# The future of membranes

## Toward the natural selection of functions

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Abstract This paper describes various strategies for the development of self-assembled supramolecular channels and their dimensional extension toward up-scaled self-organized materials, summarizing recent developments in this area. After a short non-exhaustive 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 last years in the field of *biomimetic supramolecular channel* systems. Then their inclusion in artificial polymeric/hybrid matrixes, resulting in the formation of *biomimetic artificial materials* 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 Les membranes du futur : vers la sélection naturelle des fonctions

Cet article décrit diverses stratégies récentes utilisées pour le développement de canaux supramoléculaires auto-assemblés et leur extension à des matériaux auto-organisés. Après une rapide description des systèmes de canaux artificiels supramoléculaires impliqués dans le transport ionique et d'eau à travers les membranes bicouches, ces systèmes membranaires totalement artificiels servent d'exemples de systèmes *de canaux biomimétiques supramoléculaires*. Leur inclusion dans des matrices polymère/hybrides artificielles conduit à la formation de *matériaux biomimétiques artificiels* permettant la translocation directionnelle. Des efforts pour préserver, lors du passage à une échelle supérieure opérationnelle, leurs propriétés en tant que canaux de transport dans les bicouches, sont nécessaires.

Mots-clés Canaux ioniques, eau-canaux, membranes, matériaux hybrides, auto-assemblage.

Constitutional dynamic chemistry [1-3] and its application, dynamic combinatorial chemistry [4-5], are new approaches to produce chemical diversity. Unlike conventional methods, they allow the simple generation of functional systems, amplified from a mixture of molecular and supramolecular blocks that interact and exchange reversibly. Kinetic or thermodynamic selection, self-assembly followed by covalent modification or binding and phase changes are a few helpful strategies to control and to create a convergence between self-organization and constitutional functions. These dynamic systems are of particular importance for a diverse range of applications such as medicine, catalysis, the discovery of new materials, transport systems, etc.

Constitutional dynamic chemistry implements a molecular/supramolecular reversible dynamic interface between the interacting components, promoting structural correlation of different components of the system, based on their fundamental constitutional features [6]. During the last decade, constitutional dynamic chemistry is moving towards dynamic systems with greater dimensional behaviors [7-8]. Comprehensive approaches are used to conserve the molecular self-organizing properties and to transfer them to the upper size scales. Much efforts continues to be undertaken on complex systems which have been identified as especially promising tools to explore the space with natural selection of structural and functional behaviours. This gives the possibility to extend and to engineer multivalent interactions in order to control the organization of complex matter across extended scales. It generates systems which may possess novel properties not present at molecular level [7]. This opens wide perspectives to imagine a fundamental transition from supramolecular design toward constitutional selection approaches, which might give great potential in various applications [8]. This article focuses on constitutional methods to understand and to control the flow of structural information across several orders of magnitude (figure 1). These methods show the potential to impose a specific order at 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 nanosystems. These steps are sometimes too long and research strategies should expand the fundamental understanding of the structures and the dynamics of self-assembly properties, for the creation of new products and modern production processes.

Within this context, functional supramolecular systems, representing multiple copies of the specific recognition events between reversibly interacting molecular components can generate adaptive networks of increased dimensional behaviors *via* polymerization processes (*figure 1*). This gives



Figure 1 - Up-scale transposition of self-organized functional ion-channels from supramolecular architectures toward informed materials for the directional translocation.

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].

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

This paper devoted to constitutional membrane systems is divided in three sections. The first part focuses on the implementation of the self-assembly on the elaboration of self-organized hybrid materials, emphasizing the more recent developments of *biomimetic hybrid membranes*. The second part describes recent works on the development of adaptive mesoporous membranes with special emphasis on the self-assembly approaches for building adaptive constitutional membranes. The third part presents the first advancements in the field of artificial water channels and their comparisons with natural systems. Current and potential applications of these new systems with combined characteristics of structural adaptation are presented.

#### Self-organized hybrid membranes

The concept of facilitated transport [10-12] has been connected to the concept of liquid membranes (a liquid organic interface interposed between two aqueous phases) for a long time. The main purpose of this work was to construct and synthesize specific receptors, geometrically adapted to the species being transported. The success of these approaches was conducted to ensure good molecular recognition of the solute by the receptor at the feed interface, to selectively transport the resulted host-guest mobile complex across the membrane and to release easily at the receiving interface [13]. In this context, a new approach (concept) concerning the facilitated transport through dense solid hybrid membranes for molecular recognition and self-organized materials was introduced in the recent years. The interest of the proposed approach lies directly into the design and processing of the material, which can be assimilated to a "hybrid solution". By similarity with the biological membrane channels, the structured molecules within a material selectively control the diffusion of a solute by preferential transport pathways. Because of the limited thickness of the active layer (1-2  $\mu$ m), these materials can be polarized, for example the co-transport of counter-ions.

Receptors may 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]. This may be achieved by self-organizing the receptors, in order to create channels or preferential pathways within the solid matrix for different solutes: cations, anions (figure 2a) or neutral molecules. Molecular channel-type systems have been developed by using crown ether precursors of with a specific selfassembly, via a network of hydrogen bonds between the urea groups (figure 2b). For such compounds, the formation of oligomers in solution [14] and in the solid state leads to regular nanometric arrangements, allowing the formation of ion channels (figure 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<sup>2-</sup>), against the concentration gradient and activated by competitive ionic transport [15].

The creation of ion channels in a hybrid membrane can also be done from the simpler molecules, i.e. "ureidopeptoides" containing as functional unit the side moieties of aromatic amino acids, which can interact with alkali cations *via* cation- $\pi$  interactions, which are of major significance in biology and have been recognized for many years [16].

Using these principles, and thanks to the versatility of the sol-gel process, dynamic 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 encode the required information for ionic assisted-diffusion within hydrophilic conduction pathways embedded in hydrophobic structuring nanodomains (figure 3 p. 40). 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 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 affinities between transported solutes and the membrane are related to the nature of the aromatic rings grafted on the membranes and will strongly depend on their hydrophobicity. 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, we can conclude that the transfer rate and the ability of a solute to pass through a membrane depend on thermo-



Figure 2 - a) Heteroditopic receptors for ions salts complexation: Na<sup>+</sup> ion (purple) and Cl<sup>-</sup> (green) are synergistically complexed by the receptor. b) Self-organization into macrocyclic ribbons *via* hydrogen bonding to form supramolecular ion channels. c) Dynamic organization in solution and transcription *via* the sol-gel process of directional supramolecular ion-channels in hybrid materials.

dynamic effects (solute partition between feed and receiving phases) but also kinetic effects (diffusion is facilited in dense membranes). These two aspects can be respectively connected to the chemical nature of the precursors but also to their ordered arrangement within the material [17].

Using this knowledge, the same strategy employing a combined supramolecular self-organization and sol-gel synthetic route 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]. Self-supported membrane systems, organized through the organic sulfonic and urea groups showed an increased lamellar organization in the hybrid matrix (*figure 4*). This generates therefore an efficient percolated conducting network which in turn results in correspondingly high proton conductivity 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 4*). These data are indicative of the formation of waterfilled self-organized channels and extend the applications of self-organized hybrid materials toward functional supramolecular devices.

As a preliminary conclusion, all these results concerning the self-organized functional hybrids have highlighted the wide potentialities of resolution strategies for polymorphic supramolecular self-assembly, controlled in the second step by an irreversible tandem processes, like 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. The controlled generation of connected self-organized channels along hundreds of nanometers for this class of well crystalline compound for directional diffusion of protons result in the formation of PEMs hybrid materials with high ionic conductivities up to  $\sigma$  = 160.2 mS·cm<sup>-1</sup> This value is higher than the conductivity reported for Nafion 117<sup>®</sup> commercial membrane [18].

An other important feature of molecular systems is the chirality which is often linked to the presence of asymmetric centers in the molecules. In the world of the living matter, non-chiral 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 (ionchannels). This example of a synthetic chiral functional architecture, frequently encountered in biological systems (DNA, RNA...) has attracted many scientists since forty 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 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 scaffolding pillar to obtain hexagonal twisted hybrid rods of 800 nm in diameter (*figure 5*). The heat treatment at 400 °C leads to the elimination of organic molecules and the formation of silica propellers. The propellers are several micrometers long and their chiral topology is very similar to their supramolecular congeners: the G-quadruplexes. The dynamic supramolecular



Figure 3 - Multi-scale self-assembly of a) ureidopeptoide receptors in b) hydrophilic channels and c) oriented lamellar nanodomains in hybrid materials. d) Self-organized conduction layers are generated through the membranes for oriented and synergistic translocation of ion pairs.



Figure 4 - Up-scale transfer from molecular level to nanostructures, describing the internal organization of the hybrid membrane materials for the proton conduction, with the formation of lamellar hydrophilic channels of hundreds of nanometers, structured in a hybrid matrix [18].

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. It is known that the principle of helical growth is in place to ensure the stability of the giant sequoias. In the same way, structural auto-correlation 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 trees. The process showing the transcription of supramolecular chirality of G-quadruplexes at the nanoscale is presented in *figure 5*. While using a helical growth principle to make nano-sequoias.... 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, parallel to biology, thus giving their unique properties by producing new hybrid replicas at the nanoscale [21-22].

#### Adaptive constitutional membranes

It was found that the constitutional self-assembly of supramolecular systems confined in the oriented silica mesopores leads to emerging systems 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 initiated, paving the way for the synthesis of adaptive constitutional materials, creating their own function optimized in response to external stimuli. In this context, the oriented inorganic silica mesopores are used as directional host matrix for self-organizing molecules of crown ether type forming supramolecular pathways for the transport of ions (ion channel) [23-24].

The dynamic organization of the system is ensured by the fact that the self-organized supramolecular architectures interact in a non-covalent reversible manner with the hydrophobic inorganic matrix. Their crystalline order is preserved when incorporated into the hydrophobic mesopores which might be structurally related bilayer membranes (figure 6a). Their crystallographic structures can be elucidated within the mesoporous hydrophobic materials and their possible structural transformation is determined by the presence of ionic effectors (figure 6b) [25]. This gives the possibility of controlling (changing) the constitution of the three-dimensional functional superstructure under confinement in the pores, by simply adding the ions. Such spatial self-development of supramolecular structures in the presence of ions 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: the solute allows the preparation of an optimal structure for their own transportation! This feature provides the ability to design dynamic materials



Figure 5 - The cation-templated self-assembly of guanine alkoxysilane results in the formation of *G*-quartets and *G*-quadruplexes; the supermolecular chirality of *G*-quadruplexes is transcribed in solid hybrid materials by sol-gel in the presence of templating K<sup>+</sup> cation [19].



Figure 6 - a) Generation of directional ion-conduction pathways, b) which can be morphologically tuned by alkali salts templating by the hydrophobic confinement of ureido-macrocyclic receptors within silica mesopores. c) It embodies a reorganization of the membrane configuration evolving an improved response in the presence of the solute that produced this change in the first place [29].

emerging their own functional structure in order to improve the system performances. 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 (*figure 6c*). This research opens the way for the synthesis of adaptive materials, with transport properties that mimic natural ion channels of interest to biologists with significant potential contributions in the fields of chemical separation, sensors or principles release assets.

We have shown earlier that artificial G-quadruplexes represent a dynamic architecture that presents in solution dynamic exchanges with G-ribbons and G-quartets. This dynamic equilibrium can reveal new phases organized according to various external factors such as ion effectors. It has been shown that the porous silicon (pSi) can be used as 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 Gribbons. 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 7). In addition, the G-quadruplexes with different stabilizing cations (Na<sup>+</sup>, K<sup>+</sup> or Ba<sup>2+</sup>) may be detected selectively.

These works 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 control of gene expression.

As a common feature, the systems presented in this section constitute or evolve to form organized architectures in



Figure 7 - Dynamic exchanges between supramolecular architectures of G-ribbons, G-quartets or G-quadruplexes in the presence of ionic effectors (blue sphere). Dynamic constitutional confinement of the lamellar G-ribbons and of the hexagonal cylindrical G-quadruplexes with a different molecular packing density results in a change in refractive index of a hybrid film of porous silicon used for their confinement. The formation G-quadruplexes under confinement within a pSi film by adding ions is identified by a color change from green/blue to red.

inorganic mesoporous, demonstrating their adaptivity in response to external factors resulting in a variable and flexible functionality with important applications in sensors or membranes.

### Artificial water channels: transporting water like in cells

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 trans-

fers 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-channel, 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<sup>+</sup>, K<sup>+</sup>, for example), whose regulation in living organisms is provided by aquaporins. Indeed, these waterwires can be polarized. The water molecules adopt a unique dipolar orientation and preserve the overall electrochemical dipolar potential along the channel.

Very recently we have reported that imidazole I-quartets can be mutually stabilized by inner dipolar water-wires, reminiscent of G-quartets stabilized by cation templating [29]. 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 water wires, like in aquaporin channels, form one H-bond with the inner wall of the I-quartet and one Hbond 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-guartet channels. The ion-exclusion phenomena are based on dimensional steric effects whereas hydrophobic and hydrodynamic effects appear to be less important. Water-free Iquartet-"off form" superstructure is reminiscent with closed conformation of the proton gate of the Influenza A M2 protein. The slight conformational adjustments allow the formation of water assisted I-quartet-"open form". The protons can diffuse along 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 Influenza A M2 proton channel.

### Conclusion

The most revolutionary consequences provided by the constitutional dynamic chemistry [2-3, 30] for the preparation of functional materials may reflect the exciting possibilities offered by selection, evolution, amplification, molecular recognition and replication. This paper is not a comprehensive treaty, but is a timely objective snapshot of the field of constitutional dynamic chemistry applied to the membrane materials from which the reader can get a broader view and we hope future inspiration. All the systems presented here represent prototypes of self-organized constitutional devices for directional transport of water and ionic species. Finally the results presented in this section extend the application of *constitutional dynamic chemistry* to *constitutional membrane materials* science. This feature offers to materials science perspectives towards self-designed materials evolving their



Figure 8 - Tubular G-quartet-G4 and I-quartet-I4 systems for the conduction of cations and water molecules, respectively.

own functional superstructure so as to improve their functional perf ormances. Prospects for the future include the development of these original methodologies towards dynamic materials, presenting a greater degree of structural complexity.

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