Filtration is the technique of separating two or more substances in a mixture by passing the mixture through a medium that permits some of the substances therethrough while preventing passage of other substances. Filtration theoretically possesses the ability to perform separations under low energy consumption and simple equipment to obtain high purities of the components. Filtration is a common and well-understood process for relatively large molecules. However, filtration of extremely small molecules, such as those with diameter three nanometers or smaller, poses unique challenges.

One common technology for filtration of very small molecules is reverse osmosis. Reverse osmosis utilizes industrial membranes that are composed from a continuous polymeric layer on top of an intermediate layer of a polymer that is on top of a fabric used as mechanical support. *See* [1]. Familiar examples include layers of polyamides and poly-cellulose-acetates, on top of an intermediate polysulfone, on top of polyester fabric. The selectivity of these membranes is due to the different miscibility of the materials. For illustration, even if one material is 20 times more permeable than another material through a membrane, such a difference is utilized to pass a mixture of these materials through a series of such membranes to obtain purer material.

A porous material may serve as another type of filter. Generally, the passage of a material through a layer with precise pores requires less energy than passage through a polymeric layer, because the passage is not performed via miscibility and dissolution but rather by passage through voids. For filtration of extremely small molecules, a membrane may be designed, in theory, having a pore size which is small enough to distinguish between different pico-scale and angstrom-scale molecules. For example, methane has a kinetic diameter of 3.8 Angstroms, and carbon dioxide has a kinetic diameter of 3.3 Angstroms. Filtration of these two gases from each other would proceed if they were exposed to a membrane having a pore size that precisely tailored within the 0.5 Angstrom size difference between them.

Various attempts have been made to manufacture such filtering membranes, but they all have been hindered by the technical limitations. Typically, periodic three-dimensional materials such as Zeolites, Metal-Organic Frameworks (MOF) and Covalent Organic Frameworks (COF) have been considered as porous membranes. However, fabricating continuous thin uniform membranes from the mentioned 3D materials in industrial scale is challenging.

pore of the porous substrate. For example, the channel may be built over a narrow “pit” that had been previously been formed with the solid material on the porous substrate.

The substrate may be an anodic aluminum oxide (AAO).

At least a portion of the solid material may be deposited via atomic layer deposition. In such embodiments, the material deposited via atomic layer deposition is one or more of titanium dioxide, silicon dioxide, aluminum oxide, or silicon nitride. At least a portion of the solid material may also, or alternatively, be deposited via molecular layer deposition.

A diameter of the entrance may be between 2.5 and 4.5 angstroms. Advantageously, 4.5 angstroms is the internal diameter of alpha-cyclodextrin. The internal diameter may be calibrated to even narrower than that based on the use of the tip molecules, template molecules, and/or bulky stoppers in the entrance, as discussed. The 2.5 - 4.5 angstrom minimum diameter is sufficient to filter gases and other small molecules which have diameters in that range.

According to a second aspect, a method of manufacturing a filter is disclosed. The method includes: building at least one tubular structure over at least one pore of a porous substrate that is filled with a sacrificial pore-filling material, each tubular structure comprised of a coaxial stack of associated macrocycles; filling gaps between tubular structures with a solid gap-filling material; and removing the sacrificial pore-filling material from the pores of the porous substrate; to thereby generate at least one channel in which the solid material defines a skin, an entrance of each channel is at a surface of the skin and an exit of each channel is at a pore of the porous substrate. The entrance of each channel has a diameter which is 3 nanometers or less.

Optionally, the method may include, prior to the building step, filling the pores of the porous substrate with the pore-filling sacrificial material. Prior to the step of filling the pores, the method may include layering a sacrificial layering material over the porous substrate, wherein the sacrificial layering material is configured to form associations with both the sacrificial pore-filling material and with the porous substrate. In such embodiments, the step of filling pores comprises adhering the pore-filling material to the sacrificial layering material. The method further includes, following the step of filling pores, selectively etching the sacrificial layering material to thereby leave the porous substrate with pores filled with the pore-filling material. These steps are used to render

template molecule. Optionally, this molecular bridge is performed by attaching a bulky stopper to the template molecule, to thereby form a rotaxane or polyrotaxane; forming the at least one molecular bridge when the bulky stopper is attached to the template molecule; and removing the bulky stopper and template molecule. The threading step may be performed when the tubular structures and porous substrates are immersed in solution, and optionally by ultrasonicating or heating the solution. In advantageous embodiments, the solution is a dilute solution, as this leads to a higher yield, although a saturated solution may also be used.

When a template molecule is used, following the step of filling gaps, the template molecule may be removed.

Optionally, following the step of filling gaps, the template molecule may be lengthened. The method then includes threading at least one additional macrocycle or tubular structure onto the lengthened template molecule, to thereby lengthen the channel. The step of lengthening the template molecule may be performed with click chemistry.

Optionally, a template molecule attached to a bulky stopper may be threaded into an entrance of each channel, to thereby define a passage into each channel based on dimensions of the entrance, of the bulky stopper, and of a portion of the template molecule near the entrance of each channel.

Optionally, the method may include forming the tubular structures prior to the building step by forming molecular bridges between macrocycles in solution. Advantageously, the available chemical methods available for building molecular bridges in solution may be more varied and versatile than those available for building on the porous substrates. In such embodiments, the step of building the tubular structures comprises introducing macrocycles into a solution containing template molecules, to thereby thread the macrocycles around the template molecules. The method may further include ultrasonicating the solution. The solution is advantageously a saturated solution, which generates higher yields, but may also be a dilute solution.

In embodiments in which the associations are formed in solution, the step of forming molecular bridges may include: modifying at least one functional group of each macrocycle; and forming one molecular bridge between adjacent macrocycles by associating the macrocycles at the modified functional groups, to thereby generate a train of macrocycles. The train is a versatile structure that may form the basis for additional chemical reactions. For example, the method may further include: threading the train of

macrocycles on a template molecule having a bulky stopper removably attached at one end; attaching a bulky stopper to a second end of the template molecule;
forming at least a second molecular bridge between adjacent macrocycles, to thereby generate a ladder of macrocycles; cleaving the removable bulky stopper from the template molecule; and removing the template molecule from the ladder of macrocycles.

The bridges may be formed in sequential reactions, in which each sequential reaction increases a proximity of different portions of the macrocycles to each other, thereby enabling the subsequent reactions. This may be analogized to closing of a zipper, in which initiating the closing process makes the rest of the closing easier.

The method may further include forming the bridges with at least one branched bridge using a linker molecule that forms connections between adjacent macrocycles at two or more locations. Additional functional groups may be added onto the linker molecule, following attachment of the linker molecule to the adjacent macrocycles, and additional bridges may be added between the adjacent macrocycles with the additional functional groups. In this manner, the branched bridge may grow, potentially indefinitely, to form more bridges between the adjacent macrocycles.

Optionally, the tubular structures formed in solution are asymmetric tubular structures, said asymmetric tubular structures comprising of a coaxial stack of associated macrocycles having a substantially identical internal diameter, and a molecule having a second internal diameter, said second internal diameter being narrower than the first internal diameter of the macrocycles of the coaxial stack. In such embodiments, the bridges between macrocycles that are adjacent to the tip molecule reduce a gap between said macrocycles to less than the second internal diameter. The second internal diameter may be between 2.5 and 4.5 angstroms.

The method may further include lengthening an asymmetric tubular structure in solution by associating the asymmetric tubular structure with a symmetric tubular structure. Optionally, the lengthening step comprises forming a semirotaxane including a template molecule inserted into both the symmetric tubular structure and the asymmetric tubular structure, associating the asymmetric and symmetric tubular structures, and removing the template molecule.

The method may further include, prior to the building step, modifying the tubular structures with anti-sticking functional groups on an outer shell thereof.

According to a third aspect, a method of manufacturing a filter is disclosed. The method includes: selecting a sacrificial substrate, said sacrificial substrate capable of attachment to organic compounds; attaching a template molecule to the sacrificial substrate; building at least one channel onto the sacrificial substrate, each channel comprised of one or more tubular structures comprised of a coaxial stack of associated macrocycles; filling gaps between the tubular structures by adhering a solid gap-filling material to the sacrificial substrate; attaching a porous substrate to one of the open ends of the tubular structures or the filler material; and removing the sacrificial substrate and template molecule. Optionally, the method further includes lengthening the channels by attaching additional tubular structures to the ends of the channels that had previously been associated with the sacrificial substrate.

According to a fourth aspect, a method of forming a tubular structure comprised of macrocycles connected by molecular bridges in solution is disclosed. The method includes modifying at least one functional group of two or more macrocycles; and forming one molecular bridge between said macrocycles by associating the macrocycles at the modified functional groups, to thereby generate a train of macrocycles. Optionally, the method further includes threading the train of macrocycles on a template molecule having a bulky stopper removably attached at one end; attaching a bulky stopper to a second end of the template molecule; forming at least a second molecular bridge between adjacent macrocycles, to thereby generate a ladder of macrocycles; cleaving the removable bulky stopper from the template molecule; and removing the template molecule from the ladder of macrocycles. The bridges may be formed in sequential reactions, in which each sequential reaction increases a proximity of different portions of the macrocycles to each other, thereby enabling the subsequent reactions. The bridges may be formed with at least one branched bridge using a linker molecule that forms connections between adjacent macrocycles at two or more locations. Optionally, the tubular structures formed in solution are asymmetric tubular structures, said asymmetric tubular structures comprising of a coaxial stack of associated macrocycles having a substantially identical internal diameter, and a molecule having a second internal diameter, said second internal diameter being narrower than the first internal diameter of the macrocycles of the coaxial stack. In such embodiments, the asymmetric tubular structures may be lengthened in solution by associating the asymmetric tubular structure with a symmetric tubular structure. The lengthening step may include forming a semirotaxane including a template molecule

43. The tip molecule 47 has a diameter (a "second internal diameter") which is narrower than the internal diameter of the rest of the macrocycles comprising the structure (the "first internal diameter"). The tip molecule may be selected to have a specific diameter, configured to permit the passage of selected molecules while excluding other molecules. The second internal diameter may be 3 nm or less, or even as low as 2.5 to 4.5 angstroms.

The tip molecule may be attached to the uppermost tubular structure when said tubular structure is already built onto the channel. Alternatively, the uppermost tubular structure may be pre-formed with the tip molecule in solution.

In the illustrated embodiment, the tip molecule is at the entrance of the channel. In alternative embodiments, the molecule with the second internal diameter may be located within the channel, so that the channel (and specifically the tubular structure that has the molecule with the second internal diameter) is shaped like an hourglass.

FIG. 4B illustrates a cross-section of a second embodiment of a filter 40. The filter 40 is constructed similarly to the filter of FIG. 4A, except that, in this case, the channel is constructed of a pattern of tubular structures that have different types of bridges between them. Specifically, some of the macrocycles 44 that are embedded within the filler material have the denser ligature 46 connecting between them. This configuration may be preferred if the tubular structures are formed in this manner in solution prior to building the channels on the substrate, as will be discussed further herein.

FIG. 4C illustrates a cross-section of a third embodiment of a structure that may be manufactured according to the teachings of the present disclosure. In this embodiment, a bulky stopper 49 with a template molecule 50 fills the opening. In this embodiment, instead of a passage via the opening being formed at the top of the tubular structure, the passage is via the outer shell of the tubular structure.

In order to manufacture such a configuration, a polymeric template molecule that is bonded to a bulky stopper on one end may be associated to an open end of a channel. The bulky group may then be bonded to the top of the channel at certain locations thereon, while leaving an opening at the entrance of a desired size. Optionally, the bulky stopper 49 is anchored to the tubular structure with one or more bridges 51; these need not be present in all embodiments.

The formation of such a complex between a bulky stopper and a channel may be controlled through various mechanisms. In one example, the channels may be built with

reactive functional groups (such as alcohols) at their tips. The channels may then be exposed to a surfactant molecule that contains a bulky stopper with functional groups (such as primary alkyl bromides) associated to a template molecule. The surfactants assemble into the openings of the channels. With or without drying, the alcohol or other functional groups may be activated (for example, with a base) to chemically bond the bulky stopper to the opening of the channels. The process may be repeated in order to increase the yield of the reaction. The bulky stopper-template molecule combination may be selected to fill only a small portion of the volume of the channel.

Theoretically, a similar effect may be accomplished through the use of a surfactant molecule containing a bulky stopper, which blocks the opening of the channel without being bonded thereto. In still another embodiment, the template molecule may be chemically associated with the channel in a manner that narrows the entrance of the channel, even without the bulky stopper.

Generally, a blockage may be placed at an entrance of each channel through one of three manners: a bulky stopper and elongated molecule, as discussed; an elongated molecule attached to the solid material of the skin, and inserted within a top of an uppermost tubular structure in the channel, or deposition of solid material in a manner that buries the top of the uppermost tubular structure in the channel, followed by etching of the solid material to expose the outer shell of the tubular structure.

In still another embodiment (not illustrated), regardless of whether an end-cap or bulky stopper is utilized, the bottom of the channel may be filled with a valve. The valve is oriented between the porous support and lower part of the skin. The valve may block the flux from the side of the membrane with higher pressure, so the flux could form only through the outer shell of the tubular structures.

FIG. 4D illustrates still another embodiment, in which ALD or MLD may be used to block the opening of some channels, or parts of their outer shells. The ALD or MLD may be used in place of surfactants. In such embodiments, the ALD or MLD may touch the openings of the channels, in order to expose an opening to the channel of a desired size.

In each of the depicted embodiments, the channels include tubular structures that are at least partially embedded therein. In other embodiments, this configuration is only an intermediate step, and, prior to completion of the channels, the tubular structures are

Innovative techniques for tuning parameters and characteristics of the composite layer will be described further herein. In some embodiments, depending on how the composite layer is generated, polishing and/or other means are utilized to expose the composite layer.

In some embodiments, the porous substrate is a plastic or polymer filled with gold or gold alloy. In some embodiments, gold or gold alloy nanoparticles are integrally embedded on the topmost surface of a porous material while the gaps between them are filled.

In some embodiments, the porous substrate is a layered material of two or more porous layers on top of each other, with no chemical bonds between them. In some embodiments the substrates have a high surface area, such as hollow fibers, stacked sheets and others.

In some embodiments a "linker" molecule or molecules could be associated to the surface of the porous substrate. The molecule is associated to the substrate using one of its parts while another part of such molecule will react with precursors used in the process of filling the gaps between the tubular structures, as will be discussed further herein. One example of a linker molecule is tri-ethoxy-silicon amine $(CH_3CH_2O)_3Si\text{-}(CH_2)_3\text{-}NH_2$. The silicon-tri-ethoxy group could bind ceramic surfaces, while the amine could react with silver nanoparticles. In some embodiments, the porous layer is, eventually, chemically associated with the gap-filling-layer and/or the tubular structures and/or surrounds it and/or is associated to by an accumulation of weak interactions. In another alternative, the diameter of the pores could be filled by gold, in cases of defects, where a void was not filled properly with gold, filling the gaps could also cover/block such pores if they are narrow enough.

The selection between the two main approaches of creating a membrane depends, *inter alia*, on the desired porous layer for mechanical support, which may be industrially available, and the ability to deposit such in the presence of tubular structures that may contain an organic material.

In devices constructed according to the present disclosure, a silicon wafer coated with a 100 nm film of gold (with a few nanometers of chromium as adhesion layer between the gold and the oxide layer present at the surface of the silicon wafer) was used as a substrate.

B. Attaching Sacrificial Materials to Form Composite Substrates

In this section, reference is made to a "primary sacrificial material" and a "secondary sacrificial material." A "secondary sacrificial material," also referred to herein as a "sacrificial layering material," is a material that is deposited directly on the substrate, and which may serve as a precursor for deposition of another sacrificial material, the "primary sacrificial material." A "primary sacrificial material," also referred to herein as a "sacrificial pore-filling material," is a material that is deposited onto the secondary sacrificial material while filling the pores of the porous substrate to at least some extent and which is used in order to form a base for attachment of other materials, such as template polymers and/or tubular structures.

In some embodiments, a dense layer of the secondary sacrificial material is deposited on the surface of the porous substrate. Then, the inside of the pores of the substrate are deposited with the primary sacrificial material, de novo, in order to fill the pores of the substrate. The dense layer of the secondary sacrificial material is then etched, leaving the pores filled with the primary sacrificial material. On this material, the tubular structures are deposited.

In one example, the substrate is an AAO (Anodic Aluminum Oxide) membrane. The secondary sacrificial material is silver. The silver is deposited on the exterior surface of the AAO substrate (as shown in FIG. 1B) by CVD and PVD methods, such as thermal deposition, sputtering, and e-beam. Then, electroplating (electro-deposition) of a gold (Au) as a primary sacrificial layer is carried out, filling the pores, as shown in FIG. 1C. Selective etching may then be performed, such as with nitric acid, to remove the silver layer.

Other materials may be used as substrates, with different materials requiring different types of deposition techniques, including ones having a high surface area configuration/s, possibly hollow fibers. The substrate may be formed of titanium dioxide (TiO_2), silicon dioxide (SiO_2), or silicon nitride (Si_3N_4). When the porous substrate is titanium dioxide, silver may be deposited directly with electroless deposition (ELD). ELD may then be used to deposit gold in the pores. Note that ELD processes will not deposit gold directly on titanium dioxide. This is advantageous, as it is desired to insert the gold within the pores, but not to cover the surface of the substrate with gold.

A similar two-step process may be used to deposit gold in the pores of a porous Al_2O_3.

oil interface to layer a film containing the secondary sacrificial material, activating the porous substrate prior to deposition of the secondary sacrificial material, and others.

C. Etching of the Gold Layer

In some embodiments, whether the first or the second main approach for creating membranes is used, the selective removal of gold, or a gold alloy such as gold-silver alloy, is required at the end of the process. In particular, gold could be used as a material that could fill the pores of a substrate and on top of it the construction of the tubular structures could take place, and after the gaps between the tubular structures are filled, then the gold could be removed selectively in an etching process in order to empty the pores. Gold could be selectively etched using sodium or potassium cyanide in the presence of an oxide, silicon dioxide for example. That process could also selectively etch silver. Another process for selectively etching gold is by using iodine. In other embodiments, silicon oxide is selectively removed, which could be done selectively by hydro fluoric acid and its buffers in wet conditions, or dry etching in the presence of titanium dioxide or aluminum oxide.

In some embodiments, a protective coating is first used as a molecular adhesive between the sacrificial surface and the gap-filling-layer. Such coatings could also protect the porous substrate. Such protective coatings could also be used if the materials are not the same. In some embodiments, the tubular structures could allow the passage of the etchant to the other side of the membrane, which is not desired, so they may be blocked temporarily, by adding a cap or by forming an inclusion complex with template molecules associated to a bulky group at one of its ends. In some embodiments a second porous layer is coated/deposited/placed from the other side of the membrane.

In some embodiments, before the etching, a temporary layer is coated, such as wax, in order to increase the mechanical stability and allow more aggressive stirring to be performed during the etching. Another reason is in cases where an entire layer of a continuous substrate is etched and the porous support is desired to be on the side where the continuous substrate layer was. Another reason is to hold the tubular structures intact with the gap filling layer and after the etching to thicken the outer layer of the tubular structures at the side where etching had occurred.

III. Template Molecules and Methods of Attachment Thereof to the Substrates

In many embodiments of the present disclosure, and as seen in FIG. 1E, the channels are formed on template molecules. The template molecules are attached to the substrate, e.g., to the primary sacrificial material which is overlaid onto the substrate. Following attachment of the template molecules, monomers or tubular structures of the macrocycles are overlaid onto the template molecules.

Referring to FIG. 6A, a template molecule 61, such as a polymer, is attached to a surface region of a substrate 60. A functional group, depicted as an asterisk, is positioned at the end of the template molecule 61. Although, in the illustrated Figure, only one polymer is attached to the substrate, it is understood that a network of polymers is attached to the substrate.

The template molecule is patterned on a surface position within the surface region and enables direct placement of the tubular structures at these surface positions. The template molecules are molecules that may be selected amongst any elongated molecules that have a linear backbone and at least one terminal functionality that can surface-associate to a surface region of the substrate. The template molecules may be similarly selected amongst such linear molecules which are mono-functional or optionally bi-functional, meaning that they have two or more terminal groups, at least two of which functionalized or substituted or positions at the different termini of the linear molecule (one or more terminal groups at one end and one or more same or different groups at another end). Where both termini are substituted with a functional group, one end may be selected for surface binding while the other for association with a functional group that acts as, e.g., a capping group or a stopper group once the macrocycles and/or tubular structures are threaded on the template molecule.

The selection of the functionalities depends, *inter alia*, on the template molecule used, the surface material to which the template molecules are to be associated, and on other processing parameters. The functionalities may be selected to comprise at least one heteroatom or an atom having an affinity to the surface material or an ability to associate to a capping material. Such functionalities may comprise a sulfur atom, a selenium atom, a carboxylic acid group, an ester, an activated ester, an amine group (or a nitrogen containing group including cyclic and aromatic amines), an hydroxy group (including phenols and other –OH containing molecules), an azide, aryl halides, alkyl halides, aryl pseudo-halides, alkyl pseudo-halides, and pseudo stable functionalities such as acyl halides and others.

of the deposited molecule, solvent (mixture of solvents, buffers), the concentration of the template polymer in the solution, temperature, immersion time, stirring, shaking, ultrasonication (during immersion), suction (to evaporate the solvent), and atmosphere.

Addition of other materials before or during the immersion, that cannot react chemically with the surface but only to physically adsorb into it could gain some control over the process. Physically adsorbed materials, whether the previous or another method was used, could be removed later by stirring and/or ultrasonication.

The following methods describe conditions and processes for attaching template molecules to surfaces while controlling the surface density of the template molecules, their spacing and other parameters.

As discussed above, in preferred embodiments, the substrate is a metal substrate, such as gold, or a gold layer overlaid onto another substrate. Advantageously, gold reacts with groups that may be functionalized onto polymers, such as thiols, selenols, and disulfides. The template molecule has such a group on one end, such as a thiol group. The template molecule may be functionalized on its other end with an amine or a protected amine. One example of a suitable polymer is polyethylene glycol (PEG), and more specifically one which is functionalized with a thiol group on one end and an amine on the other end.

If the template molecule does not tend to form islands on the surface, then the attachment may be performed by immersing the substrate in a diluted solution containing the polymer.

If the template molecule tends to form islands on the surface (and the distance between each molecule chain is too close in such an island and interferes with threading of the macrocycles or tubular structures then attaching a template polymer may be performed by immersing the substrate in an extremely diluted solution of thiols while heating, ultrasonicating, and/or vacuum pumping. This yields a polymer-grafted surface in which individual polymer chains are attached apart from each other, not forming islands. Oxidation of the thiols may be avoided by working under inert gas. The template polymer may be functionalized at its other end with an amine or protected amine.

In the foregoing example, the template molecule is attached to the surface in a single step. In alternative embodiments, this process may be further split into two or more steps. First, a molecule having the structure X-Y-Z-SH is attached, where: X denotes a sacrificial polymer or other functional group, optionally with a bulky group (e.g., dendron

macrocycles. Optionally, ultrasonic treatment and/or temperature control may also be utilized.

Threading of macrocycles or elongated tubular structures, for example nanotubes composed of two or more macrocycles already bonded to each other, onto a template molecule, to form an inclusion complex between them, sometimes denoted as a poly-pseudo-rotaxane or pseudo-rotaxane, is a process that depends on various factors. The factors include: functionalities and other characteristics of the template molecule, including polarity or a-polarity of the template molecule and the cavity of macrocycles, the cavity of the tubular structures, the outer shell of the tubular structures, the solvent/mixture of solvents, temperature, the flexibility/rigidity of the template molecules, the lengths of the template molecules, the macrocycles/tubular structures, and others. Often ultrasonication is used to initiate the process of threading. In some cases, threading is achieved in a saturated solution of macrocycles or tubular structures, and in other cases in diluted solutions. Some inclusion complexes are formed in water also due to hydrophobic interactions between the cavity of the tubular structures and the template molecule. After their formation, some inclusion complexes can be sustained for some time without unthreading in a solvent that could not have promoted their initial formation. For example, some inclusion complexes formed in water could be sustained for some time in a polar aprotic solvent. Some nanotubes composed of macrocycles could be threaded by template molecules in polar aprotic solvents. In some cases, even though hydrophobic interactions play a role in the formation of an inclusion complex formation, the hydrophobic cavities of the tubular structures could be threaded by template molecules having polar groups.

In some cases, a plurality of macrocycles may be associated to each other prior to surface association. In some embodiments, the outer shells of the tubular structures or a portion of them are sacrificial to some degree, i.e., could be removed selectively, for example in order to increase solubility in solutions that promote the inclusion complex, and also to generally increase the solubility of the tubular structure. In some embodiments, surfactants could be used to increase such solubility of tubular structures or a part of them. Surfactants that do not compete with the template molecules to form inclusion complexes with the tubular structures are of special interest. Such surfactants could be for example ones that all their ends are associated with bulky groups preventing threading.

In some embodiments, association is achievable by crosslinking. Crosslinking, in this context, refers to addition of an external molecule that links two different macrocycles or tubular structures. In some embodiments, association is achieved by condensation reactions between vicinal macrocycles. In some embodiments association is achieved by a combination of methods, i.e., for example by condensation reactions followed by crosslinking. Condensation reactions may require conversion/s of some group/s.

For crosslinking to be efficient, the macrocycles/tubular structures may be threaded densely on the template molecule or at least on a portion of it. Crosslinking could be performed in solution or in vapor or solid phases after drying the surface. The rate of exposure of the crosslinking agent and its shape, among other parameters, could control the rate of associations.

Various methods for vicinally linking adjacent macrocycles have been disclosed in the art. Generally, there are two basic approaches: using chemical linkages directly, and using supramolecular chemistry to achieve chemical linkages.

With respect to forming chemical linkages directly, one approach took the macrocycle Calix[4]arene and added two external opposite bridges to each of the sides of this macrocycle. Using the two bridges, a bifunctional chemical association was performed to another such macrocycle. The process could be repeated to create nanotubes of Calix[4]arenes. In some embodiments, groups at required positions are reacted more than once with a single molecule (sometimes known as a "looper"). The looper may be removed, as needed, to yield a specifically modified side of a macrocycle, following formation of different interconnections.

In some embodiments, after modifying one or both side/s of a macrocycle (by converting and/or protecting and/or deactivating groups), the side or sides could be associated with molecules functioning as “arms” that will form later bridges with other macrocycles or tubular structures containing them. One side of a cyclodextrin could be associated with two or more "full" arms, or "half" arms, or any partition, such as a single "full" arm. As used herein, a “full” arm is an arm that extends all the way from one cyclodextrin to the other in the tubular structure, while a “half” arm meets another “half” arm in the middle. The tip of any arm may be protected.

Associating cyclodextrins and tubular structures containing them may also be done utilizing supramolecular chemistry. In these embodiments, the cyclodextrins are

two adjacent macrocycles. Also, one or more bridges may have already been formed before forming the bridge between S and T. In some embodiments, S and T are both a primary alcohol. The primary alcohols are converted to primary alkyl bromides, for example, by reacting them with NBS/PPh_3. Following addition of a catalyst, a carbon-carbon bond is formed. The process may be performed to generate one bridge or more between adjacent macrocycles.

In some embodiments, a second type of bridge between adjacent macrocycles is formed, this one being an ether bridge. The process begins with each macrocycle having a primary alcohol (S=T=primary alcohol). Next, only one of the primary alcohols is converted to an alkyl bromide, while the other remains a primary alcohol. A strong base, which is not a nucleophile, is added. The base removes the hydrogen from the unreacted alcohol, thereby activating the primary alcohol to perform a nucleophilic reaction. As a result, an ether connection is formed. The bromide salt that is formed as a byproduct may be removed and discarded. Again, the process may be performed to generate more than one bridge between adjacent macrocycles.

If during this process, initially, both of the primary alcohols are converted to primary alkyl bromides, then the two alkyl bromides cannot react to form an ether bridge. Accordingly, the bromination must be reversed. NaOH base is added in order to convert one or both of the bromides back to an alcohol. At this point, the process may be performed again, in order to form the molecular ether bridges, as discussed.

In alternative configurations, one of the alcohols may be converted into a different leaving group. One exemplary is by reacting with a molecule of the type Cl-S-O_2-R.

Converting two vicinal primary alcohols into an ether bridge may be done by acid catalysis. The catalysis may be performed with any acid. A Lewis acid may also be used to perform the catalysis.

This process may be performed in order to generate a high number of links, such as up to 6 narrow-narrow links for alpha-cyclodextrin, or 8 narrow-narrow links for gamma-cyclodextrin if, for example, reacting the native primary alcohols of the narrow sides.

In certain embodiments, the formation of different bridges between different adjacent macrocycles may proceed in sequential reactions, instead of all at once, which may require to reverse certain conversions before repeating the process/processes for forming the bridge/s. Each sequential reaction increases a proximity of different portions

of the macrocycles to each other, thereby enabling the subsequent reactions. This may be advantageous because the formation of one bridge may cause other opposite functional groups to come closer together to each other, thereby enabling a reaction which was not possible when the macrocycles were merely complexed together on a template molecule. In this manner, the macrocycles may be "ratcheted" shut gradually, until a sealed structure is obtained.

In some embodiments, one of the macrocycles includes arms of the form R-CH_2-OH (=S), ending in a primary alcohol, or alternatively, S is a native primary alcohol of the opening of a macrocycle. The other macrocycle just has a non-primary alcohol/s (=T, secondary alcohol/s and/or phenol/s). The primary alcohol/s may be selectively converted into primary alkyl bromide/s, using NBS/PPh3 or Br_2/PPh3 or other leaving groups. The bromination may not be done on all of the primary alcohols at once, in a case in which more than one bridge is being formed. A non-nucleophilic base is added, to remove the hydrogen/s of the non-primary alcohol/s. The activated alcohol/s attack/s the bromide/s, and the result is formation of two ether links. It is possible to form in this process two bridges at substantially opposite positions. This process may be performed in order to generate a high number of links, such as up to 6 narrow-wide links for alpha-cyclodextrin, or 8 narrow-wide links for gamma-cyclodextrin if, for example, reacting the native primary alcohols of the narrow side with the native secondary alcohols of the wider side.

In some similar embodiments, in the two vicinal macrocycles, each one is equipped with one arm or more (of the form R-CH_2-OH) and one non-primary alcohol at 2 substantially opposite positions. The reactions proceed as described before in order to make two bridges.

Referring to FIG. 5O, in still another embodiment, a branched bridge is formed. In this embodiment, two macrocycles (and/or openings of tubular structures) are arranged vicinal to each other within the same supramolecular structure, each could be with the same functional group (S=T). The macrocycles are reacted with a group having the form X1-R1-X2-R2, and which is also referred to herein as a type of "linker." X1 is a group that is capable of reacting with S or T but not with both of them. R1 is a bridge, or part of it. R2 is a long molecule, a dendron, or a dendrimer. The volume of R2 enables the molecule to react only with one molecule S or T. The bond between X2 and R1 may be selectively cleaved, such that X2 may be reacted with a further branched molecule having at least 3 functionalities, some may be protected. After the linkage to X2, the other

D. Asymmetric Tubular Structures

As discussed above, the present disclosure teaches formation of macrocycle tubes with narrow openings at their tips, which are capable of filtering between small molecules. The macrocycle α-cyclodextrin, has an inner rim diameter of 4.5 Å. This diameter is still greater than the diameters of many molecules that are desirable to filter, such as carbon dioxide and methane. Thus, in order for the macrocycle tubes to serve as filters, it is necessary to append an even narrower opening to one entrance of the tubular structure.

In one exemplary embodiment, a narrower macrocycle (a "tip" or "endcap") is associated to the tip of a tubular structure made of wider macrocycles (i.e., macrocycles with a larger internal cavity. The tip is attached to the tubular structure with at least two external bridges on substantially opposite / relatively opposite positions of its mouth or opening. The shell between the associated narrower macrocycle and the tubular structure is less permeable than the opening in the endcap, thus ensuring that materials to be filtered enter the tube via the endcap. One or more intermediate-sized macrocycles could be used as a bridge between a smaller endcap and larger macrocycles. More than one endcap may also be applied, in a progression from larger to smaller internal diameters. A given endcap may be associated to the same tip of a tubular structure by different types of connections, where different bridges, their number and the different sites of bridging could each yield a tip with different parameters.

The modified tip presents a unique cavity whose shape and atom composition, as well as its internal cavity diameter, influence its selectivity and permeability toward different materials. The flexibility of the tubular structure also plays a role in restricting or forcing the conformations of the macrocycle. An extra layer at the surface of the membrane could also contribute to this effect.

The modifications to the tips of tubular structures may be performed when the tubular structures are already embedded into a membrane, or during/between different steps of its fabrication. The modifications may alternatively be performed on a tubular structure and even a single macrocycle before its incorporation to a membrane, where the opposite tip of the tubular structure/ macrocycle could potentially be elongated, as previously described. Such one-tip-modified tubular structures could by themselves be

tip molecule having a narrower diameter than the lower parts of the tubular structure. More generally, any combination of macrocycles of different widths may be included in the tubular structures.

In the illustrated embodiment, the tip molecules are at an end of the tubular structure. As discussed, the narrower molecules may also be at intermediate points of the tubular structures.

In the illustrated embodiment, there is a single "tip" molecule. In alternative embodiments, there may be a sequence of multiple "tip" molecules, each with a gradually narrowing diameter.

E. Removal of the Bulky Stopper and Template Molecule

In FIG. 6E, the bulky stopper and the template molecule are removed. A stacked tube of macrocycles remains on the substrate, with an internal pore. Often, this process is performed only after completion of the gap-filling layer, and, as a result, specific methods for removal of the template molecule are discussed further herein, after discussion of the gap filling.

F. Direct Attachment of the Closest Macrocycle to the Surface

Referring to FIG. 7A, the closest macrocycle to the surface 72 (the "first macrocycle") may form an association, via links 71, with the surface region 70. This may occur during the crosslinking process of FIG. 6D, or in a separate process.

In order to achieve this attachment, the first macrocycle may have one or more protected functionalities that could be activated to form such surface associations, after one or more such associations using unprotected functionalities occurred with such residues. In addition, the patterning of a surface with such tubular structures, or even single macrocycles, could be space controlled by bulky protecting groups present at different positions of the outer shell of the tubular structures. These protecting-groups serve a similar function to the dendrons of the template polymers, as discussed above. The protecting groups may be removed after the surface association. The bulky protecting groups at the outer shell or a portion of them, should be understood in its broadest context, such as oligomers, polymers, dendrons, dendrimers, branched polymers, oligomers/polymers that are too thick to be threaded by the tubular structures, or alternatively their other tip/s are associated to a bulky group to prevent threading and

the surface (and not only by the threading surface associated template molecule) so its other tip will be far enough from any possible shorter added tubular structure that could also physically adsorb to the surface. This consideration is also relevant if the tubular structure that is wished to be added is 'long' – but adsorbing to the surface means they are lying horizontally – thus shorter than their 'full extent.' After the lengthening due to the association between the tubular structures, ultrasonication could remove physically adsorbed tubular structures.

In some cases, even if an inclusion complex is formed, or could be sustained for enough time in a solvent that enables the intended chemical reactions, a poly-rotaxane should still be formed so heating and/or stirring and/or ultrasonication could be performed so groups found at vicinal tubular structures could get closer and react in order to associate the vicinal tubular structures.

The methods that will be described in this section are also compatible with tubular structures comprising cyclodextrins that are associated to each other by ether and other linkages.

Referring to FIG. 8A, a surface associated template molecule81a is threading to provide a tubular structure88a associated via means 89 to the surface 80. First, if a bulky group 83a had been associated to the top end of the template molecule 81a then it is removed, yielding a functional group FG1.

Second, FG1 is reacted with functionality FG2 present in an introduced template molecule 81b. A lengthened surface associated template molecule 81c is obtained. The lengthening of the template molecule may be performed through any known mechanism, including click chemistry. The lengthened template molecule could now thread one or more tubular structures. This is illustrated in FIG. 8B, in which a tubular structure 88b is threaded onto template molecule 81c, and a bulky stopper 83b is associated to the end of the template molecule 81c.

For example, if a rotaxane/poly-rotaxane was formed by creating a bulky amide (bulky group 83a) at the tip of the template molecule, then the amide may be selectively cleaved under extreme basic conditions, or $LiAlH_4$, or addition of an amine (by carbonyl addition-elimination), or other processes. It should be noted that some bulky amides such as FMOC could be cleaved under milder conditions, such as tertiary amines. 2,4-di-nitro-benzene-amine could be selectively cleaved under extreme basic conditions. After the cleaving, the amine could be further reacted, to form a non bulky amide for example, to

It is possible to use in advance a long enough template molecule in order to form several iterations. However, since some inclusion complexes are formed within a certain range of molecular weights of the template molecules, it may be necessary to lengthen the template molecule itself from time to time. For example, aryl bromide will not react under conditions suitable for the reaction between an alcohol/phenol and an alkyl halide. It is possible to lengthen such an aryl bromide terminated template molecule, when it threads tubular structures that contain alcohols/phenols, and not alkyl halide, with a template molecule whose tip includes a derivative of aryl boronic acid and whose other tip is aryl bromide, using a Suzuki reaction (certain protocols of this reaction could occur under the presence of alcohols). It should be noted that due to the process of this reaction it is possible that the aryl bromide that is in the same molecule with the derivative of the boronic acid will not react during the coupling with the surface associated aryl bromide, thus the presented process could be repeated. Alternatively, it is possible to perform here an "AB cycle" as well, with template molecules terminated by 2 aryl boronic acids and another template molecule terminated by 2 aryl bromides.

If the template polymer was first lengthened after cleaving a bulky group protecting an amine, and the amine was reacted to lengthen the template molecule by forming amide functionality, then conditions should be selected such that the amide will not attack the alkyl halides. First the amide may be hindered inside a tubular structure and could not react. Second, only extremely strong bases could activate an amide, while some alcohols could be activated by much weaker bases, especially some carbohydrate alcohols.

The surface may contain Si-OH or M-OH (where M is a metal) groups. Such groups, especially in the presence of a base, may attack primary alkyl halides. However, the formed bond is labile, and could be cleaved easily using water or little acidic/basic water, without cleaving ethers for example formed during the association between tubular structures. Forming a protective monolayer on top of the oxide layer in advance could also be used to avoid this scenario. The protective monolayer may contain protected functional groups that may be activated in a future process.

Still another method may be employed to lengthen tubular structures in cases where a poly-rotaxane must be formed. The tubular structures are surface-associated, as in FIG. 7A, not only via the template molecule. The functional groups at both the surface associated tubular structures and the added tubular structures are primary alcohols. The

molecules associated to the shell with thinner linking molecules. These bulky molecules may be used as anchors inside the gap-filling-layers.

The template molecules inside the tubular structures (when present) could also be used to determine the properties of the tubular structures-gap-filling-layer interface. Specifically, the template molecules cause a reduction in flexibility, and physically form a barrier from within the tubular structures, so that the gap filling structure will not have any voids to penetrate and grow within.

The properties of the interface could be tuned by the selection of the shape of the ligands of an atom used in an ALD process. An ALD process could use different ligands to the same atom, and/or change from time to time during the process the selection of the ligands, to control the properties of the tubular structures-gap-filling-layer interface.

In some embodiments, an atom or a molecule or mixtures of such are first associated to the surface, to initiate the gap-filling-process while having more functionalities that can react with ALD/MLD precursors. In some embodiments, such molecules are dendrons associated to the surface by their stems, while their 'leaves' could react with ALD precursors. Such embodiments could reduce enveloping of the bottom part of the tubular structures during the gap-filling.

In some embodiments, functionalities at the outer shell of the tubular structures and/or a bulky stopper group and/or the template molecule are protected before the gap-filling-process. The cavity of the tubular structures could be protected by a template molecule optionally associated to the surface, optionally associated at one of its ends to a bulky group. In some cases, if a bulky group at the end of the threading template molecule reacts with ALD precursors, opened pores could still be obtained once the template molecule is released with a portion of the tubular structures.

Even though ALD is sometimes considered to be a particular case of Chemical Vapor Deposition ("CVD"), the term ALD should be understood in its broadest known definition, and to include processes that achieve ALD growth even in wet conditions and a combination of wet and dry conditions, and catalytic ALD.

Between and during ALD/MLD cycles, scavengers or etchants could be used to regenerate functionalities found at the outer shell of the tubular structures, to reduce the potential for burying the tubular structures during the gap filling process. This process may also be referred to as a “super cycle.” For example, suppose that, prior to the gap-filling process, each tubular structure includes one or more exposed alcohols at an outer

results, an area selective ALD was performed using TDMAT under the presence of a THP ether and other groups comprising the tubular structures.

By such deposition, the gap-filling-layer has no chemical bonds to the tubular structures, but they are nevertheless integrally trapped within it.

If the tubular structures are poly-rotaxanes (of macrocycles, dimers of macrocycles and/or trimers of macrocycles and so on), and only the bulky stopper contains a group that could react with ALD precursors, then ALD could still be used, since the template molecule will eventually be removed alongside the bulky stopper and optionally the top portion of the tubular structures well.

3. Functional Groups on Tubular Structures for ALD for Forming Bonds at the Surface

If there are functional groups for ALD at the part of the tubular structures that is near the surface, then creating the gap-filling-layer could be done with no blocking from above and with chemical bonds between the gap-filling-layer and the tubular structures. That method also enhances the tightness of the gap-filling-layer around the tubular structures.

One way to perform this is as follows: After there is an array of tubular structures (that have functional groups for ALD at their outer shell) on a surface, the surface could be deposited to form a layer with molecules that contain a protected group that could react with ALD once activated by a small, possibly nucleophile base (such a layer may be a multilayer formed in more than a single process). Then, by activating with a large base, possibly a non-nucleophile, and for an example an alkylating agent, the functional groups of the tubular structures that are higher than the surface and are not masked by the previously formed layer could become inert to ALD (the yield may not be 100% but high so few tubular structures will be covered from above). Then a small base could break the protecting group and expose functional groups to ALD at the surface and also unmask functional groups at the tubular structures near the surface.

In some embodiments, the tubular structures have a temporary thicker outer shell at the region near the part of surface association, for controlling their surface patterning. Specifically, the thicker outer shells may be shaped like dendrimers, to help ensure minimum spacing between adjacent tubular

area, electrostatic screening, anti-stick properties, antifouling properties, anti ice-forming properties, self cleaning, and others.

While, typically, passage of materials is from the "entrance" to the "exit" of the channel, where the entrance is at the tip and the exit is at the pore of the substrate, a reverse flow may also occur, such as in a process known as "backwashing."

Without limitation, the conditions at the different sides of the membranes that influence the passage through the membrane include: pressure differences, partial pressure differences, applying suction from one side and/or applying pressure from the other side, presence of sorbent/s at a side – chemical and/or physical, chemical reaction/s, including flare/s, temperature difference including a temperature low enough to liquefy/solidify a gas, and combinations thereof.

Without limitation, the devices of the present disclosure may be utilized for one or more of the following applications:

Sorption and Extraction. Some macrocycles have known abilities to sorb certain materials. Thus, membranes composed of them, using primarily suction from one side of the membrane, could potentially increase the content of the sorbed material in that side of the membrane. Examples include: cyclodextrins and noble gases, carcerand and argon, pillararene and carbon dioxide, and nanotubes of Calix[4]arenes and NOx gases.

Sometimes if two materials are smaller than a pore, the larger material will permeate superiorly through the membrane, given a mixture of the two materials.

Catalysis. If at least one product is smaller than all the reactants, its removal, possibly continuously, could shift the equilibrium of such catalysis. Examples include: $0.5N_2 + 1.5H_2 \Leftrightarrow NH_3$, $4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O$, $3H_2 + CO_2 \Leftrightarrow CH_3OH + H_2O$ and others. In other reactions, hydrogen is released from its carrier/s (possibly organic and liquid) or produced from reacting CO with steam. Exploiting that known phenomenon (the Le Chatelier Principle), it is possible to couple a membrane with suction from one side and/or applying pressure from the other side to a reactor, using catalysis for example, to separate/extract products from reactants in real time and to influence the equilibrium. This could save energy by enabling to form the catalysis at more moderate conditions and thus preserve better the catalyst/s. This could also simplify the separation required for the production.

It is possible to associate a catalyst to the opening of the tubular structures, and by suction/applying pressure/both to couple catalysis and separation.

stick/antifouling/anti ice-forming properties. In some embodiments some of the upper part of the tubular structures is associated with antibodies/macrocycles while the surface and/or some of the bottom part of the outer shell of the tubular structures were modified to have anti-stick/antifouling/anti ice-forming properties.

Tuning the density and flexibility/rigidity of the tubular structures with or without association with hydrophobic/super-hydrophobic/hyper-hydrophobic compounds could influence the anti-stick/antifouling/anti ice-forming properties. The presence of a gap-filling-layer could be one of the means used for such tuning. The gap-filling-layer can be used for other reasons, such as protection of the underlying surface, entrapping the tubular structures and more.

One particular example of interest is where a macrocycle is associated to the tip of a tubular structure with at least two external bridges on opposite or almost opposite sites. Such association could alter the macrocycle's selectivity comparing to other associations. In another example a macrocycle is used as a bridge between vicinal macrocycles of the tubular structures.

In some embodiments, sensors could be regenerated by cleaning with solvents, with or without heating/ultrasonicating.

A membrane could be utilized to become a sensor, by using pumps and pressure sensors. When keeping one side of the membrane in sub-pressure (once or continuously or from time to time), exposure to a material or materials that can permeate the membrane will increase the pressure on the other side, which could be detected by the pressure sensor. Regeneration of such a sensor could be done via suction and tuning the pressure to the initial sub-pressure. Further cleaning with solvents with or without heating/ultrasonicating may be necessary.

Where a macrocycle is associated to the tip of a tubular structure with at least two external bridges on opposite/almost opposite sites, whether if the device is a sensor, a membrane or both , the ability to 'doubly protect' the rest of the device – its surface or gap-filling-layer and the outer shell of the tubular structures to have anti-stick/antifouling/anti ice-forming properties by modifications – presents unprecedented protection.

In some embodiments, a partially formed device, made according to the methods of the present disclosure, may serve as a sensor. Such a partially formed device may

CLAIMS:

1. A filter configured to allow communication of substances from one side to another side, and configured to separate substances passing therethrough, comprising:

a mechanically stable porous substrate;

a solid material in contact with the porous substrate, the solid material defining a skin having at least one channel, each channel having at least one entrance at a surface of the skin and at least one exit at a pore of the porous substrate;

wherein the entrance of each channel has a diameter which is 3 nm or less, and

wherein the at least one channel is comprised of one or more tubular structures comprised of a stack of macrocycles having a first internal diameter which are coaxially associated and that are at least partially embedded within the solid material.

2. A filter formed from the filter of claim 1 following a process in which the one or more tubular structures have been decomposed, so that the at least one channel is comprised of the solid material, without any additional material encased therein.

3. The filter of claim 1, wherein the macrocycles are embedded in the solid material in a manner that excludes passage between the macrocycles and solid material of materials wider than the first internal diameter.

4. The filter of claim 1, wherein the solid material is adhered to each of the macrocycles in the tubular structure.

5. The filter of claim 4, wherein the solid material is adhered to each of the macrocycles embedded by the solid material in the tubular structure with a chemical link.

6. The filter of claim 1, wherein the one or more tubular structures are partially but not completely embedded within the solid material.

7. The filter of claim 1, wherein the macrocycles are comprised of cyclodextrins, calixarenes, pillararenes, porphyrins, crown ethers, helical molecules, cubril[n]s, cucubriturils, aspherands, kekulenes, cage molecules, metallic macrocycles, carbon nanotubes, or any combination thereof.

8. The filter of claim 1, wherein each macrocycle or tubular structure in the stack is bound to one or more adjacent macrocycles or tubular structures in the stack with the solid material and/or is linked to adjacent macrocycles or tubular structures in the stack with one or more molecular bridges.

9. The filter of claim 1, wherein a top portion of each channel comprises an asymmetric tubular structure, wherein the asymmetric tubular structure includes at least one macrocycle having a second internal diameter which is narrower than the first internal diameter.

10. The filter of claim 9, wherein the at least one macrocycle having a second internal diameter is at a tip of the asymmetric tubular structure, such that the tip comprises an entrance of the channel.

11. The filter of claim 10, wherein the skin extends to above a height of the tip molecule but does not encase the entrance of the channel.

12. The filter of claim 9, wherein the at least one macrocycle having a second internal diameter is within the asymmetric tubular structure but not at a tip thereof, such that the asymmetric tubular structure has an hourglass-like configuration.

13. The filter of claim 9, wherein the at least one macrocycle having a second molecular diameter is a crown ether.

14. The filter of claim9, further comprising at least one stopper molecule and elongated molecule attached to the at least one stopper and inserted within at least a top of an uppermost tubular structure in the at least one channel, such that a gap between the stopper molecule, elongated molecule, and the top of the uppermost tubular structure is a second internal diameter, wherein the second internal diameter is narrower than the first internal diameter and comprises an entrance to the channel.

15. The filter of claim 1, wherein the entrance of at least one channel is blocked due to at least one of the following:

a) a stopper molecule and elongated molecule attached to the at least one stopper and inserted within a top of an uppermost tubular structure in the channel;

b) an elongated molecule attached to the solid material or a tubular structure and inserted within a top of an uppermost tubular structure in the channel; and

c) deposition of solid material in a manner that buries the top of an uppermost tubular structure in the channel;

and wherein a passage between adjacent macrocycles at an outer shell of the at least one tubular structure defines a second internal diameter, wherein the second internal

diameter is narrower than the first internal diameter and comprises an entrance to the channel.

16. The filter of claim 1, further comprising at least one elongated molecule inserted within at least a top of an uppermost tubular structure in the channel and chemically associated to the uppermost tubular structure in the channel or to the solid material, such that the uppermost tubular structure and at least one elongated molecule define a second internal diameter, wherein the second internal diameter is narrower than the first internal diameter and comprises an entrance to the channel.

17. The filter of claim 1, wherein the skin encases a lower portion of the at least one tubular structure and does not encase an upper portion of the at least one tubular structure; wherein the lower portion of the at least one tubular structure comprises macrocycles that are associated with each other in a manner that preserves gaps that are greater than a size of an entrance to the channel; and wherein the upper portion of each tubular structure comprises macrocycles that are associated with each other in a manner that reduces gaps between adjacent macrocycles to below the size of the entrance to the channel.

18. The filter of claim 1, wherein the solid material embeds the at least one tubular structure without being adhered thereto in a chemical link.

19. The filter of claim 1, wherein the solid material is adhered to the at least one tubular structure with at least one chemical link.

20. The filter of claim 1, wherein the at least one tubular structure further comprises one or more anti-sticking functional groups on an exterior face thereof.

21. The filter of claim 1, wherein the at least one channel extends from the entrance thereof to the exit thereof at a pore of the porous substrate, in a substantially uniform width.

22. The filter of claim 1, wherein the at least one channel comprises a narrower portion adjacent to the pore of the porous substrate.

23. The filter of claim 1, wherein at least a portion of the solid material is deposited via atomic layer deposition.

24. The filter of claim 23, wherein the solid material deposited via atomic layer deposition is one or more of titanium dioxide, silicon dioxide, aluminum oxide, or silicon nitride.

25. The filter of claim 1, wherein at least a portion of the solid material is deposited via molecular layer deposition.

26. A filter configured to allow communication of substances from one side to another side, and configured to separate substances passing therethrough, comprising:

a mechanically stable porous substrate;

a solid material in contact with the porous substrate, the solid material defining a skin having at least one channel, each channel having at least one entrance at a surface of the skin and at least one exit at a pore of the porous substrate;

wherein the entrance of each channel has a diameter which is 3 nm or less, wherein the at least one channel is comprised of the solid material, with one or more tubular structures comprised of macrocycles overlaid on the solid material.

27. The filter of claim 26, further comprising at least one stopper molecule and elongated molecule attached to the at least one stopper and inserted within at least a top of an uppermost tubular structure in the at least one channel, such that a gap between the stopper molecule, elongated molecule, and the top of the uppermost tubular structure is a second internal diameter, wherein the second internal diameter is narrower than the first internal diameter and comprises an entrance to the channel.

28. The filter of claim 26, wherein the entrance of at least one channel is blocked due to at least one of the following:

a) a stopper molecule and elongated molecule attached to the at least one stopper and inserted within a top of an uppermost tubular structure in the channel;

b) an elongated molecule attached to the solid material and inserted within a top of an uppermost tubular structure in the channel; and

c) deposition of solid material in a manner that buries the top of an uppermost tubular structure in the channel;

and wherein a passage between adjacent macrocycles at an outer shell of the at least one tubular structure defines a second internal diameter, wherein the second internal diameter is narrower than the first internal diameter and comprises an entrance to the channel.

29. The filter of claim 26, wherein the at least one channel extends from the entrance thereof to the exit thereof at a pore of the porous substrate, in a substantially uniform width.

30. The filter of claim 26, wherein the at least one channel comprises a narrower portion adjacent to the pore of the porous substrate.

31. The filter of claim 26, wherein at least a portion of the solid material is deposited via atomic layer deposition.

32. The filter of claim 26, wherein the solid material deposited via atomic layer deposition is one or more of titanium dioxide, silicon dioxide, aluminum oxide, or silicon nitride.

33. The filter of claim 26, wherein at least a portion of the solid material is deposited via molecular layer deposition.

34.A filter configured to allow communication of substances from one side to another side, and configured to separate substances passing therethrough, comprising:

a mechanically stable porous substrate;

a solid material in contact with the porous substrate, the solid material defining a skin having at least two pores;

wherein the diameter of each pore in the skin is less than 4.5 angstroms.

35. The filter of claim 34, wherein each pore in the skin has a substantially uniform diameter.

36. A nanoporous surface having at least two nanopores having different pore diameters, wherein at least the entrance of at least one pore is blocked due to at least one of the following:

a) an elongated molecule is inserted within at least the top of at least one pore, said elongated molecule having a tip attached to the nanoporous surface and/or a stopper;

b) a stopper is placed in proximity to the top of at least one pore; and

c) a solid material is deposited in a manner that buries at least the top of at least one pore.

37. A device formed from the following process:

attaching to a surface a plurality of structures, said structures comprising tubular structures, stacks of macrocycles, dendrons, dendrimers, rigid or semi-rigid sufficiently perpendicular molecules, or stretched flexible molecules;

performing a gap-filling process with solid material between the plurality of structures; and

decomposing the plurality of structures, leaving the solid material without any additional material encased therein.

38. A method of manufacturing a filter, comprising:

building at least one tubular structure over at least one pore of a porous substrate that is filled with a sacrificial pore-filling material, each tubular structure comprised of a coaxial stack of associated macrocycles;

filling gaps between tubular structures with a solid gap-filling material;

and removing the sacrificial pore-filling material from the pores of the porous substrate;

to thereby generate at least one channel in which the solid material defines a skin, an entrance of each channel is at a surface of the skin and an exit of each channel is at a pore of the porous substrate;

wherein the entrance of each channel has a diameter which is 3 nanometers or less.

39. The method of claim 38, further comprising, prior to the building step, filling the pores of the porous substrate with the pore-filling sacrificial material.

40. The method of claim 39, further comprising, prior to the step of filling the pores, layering a sacrificial layering material over the porous substrate, wherein the sacrificial layering material is configured to form associations with both the sacrificial pore-filling material and with the porous substrate, wherein the step of filling pores comprises adhering the pore-filling material to the sacrificial layering material, and further comprising, following the step of filling pores, selectively etching the sacrificial layering material to thereby leave the porous substrate with pores filled with the pore-filling material.

41. The method of claim 40, wherein the porous substrate is a high surface area ceramic material.

42. The method of claim 40, wherein the porous substrate is anodized aluminum oxide, the sacrificial pore-filling material is gold, and the sacrificial layering material is silver.

43. The method of claim 38, further comprising, prior to the building step, selecting a substrate comprised of a sacrificial layering material; depositing a porous layer on the sacrificial substrate; and filling pores of the porous layer with the pore-filling

sacrificial material, to thereby adhere the pore-filling material to the sacrificial layering material, and selectively etching the sacrificial substrate.

44. The method of claim 43, wherein the porous substrate is a high surface area material and/or a ceramic.

45. The method of claim 38, wherein the macrocycles are comprised of cyclodextrins, calixarenes, pillararenes, porphyrins, crown ethers, helical molecules, cubril[n]s, cucubriturils, aspherands, kekulenes, cage molecules, metallic macrocycles, carbon nanotubes, or any combination thereof.

46. The method of claim 38, wherein a molecular orientation of adjacent macrocycles comprises one or more of: wide-wide associations, narrow-narrow associations, and wide-narrow associations.

47. The method of claim 38, wherein the building step comprises:

patterning a template molecule on the sacrificial pore-filling material;

and threading at least a portion of at least one tubular structure around the template molecule.

48. The method of claim 47, wherein the step of patterning a template molecule comprises:

attaching a precursor molecule to the sacrificial pore-filling material, the precursor molecule formed of an X-Y-Z structure, wherein the Z functional group is configured to bond with the pore-filling material, and the X-Y bond is cleavable; and

cleaving the X-Y bond.

49. The method of claim 48, further comprising, following cleaving of the X-Y bond, bonding the template molecule to the Y group.

50. The method of claim 48, wherein X is any type of branched polymer.

51. The method of claim 48, further comprising, following the step of filling gaps, lengthening the template molecule, and threading at least one additional macrocycle or tubular structure onto the lengthened template molecule.

52. The method of claim 51, wherein the step of lengthening the template molecule is performed with click chemistry.

53. The method of claim 38, further comprising: threading a template molecule attached to a bulky stopper into an entrance of the at least one channel, to thereby define a passage into the at least one channel based on dimensions of the entrance, of the bulky

stopper, and of a portion of the template molecule near the entrance of the at least one channel; or

chemically associating at least one elongated molecule to the uppermost tubular structure of the at least one channel or to the solid material and inserting the at least one elongated molecule into a top portion of an uppermost tubular structure of the at least one channel.

54. The method of claim 38, further comprising blocking the entrance of the at least one channel due to at least one of the following:

a) inserting a stopper molecule and elongated molecule attached to the at least one stopper within a top of an uppermost tubular structure in the channel;

b) inserting an elongated molecule attached to the solid material or a tubular structure within a top of an uppermost tubular structure in the channel; and

c) depositing solid material in a manner that buries the top of an uppermost tubular structure in the channel.

55. The method of claim 38, further comprising forming the tubular structures prior to the building step by forming molecular bridges between macrocycles in solution, wherein the step of forming molecular bridges optionally includes utilizing an inclusion complex with a template molecule.

56. The method of claim 55, wherein the tubular structures formed in solution are asymmetric tubular structures, said asymmetric tubular structures comprising of a coaxial stack of associated macrocycles having a substantially identical internal diameter, and a macrocycle having a second internal diameter, said second internal diameter being narrower than the first internal diameter of the macrocycles of the coaxial stack.

57. The method of claim 56, wherein the bridges between macrocycles that are adjacent to the tip molecule reduce a gap between said macrocycles to less than the second internal diameter.

58. The method of claim 38, wherein the building step comprises patterning the at least one tubular structure directly onto the at least one pore.

59. The method of claim 58, wherein the patterning step comprises patterning tubular structures having contained therein at least one template molecule that is associated to at least one bulky stopper.

60. The method of claim 59, wherein the at least one bulky stopper is chemically linked to the at least one tubular structure.

61. The method of claim 38, wherein the filling step comprises performing atomic layer deposition (ALD).

62. The method of claim 38, wherein the solid gap-filling material is one or more of titanium dioxide, silicon dioxide, aluminum oxide or silicon nitride.

63. The method of claim 61, further comprising, prior to the ALD, attaching precursor molecules to the tubular structures, such that the gap-filling material is directly linked to the tubular structures.

64. The method of claim 61, further comprising, prior to the ALD, attaching protecting groups to the tubular structures, such that the gap-filling material does not adhere to at least some parts of the tubular structures.

65. The method of claim 61, further comprising, during the ALD process, using scavengers or etchants to regenerate functionalities found at the outer shell of the tubular structures in a super cycle process.

66. The method of claim 61, wherein the filling step comprises performing molecular layer deposition.

67. The method of claim 38, further comprising sequentially lengthening the tubular structures after the filling step, and repeating the filling step with respect to the lengthened tubular structures.

68. The method of claim 67, further comprising, after the step of filling gaps, decomposing the tubular structures, to thereby, following the step of removing the sacrificial pore-filling material, obtain channels having a skin formed solely of the solid material.

69. A method of manufacturing a filter, comprising:

selecting a sacrificial substrate, said sacrificial substrate capable of attachment to organic compounds;

attaching a template molecule to the sacrificial substrate;

building at least one channel onto the sacrificial substrate, each channel comprised of one or more tubular structures comprised of a coaxial stack of associated macrocycles;

filling gaps between the tubular structures by adhering a solid gap-filling material to the sacrificial substrate;

attaching a porous substrate to one of the open ends of the tubular structures or the filler material; and

removing the sacrificial substrate and template molecule.

70. The method of claim 69, further comprising lengthening the channels by attaching additional tubular structures to the ends of the channels that had previously been associated with the sacrificial substrate.

71. A method of forming a tubular structure comprised of macrocycles connected by molecular bridges in solution, comprising:

optionally, modifying at least one functional group of two or more macrocycles; and

forming at least one molecular bridge between said macrocycles by associating the macrocycles at the modified functional groups, wherein the step of forming molecular bridges includes utilizing an inclusion complex with a template molecule.

72. A method for lengthening at least one coaxial stack of macrocycles arranged in a planar array of a surface comprising said coaxial stacks, comprising: forming an inclusion complex between: a template molecule, the coaxial stack of said array and a tubular structure comprising stacked coaxial macrocycles; associating the coaxial stack of said array and the said tubular structure; and removing the template molecule.

73. A method of filtering a mixture of two or more substances, comprising:

exposing the mixture of substances through a filter of claim 1, wherein at least one of the substances is smaller sized, such that it is configured to pass through the channel, and at least a second of the substances is larger sized, such that it is unable to pass through the channel; and

passing at least one molecule of the at least one smaller sized substance through the filter.

74. The method of claim 73, wherein the mixture is under a chemical equilibrium.

75. The method of claim 73, wherein the mixture is in contact with a catalyst.

76. The method of claim 73, wherein the filter is the filter of claim 1, and the method further comprises passing at least one atom or molecule of the at least one smaller sized substance through the interior of the macrocycles, while blocking passage of the at least one atom or molecule of the at least one smaller sized substance through gaps between the macrocycles and the solid material.