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► **To cite this version:**

Mihail Barboiu. Biomimetic Nanofiltration Materials. Nanofiltration: Principles and Applications, In press. hal-03031124

HAL Id: hal-03031124

<https://hal.science/hal-03031124v1>

Submitted on 30 Nov 2020

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Biomimetic Nanofiltration Materials

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24.1 Introduction

Constitutional dynamic chemistry [1–3] and its application dynamic combinatorial chemistry [4, 5] are new useful approaches to create chemical diversity. Unlike conventional methods, they allow the simple generation of adaptive dynamic materials, emerged from mixtures of molecular building blocks that interact and exchange reversibly to generate variable architectures in response to internal factors or external stimuli. This might lead to new opportunities for next-generation nanofiltration membranes and materials; e.g. more specific separations based on molecular interactions that might strongly increase the performances of the membranes with a special emphasis on selectivity that is of particular importance for a diverse range of applications such as medicine, catalysis, and the discovery of new materials, biomimetic transport separations through membranes, etc., highly needed for high-performance applications.

These challenges have first inspired the incorporation of biomolecules into membranes for the design of *bio-assisted membranes* for desalination or biocatalytic processes. However, the large-scale applications of such bio-assisted systems are still suffering from high costs of the enzyme/protein production, low stability, and fabrication constraints of the membrane operating conditions. Artificial molecular or supramolecular systems have been recently proposed as the *biomimetic membrane* alternatives of biological ones, and the interest in these completely synthetic active artificial systems, embedded in the membranes, has considerably grown during the past years.

Mimicking the complex functions of natural proteins is an important exploring challenge. It is more than meaningful to mimic the key parts of active filters, giving of high selectivity, to understand the dynamics of orientating water dipoles and their role for ion/proton pumping along the channel. Moving from complex natural to simpler artificial systems, it would have the chance to understand better mechanistic and structural behaviors of such interactions, unlocking the door to the novel interactive water channels, paralleling that of biomolecular systems. Artificial systems implement supramolecular reversible

Nanofiltration: Principles, Applications, and New Materials,
Second Edition. Edited by Andrea Iris Schäfer and Anthony G. Fane.
© 2021 Wiley-VCH GmbH. Published 2021 by Wiley-VCH GmbH.

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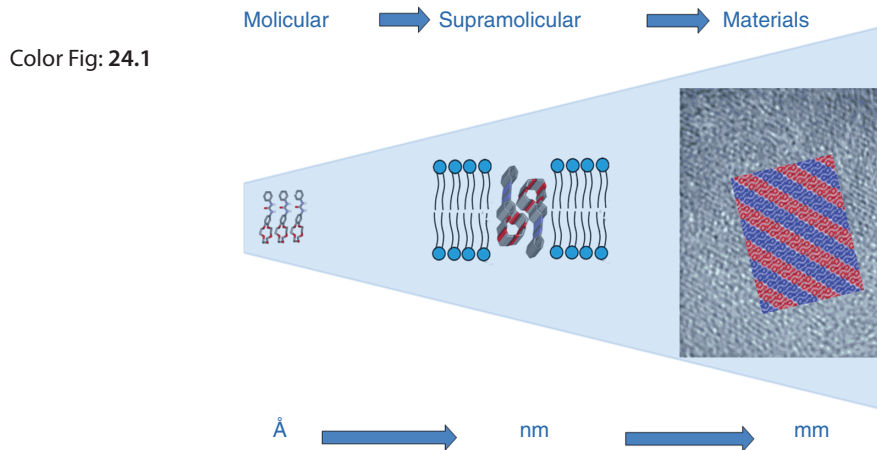


Figure 24.1 Upscale transposition of self-organized functional ion channels from supramolecular architectures toward informed materials for the directional translocation.

dynamic interfaces between the interacting molecular components, promoting structural correlation of different components of the system, based on their interactive constitutional (molecular/supramolecular) features [6]. During the past decade, the field of constitutional dynamic materials is moving toward systems with greater dynamic dimensional behaviors from molecular to nano- and mesolevels [7, 8]. Comprehensive approaches are related to upscale the self-organizing properties at the molecular level and to transfer them to the upper size scales. This gives the possibility to extend and to engineer material self-assembly via multivalent interactions in order to control the organization of complex matter across extended scales. It generates systems that may possess novel properties not present at molecular level [7]. These strategies open wide perspectives to imagine a fundamental transition from supramolecular design toward constitutional selection approaches for the construction of membrane materials, which might give great potential in various applications [8]. This chapter focuses on constitutional methods used to conceive molecular membrane materials by controlling the flow of structural information from the molecular level across several orders of magnitude toward superior scales (Figure 24.1). These methods show the potential to impose a specific order to the mesoscale and to discover new ways to obtain highly ordered materials over macroscopic distances, with the aim of shortening the essential steps to go from the molecular scale to functional nanomembrane systems.

Within this context, functional supramolecular architectures, representing a sum of multiple copies of specific recognition or self-assembly events occurring between reversibly interacting molecular components can be multiplied via polymerization processes to generate adaptive materials of increased more complex dimensional behaviors (Figure 24.1). This gives the possibility to extend and to engineer multiple supramolecular interactions in order to generate and to control the organization of functional membrane materials across extended scales [6–8].

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Several artificial membrane systems have been designed to mimic the transport properties of natural proteins, sized to work at the nanometric level, with the hope to mimic their functional complexity and performances [8]. These membrane systems appear to be strongly dependent on the self-organization domains of the material, related to the generation of preferential translocation pathways for directional transport of the solutes [9]. This leads to unique properties in terms of selectivity and flux manifested by numerous carrier and channel systems with effective biomimetic translocation mechanisms.

This chapter devoted to biomimetic nanofiltration membrane materials will be divided into *sections* with *parts*. They are described below. The first part will focus on the implementation of the self-assembly on the elaboration of hybrid membrane materials for ionic conduction, emphasizing the more recent developments of *self-organized hybrid membranes*. The second part describes the recent work on the development of adaptive mesoporous membranes with special emphasis on the self-assembly approaches for building adaptive constitutional membranes. The third part will present the first advancements in the field of biomimetic artificial water channels and their comparisons with natural systems. Current and potential applications of these new systems with combined characteristics of structural adaptation will be presented.

24.2 Self-organized Hybrid Membranes

24.2.1 Directional Nanochannels for Facilitated Ionic Conduction

The concept of facilitated transport [10–12] has been long time connected to the concept of liquid membranes (a liquid organic interface, the membrane, interposed between two aqueous phases). The main purpose of the studies related to this field was to construct and synthesize specific receptors, geometrically and structurally adapted to the solutes of interest to be transported. The success of these approaches was connected to ensure good molecular recognition of the solute by the receptor at the feed interface to selectively transport the resulted host–guest (receptor–solute) complex across the membrane and to easily release it at the receiving interface [13].

Using these concepts, it has been introduced in recent years a new approach concerning the facilitated transport through dense solid hybrid materials for molecular recognition and self-organized membranes. The force of the proposed approach lies directly in the design and processing of the material, which can be assimilated to a thin layer “hybrid solution.” Receptors can be homogeneously grafted in the solid matrix, with random spatial arrangements [12] or organized by self-assembly so that the diffusion step is minimized by decreasing the distance between the molecular recognition sites of the receptors in the network [14]. By similarity with the biological channels, the structured molecules composing the membrane material selectively control the diffusion of a solute through preferential transport pathways within the membrane. Because of the limited thickness of the active layer (1–2 μm), these materials can be polarized, for example, in the case of cotransport of counterions.

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Molecular recognition of neutral or charged organic molecules has only recently received attention in sharp contrast to the far more advanced development of the corresponding coordination chemistry of cations [9, 10]. These substrates are bulkier with miscellaneous geometries, thus are more polarizable and more strongly solvated than cations. For these reasons, artificial receptors should have a specific geometry with a correct geometrical disposition of binding sites, in order to allow a strong entrapment of the organic guest. Much interest in the field of molecular recognition of organic compounds has been focused on the amino acids. In this case, it is generally easier to complex either the hydrophobic protonated ammonium ($\text{H}_3\text{N}^+-\text{R}-\text{COOH}$) or the deprotonated carboxylate ($\text{H}_2\text{N}-\text{R}-\text{COO}^-$) forms, rather than the zwitterionic natural form of the amino acids ($\text{H}_3\text{N}^+-\text{R}-\text{COO}^-$). The selective heterocomplexation of the zwitterionic form via three hydrogen bonds of protonated ammonium moiety or the charge interactions of carboxylate form (as the counterion of the supramolecular species) can be completed by lateral specific interactions, allowing an enantiomeric molecular recognition of the amino acid [11–13].

This may be achieved by self-organization of the molecular receptors, in order to create channels or preferential pathways within the solid membrane materials for different solutes: cations, anions (Figure 24.2a), or neutral molecules. Molecular channel-type systems have been developed by using crown ether precursors self-assembled via a network of hydrogen bonds between the urea groups (Figure 24.2b). For such compounds, the formation of oligomers in solution [14] and in the solid state leads to regular arrangements, allowing the formation of nanometric ion channels (Figure 24.2b,c). These precursors have been incorporated in dense thin layer membranes via the sol-gel method and used as biomimetic pumps for the transport of adenosine triphosphate (ATP^{2-}), against the concentration gradient and activated by competitive ionic transport [15]. The generation of ion channels in a hybrid membrane can also be done from the simpler molecules, i.e. “ureidopeptoides” containing as a functional unit the side moieties of aromatic amino acids, which can interact with alkali cations via cation- π interactions, which are of major significance in biology and have been recognized for many years [16].

24.2.2 Nanochannels for Proton Conduction

Using these principles, and thanks to the versatility of the sol-gel process, self-organized supramolecular structures have been transcribed in a hybrid network with the crystallographic short-range order. Such hybrid membrane materials are composed from nanodomains of dozens of nanometers, randomly ordered in the hybrid matrix that encodes the required information for ionic diffusion along hydrophilic conduction pathways embedded in structured domains at the nanometric level (Figure 24.3). They are essential in the diffusion process and in the selectivity of the transport of hydrated alkali cations. Although these pathways do not merge to cross the micrometric films, they are well defined along nanometric distances, reminiscent with the supramolecular organization of binding sites in channel-type proteins collectively contributing to the selective translocation of metabolites. It is interesting to note that the self-assembly

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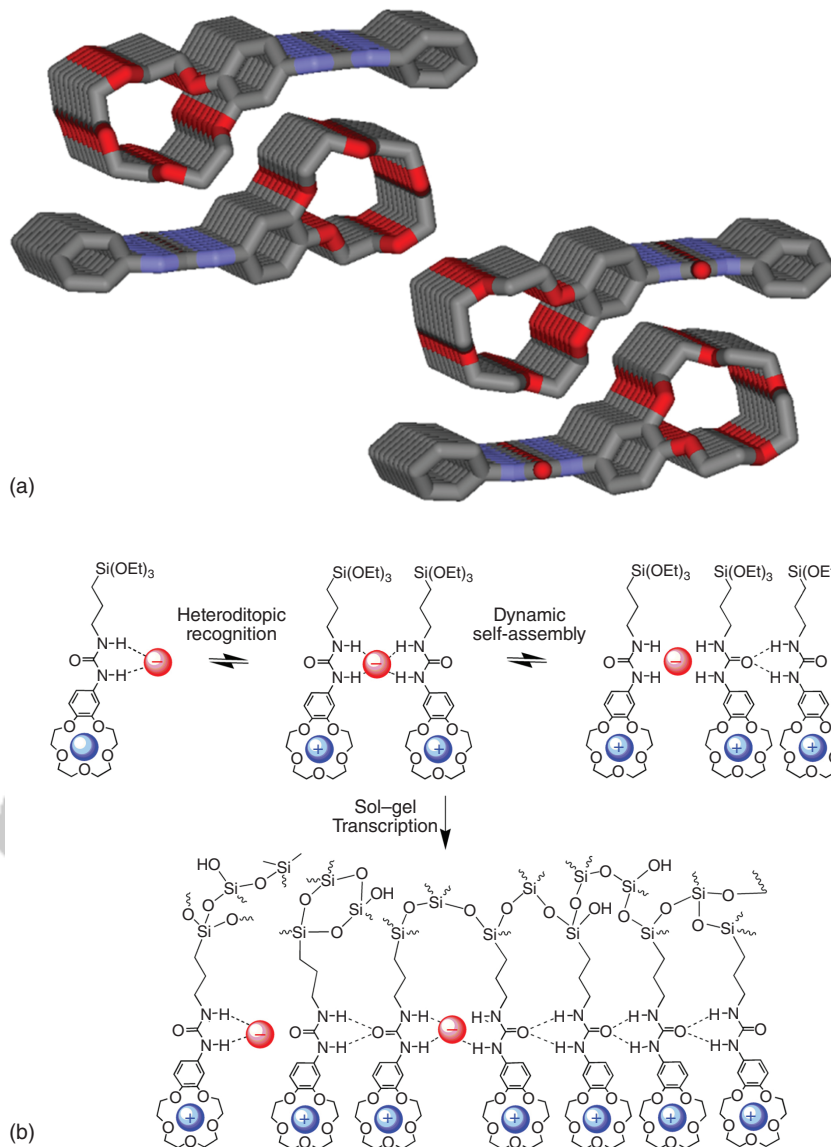


Figure 24.2 (a) Stick representation of the patching of 3 in the crystal, showing the formation of directional tubular conduction pathways and (b) schematic representation of the (top) self-organization of macrocyclic channels in solution and (bottom) sol-gel transcription of encoded molecular features into a hybrid heteropolysiloxane material. Source: Barboiu et al. 2004 [15]. Reproduced with permission of ACS Publications.

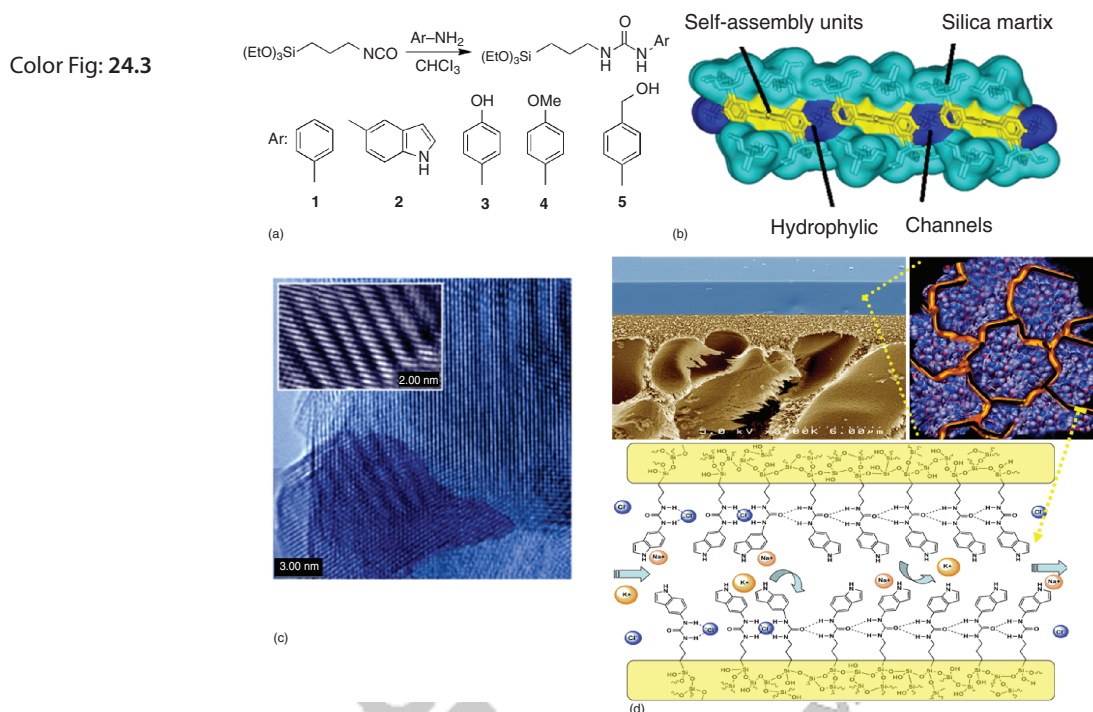


Figure 24.3 (a) Nanostructured “ureidopeptides” 1–5 receptors in (b) hydrophilic channels and (c) oriented nanodomains in lamellar hybrid materials; and (d) self-organized conduction layers are generated through the membranes for oriented and synergistic translocation of ion pairs.

of simple molecules, which collectively define transporting devices can be successfully used to transfer their overall functionality of their self-organization in hybrid membrane materials at the nanometric level.

Therefore, the affinity “solute-membrane material” is related to the nature of the molecular receptors grafted on the membranes and will strongly depend on their binding behaviors. In addition, singularities observed in transport can be a reflection of subtle interactional mechanisms, directly related to the intrinsic structural organization of the membrane sample. If one relates specifically to the transport studies, it can conclude that the transfer rate and the ability of a solute to pass through a membrane depend on not only thermodynamic effects (solute partition between feed and receiving phases) but also kinetic effects (diffusion coefficient ease in the dense membrane). These two aspects can be connected not only to the chemical nature of the precursors but also to their ordered arrangement within the material [17].

Successive H-bond urea self-assembly and sol–gel transcription steps yield to preferential conduction pathways within the hybrid membrane materials. Crystallographic, microscopic, and transport data conclude to the formation of the self-organized molecular channels transcribed in solid dense thin-layer membranes. The ionic transport across the organized domains illustrates the power

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of the supramolecular approach for the design of continual hydrophilic transport devices in hybrid membrane materials by self-organization.

The hydrophilic pathways in hybrid membranes are generally defined by the presence of the stable -Si-OH groups in the hydrophobic condensed siloxane -Si-O-Si- network. Hydrophilic organic moieties (phenol, methoxyphenyl, or indole) presenting a tight H-bond contact with the inorganic matrix enhance the hydrophobicity of the resulting hybrid material (Figure 24.3). Taking the hydrophobic phenyl-derived compound as a reference, where the transport of ions mainly occurs via hydrophilic silica pathways, the transport of protons and the hydrated alkali cations $\text{Na(H}_2\text{O)}_n^+$ and $\text{K(H}_2\text{O)}_n^+$ are amplified when phenolic groups are introduced in the membrane. Moreover, in the two cases, single or competitive transport, the smallest $\text{Na(H}_2\text{O)}_n^+$ ions are selectively transported and the transport rate is related to the diffusion coefficients of the hydrated ions along the hybrid matrix. Amazingly, the transport rates by indole-derived membranes decrease, even compared with the reference membrane, and moreover, the membranes are selectively transporting K^+ ions. Certainly, a substantial contribution to that selectivity arises from features of exchange between the hydrated ions and indole moiety: the complexation of ions is thermodynamically more favorable for K^+ ions than Na^+ . The NH indole moiety is H-bonded with the oxygen of a vicinal siloxane network; thus, the indole pathway is hydrophobic. This explains the reduced transport rates and suggests possible cation- π interactions to confer K^+ selectivity. It has been found that the pyrrolo subunit of indole (i.e. $\text{C}_2=\text{C}_3$ bond) is a strong π -donor group for K^+ cation. This suggests that voluminous hydrated $\text{Na(H}_2\text{O)}_n^+$ may be slowed in the "indole pathway," while dehydrated K^+ are transported along this pathway more easily.

Using this knowledge, the combination of the supramolecular self-assembly and sol-gel polymerization synthetic routes can be used in order to control the formation of hydrophilic *proton pathways* as a straightforward approach for the design of a novel class of proton exchange membranes (PEMs) [18]. The PEM self-supported membranes, organized through the H-bonded sulfonic and urea groups, show a nanometric lamellar organization in the hybrid matrix (Figure 24.4). Therefore, this therefore generates an efficient conducting network, which in turn results in correspondingly high proton conductivity. It results by adding to the total conductivity of all accessible conducting sulfonate groups an important supplementary contribution of the nanometric self-organization of percolated hydrophilic domains (Figure 24.4). These data are indicative of the formation of water-filled self-organized channels and extend the applications of self-organized hybrid materials toward functional supramolecular devices. All these results concerning the self-organized functional hybrids have highlighted the wide potentialities, supramolecular self-assembly strategies, controlled and stabilized via an irreversible tandem processes, and the sol-gel polymerization. The control of supramolecular self-organization can be driven by using the sol-gel process, providing simple methods for the synthesis of well-structured hybrid materials. These results imply that the control of interactions can define the self-organized architectures with *supramolecular functionality*, such as hydrophobic and hydrophilic pathways of enhanced transporting properties.

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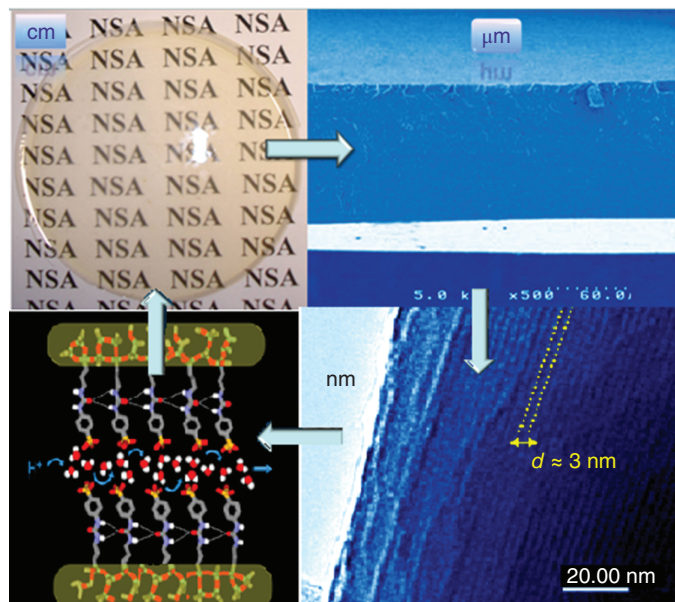


Figure 24.4 Upscale transfer from molecular level to nanostructures, describing the internal organization of the hybrid materials for the proton conduction, with the formation of lamellar hydrophilic channels hundreds of nanometers, structured in a hybrid matrix. Source: Michau and Barboiu 2009 [18]. Reproduced with permission of Royal Society of Chemistry.

The controlled generation of connected self-organized channels along hundreds of nanometers for this class of well-crystalline compound for directional proton diffusion results in PEM hybrid materials with high ionic conductivities up to $\sigma = 160.2$ mS/cm. This value is higher than the conductivity reported for the Nafion 117[®] commercial membrane [18].

24.2.3 Chiral Nanochannels

Molecular chirality is often linked to the presence of asymmetric centers in the molecules. In the world of the living matter, nonchiral molecules can form chiral assemblies, upon largely unknown self-assembly mechanisms. This type of chiral supramolecular assembly is obtained by asymmetric spatial arrangement of constitutionally interacting molecules and large-scale transcription examples of such virtual chirality remain rare.

G-quadruplexes, superstructures rich in guanine and formed by stacks of twisted G-quartets, represent a concrete example of chiral supramolecular architecture. Used in cancer therapy, they have an important role as inhibitors of telomerase, an enzyme involved in cellular aging, which plays a key role in the malign cells. G-quadruplexes, naturally constituted of nucleic, are even more surprising as they spontaneously form tubular structures for the transport of ions (ion channels). This example of a synthetic chiral functional architecture, frequently encountered in biological systems, attracted many scientists

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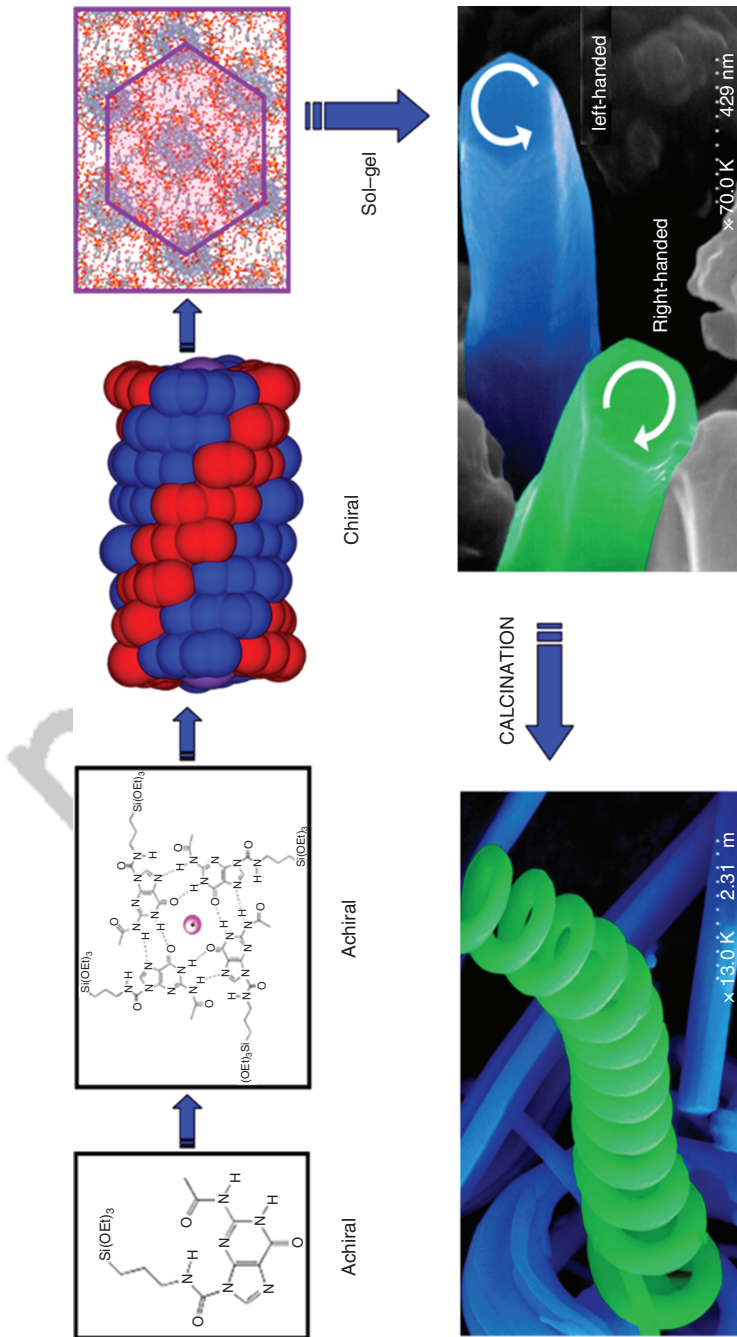


Figure 24.5 The cation-templated hierarchical self-assembly of guanine alkoxy silane gives the G-quartet in equilibrium with G-ribbons and (b) the chiral G-quadruplex transcribed in solid hybrid materials by sol-gel in the presence of templating K^+ cation. Source: Arnal-Heraut 2007 [19]. Reproduced with permission of John Wiley and Sons.

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since many years. Recently, it was demonstrated that the amplification and transcription of the supramolecular chirality G-quadruplex guanine can be amplified at the nanometer scale by using the sol-gel process (Figure 24.5) [19, 20]. G-quadruplexes with a twisted geometry communicate their chiral information to near neighbors, organized in a hexagonal lattice. This dynamic supramolecular construction was used as a scaffolding pillar to obtain hexagonal twisted hybrid rods of 800 nm in diameter (Figure 24.5). The slow heat treatment at 400 °C leads to the elimination of organic molecules and the formation of silica spirals. The spirals are several micrometers long and their chiral topology is very similar supramolecular to their congeners: G-quadruplexes. The dynamic supramolecular organization is so hierarchically controlled over several orders of magnitude. The “dynamic marriage” between the supramolecular self-organization and the inorganic polymerization leads to the transcription of the chiral supramolecular information within a hybrid material from molecular level to nanometric/micrometric dimensions. The principle of helical growth is in place to ensure the stability of the giant sequoias. The helicity is necessary for the growth and the stability of giant sequoias! In the same way, structural autocorrelation ensuring the control of the organization to the supramolecular level, while producing a helical hybrid replica at the nanoscale, surprisingly resembles the helical architecture that ensures the stability of the sequoias. The process showing the transcription of supramolecular chirality of G-quadruplexes at the nanoscale is presented in Figure 24.5. This work opens two new perspectives. On the one hand, they provide insights by using a simplified system, to understand how the transcription mechanisms of the supramolecular information operate in order to form materials of nanometric scale. On the other hand, they open the door to the world of new materials, biomimetic in nature, thus giving their unique properties by producing new hybrid replicas at the nanoscale [21, 22].

24.3 Adaptive Constitutional Membranes

It was found that the constitutional self-assembly of supramolecular systems confined in the oriented silica mesoporous membranes leads to emerging membrane materials with unique transport properties of ions comparable to those of natural membrane proteins [23]. To achieve this performance, the development of “dynamic hybrid materials” was recently proposed by our group, paving the way for the synthesis of adaptive constitutional materials, creating their own function optimized in response to external stimuli. To reach this objective, the oriented inorganic silica mesopores are used as directional host matrix for the self-assembly of macrocyclic components in order to generate dynamic supramolecular pathways for the transport of ions (ion channels) [23, 24].

The membrane system is dynamically switchable via noncovalent reversible hydrophobic contacts with the inorganic mesoporous matrix, which is structurally relating the bilayer membrane structure (Figure 24.6). Their directional order and their adaptive functional binding behaviors for different ionic species

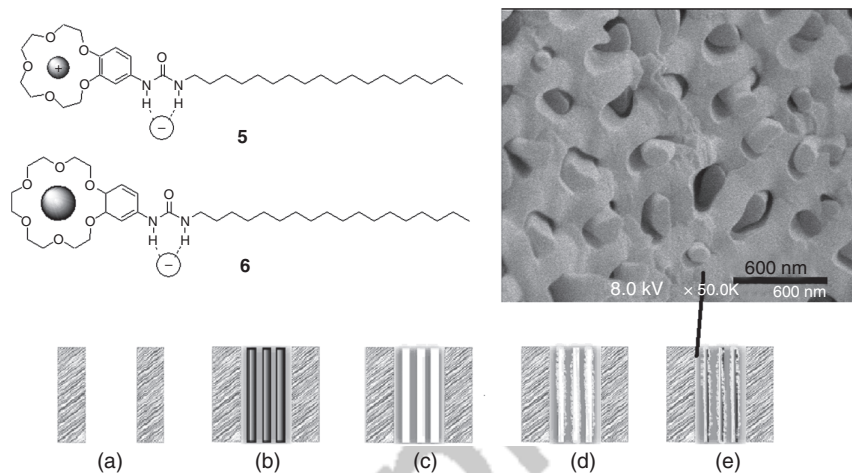


Figure 24.6 Schematic representation of the synthetic route to obtain dynamic functionalized mesostructured silica membranes in the AAMs: (a) anodic alumina membrane (pore diameter = ~ 200 nm, thickness = ~ 60 μm , diameter of membrane = 47 mm), mesostructured silica-surfactant before (b) and after (c) calcination, ODS-hydrophobized silica before (d) and after (e) inclusion of the hydrophobic carriers 5 or 6. SEM micrograph of the alumina membrane. Source: Cazacu et al. 2009 [23]. Reproduced with permission of PNAS.

are easily controllable when self-organized crown ribbons are incorporated into the directional mesopores.

Their crystallographic structures can be elucidated within the mesoporous matrix and their possible structural transformation is possible in the presence of ionic effectors [25]. Based on hydrophobic interactions and specific hydrogen bonds such as urea-urea or urea-anion interactions, molecular carriers can be noncovalently trapped in an inorganic matrix, which allow us to prepare very promising dynamic-site complexant molecular channel membranes. Hybrid organic-inorganic membranes have been prepared by filling a porous alumina membrane coupled with the sol-gel process. The MCM41-type functionalized materials were successfully oriented along the alumina membrane pores. These membranes have been tested in selective Na^+/K^+ transport. Periodic mesoporous materials have attracted considerable attention during the past decade because of their promising applications as membranes or as hosts for functional membrane materials. Many of these applications benefit from arrangements of preferentially aligned, ordered arrays of certain mesostructures. The evaporation-induced self-assembly method has been established as an efficient process for the preparation of thin films with mono-oriented materials. However, the most frequently obtained films display hexagonally ordered channels that are aligned in a nonfavorable orientation, parallel to the surface of the substrate. Recently, the synthesis of mesoporous materials within the regular 200 nm channels of Anodic alumina membranes (AAMs) has been explored with the aim of attaining greater control over the morphology (orientation) of the mesoporous system. It was then demonstrated that porous anodic alumina can serve as support material to form silica-surfactant nanocomposites with

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a desirable orientation of nanochannels perpendicular to the surface of the support and consequently parallel to (along) the alumina pores. Therefore, this method was also applied by us for the preparation of our membranes in order to allow preferential transport nanopaths for molecules. In the first step, the AAMs were filled in with a surfactant (CTAB) template silica and then calcinated to remove CTAB. Afterward, silica was reacted with octadecylsilica (ODS) followed by the incorporation of long-chain hydrophobic carriers [23, 24]. In the absence of the silica–surfactant–receptor nanocomposite in the alumina membrane, Na^+ and K^+ cations are transported through the membrane in a similar proportion. In contrast, the hybrid crown alumina membranes, including the silica-surfactant composite, show a selective transport of ions depending on the receptor selectivity **5** or **6**, respectively. In every case, we can distinguish two stages for the transport mechanism: (i) a simple and (ii) a facilitated diffusion. In the first one, the membranes are functioning like a “sponge,” and the simple rapid diffusion through the membrane is accompanied with the selective complexation of the fittest cation (Na^+ for **5** and K^+ for **6**, respectively); it is the so-called “membrane self-preparing step.” The selective transport of the specific cation occurs in the second stage much faster. Thus, one can conclude that the membrane with **15C5** receptor facilitates in the second step the transport of Na^+ , whereas **18C6** receptor facilitates the transport of K^+ . These experimental results suggest that the self-assembly of receptors inside the surfactant-templated silica nanochannels of the columnar alumina pores can reorganize during the molecular transport, the mechanism being characterized by an initial self-preparing step. This gives the possibility of controlling (changing) the constitution of the three-dimensional functional superstructure present under confinement in the pores, by simply adding the ions. Such spatial self-emergence of specific ion-induced supramolecular structures leads to a significant improvement of transport performance (transport rate and selectivity). These constitutional dynamic systems also demonstrate a flexible adaptation to a self-customized recognition for the dimensionally compatible ions selected from mixtures of ions. This concept led to the identification of effective self-evolved ion channels adapted to ions that initially create this superstructure. More precisely, the solute allows the preparation of an optimal membrane structure for their own transportation!

This feature provides the ability to self-design dynamic membrane materials emerging their own functional structure in order to improve the system performance. This work opens other new perspectives. By their ability to change their constitution in response to external stimuli, to produce the most efficient superstructure, these materials lead to the definition of “systems membranes,” [6] with adaptability and emerging functionality. This research opens the way for the synthesis of adaptive membrane materials, with transport properties that mimic natural ion channels of interest to biologists with significant contributions in the fields of chemical separation, sensors, or release assets.

It has been shown earlier that artificial G-quadruplex represents a dynamic architecture that presents in solution dynamic exchanges with G-ribbons and G-quartets. These dynamic equilibriums can reveal new phases organized according to various external factors such as ion effectors. It has been shown

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that porous silicon (pSi) can be used as a protective matrix slowing the dynamic exchanges observed in solution and allowing their stabilization and also more importantly the optical detection of artificial G-quadruplexes [26]. Indeed, the formation in real time of the G-quadruplexes in the host matrix pSi induces controlled changes in the refractive index of the matrix, depending on the molecular packing density, which is different for G-quadruplexes and G-ribbons. When the confined G-quadruplexes are formed, the initial green/blue color of the pSi films changes to red. Their presence can be easily detected with the naked eye (Figure 24.7). In addition, the G-quadruplexes with different stabilizing cations (Na^+ , K^+ , or Ba^{2+}) may be detected selectively. These examples of work open up new perspectives: on the one hand, they open the way for the design of materials for simultaneous stabilization and detection of dynamic supramolecular architectures. In addition, they will provide a better understanding about the role of G-quadruplexes in molecular information transcription mechanisms and the control of gene expression. As a common feature, the systems presented in this section constitute or evolve to form organized architectures in inorganic mesoporous scaffolds. Moreover, they demonstrate their adaptivity in response to external factors resulting in a variable and flexible functionality with important applications in sensors or membranes.

24.4 Artificial Water Channels (AWCs)

24.4.1 Artificial Water Channels in Bilayer Membranes

In living organisms, the physiological processes are governed in part by the translocation events of metabolites across the cell bilayer membrane, the most effective and the most complex of the membranes at all. These membranes use channels, specifically dedicated to these exchanges. The chemist has long been trying to understand these transfers regulated by various proteins in an attempt to reproduce them in artificial molecular systems. In this context, many artificial membranes have been constructed to control the conduction of ions through artificial ion channels, specially dedicated to this function. However, there has been less progress in the area of synthetic water channels, whose role is to ensure the selective transport of water against ions [27, 28]. In these channels, oriented water wires are formed from water molecules intermolecularly linked via hydrogen bonding and synergistically interacting with inner moieties on the wall of the channel. It is indeed not easy to build such architectures because of the synergistic control and correlation of channel–water and water–water interactions. Even more difficult is to achieve systems that selectively conduct water against ions (Na^+ , K^+ , for example), whose regulation in living organisms is provided by Aquaporins (AQPs). Indeed, these water wires can be polarized. The water molecules adopt a unique dipolar orientation and preserve the overall electrochemical dipolar potential along the channel. There are until now in the literature only very few examples of artificial water channels that integrate only synthetic elements in their water-selective translocation unit [29].

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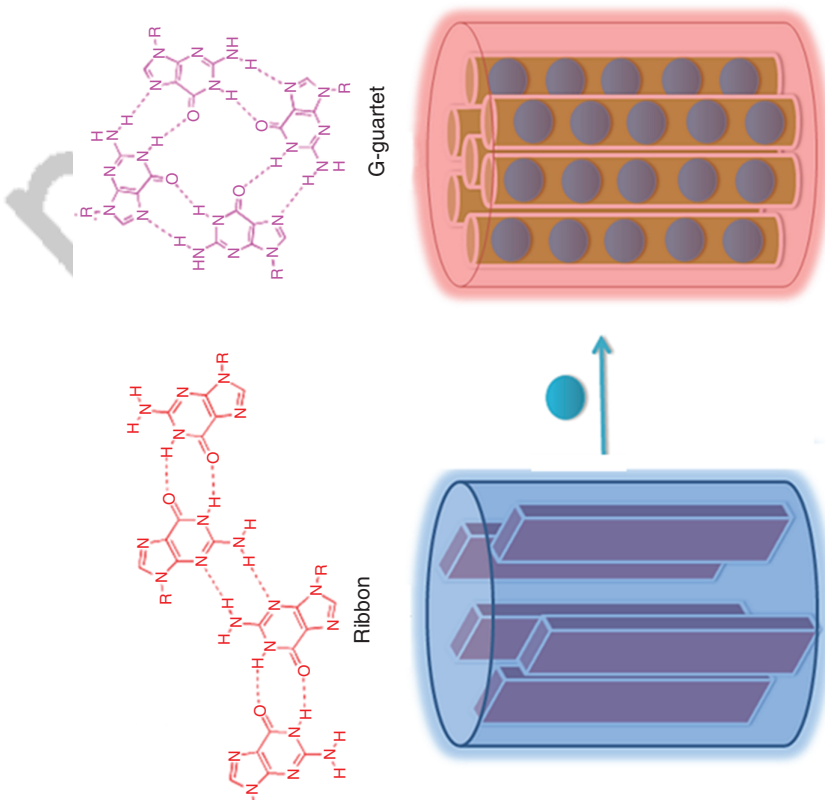
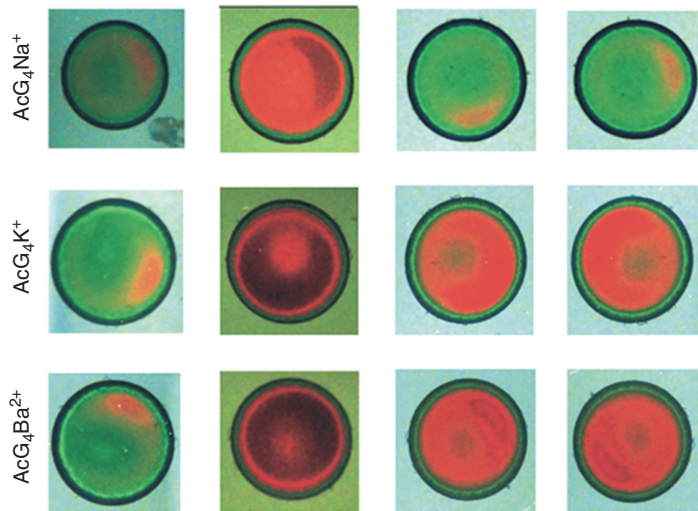


Figure 24.7 Dynamic exchanges between supramolecular architectures of G-ribbons, G-quartets, or G-quadruplex in the presence of ionic effectors (blue sphere). Dynamic constitutional confinement of the lamellar G-ribbons and the hexagonal cylindrical G-quadruplex with a different molecular packing density results in a change in the refractive index of a hybrid film of porous silicon used for their confinement. The formation of G-quadruplexes under confinement within a pSi film by adding ions is identified by a color change from green/blue to red.

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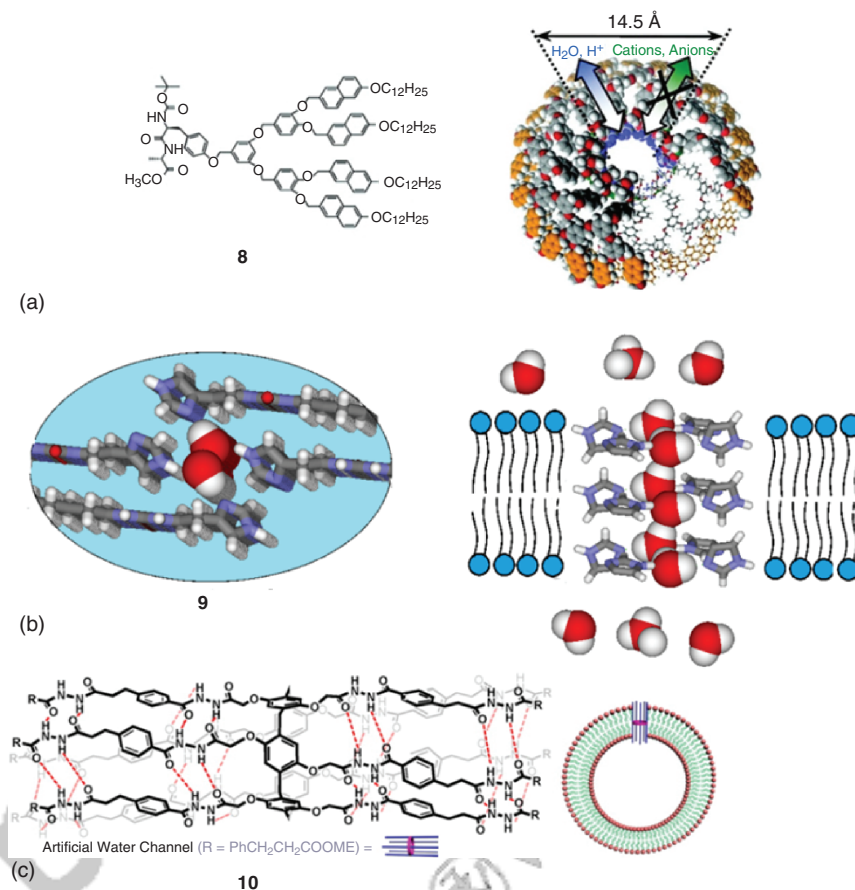


Figure 24.8 (a) Top view of the helical pore assembled from dendritic peptides, **8**; (b) the I-quartets, **9** presenting supramolecular chirality can accommodate dipolar water wires along the length of the channel; and (c) the Pillar[5]arene hydrazone units, **10** form pentameric cylinders.

Synthetic building blocks have been used to generate such systems where water was shown to transport through hydrophilic, hydrophobic, or hybrid hydrophobic/hydrophilic tubular superstructures inserted within the bilayer membranes very efficiently. Dendritic dipeptides, **8**, self-assemble via enhanced peripheral π -stacking to form stable cylindrical helical pores (14.5 Å in diameter) of reasonable thermal stability (Figure 24.8a). They selectively transport water molecules against ions through self-assembled hydrophobic nanotubes stable in phospholipid membranes. The ion exclusion phenomena are based on hydrophobic effects that appear to be very important [30].

Later, it has been reported that imidazole (I) quartets, **9** can be mutually stabilized by inner dipolar water wires, reminiscent of G-quartets stabilized by cation templating (Figure 24.8b) [31]. The I-quartets are stable in solution, in the solid state, and within bilayers, leading to the tubular channel-type chiral

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superstructures. These systems have provided excellent reasons to consider that the supramolecular chirality of I-quartets and water-induced polarization within the channels may be strongly associated. Recently, Hou and coworkers proposed a very elegant artificial system that functions exclusively as single-molecule water channels (Figure 24.8c) [32]. Hydrazide-incorporated pillar[5]arenes, **10**, were used to form H-bonded superstructures that are robust when embedded in bilayer membranes.

Unlike ions and water molecules that can be transported across membrane as isolated entities, protons need a carrier on which the charged monoatomic particle hops from one to another. Water can be the appropriate media, in the hydronium form, or many other organic moieties. Although several well-known membrane examples are identified to transport protons, such as sulfonic acid functions in Nafion[®] or proton pumps in transmembrane ATPases, rare examples of synthetic bilayer membranes transporting H⁺ can be found. Hou's group has developed artificial transmembrane channels based on the same pillar-arene superstructures in which water formed wires. It was shown that proton migration occurred along the water wire according to the Grotthus mechanism [33] using the isotope effect of H vs. D (deuterium). The H-bonding of these I-quartets leads to tubular solid-state structures and, in a membrane environment, to a barreled channel. Within the I-quartet nanotubes, water molecules of unique dipolar orientation can preserve the electrochemical potential along the channel. These results indicate that protons can permeate bilayer membranes through I-quartet channels. No example of proton transport across a bilayer membrane with a different media than water wires could be found.

Moreover, the imidazole I-quartets can be mutually stabilized by inner dipolar water wires, reminiscent of G-quartets stabilized by cation templating [34]. The I-quartets are stable in solution, solid state, and within bilayers, leading to the tubular channel-type chiral superstructures. These systems have provided excellent reasons to consider that supramolecular chirality of I-quartets and water-induced polarization within the channels may be strongly associated. The confined supramolecular water wires, as in AQP channels, form one H-bond with the inner wall of the I-quartet and one H-bond with an adjacent water molecule. Moreover, the water molecules adopt a unique dipolar orientation and preserve the overall electrochemical dipolar potential along the channel. These results strongly indicated that water molecules and protons can permeate the bilayer membranes through I-quartet channels. The ion exclusion phenomena are based on dimensional steric effects, whereas hydrophobic and hydrodynamic effects appear to be less important. The water-free *I-quartet*-“off form” superstructure is reminiscent of the closed conformation of the proton gate of the Influenza A M2 protein. The slight conformational adjustments allow the water-assisted formation of the *I-quartet*-“open form” through which protons can diffuse along the dipolar oriented water wire in the open-state pore-gate region. These artificial I-quartet superstructures obtained by using a simple chemistry are in excellent agreement with structural X-ray and NMR results as well as theoretical results providing accurate structural issues for water/proton conductance mechanisms through the Influenza A M2 channel (Figure 24.9).

Color Fig: 24.9

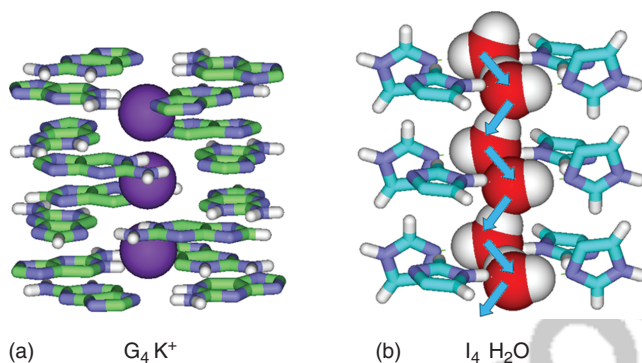


Figure 24.9 (a) G-quartet-G4 and (b) I-quartet-I4 for the transport of cations and water molecules, respectively.

24.4.2 Biomimetic Membranes Using Aquaporins and Artificial Water Channels

During the past decade, the basic research on Artificial Water Channels (AWCs) has been focused on their design, direct synthesis, molecular simulations, and transport properties in lipid bilayer membranes [29, 35]. The osmotic water permeability of several artificial systems embedded in lipid bilayers ranges – [36] to 2 orders [37] of magnitude lower than that of AQP1 ($\sim 10^8$ – 10^9 molecules/s/channel), with similar or even better values for CNTs [38].

The large cross-sectional area of AQPs (9.0 nm^2) is somewhat disproportionate with regard to the size of its active functional pore for which the narrowest region diameter is only 3 \AA [39]. It is important to note that the effective cross-sectional area of the AWC molecular channels in 2D layers will take up significantly less space than proteins. From an engineering point of view, this could potentially increase by orders of magnitude the permeability of AWCs per surface area when compared with AQPs (Table 24.1).

The two main challenges for AWCs are (i) to make tailored channels that reject salt but allow the easy passage of water molecules and (ii) the transfer of the AWCs from the nanomolecular level to that of large-scale membrane materials. Although this has been achieved using AQPs [41], no studies have been reported yet on integrating the AWCs within active layers casted onto polymeric membrane supports.

Kumar et al. published a first paper that proposed the idea of incorporating AQPs in block copolymer (BCP) vesicles and even for low density of Aquaporin Z (AQPZ)-incorporated polymer, the productivity of the membranes was at least an order of magnitude larger than values for existing salt-rejecting polymeric membranes [40]. Then, another parallel inspiring method using the direct fusion of AQP-embedded bilayers on a hydrophilic membrane surfaces led to supported lipid membranes, showing low reconstitution of membrane proteins [42, 43]. The morphology of self-assembled biofilms follows similar behaviors for all these systems, showing discontinuous phases on the surface function

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Table 24.1 Performance overview of artificial water channels and pores reported until now.

Water channels	Net permeability for water/single-channel permeability	Selectivity	References
Aquaporins (AQPs) hourglass structure with a narrowest constriction of 2.8 Å	167 $\mu\text{m}^2/\text{s}/\text{bar}$ 4×10^9 water molecules/s/channel	High selectivity for water, perfect rejection of ions and protons	[40]
Carbon nanotube's (CNTs) estimated diameter = 15 Å	300 $\mu\text{m}^2/\text{s}/\text{bar}$, 1.9×10^9 water molecules/s/channel	—	[38]
CNT's estimated diameter = 8 Å	520 $\mu\text{m}^2/\text{s}/\text{bar}$, 2.3×10^{10} water molecules/s/channel	Ion rejection in dilute solutions	[38]
Hydrophilic I-quartets, channel (2.6 Å)	3–4 $\mu\text{m}^2/\text{s}/\text{bar}$ 1.5×10^6 water molecules/s/channel	High selectivity for water, reject all ions except protons	[37]
Peptide-appended pillar[5]arenes, PAP2 unimolecular channel (5 Å)	Swelling: 30 $\mu\text{m}^2/\text{s}/\text{bar}$ or 3.5×10^8 molecules/s/channel shrinking: 1 $\mu\text{m}^2/\text{s}/\text{bar}$ or 3.7×10^6 molecules/s/channel	No selectivity for water, good conduction for alkali cations	[36]
RO membrane	2 $\mu\text{m}^2/\text{s}/\text{bar}$	99.8% rejection of salts vs. water	[40]

Source: Adapted from [29, 35].

on the volume fraction occupied by AQP in the bilayer. While the average stability times are qualitatively correct, it appears that such strategy limits the amount of functional protein that can be incorporated into membrane. Despite all these results, the major challenge relates on how scaled-up reconstituted high-density membranes of reasonable available filtration area surface can be prepared. Then, successful high-density reconstitution of AQP in various BCP systems has been demonstrated by a significant number of papers. The simple BCP vesicle rupturing strategy was demonstrated successfully to prepare high-density active AQP-confined polymer membranes on the surface or within porous membrane substrates (reviewed in Ref. [41]) [44–46]. Polymerization of protective cross-linked matrixes or controlled dialysis procedures have been used to incorporate AQP-confined vesicles into thin-film composites. The AQP-vesicle-containing films will combine the partial performances of the AQP-vesicles and of the cross-linked polyamide (PA) matrix materials.

Designing stable membranes capable of keeping AWCs in their active state will prove crucial for future nanofiltration or reverse osmosis (RO) processes. The use of lipid bilayers or hydrophobic polymers as host matrixes, which certainly can be affected by the presence of organic solutes or surfactants in water, is not a necessary option. They have been used until now to compare the performance of AWC with the AQP ones. One strategy to obtain modified active layer is to incorporate

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the AWC networks while forming the PA layer of RO membrane or to imagine new cross-linked polymers in order to obtain networks of AWC within the thin layers on the top of nanofiltration membranes. If AWCs are covalently attached to thin film composites (TFC), there is no degradation of layer, only temporary channel destabilization. This way, the nanometric AWCs are dense and highly robust, would be encapsulated in the dense part of the membrane, while the PA matrix should be responsible for the rejections of organics.

To compete with polymeric reverse osmosis RO membranes, the current gold standard for desalinating seawater, water flux, and rejection rates for AWCs need to be very close to that of AQPs. While having even higher flux values will not have a substantial impact on membrane filtration performances, highly water specific membranes will improve the quality of water produced as well as remove unnecessary pretreatment processes [47]. An optimal bonding of water clusters within the channel is needed for selectivity, while less friction/interaction with the channel structure is desired to increase the water permeability. These key features must be combined in order to exploit both the selectivity of hydrophilic H-bonding channels like I-quartets and the high permeability of hydrophobic carbon nanotubes (CNTs). Shorter channel lengths, more dense channels per unit area of surface, will play an important role in developing efficient water filtration systems based on AWC technology. Given the importance of developing even more efficient membranes for desalination, this will be an exciting and challenging project, potentially redefining the paradigms of desalination.

24.5 Conclusions

Controlled formation of three-dimensional functional devices in silica makes hybrid membrane materials as presented here of interest for the development of a new supramolecular approach to nanoscience and nanotechnology through self-organization, toward systems of increasing behavioral and functional addressabilities (catalysis, optical and electronic applications, etc.). The above results describe a simple synthetic hybrid material that successfully formed molecular recognition devices, transport patterns so as to enable efficient translocation events. To our knowledge, the present systems are the first example of a hybrid nanomaterial where the concept of self-organization and a specific function (generation of specific translocation pathways in a hybrid solid) might in principle be associated. Finally, these findings show that the sol-gel may be used for reading biomolecular information. This is a new way of embedding base-pairing or transcribing the supramolecular chirality in materials of interest for developing a new sol-gel approach for nanoscience and nanotechnology.

The combined features of structural adaptation in a specific hybrid nanospace and of dynamic supramolecular selection process make the dynamic-site membranes, presented in the third part, of general interest for the development of a specific approach toward nanomembranes of increasing structural selectivity. From the conceptual point of view, these membranes express a synergistic adaptative behavior: the addition of the fittest alkali ion drives a

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constitutional evolution of the membrane toward the selection and amplification of a specific transport crown-ether superstructure in the presence of the solute that promoted its generation in a first place. It embodies a constitutional self-reorganization (self-adaptation) of the membrane configuration producing an adaptative response in the presence of its solute. This is the first example of dynamic “smart” membranes where a solute induces the upregulation of (or even prepares itself) its own selective membrane.

Acknowledgements

This work was also conducted within ANR-15-CE29-0009 DYNAFUN.

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Abstract

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This chapter describes various strategies for the development of biomimetic channels and their dimensional extension toward up-scaled nanofiltration membrane materials, summarizing recent developments in this area. After a short nonexhaustive description of the artificial supramolecular channel systems involved in water, proton, and ion transport processes through bilayer membranes, these *all-made* artificial systems are described as a source of inspiration by presenting several breakthroughs of the past years in the field of *biomimetic nanofiltration materials*. Then, their inclusion in artificial polymeric/hybrid matrixes, resulting in the formation of membranes for directional translocation *via* channeling pathways, is described, highlighting all the efforts necessary to maintain their channel-transporting functions observed within bilayer membranes under up-scaled operating conditions.

Keywords

ion channels; water channels; membranes; hybrid materials; self-assembly