group of a surfactant, or a co-template; and

hydrothermally treating the aqueous suspension at a temperature of 110-250 C for 12-96 hours and (a) forming oligomeric units of the parent crystalline microporous material, (b) form shaped micelles of the supramolecular template, and (c) assembling the oligomeric units around the shaped micelles, in which a solid is formed as the hierarchically ordered mesostructures that have a high-degree of long-range mesoporous ordering including mesopore periodicity repeating over a length of greater than 50 nm with pores characterized by crystalline microporous walls that retain the underlying microporous structure.

2. A method according to Claim 1, in which the shape of the micelles is tuned by selection of the supramolecular template.

3. A method according to Claim 1, in which the aqueous suspension further comprises an ionic co-solute that is separate from an anion associated with the supramolecular template, and in which the shape of the micelles is tuned by selection of the supramolecular template and the ionic co-solute.

4. A method according to Claim 3, in which the ionic co-solute is selected from the group consisting of $CO3_2^-$, SO_4^{2-}, $S2O_3^{2-}$, $H_2PO_4^-$, F^-, Cl^-, Br^-, NO_3^-, I^-, ClO_4^-, SCN^- and $C_6H_5O_8^{-3}$.

5. A method according to Claim 3, in which the ionic co-solute is selected from the group consisting of SO_4^{2-}, NO_3^-, and ClO_4^-.

6. A method according to Claim 3, in which the ionic co-solute comprises NO_3^- and in which the hierarchically ordered mesostructures possess a cubic mesophase symmetry.

7. A method according to any of Claims 3 to 6, in which the hierarchically ordered mesostructures possess a cubic mesophase symmetry and the mesophase transition is characterized by a surfactant packing parameter g in the range of 0.4-0.8, in which

$g = V/a_0l$

in which

V = total volume of surfactant tails of the supramolecular template,

a_0 = area of the head group of the supramolecular template, and

l = length of surfactant tail of the supramolecular template.

8. A method according to any of Claims 3 to 6, in which the hierarchically ordered mesostructures possess a cubic mesophase symmetry and a molar ratio of supramolecular template to co-solute is in the range of 0.8-1.3.

9. A method according to Claim 3, in which the ionic co-solute comprises SO_4^{2-} and in which the hierarchically ordered mesostructures possess a hexagonal mesophase symmetry.

10. A method according to any of Claims 3 to 5 or 9, in which the hierarchically ordered mesostructures possess a hexagonal mesophase symmetry and the mesophase transitions is characterized by a surfactant packing parameter g in the range of 0.4-0.6, in which

$g = V/a_0l$

in which

V = total volume of surfactant tails of the supramolecular template,

a_0 = area of the head group of the supramolecular template, and

l = length of surfactant tail of the supramolecular template.

11. A method according to any of Claims 3 to 5 or 9, in which the hierarchically ordered mesostructures possess a hexagonal mesophase symmetry and a molar ratio of supramolecular template to co-solute is in the range of 0.8-1.3.

12. A method according to Claim 3, in which the ionic co-solute comprises ClO_4^- and in which the hierarchically ordered mesostructures possess a lamellar mesophase symmetry.

13. A method according to any of Claims 3 to 5 or 12, in which the hierarchically ordered mesostructures possess a lamellar mesophase symmetry and the mesophase transitions is characterized by a surfactant packing parameter g in the range of 0.9-1.1, in which

$$g = V/a_0 l$$

in which

V = total volume of surfactant tails of the supramolecular template,

a_0 = area of the head group of the supramolecular template, and

l = length of surfactant tail of the supramolecular template.

14. A method according to any of Claims 3 to 5 or 12, in which the hierarchically ordered mesostructures possess a lamellar mesophase symmetry and a molar ratio of supramolecular template to co-solute is in the range of 0.2-0.7.

15. A method according to Claim 1, in which the supramolecular template contains least one moiety, as a head group or a tail group, selected from the group consisting of organosilanes, hydroxysilyls, alkoxysilyls, aromatics, branched alkyls, sulfonates, carboxylates, phosphates and combinations comprising one of the foregoing moieties.

16. A method according to Claim 1 or 15, in which the supramolecular template contains at least one cationic moiety selected from the group consisting of a quaternary ammonium moiety and a phosphonium moiety.

17. A method according to Claim 1 or 15, in which the supramolecular template contains at least one quaternary ammonium group having a terminal alkyl group with 6-24 carbon atoms.

18. A method according to Claim 1 or 15, in which the supramolecular template contains two quaternary ammonium groups in which an alkyl group bridging the quaternary ammonium groups contains 1-10 carbon atoms.

19. A method according to Claim 1, in which the supramolecular template contains at least one quaternary ammonium group, and an organosilane as at least one head group moiety.

20. A method according to Claim 1, in which the supramolecular template contains at least one quaternary ammonium group, and at least one head group moiety selected from the group consisting of organosilanes, hydroxysilyls, alkoxysilyls, aromatics, branched alkyls, sulfonates, carboxylates, phosphates and combinations comprising one of the foregoing moieties, in which an alkyl group bridging at least one of the quaternary ammonium groups and at least one of the head groups contains 1-10 carbon atoms.

21. A method according to Claim 1, in which the supramolecular template comprises dimethyloctadecyl(3-trimethoxysilyl-propyl)-ammonium or a derivative of dimethyloctadecyl(3-trimethoxysilyl-propyl)-ammonium.

22. A method according to any preceding claim, in which the alkaline reagent is urea, in which during hydrothermal treatment, urea reacts to form ammonium hydroxide, thereby controlling hydrothermal treatment.

23. A method according to any of Claims 1 to 21, in which the as-formed hierarchically ordered mesostructures are calcined, in which calcining reduces amorphous content of the hierarchically ordered mesostructures.

24. A method according to any of Claims 1 to 23, in which the parent crystalline microporous material comprises a zeolite or zeolite-type material selected from the group consisting of aluminophosphates, silicon-substituted aluminophosphates, metal-containing aluminophosphates and zeolitic siliceous only framework material.

25. A method according to any of Claims 1 to 23, in which the parent crystalline microporous material is a zeolite having a framework selected from the group consisting of AEI, *BEA, CHA, FAU, MFI, MOR, LTL, LTA and MWW.

26. A method according to any of Claims 1 to 23, in which the parent crystalline microporous material is a zeolite having FAU framework.