

# Chapter 2

## Hydrogen Bonding in Supramolecular Nanoporous Materials

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**Abstract** This chapter provides an overview of the use of hydrogen bonds for the construction of nanoporous materials. These materials attract a great deal of interest because of their large surface area to volume ratio and their applications in areas such as filtration, separation, adsorption, catalysis, and ion conduction. Organic materials are especially appealing for these applications, because their properties can be tailored. The use of supramolecular interactions is required to control the organization of materials at the molecular level. Hydrogen bonds are ideal supramolecular interactions for the construction of these nanoporous materials, thanks to their directionality and reversibility. The directionality causes the positioning molecules in such a way that voids have been created in between the molecules, such as in two- and three-dimensional hydrogen bonded organic frameworks. In a second approach, hydrogen bonded template molecules have been removed from a polymer to create pores. This method is successfully applied to hydrogen bonded block copolymers and liquid crystalline polymers.

### 2.1 Introduction

Nanoporous materials are frameworks with a porous structure. The size of these nanopores is generally 100 nm or smaller. According to IUPAC (International Union of Pure and Applied Chemistry), the following subdivisions in pore size [1] can be made: macroporous: 50 nm–1  $\mu\text{m}$ , mesoporous: 2–50 nm, and microporous: less than 2 nm. Nanoporous materials attract a great deal of interest [2–10] because

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of their large surface area to volume ratio and their applications in areas such as filtration, separation, catalysis, ion conduction, and drug delivery. The small pore size in these materials makes discrimination between molecules and ions based on size and shape possible. The confined environment within the material can also be used to enhance chemical reactions or to make them product selective. The pore size can be tailored to slow down the passage of molecules, which makes these materials suitable for controlled drug delivery [11].

Inspired by biological cell membranes, chemical engineers have fabricated almost all kinds of nanoporous materials. Inorganic materials such as silica [8], zeolites [9], and metals [10] have been used as porous materials because of their long-term stability. However, it is generally hard to tailor their properties. Organic materials are much easier to modify and tune for specific applications. Polymers are widely used as nanoporous materials thanks to their easy processability into a variety of geometries [12]. Top-down, bottom-up, and combined approaches have been used to make porous hierarchical structures. Various strategies are used to reduce the pore size toward the nanometer level, which is the size of small molecules and ions. The use of supramolecular interactions is often required to control the organization of materials at the molecular level.

Supramolecular noncovalent interactions [13], such as metal coordination, hydrogen bonding, hydrophobic forces, van der Waals forces, pi-pi interactions, and electrostatic interactions, are very appealing for the self-assembly of molecules, and they could be used to create nanostructured materials. Metal coordination, for instance in metal organic frameworks (MOFs) [14] or coordination polymers [15], has been applied to construct nanoporous supramolecular networks.

Hydrogen bonds (H-bonds) are ideal noncovalent interactions to construct supramolecular nanoporous architectures since they are highly selective and directional [16]. H-bonds are formed when a donor with an available acidic hydrogen atom interacts with an acceptor that carries available nonbonding electron lone pairs. The strength of the H-bond depends mainly on the solvent and number and sequence of the H-bond donors and acceptors. Various supramolecular polymer materials have been developed which use H-bonds as structural element to position molecules. After removal of these molecular templates, a porous material is obtained to fabricate molecule specific systems.

This chapter provides an overview of the use of H-bonds for the construction of nanoporous materials. Systems are discussed where the formation of H-bonds directly induces porosity and approaches are presented where the rupture of H-bonds leads to porous materials. First, we describe the use of small molecules capable of forming H-bonds, which directly induces porosity in 2D and 3D H-bonded networks. Next, block copolymers are discussed which self-assemble in nanostructured materials. The removal of H-bonded template molecules leads to porous polymer materials. Finally, H-bonded polymerizable liquid crystals having even smaller pores are discussed. Molecular imprinted polymers that do not contain pores are beyond the scope of this chapter.

## 2.2 Supramolecular Hydrogen Bonded Nanoporous Frameworks

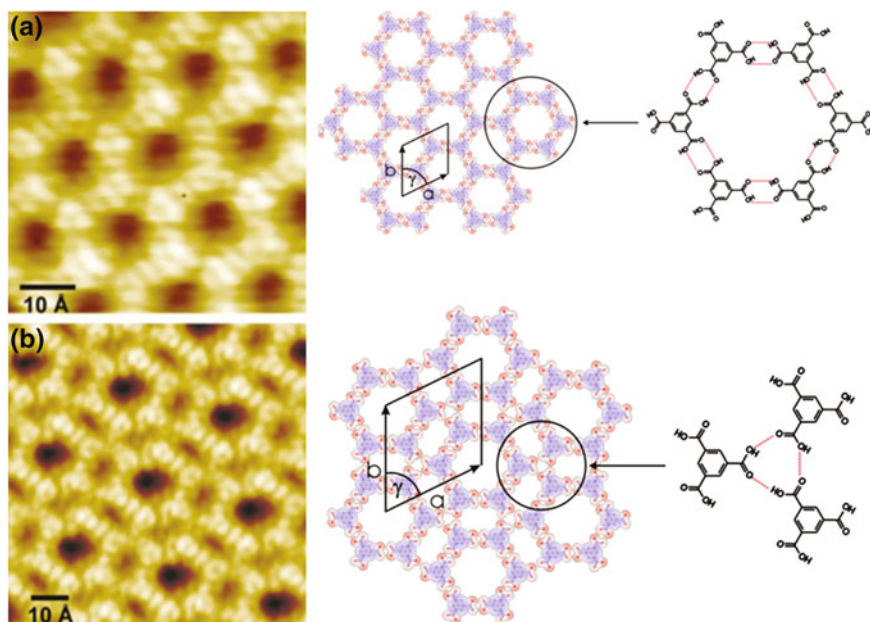
Small molecules capable of forming H-bonds can self-assemble in porous networks [17–19]. Here the porous morphology that is obtained is directed by the H-bonding units present in the molecule. Two-dimensional H-bonded nanoporous networks have been obtained at surfaces and mostly visualized by scanning tunneling microscopy (STM). Three-dimensional H-bonded nanoporous networks have also been fabricated and analyzed.

### 2.2.1 Two-dimensional Hydrogen Bonded Nanoporous Networks

A pioneering example of a nanoporous self-assembled network is based on H-bonding interactions between trimesic acid (TMA, 1,3,5-benzenetricarboxylic acid) building blocks [20]. Porous networks are formed through dimerization of the carboxylic acid groups. The planar structure of the molecule and the positioning of the three functional groups results in the formation of a 2D network. Primarily two networks are found which are referred to as the “honeycomb” and the “flower” structures (Fig. 2.1). In the honeycomb structure, each pore is surrounded by six TMA molecules which are all connected via double H-bonding interaction between the carboxylic acids. The pore diameter in this structure is 15 Å. In the flower structure, the TMA molecules are arranged in similar sixfold rings, but these rings are more closely packed. This is in contrast to the honeycomb structure, where one of the carboxylic acid groups of each TMA molecule actively participates in the hydrogen bonding seam of a neighboring ring of the network. They serve here as a bridge to two neighboring rings via a three-point interaction with two adjacent carboxylic acid groups. The flower structure results in a network with pore diameters of 15 and 7.5 Å.

Simple modifications in a molecule, which is encoded to form a network by H-bond interactions, can afford a certain degree of control over the resulting pore size. Longer derivatives of TMA, such as 1,3,5-tris(10-carboxydecyloxy)-benzene (TCDB), can form extended networks [21]. This molecule, which has three long aliphatic C10-spacers between the core and the hydrogen bonding functionalities, forms a pseudo-rectangular network. Two carboxylic acid groups of each molecule form H-bonds with a neighboring molecule to form a pore, whereas the third carboxylic acid dimerizes via H-bonds with the carboxylic acid of a more distant TCDB molecule. Tetragonal cavities were formed with a pore dimension of 23 Å × 13 Å.

H-bonding interactions are also suitable for assembling multi-component networks. In an illustrative example, melamine [17, 22], a H-bonded molecule with threefold symmetry, was assembled together with perylene tetracarboxylic diimide (PTCDI) [23]. These molecules interact strongly via complementary triple H-bonds. A hexagonal network with pores that have a size of approximately 2 nm were



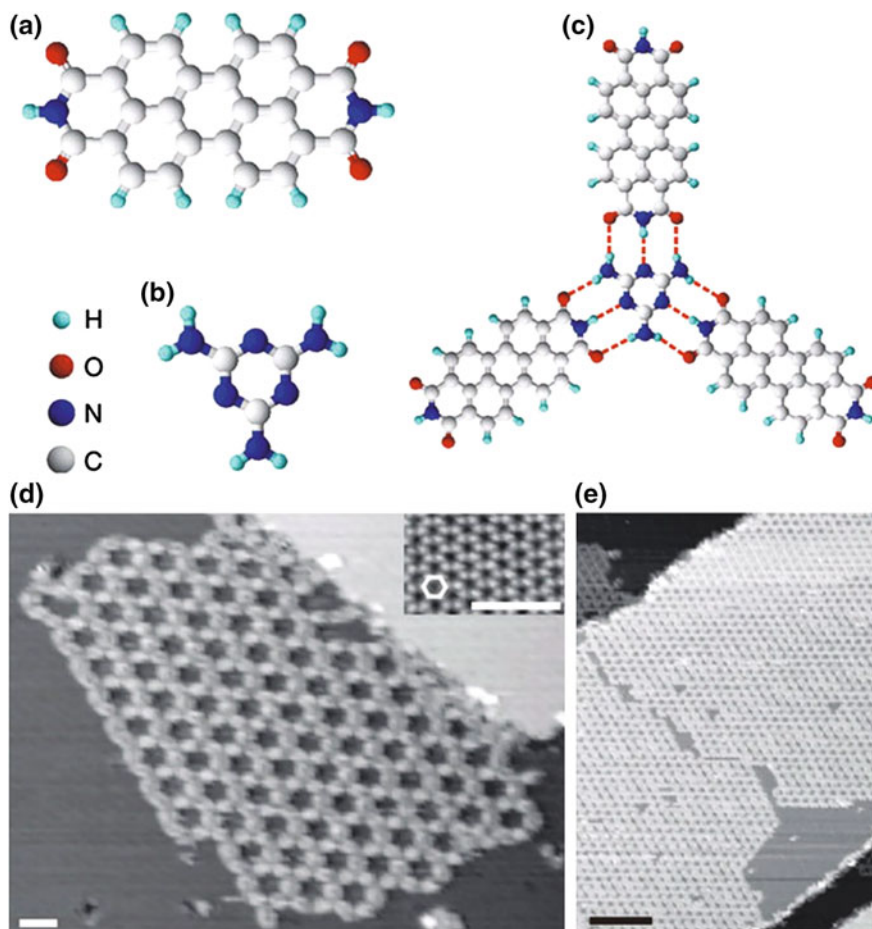
**Fig. 2.1** Ultra-high-vacuum STM image and the molecular model of the honeycomb structure (a) and the flower structure (b) formed by H-bonded TMA molecules on a graphite substrate. Adapted from Ref. [20] by permission of John Wiley & Sons Ltd

formed, in which the melamine molecules served as the junctions and the PTCDI molecules as the sides (Fig. 2.2) [23].

The small complementary molecular building blocks used are relatively easy to synthesize. These nanoporous surfaces could be used to immobilize and host a large variety of guest species [23, 24]. These research activities, however, have revealed a number of important aspects of monolayer formation, such as the role of concentration, surface coverage control, self-recognition, and self-selection [17]. Although directional supramolecular interactions, such as H-bonding, have proven to be quite predictable, other factors that play a role in the formation of the self-assemblies, such as entropy and the influence of surface, are less understood and difficult to control.

### 2.2.2 Three-dimensional Hydrogen Bonded Molecular Nanoporous Networks

Strong directional interactions, such as H-bonds, can be used to create porous 3D networks with a significant capacity for inclusions [25, 26]. Most molecules form crystals that are considered to be closely packed, with no capacity to include guests. The small residual spaces between molecules generally remained unfilled.

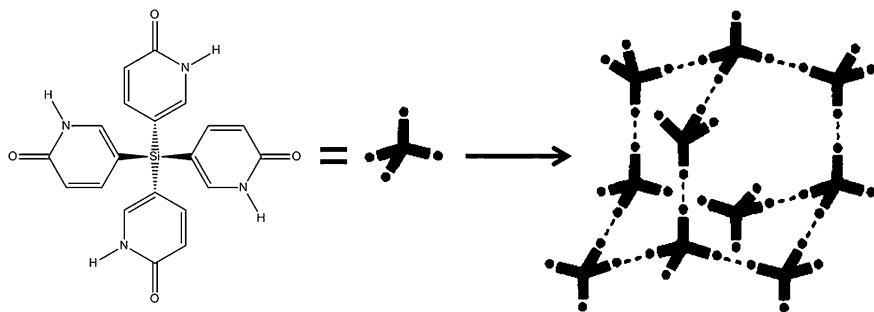


**Fig. 2.2** Example of a multi-component network of PTCDI (a) and melamine (b). c Melamine serves as the junctions between the sides of PTCDI. d STM of this H-bonded network, scale bar 3 nm. e STM image of large-area network, scale bar 20 nm. Adapted by permission from Macmillan Publishers Ltd: Ref. [23], copyright 2003

These unoccupied spaces typically add up to about 30 % of the total volume of the crystals, although none of these voids would accommodate a probe sphere 2.4 Å in diameter, which is roughly the size of a water molecule.

H-bonds have been used to pack molecules in such a way that larger voids are formed. A good example can be seen in crystals of tetrapyridinone having H-bonding units in 3D (Fig. 2.3) [27]. In these crystals, 60 % of the volume is accessible to guests, while no voids are observed in crystals of the close structural analogue, which lacks the crucial ability to form strong directional intermolecular interactions.

The 2,4-diaminotriazinyl (DAT), which was pioneered by Wuest et al. [25, 28], is a very powerful hydrogen bonding motif for the construction of porous robust



**Fig. 2.3** This molecule forms a porous 3D network induced by the directionality of the H-bonds. Adapted with the permission from Ref. [27]. Copyright 1994 American Chemical Society

networks. An H-bonded organic framework (HOFs) from a homochiral backbone which is connected to DAT motifs [29] was fabricated. The chiral porous nature allows enantioselective separation of small molecules. They exhibit separation of racemic secondary alcohols with up to 92 % selectivity. In particular, aromatic alcohols reached high separation values: X-ray studies revealed that the framework encapsulates exclusively right-handed chiral isomers. The specific recognition can be attributed to the combination of the confinement of the chiral pockets and the directionality of H-bonds between the framework and the alcohol guest molecules.

HOFs have some advantages and disadvantages compared to other nanoporous materials, such as zeolites and MOFs [25]. The most important advantages are: solution processability and characterization, easy purification, straightforward regeneration, and reuse by simple recrystallization. The H-bonds are weaker interactions compared to the covalent bonds in zeolites, resulting in less robust materials. On the other hand, the molecular networks combine a certain robustness with plasticity which is better suited to make materials that can adapt to guests and include them with high selectivity. Some porous HOFs might be implemented in industrial and/or pharmaceutical applications such as enantioselective separation [29]. It is anticipated that the emerging HOF chemistry will prosper and more functional porous HOF materials will be targeted for their applications in gas storage, separation, sensing, and heterogeneous catalysis in the near future [26, 30]. HOFs offer crystal engineers a very powerful tool to control pore sizes and will continue to be a source of new crystalline materials with tunable structural features and properties.

### 2.3 Hydrogen Bonding in Block Copolymers as Nanoporous Networks

Polymers are commonly used as porous materials due to their relatively easy processability into a variety of geometries. Much effort has been taken into controlling the structure of various porous polymers. This can be achieved with

different top-down techniques, such as photolithography, photoembossing, and inkjet printing. To control the structure at the nanometer level, bottom-up approaches are appealing. Supramolecular interactions, such as H-bonds, are a powerful tool that can be used to fabricate functional nanoporous materials. Often, these H-bonds in polymers do not directly induce porosity, which is the case for the small H-bonding molecules described above. Mostly, the pore structures are created after breaking the H-bonds between the polymer and template moieties and subsequent removal of the templates.

Covalently connecting incompatible polymers at their ends leads to self-assembled nanostructured materials [31, 32]. It is well-known that block copolymers, depending on the number of blocks, their chain length, and flexibility, volume fraction and the extent of repulsion between the covalently connected blocks, self-assemble into a variety of structures. A number of morphologies have been identified; spherical, cylindrical, gyroid, lamellar, as well as more complicated structures (Fig. 2.4) [33]. Nanopores can be created by removing of one of these blocks. The different morphologies result in a variety of pore shapes and sizes ranging from 3 to 50 nm.

One of the first examples of a nanoporous polymer made from an ordered block copolymer was reported in 1988 by Lee et al. [34]. In recent decades a number of strategies to remove the minor phase have been published [12]. This is mainly done by degradation of one of the blocks or cleavage of the block junction. Those strategies generally require the use of harsh conditions such as etching [35–37], ozonolysis [38, 39], hydrolysis [40], or depolymerization [41]. One appealing approach is the use of noncovalent H-bonds, which can be broken easily under mild conditions.

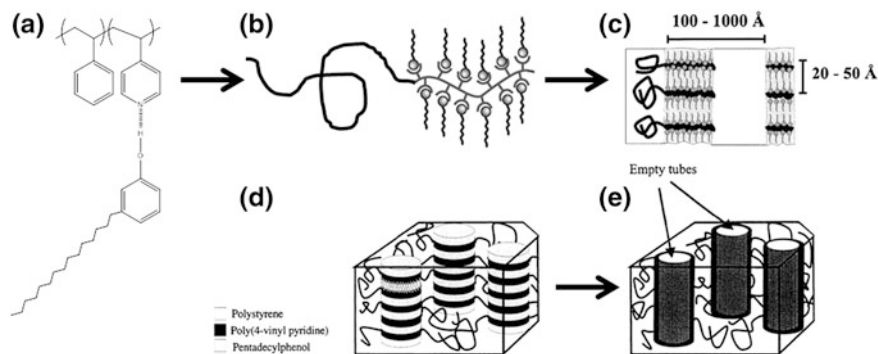
To use H-bonding in the formation of nanostructured materials, the concept of recognition is used [42]. Two molecules with molecularly matching complementary interactions are able to shape recognize each other. For example, the H-bonding interaction between pyridine and phenol has been used. The phenol acts as the H-bond donor and the pyridine acts as the H-bond acceptor.

Combining recognition with the self-assembly of block copolymers have been used to create hierarchical porous structures. Using the above-mentioned recognition between pyridines and phenols, a block copolymer has been constructed by a poly(4-vinylpyridine) (P4VP) polystyrene (PS) block copolymer (Fig. 2.5) [43]. PS was used for the glassy rigid state while the P4VP block forms H-bonding



**Fig. 2.4** Different morphologies of block copolymers. From *left to right* an increasing fraction of the *blue block*, resulting in *spherical, cylindrical, gyroid, lamellar, and the inverse structures*, respectively. Adapted with the permission from Ref. [33]. Copyright 2010 American Chemical Society





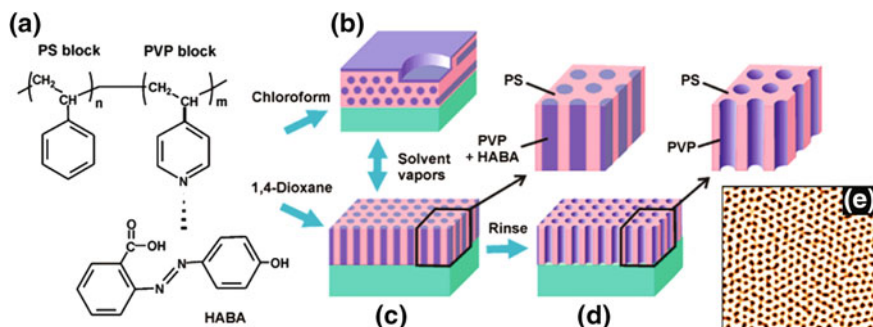
**Fig. 2.5** **a** H-bonded supramolecule obtained by H-bond recognition of pentadecylphenol and PS-P4VP block copolymer. **b** Schematic representation of the supramolecule which self-assembles **(c)** in nanostructured materials **(d)**. **e** Nanopores are obtained by breaking the H-bonding interactions, under mild conditions, resulting in a cylindrical structure. Adapted from Ref. [43] by permission of John Wiley & Sons Ltd

interactions with stoichiometric amounts of pentadecylphenol (PDP), resulting in a comb coil diblock copolymer. This block copolymer was capable of forming a cylindrical morphology in a glassy rigid PS matrix, where the P4VP-PDP blocks were organized in a lamellar phase within the cylinders. The PDP was removed in a simple mild washing step in methanol, resulting in hollow cylinders with P4VP brushes on the interior walls. The cylinders have a diameter of several nanometers and a relatively high macroscopic order. This concept permits generalization and tailoring, and such “hairy tubes” open the possibilities for controllable nanoporous materials, as the conformation of the brushes depends on the solvent.

Pyridine moieties can also have H-bonding interactions with other H-bond donors to create nanostructured materials, as shown by Stamm et al. [44]. Well-ordered nanostructured thin polymer films from the supramolecular assemblies of PS-P4VP and 2-(4'-hydroxybenzeneazo)benzoic acid (HABA) have been fabricated (Fig. 2.6) [44]. This assembly formed cylindrical P4VP-HABA nanodomains surrounded by the PS matrix.

For many applications, the orientation of pores is important. For instance, for membranes a perpendicular pore orientation through the materials is desired. Normally, the orientation of the cylinders can be controlled by the surface composition or by applying external stimuli, such as an electrical field or a shear flow. In the case of HABA-P4VP assemblies, the alignment of the domains has been shown to switch upon exposure to vapors of different solvents from the parallel to perpendicular orientation to the confining surface and vice versa. The alignment of the cylindrical nanodomains was insensitive to the composition of the confining surface thanks to the self-adaptive behavior of the supramolecular P4VP-HABA assembly. Re-alignment in different solvents was a relatively fast process; it only took tens of minutes.





**Fig. 2.6** Illustration of the nanotemplate fabrication approach based on the H-bonded block copolymer columnar assembly (a). The columnar alignment can be switched by different solvent vapors, chloroform (b) and 1,4-dioxane (c). H-bonded HABA is removed by washing with methanol (d) resulting in a porous network. **e** AFM image of the 1,4-dioxane vapor exposed, dried, and washed film, lateral scale 500 nm  $\times$  500 nm. Adapted with the permission from Ref. [44]. Copyright 2003 American Chemical Society

HABA molecules were selectively and completely extracted with a selective solvent, such as methanol, resulting in nanoporous membranes with a hexagonal lattice (24 nm in the period) of hollow channels of 8 nm in the diameter crossing the membrane from the top to the bottom. The walls of the channels were again constituted from reactive P4VP chains.

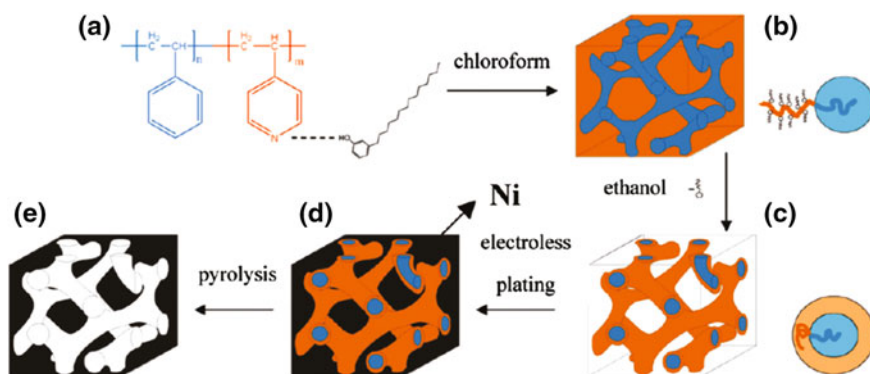
The need to orientate the pores can also be circumvented by a gyroid morphology (Fig. 2.4). In this structure, the pore orientation is continuous in three directions and alignment is no longer an issue. These continuous morphologies have been reported for triblock copolymers, for example, poly(*tert*-butoxystyrene)-*block*-PS-*block*-P4VP [45]. To generate the most unfavorable interactions between the different blocks less than stoichiometric amounts of PDP were used to form H-bonds with the P4VP block. A self-assembled core-shell gyroid morphology was formed. After removing PDP well-ordered nanoporous films with continuous pores were obtained.

The pore chemistry is important as well. The most reported porous polymer systems are based on P4VP-PS [42–44], which results in a pyridine pore interior. Other block copolymer systems were used to create pores with a different surface chemistry. Poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) copolymers were used to create an anionic pore interior [46]. Blends were made with this block copolymer and a poly(ethylene oxide) (PEO) homo polymer. Generally, polymers with different repeating units do not mix well. But, the ether groups in PEO forms H-bonds with the carboxylic acid groups in PAA block. The presence of these H-bonds is interesting because it enhances the miscibility of those blends. With appropriate amounts of PEO the block copolymer phase separated into a cylindrical morphology constituted of PAA-PEO cylinders in a PS matrix. If more PEO was added, a lamellar morphology was found. However, when PEO was removed the polymer layers collapsed or fell apart since the layers were no longer connected. PEO was removed with a slightly alkaline mixture of methanol and water. The carboxylic

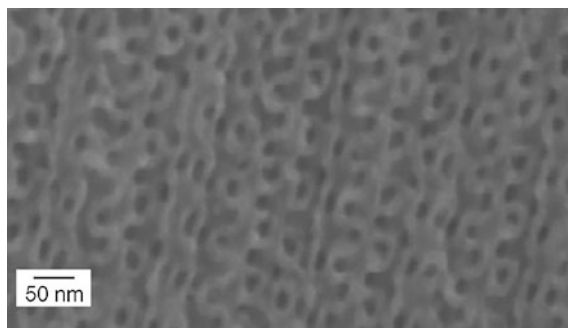
acid moieties transformed into deprotonated carboxylate units and hence disrupt the H-bonds. This resulted in cylinders with a diameter of 13 nm and an anionic carboxylate interior.

Nanoporous materials based on hydrogen bonded block copolymers could be used in various application such as separation, filtration, ion exchange, catalysis, and sensors [47]. Ten Brinke, Loos et al. successfully applied nanoporous materials based on hydrogen bonded block copolymers as a template for the fabrication of highly porous metal foams [44–46, 48]. These foams combine the properties of porous polymer materials with those of metals and might be used in applications such as high-power density batteries, catalysts, or hydrogen storage materials. A PS-P4VP-(PDP) block copolymer was used to self-assemble into a bicontinuous gyroid morphology. The block lengths were chosen in such a way that the channels consisted of PS in a P4VP(PDP) matrix. After dissolving the PDP, the P4VP collapsed onto the PS struts and a free-standing bicontinuous gyroid template of interconnected, uniformly sized pores was formed (Fig. 2.7) [48]. The hydrophilic P4VP corona facilitated the penetration of water-based plating reagents into the porous template and enabled successful metal deposition. After plating, the polymer is simply degraded by heating, resulting in a well-ordered inverse gyroid nickel foam (Fig. 2.8) [48]. It is essential in this approach to remove the H-bonded part of the matrix, PDP. This is why the template accounts for 50 % v/v or more. The porosity characteristics—amount, size of pores—can be tuned by selecting the appropriate copolymer and by adjusting the amount of hydrogen bonded PDP.

In the above-mentioned strategies H-bonded side groups or polymers are removed to induce porosity. However, others strategies were also developed to create porous structures. In one strategy, the network is made by using a phenolic resin in combination with an H-bonding block copolymer. This procedure was

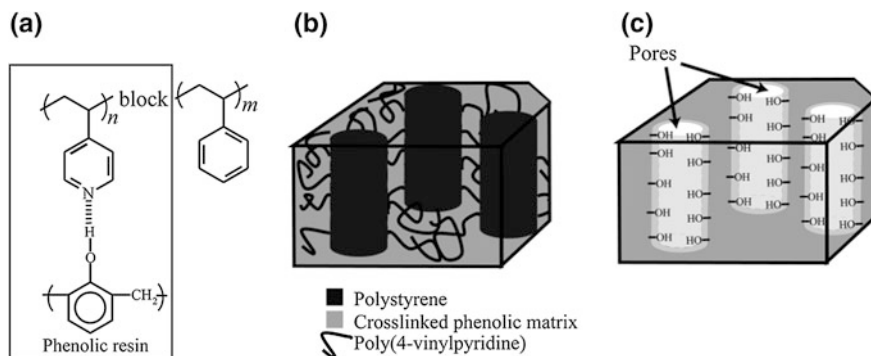


**Fig. 2.7** Schematic representation of the preparation of gyroid metallic nanofoam. **a** Chemical structure of the supramolecular complex PS-*b*-P4VP(PDP). **b** Bicontinuous gyroid morphology of PS-*b*-P4VP(PDP). **c** Nanoporous template after PDP was removed. **d** By electroless deposition, the pores between PS struts are filled with nickel. **e** Gyroid nickel nanofoam after the polymer template was removed by pyrolysis. Adapted with the permission from Ref. [48]. Copyright 2011 American Chemical Society



**Fig. 2.8** SEM image of the inverse gyroid nickel replicas obtained after the polymer template removal by pyrolysis. Adapted with the permission from Ref. [48]. Copyright 2011 American Chemical Society

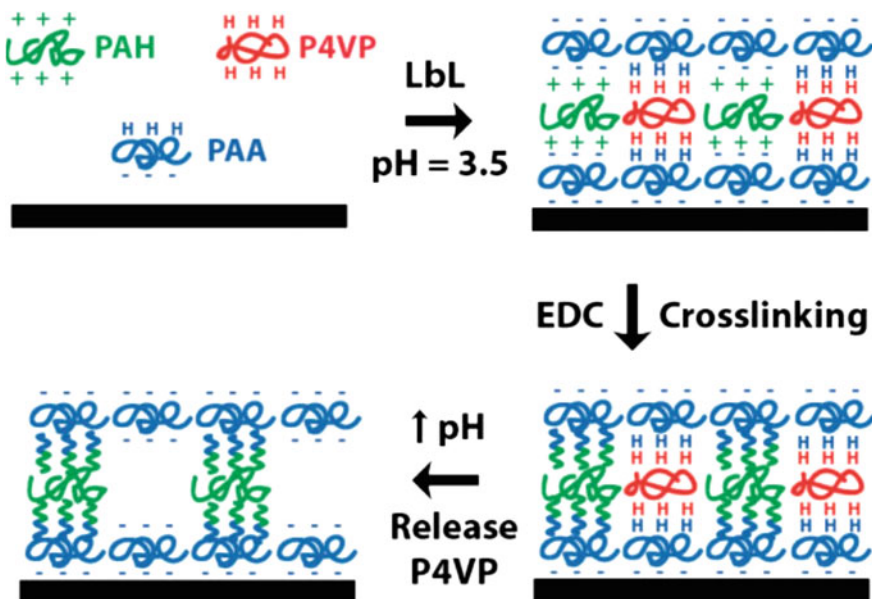
developed by two research groups independently [49–51]. In this method, porous films were constructed by crosslinking the resin in the presence of a self-assembled block copolymer. The block copolymer plays two important roles in the fabrication process. First, it directed the formation of the resin nanostructure, and second, it served as a template for the nanopores. In this case, PS-P4VP block copolymers were used and they were dissolved and mixed with a resin, for instance resorcinol. The acidic resin monomers formed H-bonds with the basic P4VP blocks. The initial block copolymer has equal block lengths resulting in a lamellar phase. However, the enrichment of the P4VP domain with the resin significantly increases the volume fraction, resulting in a hexagonal structure. The PS block was the minor component which formed the cylindrical microdomains in the self-assembled film. After controlled solvent annealing to remove the solvent the nanostructured film was exposed to a crosslinker agent (formaldehyde in the case of resorcinol) to crosslink the resin molecules. The resin monomers formed a highly crosslinked phenolic network, which is located in the PV4P domains. Pores were created in the final step by removing the block copolymer with pyrolysis (Fig. 2.9) [49]. Although this is a quite harsh treatment, it has been shown to be controllable and selective. Monomodal porous structures were created where only the PS block was hydrolyzed and the pore surface contains a large number of phenolic groups. Such pores can be used for selective adsorption or further functionalization. Selective dye adsorption was achieved by exposing the porous material to an aqueous dye solution. The material was able to adsorb methylene blue (MB) over rhodamine 6G due to H-bonding interaction between MB and the phenolic matter. This proves the importance of the chemistry of the pore. However, the adsorption took over 400 h. Brunauer–Emmett–Teller (BET) gas adsorption experiments revealed mesoporous surface areas of around 25–100 m<sup>2</sup>/g. Even hierarchical porous materials can be made when both blocks were pyrolyzed in a controlled fashion. This resulted in materials with mesoporous cylindrical pores and micropores in the resin matrix. These hierarchical materials exhibit an inner surface area up to 500 m<sup>2</sup>/g.



**Fig. 2.9** **a** The H-bonds between the PS-P4VP block copolymer and a phenolic resin. **b** As a result of H-bonding, the phenolic resin and P4VP are confined within the same self-assembled domains as they have microphases separated from the nonpolar PS domains. Crosslinking at elevated temperatures “locks” the structure. **c** Depending on the pyrolysis procedure, different pores are created with hydroxyl groups in the pore interior. Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd

In addition to using the self-organization properties of block copolymer, other bottom-up strategies can also be applied to create nanoporous polymer structures. An example has been demonstrated with a polyelectrolyte multilayer approach [52–54]. Structured polymer layers can be built up by layer-by-layer deposition. In this approach, electrostatic interactions are combined with H-bonded interaction to create alternating layers of cationic and anionic polymer layers and H-bonded areas. Various combinations of polymers have been applied to create microporous materials, but some of them are only porous in small pH range due to electrostatic repulsions, which cause the polymer layers to disintegrate. Caruso et al. prepared stable porous polymer films from assemblies of poly(acrylic acid) (PAA) in alternations with a blend of polyelectrolyte (poly(allylamine hydrochloride) (PAH) and a H-bonding polymer P4VP [55]. Pore formation was achieved by chemically crosslinking the electrostatic component (PAA/PAH) and removing the H-bonded polymer by increasing the pH (Fig. 2.10) [55]. Interconnected pores are created throughout the film, which was proven by ion diffusion. Only after crosslinking and release of the H-bonded polymer does the film show ion diffusion characteristics.

De Geest et al. [56] demonstrated that nanoporous H-bonded polymers can be used in the biomedical field, for instance to carry vaccines. They produced polymer particles, based on H-bonding between poly(*N*-vinylpyrrolidone) and tannic acid. These H-bonds are stable at a wide range of physiological conditions. In the production of the polymer particles, they used a pore former template molecule. After particle formation, the pore former can be simply removed by a washing step in water. This nanoporous framework is able to carry vaccines and proteins and it is anticipated that this technology holds great promise for the formulation of vaccines for developing countries or for pandemic vaccines where long-term storage under refrigerated conditions is a major issue.



**Fig. 2.10** Procedure used for producing porous polymer films from PAA/(P4VP/PAH) multilayers. Initially, a multilayer thin film is formed by adsorbing PAA in alternation with a blend of H-bonding interactions between P4VP and PAH. Subsequently, the film is crosslinked, forming covalent bonds between PAA and PAH polymers. Finally, P4VP is released by elevating the pH to disrupt the H-bonds. Reproduced from Ref. [55] by permission of John Wiley & Sons Ltd

## 2.4 Hydrogen Bonding in Liquid Crystals as Nanoporous Networks

The self-organization of block polymers has been used to create nanoporous materials, but the pore size is limited to approximately 5 nm and above. To create smaller pore dimensions, smaller building blocks are required. This is why the self-organization of liquid crystals (LCs) and their polymers are very appealing. Here, the pore size can be decreased to below 1 nm, while the assemblies themselves can have much larger dimensions.

Liquid crystals represent an intermediate state of matter between a crystalline solid and an isotropic liquid phase [57]. Generally, most solids when heated directly transform to a liquid state. However, some solids do not change directly to a liquid state on heating but instead pass through a phase that has properties of both solids and liquids. This phase is known as liquid crystalline phase and the molecules comprised of them are known as liquid crystals.

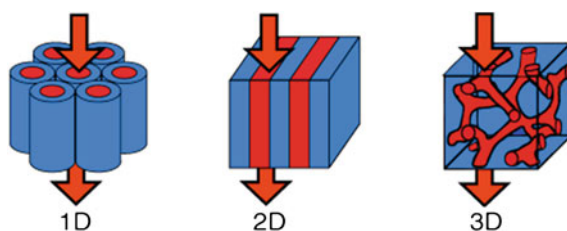
LCs can be divided into two categories: lyotropic and thermotropic LCs [57]. Lyotropic liquid crystals are obtained when an appropriate concentration of a material is dissolved in a solvent. The most common systems are those formed by

water and amphiphiles. Thermotropic liquid crystalline phases occur in a certain temperature range and the phase is stable over a certain temperature interval. If the temperature is increased, thermal motion will destroy the ordering of the liquid crystalline phase resulting in isotropic liquid phase. Transitions between the various liquid crystal mesophases generally occur at defined temperatures and with little hysteresis observed between heating and cooling cycles.

LCs can self-organize in a number of phases (Fig. 2.11) [57, 58]. One of the most common LC phases is the nematic phase. In this phase, the rodlike or calamitic organic molecules have no positional order, but they self-align to have long-range directional order with their long axes parallel. Nematics have fluidity similar to that of isotropic liquids, but they can be easily aligned by an external magnetic or electric field. The nematic phase is the least-ordered liquid crystalline phase. The smectic phase is another well-known phase. This mesophase is more ordered than the nematic phase where, in addition to the orientational order, the molecules possess positional order, such that the molecules organize in layered structures. Many other phases are known.

Mesophases can be locked into a polymer network by making use of polymerizable LCs [59]. These molecules contain moieties such as acryloyl, diacetylenic, and diene. Self-organization and in situ photopolymerization under UV irradiation will provide ordered nanostructured polymers maintaining the stable LC order over a wide temperature range. A number of thermotropic liquid crystalline phases, including the nematic and smectic mesophases, have been successfully applied to synthesize polymer networks. Polymerization of reactive lyotropic liquid crystals also have been employed for preparation of nanoporous polymeric materials [58, 60]. For the construction of nanoporous membranes, lyotropics hexagonal or columnar, lamellar or smectic, and bicontinuous cubic phases have been used, polymerized, and utilized demonstrated in a variety of applications (Fig. 2.11).

For the construction of nanoporous polymeric structure materials, scientists often make use of H-bonded LCs. The first H-bonded LC was published in 1989 by Kato and Fréchet [61]. Since then a variety of H-bonded LCs have been synthesized and applied for a number of applications, including nanoporous materials [62]. In these LC systems, H-bonds have been used to position template molecules. By careful design of



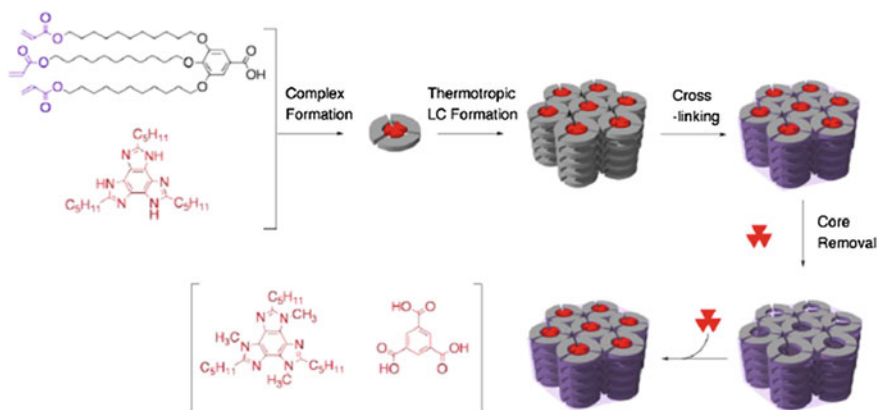
**Fig. 2.11** The different phases that have been used in the construction of nanoporous membranes: columnar or hexagonal (1D), smectic or lamellar (2D), and bicontinuous cubic (3D) phases. The red part represents the pore, while the blue fraction is the molecular region. Reproduced from Ref. [58] by permission of John Wiley & Sons Ltd



the components, channels complementary to the template unit could be created. This might enable scientists to control the structure and properties of the resultant pores.

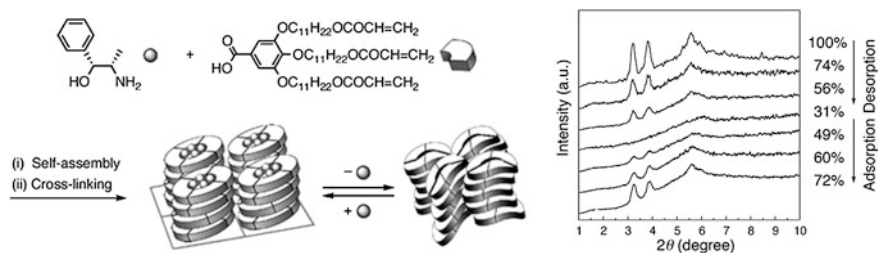
In the last decade, Kim and co-workers synthesized one of the first nanoporous materials based on thermotropic LCs [63]. Their system consists of a benzotri (imidazole) core and polymerizable trialkoxybenzoic acid acrylate. These molecules self-organize in a 1:3 supramolecular complex through H-bonding and they spontaneously form a hexagonal columnar LC phase (Fig. 2.12) [2, 64]. This LC phase is stable over a broad temperature window. Irradiation of the material with UV light induces polymerization of the acrylate moieties at the termini of the alkyl chains to give a crosslinked polymer film. Subsequently, acidified methanol is used to break the H-bonding interactions. This results in the extraction of the benzotri (imidazole) core and a porous polymer network is formed. 90 % of the core molecules can be removed and nitrogen adsorption tests reveal the porous nature of the material. It is worth noting that gas permeability constant of this porous polymer was four orders of magnitude higher than that of low-density polyethylene. Furthermore, the X-ray diffraction pattern is nearly identical to the crosslinked supramolecular polymer network, revealing that the hexagonal columnar organization is maintained. Another interesting feature of this material is the ability to recognize structural differences of guest molecules. The “de-cored” polymer readily incorporates the original core template, while other guest molecules with the right size to fit into the channel were hardly captured, such as the tri-*N*-methylated derivative of benzotri(imidazole) and 1,3,5-benzenetricarboxylic acid. Although the experimental details of the host–guest chemistry were not given, this proves the shape selectivity in porous materials.

In a similar approach, Saigo et al. have prepared a chiral columnar LC structure [2] using the same benzoic acid derivative and a chiral amino alcohol (Fig. 2.13) [64–66]. The columnar phase could be photopolymerized and powder X-ray



**Fig. 2.12** The H-bonded liquid crystal is able to form a columnar structure. After polymerization the structure is locked into a polymer network. The core molecule can be removed and incorporated later, while structure analogue are hardly adsorbed. Reprinted from Ref. [64]





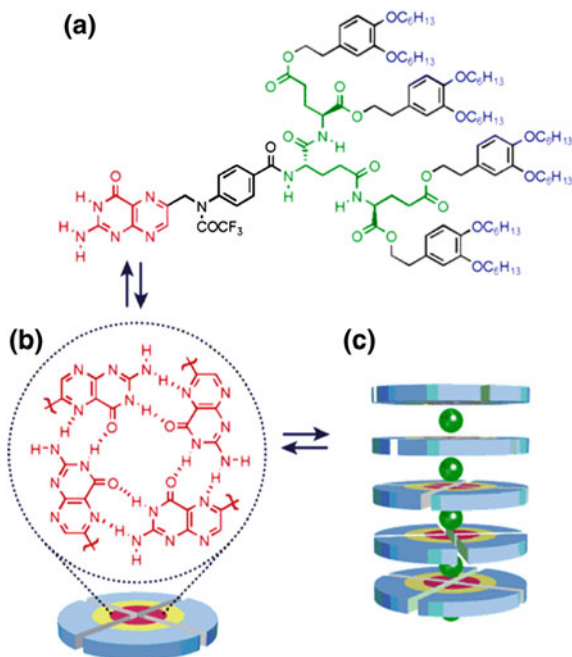
**Fig. 2.13** *Left* the chemical structures and a schematic representation of desorption and adsorption of **9** in the nanoporous columnar liquid crystalline polymer film. *Right* the X-ray diffraction of the crosslinked network at different stages of adsorption and desorption. Adapted with the permission from Ref. [66]. Copyright 2006 American Chemical Society and Ref. [64]

diffraction analysis revealed that the rectangular columnar structure is maintained after polymerization [65]. An acidic aqueous solution was used to desorb the amino alcohol and FT-IR measurements reveal that the desorption process involves a simple ion exchange reaction. Furthermore, the intensities of the X-ray diffraction peaks attributed to the rectangular columnar structure became undetectable (Fig. 2.13), indicating that columnar phase was lost after removal of the template. The re-adsorption of the amino alcohol was investigated by immersing the polymer network in a methanol solution of the amino alcohol. Interestingly, FT-IR spectroscopy showed that the adsorption is based on the formation of the ammonium-carboxylate salt. Furthermore, X-ray diffraction signals indicative of the rectangular columnar structure became detectable again [66]. These results showed that H-bonding interactions can be used to bind guest molecules in materials by molecular imprinting. More recent studies have demonstrated that the polymer porous material also readily incorporates other guest molecules with sizes that fit in the chiral nanochannels [67]. Detailed studies indicate that modification of the polymer porous material has large effects on properties such as structural order, guest recognition and release, and its repetitive switching [64, 68].

A similar approach can also be applied to create a nanoporous network having two different polymerizable units. Lee published an LC formed by H-bonds between phloroglucinol and pyridine derivatives [69]. These molecules were mixed in a 1:3 ratio to form a star-shaped discotic columnar phase. The pyridine derivative contains two different photoreactive polymerizable groups in the alkyl chain. These groups, diacetylene and acrylate, might be selectively polymerized along the vertical and horizontal axes. The core molecules are removed with a sodium hydroxide treatment, to create the nanoporous conjugated network. These pores have a pyridine interior and an estimate pore size of 1 nm.

Nanoporous columnar structures have also been constructed without removing the core molecule [70, 71]. An illustrative example is a rosette-like structure formed by H-bonded folates. These folic acid derivatives exhibit a thermotropic columnar LC phase through the formation of H-bonded pterin rings (Fig. 2.14) [70]. These columns exist over a wide temperature range thanks to the stabilization of the

**Fig. 2.14** Self-assembly of folate (a) into an H-bonded rosette (b) and c with a central string of cations. Adapted with the permission from Ref. [70]. Copyright 2006 American Chemical Society



amide H-bonds. The tetramer ring of pterins is organized in such a way that a small pore of only 3.7 Å is formed in the middle. The pore exhibit cation selective transport properties and it is suggested [70] that this ion transport is based on tunneling through the supramolecular macrocycles. Furthermore, big cations are able to go through the small pore thanks to the dynamic behavior of the H-bonds: this is not possible with covalent macrocycles such as crown ethers and calixarenes.

Another system which directly forms porous columnar structures is described by Percec and co-workers [72]. They reported that dipeptide moieties can be used to self-assemble in cone-shaped dendrons to form nanometer-sized hollow columns. The self-assembly is based on the H-bonds between the dipeptides. The porous columns were used as ion channels, for instance for proton transport.

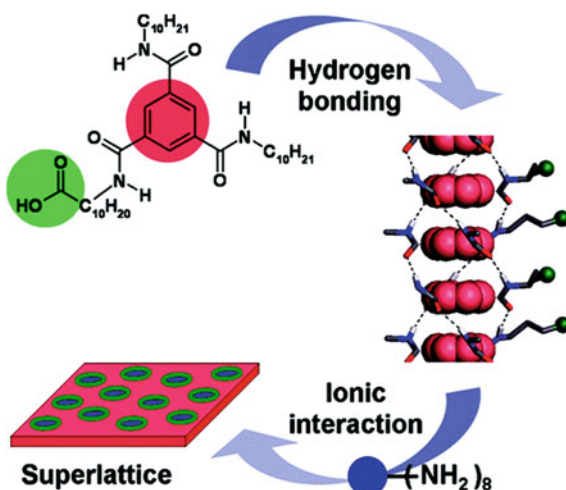
In the previous examples of nanoporous materials based on H-bonded liquid crystals, the H-bonds are generally formed between a core molecule and a few molecules containing polymerizable groups, or molecules capable of forming H-bonds directly inducing porous structures. H-bonds could also be formed between discotic molecules within a column. Fitié et al. reported a procedure to use these H-bonded columns to create a nanostructured material with potential use as a nanoporous network [73].

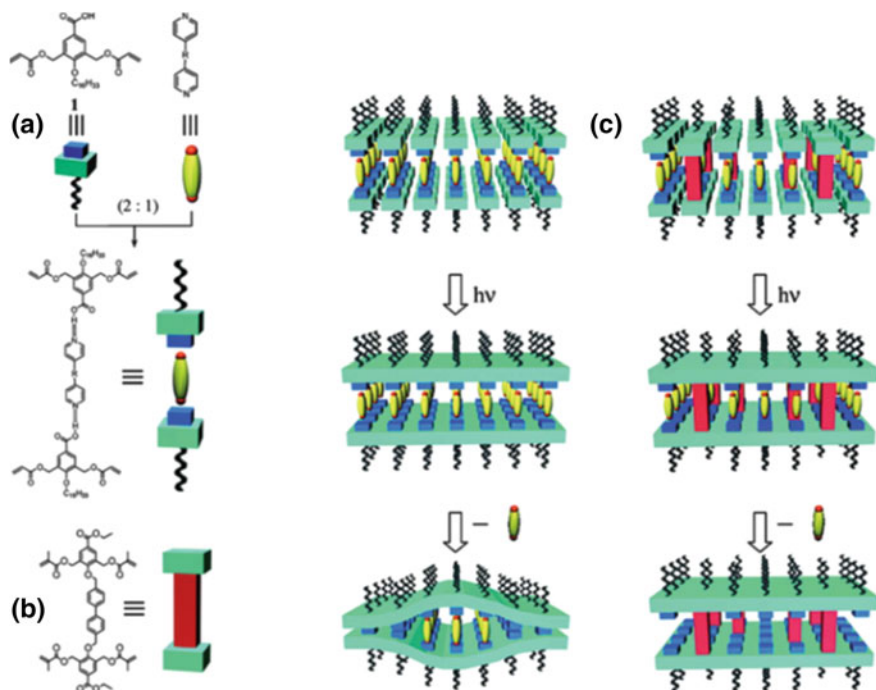
Discotic molecules with a benzene-1,3,5-tricarboxamide (BTA) core are used to form a columnar LC phase through threefold intermolecular H-bonding. The BTAs are functionalized with a carboxylic acid moiety, which is able to form an ionic interaction with amines. A well-ordered superlattice is formed by mixing the BTAs

with a second-generation poly(propyleneimine) (PPI) dendrimer with amine end-groups. The orthogonal combination of H-bonding in the columnar direction and ionic interaction in the plane perpendicular to the columns gives rise to a structure in which the dendrimer is confined to separate columnar domains. Polymerizable analogues of the BTA (depicted in Fig. 2.15) [73] are used to fixate the superlattice in a supramolecular network. Nanostructured materials were obtained with a periodicity of 2–10 nm. A simple washing step should result in a porous structure, but unwanted crosslinks between the BTAs and PPI dendrimers prevented this. The side reaction should be reduced by optimizing the processing conditions to really form a porous superlattice. However, this is another promising route for the construction of nanoporous H-bonded materials.

The crosslinked hexagonal columnar structures discussed in the previous section have the advantage of maintaining structured after removal of the H-bonded template molecule [2]. The pore size is retained thanks to the rigidity of polymerized honeycomb structures. This approach cannot be applied to a lamellar structure (Fig. 2.11), since the polymerized regions exist in sheets which are not covalently connected to each other. H-bonds hold the polymer sheets together and rupture of the H-bonds results in the collapse or disintegrations of the lamella structure. To circumvent the breakup, Kishikawa et al. developed a method to prepare lamellar structured nanoporous films [74]. A smectic LC mixture was used in which the majority is an H-bonded LC that organizes in a smectic A fashion. In addition, a small fraction of “nanopillars” was added. These nanopillars are able to maintain the lamellar structure after removing the template molecules (Fig. 2.16) [74]. These nanopillar crosslinkers were synthesized in such a way that they are quite similar in size and shape to the H-bonded LC. Both LCs have a rodlike shape and two polymerizable units at each end. The LCs mixture is organized in a smectic state and subsequently photopolymerized to lock in the smectic state in a polymer

**Fig. 2.15** The 3D structure of the H-bonded column. Reprinted with the permission from Ref. [73]. Copyright 2008 American Chemical Society





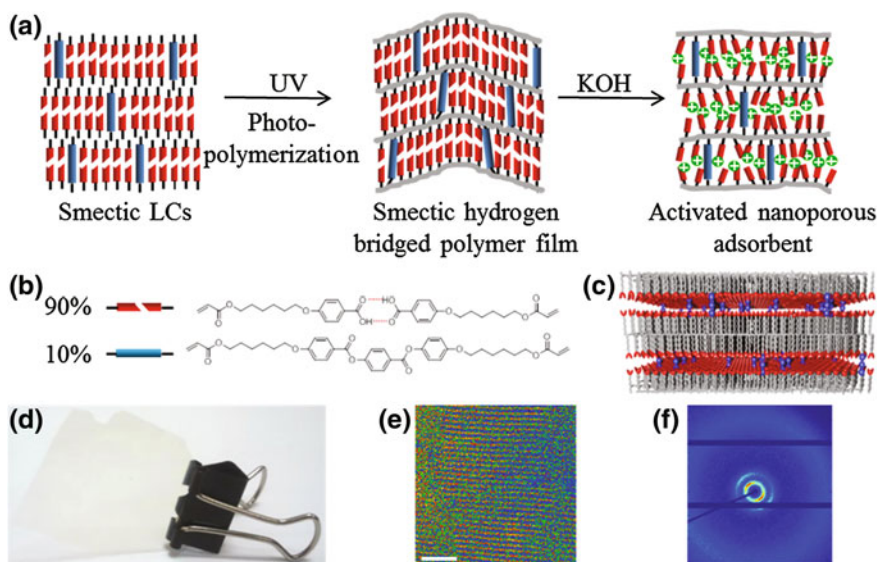
**Fig. 2.16** Chemical structure and schematic representation of the supramolecular monomer (a), the pillar molecule (b) and both processes (without pillar and with pillar) to build nanoporous layered polymers (c). Adapted with the permission from Ref. [74]. Copyright 2008 American Chemical Society

network. After removal of the template, nanoporous layered structures are obtained that are held together by the pillar moieties and do not collapse.

In a similar approach, nanoporous membranes have also been prepared without the use of a template [75]. These membranes were also built from a mixture of two LCs, an H-bonded dimer and a covalent linker. The membranes were created by photopolymerization to lock the smectic structure into a network followed by an alkaline treatment to create the pores (Fig. 2.17a) [76]. The H-bonds were formed between two benzoic acid monomers and after deprotonating of the acid moieties the H-bonds break and a carboxylate pore interior was created. The smectic nature of the material resulted in straight pores with a 2D geometry and transmission electron microscopy (TEM) (Fig. 2.17e) revealed a periodicity of approximately 3 nm and pores around 1 nm.

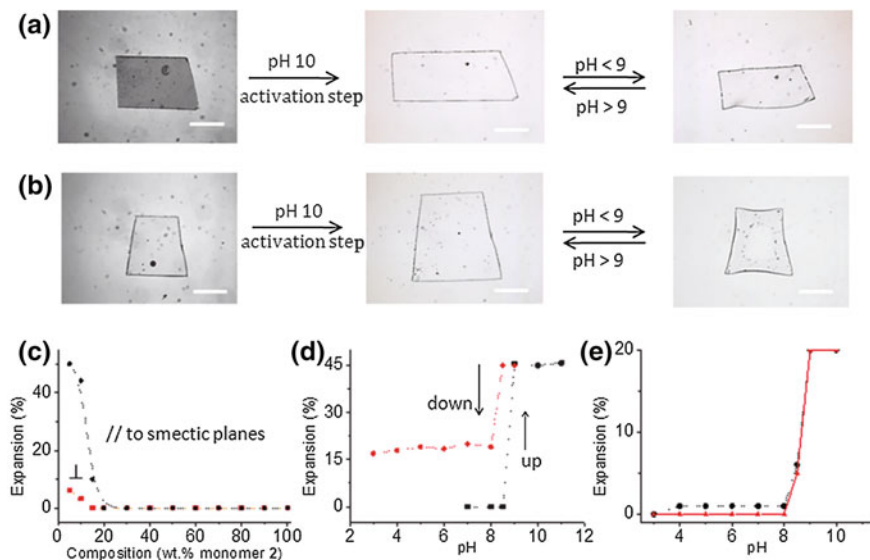
A unique feature of this kind of highly ordered LC networks is their anisotropic swelling [77]. The polymer films swells only perpendicularly to the molecular director (Fig. 2.18) [77].

This material exhibits appealing adsorption behavior [76]. The adsorption study was performed with dyes as model compounds. Cationic methylene blue (MB) was

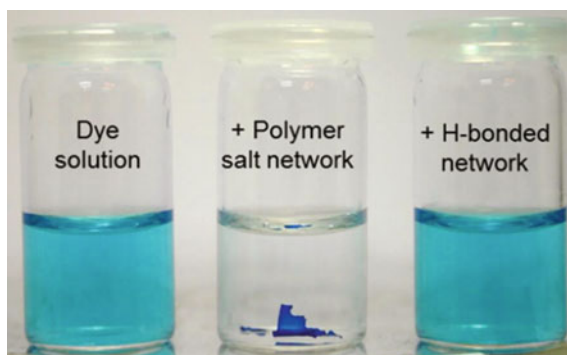


**Fig. 2.17** **a** Schematic representation of the formation of the nanoporous membrane based on smectic liquid crystals. **b** The chemical structure of the LCs. **c** Simplified artistic view of the nanopores in the layered network. To visualize the 2D pores the counter ion is not shown and the benzoic acid derivatives are drawn highly ordered. **d** A free-standing H-bonded polymer network. **e** TEM of the nanoporous polymer network filled with barium ions, scale bar 20 nm. **f** X-ray diffraction pattern of the alkaline treated network. Adapted from Ref. [76] by permission of John Wiley & Sons Ltd

very efficiently removed from an aqueous solution. A high capacity of 1 g of MB could be adsorbed in 1 g of material. This corresponds to 100 % occupation of the adsorption sites. The H-bonds in this material play a crucial role; only the material where the H-bonds were broken was able to adsorb the dye (Fig. 2.19) [76]. The adsorption rate constant was competitive too. These properties indicate the good and fast access to the adsorption sites, caused by a combination of the porous nature and the nanostructure achieved by the self-organization of the LCs. This material is also quite selective. The nanopores only adsorb small ions and the anionic carboxylate pores only allow molecules with cationic moieties and have a large preference for molecules with solely cationic moieties. The ability to reform the H-bonds is beneficial for the reuse. A simple acid treatment results in the protonation of the carboxylate moieties, the formation of the H-bonds and the desorption of the adsorbate. This makes these nanoporous materials interesting candidates for selective adsorption of valuable chemicals or for water purifications purposes, including adsorption and membrane filtration. Potentially they could be used in drug delivery systems. Additionally, the self-organization of LCs can easily be combined with top-down techniques, such as inkjet printing and photolithography [77], which could be interesting to apply them in microfluidic devices.



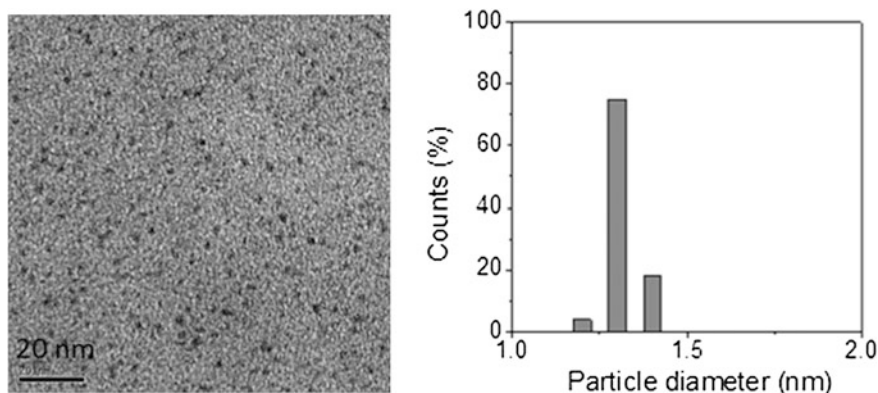
**Fig. 2.18** Swelling and deswelling of thin films of a planar aligned smectic network (a) and a homeotropic smectic network (b) (scale bar corresponds to 500  $\mu\text{m}$ ). Swelling depends on the concentration of covalent crosslinker and on the direction with respect to the molecular orientation (c) and shows hysteresis upon cycling during the activation step and the first cycle (d) and repeated cycle (e) Reproduced from Ref. [77] by permission of The Royal Society of Chemistry



**Fig. 2.19** Adsorption of MB in the polymer network as shown in Fig. 2.18. From left to right the MB solution without adsorbent, with adsorbent and with H-bonded adsorbent. Adapted from Ref. [76] by permission of John Wiley & Sons Ltd

Furthermore, this smectic nanoporous network could be used as reaction medium, for instance for the formation of silver nanoparticles (NPs) [78]. The pores were first filled with silver ions and subsequently the ions were reduced to form Ag nanoparticles. The NPs are monodisperse (Fig. 2.20) [78], and interestingly, the size





**Fig. 2.20** TEM image along with the particle size distribution of an ultramicrotomed section of a planar Ag nanoparticle smectic hybrid film as shown in Fig. 2.18. Adapted with the permission from Ref. [78]. Copyright 2013 American Chemical Society

is controlled by the length of the covalent linker. A crosslinker with a larger molecular length results in larger NP. This strategy can in principle be extended to fabricate micropatternable anisotropic plasmonic or semiconducting hybrid structures. The nanoporosity of the hybrid polymer films makes them interesting for a wide variety of applications, ranging from nanoreactors to antimicrobial patches.

## 2.5 Conclusions and Outlook

This chapter presents the possibilities of using H-bonded nanostructured materials to construct nanoporous networks. H-bonds are ideal supramolecular interactions for these porous materials, thanks to the directionality of the H-bonds. Especially, for the H-bonded organic frameworks, this directionality is used to position molecules in such a way that nanometer-sized voids are created between molecules. These materials can be regenerated and reused by simple recrystallization thanks to the reversibility of the H-bonds. The H-bonds are weaker interactions compared to covalent bonds, causing an interesting combination of robustness and plasticity, resulting in materials which can adapt to guests and included them with high selectivity. However, the weaker interactions also affect the stability of the materials, which makes these types of materials less suitable for applications such as filtration.

More stable nanoporous materials have been constructed by making use of recognition and self-assembly of H-bonded block copolymers. The H-bonds do not directly induce porosity, which is in contrast to the H-bonded organic frameworks. A well-defined nanoporous structure is created after breaking the H-bonds and the release of a template molecule. A great advantage is that the H-bonds can be broken under mild conditions, while for covalently bonded block copolymers harsh



conditions are needed to create porosity. Nanoporous polymers have been constructed with a variety of pore structures and functionalities, and a number of strategies have been applied to create novel porous polymer networks with pore diameters of few nanometers and above. The use of H-bonded block copolymers is a promising route for the synthesis of porous materials, although the number of applications described in the literature is limited.

H-bonded reactive LCs are a promising class of materials to construct nanoporous materials with smaller pore dimensions. Self-organization of LCs is essential to control the material structure at the nanometer level and each liquid crystalline phase can be fixed by polymerization, allowing a wide variety of highly ordered organic materials. H-bonds play a crucial role in both the directionality of the molecules and formation of the pores by breaking the H-bonds. Highly porous materials with sub-nanometer-sized monodisperse pores have been made and applied for ion and proton transport, host–guest chemistry, and selective adsorption. For all applications, it is important to integrate and align the nanoporous liquid crystalline polymers in devices. This issue has not been addressed extensively, but will be crucial for the success of this class of materials [79]. Furthermore, they could also be used in applications as ion selection, desalination, and blue energy. This is why the control over the pore size and pore size distribution is a crucial parameter in porous materials.

Although the development of hydrogen bonded nanoporous materials is still in its infancy, this chapter shows that these materials have appealing properties and have promise in fields such as filtration, separation, adsorption, ion conductivity, enantioselective separation, and molecular recognition. For the development of well-performing devices, these types of materials should be used in hierarchical structures to create stable materials with excellent performances.

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