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Main Manuscript for

Tunable membranes incorporating artificial water channels for high-performance brackish/low salinity water reverse osmosis desalination

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Abstract

Membrane-based technologies have a tremendous role in water purification and desalination. Inspired by biological proteins, artificial water channels (AWC) have been proposed to overcome the permeability/selectivity trade-off of desalination processes. Promising strategies exploiting the AWC with Å-scale selectivity, have revealed their impressive performances when embedded in bilayer membranes. Herein, we demonstrate that self-assembled imidazole-quartet (I-quartet) AWCs are macroscopically incorporated within industrially relevant reverse osmosis membranes. In particular, we explore the best combination between I-quartet AWC and m-phenylenediamine (MPD) monomer to achieve a seamless incorporation of AWC in a defect-free polyamide membrane. The performance of the membranes is evaluated by cross-flow filtration under real reverse osmosis conditions (15-20 bar of applied pressure) by filtration of brackish feed streams. The optimized bio-inspired membranes achieve an unprecedented improvement, resulting in more than twice (up to $6.9 \text{ L m}^{-2}\text{h}^{-1} \text{ bar}^{-1}$) water permeance of analogous commercial membranes, while maintaining excellent NaCl rejection (>99.5%). They show also excellent performance in the purification of low-salinity water under low-pressure conditions (6 bar of applied pressure) with fluxes up to $35 \text{ L m}^{-2}\text{h}^{-1}$ and 97.5-99.3% observed rejection.

Significance Statement

Inspired by biological models, artificial water channels can be used to overcome the permeability/selectivity trade-off of traditional desalination membranes. We demonstrate that rational incorporation of I-quartet artificial water channels in composite polyamide membranes synthesized *via* interfacial polymerization, provide defect free biomimetic membranes with intrinsic water-to-salt permeability on the operational Brackish water reverse osmosis-BWRO/ Tap water reverse osmosis-TWRO desalination pressure and medium/low salinity conditions.

Introduction

Competition over increasingly contaminated freshwater resources during the last decades has made the availability to safe drinking water a serious global challenge for the 21st century. Desalination is one of the solutions to the problem of freshwater scarcity, along with environmental remediation technologies and sustainable conservation policies.^{1,2} Currently, about 100 million m³/day of desalinated water is being produced, with an annual increase of more than 10%. Traditional reverse osmosis (RO) membranes are thin-film composites (TFC), which rely on a supported polyamide layer to perform water/solute separations.^{3,4}

Synthetic membranes act by dissolving and diffusing solutes with scale selectivity through their polymeric matrix: a material property that leads to a permeability-selectivity trade-off behavior.⁵ Numerous approaches have been proposed to overcome this limitation, including membrane grafting, chemical functionalization, and processes optimization.⁶⁻¹⁰ Despite several elegant design strategies, membrane-based technologies always report an improved water permeability at the expense of lower selectivity, or vice versa.¹¹ Although membrane-based separation offers energy efficiency, excellent water quality, and capability for implementation at industrial scale, there is a pressing need for membranes with both improved selectivity and enhanced permeability, especially for increasing the efficiency of the RO purification technology.^{2,4}

Recent advances have made materials prepared under molecular control increasingly more attractive to researchers, offering the possibility of stable and high efficiency bio-inspired membranes.^{1,2} Due to their unique functional design, biological aquaporins and artificial water channels (AWC), with proven high performances at the Å-scale, when embedded in lipid bilayers, have inspired their incorporation into desalination membranes.^{12,13} Self-assembled^{14,15} and unimolecular¹⁶ AWCs have been developed during the last decade with the hope to mimic the complex biological machinery.¹⁷⁻¹⁹ These approaches have shown that AWCs are mostly active when embedded in lipid bilayers, but upscaling methods toward biomimetic RO polymeric membrane that can be prepared at industrial standards is possible.²

The defects created at the interface between active AWCs and surrounding matrices are critical for the performances of RO membrane for desalination. When fabricating a high-performance RO membrane for desalination, a number of necessary characteristics need to be achieved to maximize the productivity, including suitable mechanical resistance, high density of the functional channels per unit area and, perhaps the most ambitious of all, the absence of defects.¹ We postulated that one of the creative strategies for addressing the scale-up challenges and improved performances is to combine the established polyamide (PA) material prepared *via* interfacial polymerization (IP) and known for its easy scalability *via* the integration within a typical roll-to-roll processing system, with both permeable and selective AWCs.²

We previously reported the fabrication of a biomimetic membranes, containing I-quartet AWCs embedded in a classical polyamide PA.² We know that compositional diversity of PA components and additives have a tremendous impact on membrane structure and performances.¹ In the present report, our novel strategy leads to a greater fundamental understanding of how AWC incorporation influence the performance of PA/AWC membranes. The novel reported hybrid AWC-PA materials can be optimized at the nanoscale with different morphologies and chemical properties by the optimal mixing of various recipes exploiting variable amounts of AWCs and PA components. Specifically, we investigate valuable insights into fabrication-structure-performance relationship and discuss the effect of composition of AWC and *m*-phenylenediamine components for improving and discovering new performances of bioinspired membranes. The novelty here is related to the straightforward quantification of specific compositions, that allow obtainment of seamless active layers in which AWCs are gently and optimally incorporated without creating defects, in all cases. Homogeneous sponge-like superstructures of hybrid PA-AWC materials are thus achieved and applied under new filtration conditions real brackish water and low-salinity-water RO desalination conditions.

Results

Formation pathways of control and bioinspired reverse osmosis membranes. The imidazole-quartet, I-quartet,^{14,15} comprises stacks of four molecules **HC6** and two water molecules that form a pore diameter of 2.6 Å filled with oriented single water wires (Fig. 1a).²⁰ The water orientation²¹ is of prime importance for enhancing its translocation in the range of 10^6 - 10^7 water molecules·s⁻¹ per channel, with a perfect salt rejection via a single wire²⁰ or sponge cluster¹⁷ mechanism. The crystal packing reveals parallel sheets of the alternative I-quartets self-assembled in a lamellar phases of parallel single water channels (Fig. 1c,d) and matching well with the ordered rows observed in the TEM micrograph of a crystalline powder obtained from the evaporation of an ethanolic aqueous casting solution of **HC6** (Fig. 1b).

The RO membranes in this study were prepared by interfacial polymerization (IP) of m-phenylenediamine (MPD) and trimesoylchloride (TMC), resulting in the formation of polyamide (PA) layers onto a commercial polysulfone (PSf) support. For the synthesis of bioinspired PA layers, the conventional IP procedure was preceded by the incorporation of AWCs (Fig. 1e). In a first step, an ethanolic aqueous solution of **HC6** results in the formation of stable colloidal aggregates ($D_h = 200$ nm), observed by dynamic light scattering DLS when water was added to ethanolic solutions of **HC6**, without any visible precipitation. Please note that compared with other previously studied channels **HC4-HC8**, **HC6** with an optimal solubility, avoid precipitation under described IP experimental conditions leading to the formation of free defect membranes. This aqueous solution was poured onto the PSf support which was then immersed in an aqueous MPD solution, resulting in the formation of hybrid AWC/MPD nanosized colloidal aggregates. The DLS analysis shows that smaller aggregates ($D_h = 70$ nm) (See SI Appendix, Fig. S1) were obtained when an aqueous solution of MPD was used instead of pure water, reminiscent of H-bonding interactions between AWC and MPD.² The integration of AWC into PA hybrid layers is firstly related to a nucleation process of such colloidal structures; then, a heterogeneous nucleation is promoted by H-bonding interactions between MPD and colloidal AWC nano-aggregates, as shown by DLS, while any precipitation process was observed. Based on this information, different **HC6**/MPD ratios were investigated to explore the effect of the composition on the material morphology that control and tune the membrane transport performances (See SI Appendix, Table S1). We know that, over the period of incipient formation of the PA film, the polymer growth remains nearly constant, being determined by the diffusion rate of the MPD monomers in the organic phase.²² An excess of MPD is required to promote a significant diffusion into the organic phase during film formation; therefore, an equal or sub-stoichiometric amount of MPD may result in a lower polymerization degree.^{23,24} After the immersion of the support layer into the MPD solution, the excess solution was removed with an air gun from the surface, and the **HC6**-MPD-saturated support was immersed into a TMC solution to form the PA layer. In this step, the AWC/MPD amphiphilic colloidal aggregates might help the migration of the MPD to the organic phase, favoring the IP reaction, while they may synergistically interact with the growing PA segments *via* H-bonding. We surmise that this process results in the formation of cross-linked hybrid AWC-PA materials. Following the IP procedures to prepare both the control and the bioinspired membranes, they were cured in DI water at 95 °C, dipped in a 200 ppm NaOCl aqueous solution, and then in a 1000 ppm NaHSO₃ aqueous solution. The membranes were finally rinsed and stored in DI water at 4 °C before testing or characterization.

Morphological / structural properties of the bioinspired membranes. Evidence of AWCs incorporation. Fourier Transform Infrared (FTIR) spectra demonstrate the formation of a hybrid PA-AWC networks (See SI Appendix, Fig. S2 a,b). Vibration bands associated with amide bonds of the PA are visible in all IR spectra, namely, the peaks at 1502 cm⁻¹ (amide-II, N-H in-plane bending) and 1666 cm⁻¹ (amide-I, C=O stretching vibration).²² Evidence for AWCs incorporation within hybrid PA membranes was obtained from the vibration shifts at 1585 cm⁻¹ and 1609 cm⁻¹, assigned to the C=C stretching of the imidazole and to the C=O stretch of the urea groups, as well as the -CH_{2,as} and -CH_{2,sym} stretch modes of the alkyl chains of **HC6** visible in the range 2750

and 2957 cm^{-1} , respectively. The sharp band centered around 3400 cm^{-1} is attributed to the O-H stretching vibration of strongly H-bonded water within I-quartet channels. This band became broad for the TFC-**HC6** membrane, due to the presence of more mobile less dense H-bonded water within the matrix of the bioinspired layer. This new type of PA-AWC hybrid material generated *via* a nucleation/IP mechanism, is reminiscent of the emergence of self-assembled I-quartets within a porous sponge-like membrane that theoretically present enhanced water permeation as showed by our previous molecular modeling studies.¹⁷ They are suggestive of dynamic superstructures to provide cooperatively interconnected membrane-spanning pathways through water networks.

Fig. S2b, See SI Appendix, presents the average elemental mass fraction X% obtained from energy dispersive X-ray spectroscopy (EDX) analysis for bioinspired membranes prepared by keeping constant the amount of **HC6** and varying MPD concentration. When compared to the control TFC membranes presenting a C % of 61-67 w % as previously reported in literature for traditional PA membranes,^{23,24} the C % of 80-85 w % was significantly higher in all the bioinspired PA-AWC layers. This result is expected because the C/O mass ratio of **HC6** is significantly higher (~10) than that of PA (~3.5-4), thus providing additional evidence of AWCs incorporation in hybrid AWC-PA layers. By reducing the MPD molar ratio, thereby decreasing the density of amine moieties and amide bonds, the N % decreased and the relative C % increased by roughly 4%.

Scanning electronic microscopy (SEM) micrographs (Fig.2 and See SI Appendix, Fig. S3) suggest that the morphology of the layer and the level of **HC6** incorporation can be tuned by adjusting the MPD/**HC6** ratio during membrane fabrication. All the bioinspired layers appeared continuous and free of microscopic defects. The nano- and micro-structures of PA-layers governing mass transport is strongly dependent on the cross-linking degree of PA, influencing the density and distribution of AWCs within the PA matrix. In general, with a constant **HC6** load, as the concentration of MPD was reduced in the fabrication solution, the top surface evolved from a “ridge-and-valley” morphology (an effect of the rapid diffusion of concentrated MPD into the organic phase), typical of conventional PA layers, to a “flake-like” morphology (See SI Appendix, Figs S4, S5) observed for lower MPD concentrations. In addition to a change in the surface roughness, the bioinspired membranes with higher **HC6** loads and medium to high MPD concentrations displayed a distinct, highly porous core structure, with a relatively large thickness ranging from 150 to 300 nm. Even more interestingly, all the layers prepared in the presence of **HC6** further comprised a diffuse distribution of sponge like-packed superstructures that spanned the whole active layer (Fig. 2a,b and See SI Appendix, Fig. S6). These innovative inner nanostructures and overall morphology appeared to be pronounced for the membrane referred to as 0.8-**HC6** (0.8% w/w MPD and the optimal load of 1.5% w/w **HC6**), shown in Fig. 2c,d. Clearly, the cross-section of this representative bioinspired membrane was characterized by: (i) a smoother upper surface compared to the control TFC membrane, (ii) a highly porous multi-layer structure comprising large voids, (iii) a greater overall thickness and (iv) the presence of high-density and homogeneously distributed nanoparticles embedded in the PA matrix. The best combination of productivity and selectivity was obtained with this membrane in experimental brackish water reverse osmosis tests (*vide infra*). When bioinspired PA-AWC layers were instead prepared with a sub-stoichiometric MPD molar ratio ($\leq 0.4\%$ w/w), the concentration of this monomer became the dominant factor governing the final film structure: these layers were generally free of underlying large voids and were characterized by a much smaller average thickness of 50 nm; see the representative samples in Fig. 2e-f. The sponge-like nanostructures embedded in the layer were still observed, although with apparently lower density, possibly due to a more difficult incorporation in thin-films with smaller polymerization degree. This result suggests that the complex core structure of the selective layer embedding self-aggregated AWC-PA sponge-like superstructures is a strong function of both the **HC6**/MPD ratios and the absolute monomer concentrations employed during fabrication, and that the layer architecture can ultimately be controlled by these parameters to tune and improve the RO performance, which is described in detail below.

The surface morphology of the bioinspired PA layers was further investigated by atomic force microscopy-AFM (See SI Appendix, Fig. S7). In agreement with the SEM analysis, revealing the disappearance of the rough ridge-and-valley features, values of RMS <100 nm roughness were found for membranes fabricated with MPD concentrations below 2% w/w. These RMS values are lower than typical values of 100 - 300 nm often observed for classical PA membranes.²⁷ The average roughness, indicative of the overall thickness of the layer, increased when the bioinspired membranes were fabricated using 1.5 % w/w **HC6** and 0.8-1.2 % w/w MPD (Fig. 3a-f), in accordance with the greater internal porosity and thickness of the morphologies observed in SEM micrographs.

Transmission electronic microscopy (TEM) cross-sectional images in Fig. 3 also evidence that by increasing the MPD concentration from 0.2 to 2.0% w/w while keeping constant the amount of **HC6** (1.5% w/w) leads to an increase of membrane thickness; the maximum height of the PA layer correlates with the amount of MPD, with alternating thinner / thicker regions on the top of the PSf support. For 0.2 and 0.4 w/w % MPD (Fig. 3a, b), the PA layer has a more irregular aspect, encompassing larger portions (up to 1 μm , as observed in TEM cross-sections of the 0.2-HC6 membrane) with 20 - 40 nm thickness, portions with more regular aspect of ridge and valley and areas with higher thickness (up to 240 nm and 170 nm for 0.2 and respectively, 0.4-HC6). Starting with 0.8-1.8 w/w % MPD, (Fig. 3c-e) the IP layer has a more uniform aspect with ridge and valley morphology. In addition, more developed areas with branches more equally grown in all dimensions (with flower/rose-like morphology) are being observed. For these membranes, the PA layer has a more tortuous appearance and therefore, a higher surface area. It is also clear that the IP layer has a complex internal structure when the AWC are added, with specific nanoparticulate domains present over its whole thickness. AWC/PA nanoparticles, corresponding to the brighter spots and having a diameter of $\sim 15\text{-}20$ nm in the middle of the PA layer for 0.2 and 0.4 w/w % MPD, while higher density of nanoparticles are observed for 0.8-1.8 w/w % MPD. In addition, they are more equally distributed across the membranes thickness, from the top to the bottom of the layer. These less dense white regions are filled by porous nanoparticles of AWC/PA hybrids during the PA formation. This apparent lower layer density may lead to a lower resistance to transport that would in part explain larger water permeance values observed for the TFC-**HC6** films. In summary, a low concentration of MPD promoted the formation of a smoother surface, while the presence of **HC6** during IP produced thicker and more porous selective layers compared to their reference TFC counterparts free of **HC6**. In addition, appropriate loadings of MPD above 0.4 % w/w and of **HC6** below 1.8% w/w, together with an appropriate ratio of **HC6**/MPD of 0.7-1.9 (w/w) during fabrication, allowed suitable embedding of self-assembled AWC/PA nanoparticles within the PA layer, which are hypothesized to promote faster and selective water passage during membrane filtration.

Performance of the membranes in low-pressure RO filtration of brackish water. The filtration performance of bioinspired membranes was measured in brackish water reverse osmosis (BWRO) and tap water reverse osmosis (TWRO) desalination.²⁵

First, the BWRO performances (i.e., water permeance, A , and the solute permeability coefficient, B) were evaluated for membranes prepared by varying the **HC6** loading from 0 % (control TFC) to 1.8% w/w, while keeping the MPD concentration constant (3.4 % w/w) (Fig. 4a,b). By increasing the **HC6** loading, membranes exhibited progressively higher water permeance increasing from 1.5 to 3.5 $\text{L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, with up to 185% increase with respect to the control TFC membrane, while maintaining very low and near uniform salt fluxes up to around 1.3% w/w **HC6** of initial loading. Above this concentration, a drop of performance was observed. This result is rationalized with the **HC6** concentration at the highest loading of 1.8 % w/w, which inhibited the formation of a defect-free selective layer during IP, also suggested by the large error bars related to erratic filtration performance of different samples fabricated using the same procedure. This set of filtration results translated into values of A/B with a peak for concentrations of 0.9 % w/w **HC6**. Then, we observed that by lowering the MPD concentration to 2 % w/w, higher values of water

permeances were obtained with an average A of $4.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and low salt passage: 99.8 % real NaCl average rejection were observed up to 1.5 % w/w **HC6** loading (empty symbols in Fig. 4 a,b).

We know that the MPD concentration control its diffusion into the organic phase when IP reaction is occurring,²³ but this parameter also interferes with the **HC6** aggregation through H-bonding. Therefore, the **HC6**/MPD ratio clearly determines the final layer morphology and transport properties. With these assumptions in mind, further experiments aimed at investigating lower MPD concentrations, from 2 % to 0.2 % w/w, combined with an optimal **HC6** loading, fixed at 1.5 % w/w (Fig. 4c,d). The best samples prepared with this loading showed a consistent value of A/B close to $\sim 35 \text{ l/bar}$, thus associated with an overall remarkable permeability-selectivity combination to be applied in BWRO desalination, whereby membranes with a permeance of $>3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ are required. Under BWRO conditions, the water permeance increased significantly and reached a peak of $\sim 6.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the MPD concentration of 0.8-1.2 % w/w, while maintaining very low associated salt fluxes rates. This result represents an exceptional $\sim 360 \%$ increase in water permeance at equivalent A/B ratio, with respect to the best membrane fabricated using 3.4% w/w MPD concentration and a $\sim 130\%$ increase in water permeance compared to commercial BW30 membranes (permeance of $\sim 3.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 99.5 % NaCl rejection), with comparable observed NaCl rejection of $\geq 99.4\%$. We noted that the membrane performance dropped rapidly by using sub-stoichiometric MPD concentrations lower than 0.8 % w/w. The data suggest that a maximum loading of **HC6** of 1.8% w/w and minimum loading of MPD of 0.4% w/w are needed to construct the optimal porous sponge-like AWC/PA structures and to prevent the formation of defects in the selective layer. Also, there is a clearly optimal combination of 0.8-1.2% w/w MPD with 1.5% w/w **HC6**, for a resulting **HC6**/MPD ratio of roughly 1.2 w/w to achieve high-performance defect-free bioinspired membranes.

Performance of the membranes in low-pressure RO filtration of Tap water. This study also aimed at evaluating the performances of bioinspired membranes for TWRO desalination. The water flux followed the performances measured under BWRO desalination, decreasing from $34 \text{ L m}^{-2} \text{ h}^{-1}$ by increasing the MPD concentration from 0.8% w/w to 1.8% w/w with a constant optimal **HC6** load of 1.5% w/w (applied pressure of 6 bar, Table S5, S6). Simultaneously, the observed rejections based on global conductivity measurements grew accordingly, from 97.5% to 99.3% (Fig. 4e). These values are in the same range, and in some cases slightly higher, of those measured under the same experimental conditions with commercial TWRO membranes ($31 \pm 1 \text{ L m}^{-2} \text{ h}^{-1}$; 97.5 % observed rejection), such as the TW30 from DuPont. Furthermore, multivalent cations including Ca^{2+} were rejected at a higher rate of 99.8 % compared to Na^{+} and K^{+} cations, due to size exclusion mechanism,²⁶ specifically indicating the potential of these membranes for water softening applications (Fig. 4f).

Discussion

Relationship between structural behavior and transport performance of the biomimetic membranes. The present study leads to the discovery of an unexplored mechanistic strategy allowing homogeneous AWC incorporation starting from their in-situ colloidal self-assembled superstructures leading to the identification of sponge-like particles present within the hybrid PA-AWC materials. During IP, the MPD is interacting with soft self-assembled **HC6** colloidal nanoparticles *via* H-bonding. Due to their amphiphilic properties, the AWC aggregates may also contribute to enhance the diffusion of the MPD into the organic phase to react with the TMC as revealed by previous studies.²⁷ The formation of the hybrid layers may be further generated *via* the interaction of the amphiphilic AWC/MPD nanoparticles with nascent PA oligomers *via* H-bonding. These interactions depend strongly on the **HC6**/MPD ratio and under favorable conditions, they effectively promote the PA formation and facilitate the gentle incorporation of AWC aggregates, whereby preventing the formation of defects, which are commonly observed when solid state nanoparticles are directly incorporated within the PA.^{1,2} Other than the seamless

in-situ adaptive incorporation of distributed AWC/PA-sponge like nanostructures into the PA layer, a morphological result observed in this study suggests the homogeneous formation of unique highly porous AWC/PA structures with reduced water transport resistance at the interface of the selective layer with the PSf support. Such membranes provided the best performances in terms of water transport and selectivity, and the porous structure did not affect the mechanical resistance or the membrane properties under RO filtration, unlike previous results reported for PA membranes prepared with additives.^{25,28}

It can be concluded that the improved transport performances stem from a combination of higher porosity of the overall PA-based layer, the absence of defects, and the occurring fast transport through the **HC6** nanostructures, whose excellent supramolecular adaptive properties confirm their ability to selectively translocate water while rejecting small ions even when incorporated into hybrid PA-AWC membranes. A significant loss in the perm-selectivity was instead observed for the membranes fabricated with too low MPD concentration or too high **HC6** loadings. For example, membranes fabricated with insufficient MPD exhibited a dense, more symmetric, and extremely thin selective layer. These results suggest that the presence of an excess of MPD seems to be imperatively needed for synthesizing defect-free bioinspired layers.²⁹

We know from literature data that the use of a spray coated CNT layer on the PES support before the IP, provides an interface that enables the generation of a highly permeable and selective PA layer with a large effective surface area for water transport.³⁰ Some similarities may explain the formation mechanism related to this study, whereby the incorporation of **HC6** in the PA layer leads to combined effects, such as the formation of a gutter layer or the generation of higher surface roughness and/or a leaf-like morphology that might be related to the amphiphilic properties of the **HC6** (in contrast to the use of additives, such as SDS). Nonetheless, if we look at the experimental results in the upper bound graph (Fig. 5c), our membranes show to be highly permeable and selective, lying at the limit that exists between BWRO and SWRO regions. High recovery and fouling experiments (See SI Appendix, Figs S8, S9) confirm the high-quality features of our biomimetic membranes. Therefore, in the range/area that delimitates the BWRO membranes, our membranes are highly selective, more selective than the other membranes prepared on laboratory scale, including thin-film nanocomposites (TFN) obtained using nanofillers (i.e., zeolites, carbon nanotubes, graphene oxide), additives (i.e., proton acceptors, surfactants, acids), or optimized by using salts/hydrophilic additives, different solvent or co-solvent, or by varying other experimental conditions (i.e., pH, T or concentrations in the casting solutions) during the membrane fabrication.¹¹

Of particular interest is the potential ability of such PA films to present directional pathways for water transport. Herein, microscopy studies revealed that such hybrid PA-AWC materials are composed by AWC crystalline nanoparticles, randomly dispersed in the PA matrix (Fig. 5b). For 1.2-1.8 % w/w MPD these particles are homogeneously and densely distributed within all the thickness of the PA layer, while for lower concentration of 0.2-0.8 % w/w MPD they are less dense and are situated in the middle part of the PA layer. For the sponge like nanoparticles¹⁷ of 20-40 nm the permeability of water can be theoretically estimated up to $P_{AWC} = 131 \text{ L}\cdot\text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (see SI Appendix). Independently of what is possible by microscopy or not, a high density of channels percolating from one side to the other of the membranes would be ideal, but we are not there yet. It is not about alignment which is clearly proved to occur along nanometric distances of crystals of AWC that are showing order. It is about percolation and high density of channels that for the moment is achieved at this nanometric scale. Although these nanoparticles do not merge to cross the μm etric PA films (Fig. 5a), they are randomly distributed within the PA layer ($P_{PA}=1 \text{ LMH/bar}$). The AWC crystals locally contribute to enhance translocation of water, as $P_{AWC} \gg P_{PA}$ (Fig. 5b). We do not intend to prove anything in a definite or exactly mathematical way here it is only an intuitive way to explain our results on AWC-PA membrane permeabilities that are experimental and unquestionable. The hybrid PA-AWC materials are reminiscent with previous hybrid ion-

channels siloxanes, providing high ionic conduction through their nanometric self-organization of binding sites in hybrid materials.³¹⁻³³

The assumption is that, beside 1. the tunable formation of colloidal nanoparticles within the PA, 2. the formation of inner porosity/voids (as a consequence of the effect of the **HC6** “interlayer”), and 3. the gutter layer-like structure, there is the diffusion of hydrophilic and selective sponge-like AWCs-PA (which we surmise are also in the form of I-quartets). Thus, we assume that this performance is achieved thanks to the combined effect of all these aspects. It is also true that the AWCs are intrinsically “nanofillers” but, by comparison, our membranes are more selective and permeable, possibly due to the compatibility of the **HC6**. Obviously, a high density of channels is desired to promote high permeance. Alignment is not essential, but the percolation of AWC particles is important and should be optimized to have the water transport mainly taking place through the channels. Homogeneous distribution with particle percolation should be preferred. High density of particles without aggregation should be obtained. Achieving these conditions was a main goal of the optimization in this work.

In this work, bioinspired membranes for low salinity BWRO and TWRO water desalination were fabricated by incorporating I-quartet AWC in the classical PA layer. Specifically, the performance of hybrid AWC-PA membranes was tuned by studying the effect of the optimal AWC loads and that of MPD monomer concentration during IP, thus optimizing the selective layer. It may be concluded that self-aggregated AWC colloidal nanoparticles were incorporated by means of their supramolecular interactions with MPD monomer and their presence altered the IP process, and thus the final layer properties. These dynamic self-assembly processes amount to adaptive colloidal entities with the nascent PA oligomers.

This study illustrates a complete interplay of supramolecular aggregation and IP processes:

a) related to supramolecular aggregation, once the AWC load is increasing, the selective PA-AWC layers became more porous and AWC nanoaggregates were homogeneously distributed within the hybrid PA, resulting in high-performance membranes. However, overly high concentrations of AWC nanoaggregates led to the formation of defects, resulting in the poorest performances.

b) The MPD monomer concentration had also an important effect during membrane fabrication and seamless biomimetic layers were synthesized by adjusting this parameter reaching the optimal **HC6**/MPD ratio between 0.7 and 1.9 w/w. In general, a minimum concentration of MPD (~0.8% w/w) was required to obtain high selectivity. However, even this concentration should not be too high in order to maintain high water fluxes. In particular, the membranes fabricated with 1.2 % w/w MPD and 1.5% w/w **HC6** provided a ~360% increase in water permeance at equivalent water to salt flux ratio with respect to the membrane fabricated using 3.4 % w/w MPD.

The best membranes displayed excellent productivity of 110 L m⁻² h⁻¹ under 15.5 bar applied pressure and 35 L m⁻² h⁻¹ under 6 bar applied pressure, while maintaining high selectivity properties, outperforming current BWRO and TWRO commercial membranes. Ultimately, we demonstrated that bioinspired membranes incorporating I-quartet AWCs own the potential for improving existing low-pressure RO applications and their composition can be adjusted to tune their superstructures and performances to target different applications.

Methods Section

Chemicals, Membrane morphological and physio-chemical characterization, Dynamic light scattering (DLS) measurements, Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Scanning electron microscopy (SEM), Transmission Electronic Microscopy (TEM) and Membrane performance evaluation are presented in supporting information -see SI appendix

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Figures and Tables

Fig. 1. Membrane synthesis a) I-quartet AWC, b) High TEM magnification of the lamellar crystalline nanoparticles, obtained from the evaporation of an ethanolic/aqueous solution of HC6 and c) top and d) lateral views of single-crystal lamellar packing of I-quartet AWC; e) Synthetic procedure for the hybrid PA/AWC membrane preparation: impregnation 1 of PSf support with a solution of HC6 -formation of colloidal lamellar phases of AWCs, followed by the impregnation 2 with an aqueous solution of m-phenylenediamine (MPD)-interacting *via* f) H-bonding with AWC colloidal particles and by the impregnation 3 with a hexane solution of trimesoylchloride (TMC) resulting in the formation of hybrid H-bonded PA/AWC layers *via* the nucleation/IP processes.

Fig. 2. Representative cross-section SEM micrographs of (a,b) H-0.9; (c,d) 0.8-HC6 and (e,f) 0.2-HC6. MPD concentrations in the casting solutions were (a,b) 3.4%; (c,d) 0.8%; (e,f) 0.2% (w/w). HC6 concentrations in the casting solutions were (a,b) 0.9%; (c,f) 1.5% (w/w).

Fig. 3. TEM cross-sectional image of a) 0.2-HC6, b) 0.4-HC6, c) 0.8-HC6, d) 1.2-HC6, and e) 1.8-HC6 membranes, % w/w MPD, 0.1 w/w% TMC and 1.5% w/w HC6 stained with $Zn(NO_3)_2$ showing the detail of the top hybrid layer containing AWC/PA white nanoparticles embedded with high precision in darker PA matrix.

Fig. 4. BWRO desalination performances at 15.5 bar as a function of (a,b) HC6 and (c,d) MPD concentrations. Experimental conditions: pure water for the measurement of *A*; 100 mM NaCl in the feed solution for the measurement of *B*. TWRO desalination performance at 6 bar e) Permeate flux and observed rejection at steady-state as a function of MPD concentration. f) Observed rejection of different cations and anions at steady-state of 1.6-HC6 membranes under TWRO conditions. Lines connecting the data points are only intended as a guide for the eye.

Fig. 5. Enhancement permeation mechanism. a) the ideal membrane with perfectly aligned channels though the whole thickness of the PA membrane (blue); b) uniform aleatory distribution of AWC nanoparticles within the layer. Enhanced permeation at the nanometric level relates to AWCs nanoparticles regions-see text for the details; c) Water permeance and selectivity of commercial seawater reverse osmosis (SWRO, red), brackish water RO (BWRO, blue) and NF membranes (green). Blue dash lines correspond to the NaCl rejection of 99% and 90%, respectively, at a flux of $20 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. The yellow star highlights the perm-selectivity performance of our optimized BWRO membranes prepared using AWCs, while the empty symbols represent all the other laboratory scaled membranes¹¹ Fig. adapted from ref. 11 Copyright Elsevier 2019.









