Prospective Applications of Nanometer-scale Pore Size Biomimetic and Bioinspired Membranes

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Highlights:

- Biomimetic and biomimetic membranes (BBMs) are separation membranes containing biological functional molecules or bioinspired functional elements that can mimic the structure and special function of biological molecules.
- BBMs can be used to develop sub-nanometer pore size membranes with uniform pore size distribution.
- BBMs are by their very nature monodisperse, and they can achieve ideal size-based separation properties with a sharp solute rejection curve.
- Membrane protein channels, artificial water channels, and carbon nanotubes can be considered functional elements of BBMs.
- Prospective applications of BBMs include antibiotic separations, organic acid separations, gas separations, homogeneous catalyst recovery, organic solvent nanofiltration, food processing, protective and breathable fabrics, and ion/ion separations.

Abstract

Biomimetic and bioinspired membranes (BBMs) have garnered significant attention as innovative platforms for membrane-based separations and purification. These membranes typically consist of highly permeable biological or bioinspired pore structures or channels with well-defined pore geometries. The pore structures are embedded in a relatively impermeable synthetic membrane matrix, and the overall membrane demonstrates high performance, functionality, and selectivity originating primarily from the pore properties. The channels utilized have well-controlled and uniform inner pore diameters, leading to a completely uniform pore size distribution, in direct contrast to the wide pore size distribution common in current commercial membranes. Biomimetic membranes thus have the potential to target specific separations that require precise selectivity, particularly in the challenging sub-nanometer to nanometer size ranges. So far, the discussion around BBMs has largely focused on water purification. However, these membranes could provide significant benefits in other potential applications, such as antibiotic separations, homogeneous catalyst retention, organic acid separations, gas separations, organic solvent nanofiltration, and food processing. This review first illustrates the importance of monodisperse pore size distribution to selectivity in nm-scale separations, and then discusses potential applications of BBM membranes. Provided that defect-free biomimetic membranes compatible with the environments used in these applications can be engineered, these membranes may provide a path to move beyond the permeability-selectivity tradeoff that limits the separation properties of current synthetic membranes.

Introduction

Biomimetic and bioinspired membranes (BBMs) are separation membranes that contain biological or bioinspired molecules and aim to provide enhanced transport rates combined with the exquisite specificity typical of biologically mediated separations [1]. The functional components of such membranes include biological membrane proteins (MPs) [2, 3], artificial water channels (AWCs) [4-6] and carbon nanotubes (CNTs) [7]. Metal-organic frameworks (MOFs) may also be considered an example of bioinspired channels. BBMs with well-defined porous components have been developed with a view to enhancing membrane permeability and separation efficiency critical to many challenging separations and industrial applications [1, 8, 9]. A distinct feature of biomimetic membranes is the "division of labor" between the functional components (transport channels) and the matrix components of the membrane [10]. This contrasts with current polymeric membrane systems where the same materials provide both the matrix and the transport element (pores or voids).

In an ideal BBM system, the functional channel has a well-defined pore geometry. BBM channels are uniform in size, and they possess specific functionality that can be designed to exclude or transport specific components efficiently from complicated mixtures, owing to molecular size sieving effects [11] and specific pore-solute chemical interactions [12]. Channel mediated biomimetic membranes and molecular scale designed porous materials have emerged as strong candidates for membrane-based purifications and separations [8, 13]. The pore size distribution, pore density, apertures and dimensions of porous membranes are key factors that determine membrane performance and function for anticipated applications [14-16]. With the emergence of channel mediated membranes, the influence and significance of pore size distribution on small molecule rejection and challenging size-based separations for sub-nanometer porous membranes is important to emphasize. A simple modeling exercise reveals the importance of pore size distribution, particularly uniform pore size distribution on selectivity in nanometer scale pores (see **Figure 1a**, **Supporting Information**), this idea is supported by several other studies (**Figure 1b-d**). Further, with new synthetic strategies, and well-controlled pore dispersity in the membranes, we should be able to design separation membranes geared towards specific applications and succeed in some challenging separations [17] (**Figure 1**).

In this review, we investigate the theoretical rejection properties and trends of porous nanofiltration (NF) membranes using previously published models [18]. We also propose added benefits and potential applications of monodisperse biomimetic membranes based on existing theoretical studies of NF membranes [18-20]. We then review the current types of biological channels, bioinspired channels, and porous materials for biomimetic and bioinspired membrane development. We then evaluate prospective applications in homogeneous catalysis, pharmaceutical separations, gas separations, food processing, and industrial chemistry where membranes with uniformity of sub-nanometer pore size distribution may have marked advantages in the future. For example, the superior selectivity of a monodisperse membrane would benefit a number of potential applications, such as the retention of expensive or toxic homogeneous metal catalysts in chemical and pharmaceutical synthesis [21, 22], or the recovery of low concentrations of small helium atoms in natural gas streams composed primarily of larger methane molecules [23, 24]. These are discussed in more detail in the following sections.

The potential challenges to fabricating membranes and conducting separations are also reviewed as most channel-mediated membranes (especially biomimetic membranes) are designed to operate at ambient temperatures in aqueous solutions. Hence, the harsh conditions, such as high temperature, corrosive solvents, and extreme pH values, involved in certain applications would prevent the use of these channel types in some circumstances [25]. Nevertheless, size-based membrane separations can be carried out with significantly greater thermodynamic efficiency than can competing separation methods, such as distillation [21, 26-28], and in some cases could avoid the use of extreme temperature that denature the components in product streams [21]. Consequently, the design and control of such monodisperse separation membranes would allow significant energy and material savings, making it an intriguing possibility for scientists and engineers working on a variety of applications.

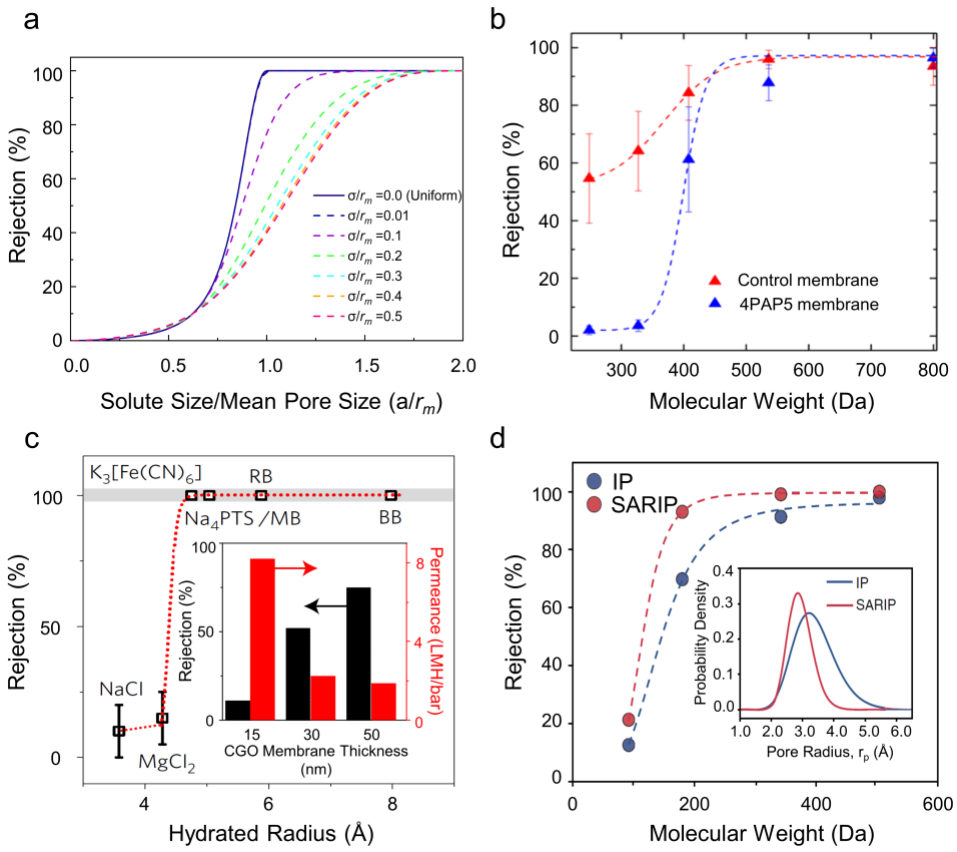


Fig. 1 The significance of pore size distribution in nanofiltration membranes. (a) Calculated solute rejection of membranes with different pore size distributions (based on a Donnan Steric Pore Model for NF membranes, see SI for details). As the pore size distribution of the membrane widens ($\boldsymbol{\sigma/r_m}$ increases), the rejection of solutes decreases and leads to a less effective separation of large solutes from small solutes. $\boldsymbol{\sigma/r_m = 0}$ here represents a membrane with uniform pore size where there is perfect rejection of solutes with sizes larger than the pore size ($\boldsymbol{a/r_m = 1}$). The $\boldsymbol{\sigma/r_m}$ value of conventional commercial membranes with widely dispersed pore size distribution is in the range of 0.14 to 1.59 (**Table S1**). The fixed parameters used for this calculation are $\boldsymbol{r_m}$ (mean pore size) = 0.5 nm, $\boldsymbol{\Delta p}$ (pressure difference across membrane) = 3 MPa, $\boldsymbol{T_0}$ (temperature) = 293 °K, $\boldsymbol{\eta_0}$ (dynamic viscosity of water) = 1 cP. **(b)** A sharp separation performance of a 4PAP5-inserted lamellar membrane [10], Copyright 2019 American Chemical Society. **(c)** A sharp and precise cut-off at 0.45 nm with 8 nm thick highly laminated graphene oxide (HLGO) membranes [29], Copyright 2017 Nature Publishing Group. **(d)** A sharper separation curve is achieved by a polyamide membrane with tighter pore size distribution fabricated by surfactant assembly regulated interfacial polymerization (SARIP) compared to conventional interfacial polymerization (IP) method [30], Copyright 2020 Nature Publishing Group.

Types of BBMs

The common types of BBMs, based on their incorporated channel types, are summarized in **Table 1**, shown in **Fig. 2**, and discussed in more detail in the following sections. In brief, the biological or bioinspired channels include (1) membrane protein (MP) channels, (2) self-assembled and single-molecule artificial water channels (AWCs) as well as (3) carbon nanotubes (CNTs). For comparison to other approaches currently used to tailor and mediate the pore aperture of membranes in the nanometer to sub-nm scale, metal-organic framework (MOF)-based membranes and carbon molecular sieves (CMS) are described, along with their proposed applications in gas separations, energy storage and catalysis.

Table 1
Properties of BBMs and comparable approaches allowing size-selective separation of sub-nanometer-sized molecules

Channel/ Porous Element Type	Pore Diameter	Requirements to maintain stability
Membrane proteins (MPs)	≥ 0.3 nm (monodisperse pores) [1]	Amphiphilic and anisotropic environment [31]
Artificial water channels (AWCs) (PAH[4], PAP[5], Imidazole I-quartets, dendritic dipeptides, foldamers, others)	0.26-1.45 nm (monodisperse pores) [4]	Hydrogen bonding in the solvent but not in the membrane matrix for self-assembled channels [5]
Carbon nanotubes (CNTs)	0.4-100 nm (standard deviation typically ≤ 1 nm) [32]	Chemical, thermal and solvent stability [33, 34]
[non-BBM model porous materials (for comparison)]		
Metal-organic frameworks (MOFs)	≤ 20 nm (monodisperse pores) [35]	Chemical, thermal and mechanical stability [36], less stable in water [37]
Carbon molecular sieve (CMS)	≤ 20 nm (polydisperse pores) [38]	Chemically and thermally stable, but brittle

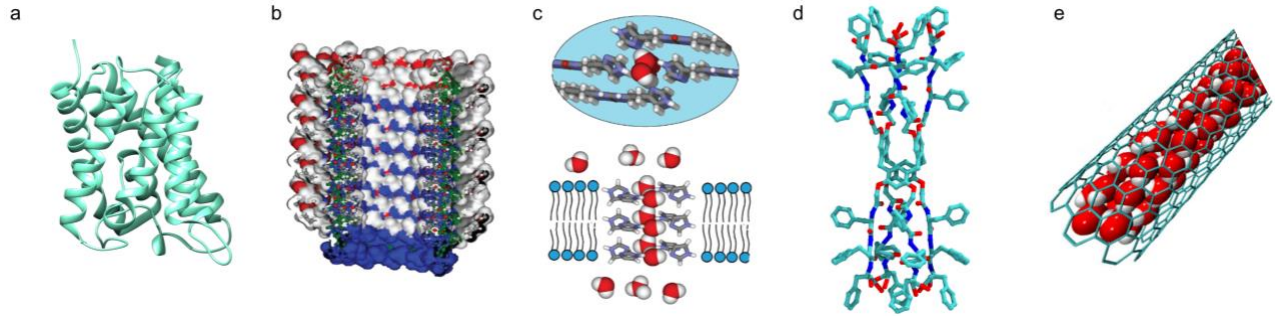


Fig. 2. Biological molecules and artificial water channels with precise sub-nanometer sizes. **(a)** Aquaporin Z, a biological membrane protein water channel (PDB: 1RC2). **(b)** A synthetic helical pore self-assembled by dendritic dipeptides. Copyright 2007 American Chemical Society; **(c)** A synthetic water channel self-assembled from imidazole I-quartets. Copyright 2013 American Chemical Society; **(d)** A peptide-appended hybrid[4]arene (PAH[4]) water channel. Copyright 2019 Nature Publishing Group; (e) A unimolecular carbon nanotube ion/water channel with sub-nanometer inner diameter. Copyright 2017 American Chemical Society.

Membrane protein channel — embedded biomimetic membranes

Membrane proteins (MPs) exist in nearly all cell membranes and conduct essential processes for cell viability including: (1) water and nutrient transport, as well as small molecule separations [39]; (2) ion transport across cell membranes, used to maintain transmembrane ion concentration difference [40]; and (3) biomolecular and signal sensing for intercellular communication [41, 42]. Based on their structures and functions in the cell membrane, MPs involved in transport properties can mainly be classified as MP channels, electrochemical potential-driven transporters, primary active transporters, group translocators, or transmembrane electron carriers [43]. Among these different types of MPs, MP channels have commonly been reconstituted into biomimetic separation membranes, owing to their simplicity of function (passive bidirectional transport) and specific molecular recognition and transport [44-46]. The molecular transport rate through MP channels, which is usually an energy-independent passive diffusion down a concentration gradient, is an order of magnitude (or more) faster than transport through other types of MPs [1]. In general, the functions of MP channels relevant to membrane applications include water

permeation, ion transport/separation (e.g. K^+, Na^+, Cl^-, and H^+ channels), and size-selective small molecule transport, as well as protein and DNA transport [43, 47].

With the features of rapid water permeability, high specificity and small molecule selectivity, MP channels have thus emerged as a promising platform for the development of biomimetic membranes in several applications, such as sensors [48], dialysis and water treatment [49]. The incorporation of functional MP channels into polymeric membranes can narrow pore size distribution, improve solute selectivity, and enhance membrane permeability (**Fig. 3**). However, the compatibility between protein channels and polymeric or biomimetic matrix is not well-established, resulting in large defects, low channel insertion, and productivity [13]. Aquaporins (AQPs) are well-studied tetrameric MP channels and have been proposed to have ideal internal pore geometry for selective and highly permeable water channels used for desalination [45, 50, 51]. The high ion selectivity ($>10^9$ water over monovalent ion selectivity), and fast water transport ($>10^9$ water molecules per second per unit osmolar gradient) [8, 52] of classical aquaporins has become a standard to aspire towards for desalination membranes (**Figure 3a, I**) [53, 54]. Among classical aquaporins, the *Rhodobacter sphaeroides* aquaporin (RsAqpZ) has the highest single channel permeability, 4.29×10^{-13} cm^3 s^{-1} or 1.43×10^{10} H_2O s^{-1}, note that the water permeability P_f value is updated by the correction factor presented by Hannesschläger *et al.* [55, 56]. Additionally, a recent study has proposed novel designs for outer membrane protein F (OmpF) mutants with precise angstrom-scale pore sizes in the range of 3-10 Å to achieve specific solute selectivity and high osmotic water permeabilities, which could be applied to development of membranes that separate molecules by size in the challenging sub-nm to nm ranges (**Figure 3a, II**) [2]. Several recent successes have been reported with AQP-reconstituted reverse osmosis (RO) membranes [44, 45], but their overall performance still falls short of AQP-containing biological membranes due to impermeable matrix selection (**Figure 3a, III**), insufficient protein content in membrane matrices and the use of vesicular structures of proteo-liposomes (**Figure 3b, IV**) [57]. Additionally, high performance MP-based membranes are currently considered challenging for scalable fabrication due to several shortcomings, including the use of detergent for protein purification and vesicle assembly, limited protein insertion into polymer matrices (**Figure 3c, VII**) or lipid bilayers (**Figure 3c, VIII**) [58], and low structural stability with regard to fabrication [59]. Although interfacial polymerization method is a well-established process to create a thin selective layer scalable to the industrial scale, insertion efficiency and alignment are still difficult to control and optimize. Lipid bilayers match the length of embedded MP channels and maintain their functionality; however, they are not stable in the absence of an aqueous environment and are prone to rapid degradation (within hours) by oxidation. Recent work demonstrated protein channels integration into polymer matrices forming two-dimensional (2D) crystal or nanosheets in a 2-hour organic solvent extraction method, which may offer potential for developing MP-based membranes in industrial practice (**Figure 3b, V**). The formation of 2D protein crystals also indicate an optimized packing density of MP into membrane matrix, which is ~ 2 orders of magnitude higher than that in proteoliposomes. Further, this study described methods that could be generalized to fabricate MP-copolymer membranes with protein channels of different pore sizes or chemical morphologies for conducting targeted molecular separations [3]. The co-assembly of MP or synthetic channels and BAB triblock copolymers to form a lamellar structure is another insertion strategy, which forms a thin selective layer containing aligned channels in a single step. This could be considered as a robust and scalable alternative to lipid bilayers (**Figure 3b, VI**) [10]. A chemically cross-linkable and thin nanosheet layer could confer higher stability and mechanical properties for filtration (**Figure 3c, IX**). A chemically cross-linkable and thin nanosheet layer could confer higher stability and mechanical properties for filtration (**Figure 3c, IX**). Nevertheless, nanoscopic gaps and defects between layers are a current challenge for MP membranes made with such a strategy. Further exploration may need to be invested in synthesizing sealing materials or developing robust defect-filling fabrication processes. The size of membranes demonstrated with this strategy is limited to ~ 41 cm^2 [3]. The appropriate membrane module designs for practical applications to withstand harsh conditions in industry would need to be further investigated [60].

Procedures to further develop MP-based biomimetic membranes could include MP channel redesign for higher solvent resistance and thermal stability, which would enable broader application of MP-based membranes and AQP-integrated RO membranes. Durable and robust membrane fabrication may be required to extend applications for

long-term process with tangential flow, substantial concentration polarization and corrosive conditions [60]. In addition, strategies to preserve the protein structure, functionality, and transport properties under dehydrated conditions could extend applications of MP-based membranes to create breathable but protective fabrics for biological and chemical agent barriers. A further exploration on the biocompatible and flexible membrane matrix could be an added benefit for applying the fabrics for medical protections and barriers. These MP-based biomimetic membranes may even allow the expansion of MP-based applications to include biochemical separations, gas/vapor separations and homogenous catalysis retention, as discussed in later sections.

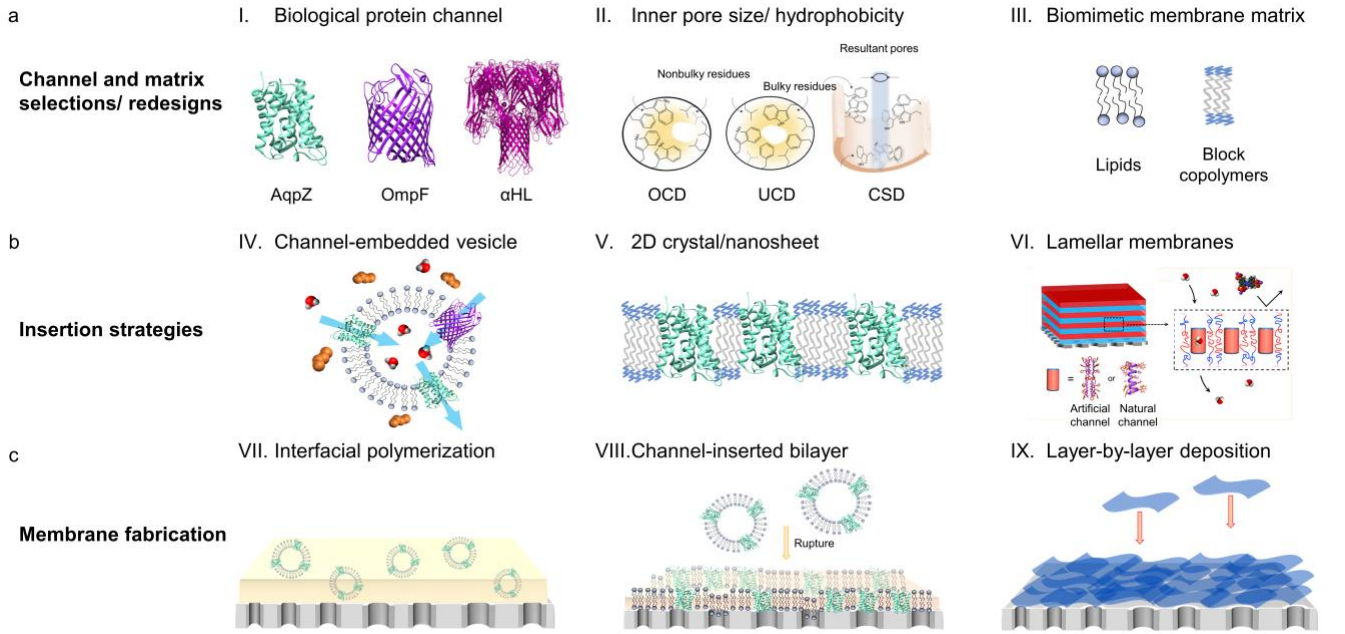


Fig. 3. Summary of current strategies for BBM fabrication. (a) Protein channel and matrix selection/redesign: **I**. Select biological protein channel: the *Escherichia coli* aquaporin-Z (AqpZ, PDB: 1RC2), Outer membrane protein F (OmpF, PDB: 2OMF), and alpha-hemolysin (αHL, PDB: 7AHL) are examples; **II**. Tailored angstrom-scale pore sizes in the range of 3-10 Å and hydrophobicity by the addition of hydrophobic amino acids to the inner pore of OmpF channels [2], Copyright 2018 Nature Publishing Group; **III**, Biomimetic membrane matrix: native phospholipids, block copolymers (BCPs) mimic the amphiphilic amphipathic properties of phospholipids [61]. **(b)** Insertion strategies: **IV**. vesicles containing channel proteins; **V**. Two dimensional (2D) nanosheets or crystals embedded with MPs or AWCs within BCP matrices [3, 62]. **VI**. Co-assembly of MPs/Artificial channels and polymeric matrices into a lamellar structure [10], Copyright 2019 American Chemical Society. **(c)** Membrane fabrication: **VII**. Incorporate proteo-liposomes into a thin selective layer using interfacial polymerization (IP) method [54]; **VIII**. Form a bilayer structure through the rupture of proteo-liposomes on a porous substrate; **IX**. Fabrication of a robust selective layer via crosslinked layer-by-layer structure [3].

Artificial channels—inserted biomimetic membranes

Artificial water channels (AWCs) are transmembrane synthetic molecules designed to mimic the function of biological MP channels, such as AQPs [4, 50, 63]. AWCs are expected to possess transport mechanisms with high water transport and efficient molecular separations while providing structural stability, mechanical strength, flexible functional modification and reduced fabrication costs [64, 65]. There are two primary types of AWCs: self-assembled channels and unimolecular transmembrane channels [66]. A third type has recently emerged where single channels work cooperatively, resulting in self-assembled channel networks that have enhanced transport compared to the individual channels [67]. Self-assembled synthetic water channels are organized based on the intermolecular interactions between organic building blocks. Self-assembled channels include dendritic dipeptides that self-assemble through π-π stacking interactions to form channels [68], as well as imidazole-quartet channels that are

stabilized by inner water-wires with a reported inner pore diameter of 2.6 Å [69], triazole channels [35], and hexa(m-phenylene ethynylene) channels [36]. Peptide-appended pillar[5]arenes (PAP[5]) are unimolecular transmembrane channels with ~4.7 Å diameter pores. Each PAP[5] contains a pillar[5]arene backbone that forms the pore and tripeptide chains that stabilize the channel structure through the interactions of hydrogen bonds between the chains [62]. Aquafoldamer channels are helically folded unimolecular structures formed via hydrogen-bonded aromatic amide foldamers with an internal cavity of ~2.8 Å [63, 70]. Cluster-forming peptide-appended hybrid[4]arene (PAH[4]) with the pore size of ~3 Å demonstrated rapid water permeation (>10^9 water molecules per second per channel) and water/NaCl selective transport properties, which is comparable to biological elements [67].

Synthetic AWCs are generally considered more favorable for large-scale development of channel-mediated membranes than biological channels, owing to the AWCs' chemical, mechanical and structural stability, as well as their potential for simple functional modifications [62, 71]. A few recent attempts have been made to incorporate AWCs into polymeric membranes. PAP[5]-BCP membranes were fabricated using layer-by-layer depositions of 2D crystals with high packing density [62]. In another approach, lamellar multilayered membranes were created with co-assembly of BAB triblock copolymers and PAP[5] or gramicidin A which required short preparation times (**Figure 3b, VI**) [10]. Most recently, the IP method was used for incorporation of I-quartet AWCs in Polyamide (PA) membranes - this approach could be scaled for meter-sized and industrially relevant membrane areas [72]. Nevertheless, the designed performance of single AWCs was well leveraged in this demonstration after being embedded into interfacially polymerized polymeric membranes. Membrane fabrication with high insertion efficiency, vertical alignment, and optimized packing density compatible with impermeable matrices the preserve the high permeability and selectivity of individual channels may need to be further explored.

There have been several efforts and success with trying to mimic biological ion channels by using pore-containing macromolecules (**Table 2**). These artificial ion channels demonstrate the versatile features and robust structures. However, membrane development around these channels have been limited [9, 73-76]. Selective separations including rare earth elements (REE) separations and lithium ion separation could be greatly enhanced if specific ion channel mimics are developed and incorporated into membranes [65, 77-79].

Table 2. Biological/ biomimetic ion channels and ion selectivity

Ion channels	Ion selectivity	Reference
KcsA	$K^+/Na^+ = 10^4$	[47]
M2 proton channel	Proton/monovalent cations = 10^5	[80]
Pyridine/oxadiazole-based helical foldamer ion channels	$K /Na^+ = 16.3$	[73]
Heptapeptide ion transporters	$Cl^-/K^+ > 10$	[81]
Porphyrin-based covalent organic cage	$I^-/Cl^- > 60$	[82]
Liquid-crystalline lithium-selective receptors	$Li^+/Na^+ = 10.35$	[83]
Helical macromolecule channels	$K^+/Cl^- = 5.7$	[84]
Helical Oligomers	$K^+/Na^+ =22.5$	[85]

Carbon nanotube membranes

Carbon nanotubes (CNTs) are size-selective channels that consist of rolled up sheets of monolayer carbon atoms. CNTs can remain stable in a variety of chemical environments, including aqueous and organic solvents, as well as at high process temperatures [86, 87]. CNTs are stable under a wide range of temperatures (up to 1,600 °C for single-walled nanotubes and even higher for multi-walled nanotubes [88, 89]), a significant advantage for broad applications in industrial processes [34]. CNTs have been synthesized with a series of different pore sizes, diameters from about 0.4-100 nm [90], and 1.5-4 nm with uniform distributions (standard deviation typically ≤ 1 nm), which

could be useful in targeting specific small molecule separations [91]. Most small CNTs (0.8 nm diameter) have uniform pore diameters and have shown higher water permeability than do biological water transporters and wider CNT pores [7]. CNT channel-based membrane with sub-5 nm pores have also been applied to create protective fabrics while allowing high water vapor transport rates [92].

In addition to allowing precise size-selectivity, CNTs possess charge selective transport in solutions with a high dielectric constant, such as aqueous solutions. The terminal carboxyl groups of the CNT can be replaced with various molecules (such as alkane chains, dye molecules, and peptides) to promote charge-selective rejection of certain solutes, leading to charge-selective as well as size-selective transport [87, 93]. If one ion from a divalent salt is rejected in this way, the counterion will also be rejected due to the requirement of charge neutrality, so that these nanotubes can have higher salt rejection than would be predicted based solely on their diameters [93]. Finally, CNTs have a hydrophobic interior surface, making it thermodynamically unfavorable for water to exist near the nanotube walls [94]. This allows CNTs of diameter ≤ 0.8 nm to reject ions by preventing them from entering with an intact hydration shell [94]. Although commercial access to CNTs is less problematic than MPs, and membrane fabrication using IP, surface spray coating, or phase inversion to immobilize CNT into polymer matrix are now established, their large-scale application has been hampered by difficulties with controllable loading and dispersion of CNTs in membranes, translation of desired performance observed at the small scale to the entire large membrane area, and membrane fabrication with vertically aligned CNTs (VACNT) [32, 95]. A recent study demonstrated fabrication of 1.7 nm single-walled carbon nanotubes (SWCNTs) using chemical vapor deposition (CVD) on a silicon wafer. A 60 cm^2 SWCNTs/parylene membrane demonstrates negatively charged dye rejection and water permeability >200 LMH bar^{-1} exceeding commercial nanofiltration membranes of similar pore sizes [96]. In addition, commercial CNTs comprising membranes with CNTs of 0.67 to 1.27 nm diameter in a nonporous polysulfone film (20.3 cm by 27.9 cm) demonstrated pure water permeability of ~5 liter m^{-2} h^{-1} bar^{-1} (LMH/bar), which is 3 orders of magnitude higher than the predicted Hagen-Poiseuille flow. These membranes also manifested NaCl and $MgSO_4$ rejection (> 10 %) at high ionic strengths (> 30 mM), as well as dye solute rejection. In addition, the membranes demonstrated gas selectivity (analyte/He selectivity), providing further potential evidence of dominant surface diffusion transport along the wall of sub-nanometer CNT pores. These results indicate the potential for applying CNT membranes to both aqueous and gas separations in centimeter-scale purifications [97].

Metal-organic framework composite membranes

MOFs are composed of metal ions or metal clusters that are connected by organic linkers through metal–ligand coordination bonds [98, 99]. The arrangements of linkers and functional groups could be combined in different topologies to create a number of tailorable, functional and unique MOFs as solid sorbents, heterogeneous catalysts and molecular sieving materials [100]. MOFs appear as innovative porous materials in several proposed applications, such as gas adsorption, gas storage, water purification, energy storage, sensors [101], heterogeneous catalysis, metal ion separations and drug delivery [102-106]. Additionally, high porosity, tunable pore size, high surface areas, large pore volumes, and high concentrations of active sites make them an appealing class of materials for potential applications [98]. MOFs have been studied extensively for chemical sensing, catalysis, preferential adsorption and removal of hazardous molecules such as SO_2, NO_x, CO, and CO_2 from flue gas, as well as for degradation of chemical warfare agents (CWAs), including sarin, soman and sulfur mustard [98, 107, 108]. Due to the molecular sieving effect of MOFs, they have been synthesized as selective layers on top of a porous support (such as polyethersulfone, polyimide or polydimethylsiloxane) and formed as mixed-matrix membranes (MMMs) for NF, liquid separations, and solvent resistant nanofiltration (SRNF) [109, 110]. In addition, biocompatible MOFs have recently emerged in biomedical and nanomedical applications, owing to features such as high capacity for active ingredients and decreased *in vivo* toxicity, which could be utilized to capture toxins and deliver drugs [111, 112]. Bioinspired design of MOFs could also be applied in the development of biomimetic enzymes and catalysts to enhance their robustness and to detect biomolecules [113]. MOFs were used successfully as the precursor or as the template for the synthesis of porous carbon materials with a tunable surface area (> 800 m^2 g^{-1}) and a controllable pore-size distribution that exhibited promising capacitive performance [114]. Hence, the development of two-

dimensional MOF nanosheet-based membranes could also provide efficient separation and high selectivity properties, owing to their molecular-unit thickness, large surface area and low transfer barrier [115-117]. In particular, highly oriented and ordered MOF film fabrication may contribute to applications that require highly specific separations [118, 119].

Carbon molecular sieve membranes

Carbon molecular sieves (CMSs) are a special class of nano-porous activated carbons with tailorable transport properties for gas, vapor, and aqueous separations [120]. CMSs arise from the controlled pyrolysis of polymeric precursors under controlled pressure and a specific temperature-mediated procedure. During heat treatment, heteroatoms (essentially oxygen and hydrogen) from the polymeric bonds are progressively removed and produce carbon skeletons with amorphous and porous structures that consist of disordered graphene layers. The pore geometries of carbon depend on the morphology of the organic precursor and the chemistry of pyrolysis [121]. The porous structures derived from adjacent graphene sheets form a network of inter-connected pores: relatively wide openings with narrow constrictions, responsible for the molecular sieving effect [121]. The constrictions contribute to molecular selectivity on CMS membranes, while the cavities increase the membrane adsorption capacity and enhance permeabilities through the membranes. A significant feature of CMS is that the pore network can be tailored or adjusted by employing different pre- or post-heat treatments, tuning the permeation properties of the membrane in order to suit a given application [122]. CMS transport properties depend on a slit-shaped pore structure constructed by a distribution of larger (0.7 to 2 nm) micropores connected by smaller (< 0.7 nm) ultra-micropore windows. While bimodal ultra-micropore−micropore distributions provide large sorption capacity and diffusion selectivity, the non-uniform pore size distribution of CMS membranes may constraint the separation performance of CMS in similar molecules [123].

Other porous material-embedded membranes with tunable porosity

Macrocycles are molecular structures that contains cyclic frameworks of at least twelve atoms including pillar[n]arene [124], crown ethers [125], calix[n]arenes [126], cyclodextrins [127], and cucurbit[n]urils [128] molecules (**Table S2**). These cyclic molecules possess nanoscale hollow cavity structure for ion transport, ion absorption [129], molecular separation [130], and drug delivery [131]. The porosity and pore size distribution of membranes can be tailored by the addition of the nanoporous materials or macrocycles with defined cavities. Few attempts are made recently by incorporating macrocycles into polymeric membranes for enhanced filtration and solute selectivity. For instance, a composite membrane was developed by a layered structure of polymerized β-cyclodextrin (β-CD) using interfacial polymerization for organic solvent nanofiltration and shape selectivity owing to the cavity of β-CD [43]. In addition, membrane filtration performance and chlorine resistance are improved by the intrinsic properties of β-CD and compatibility of graphene quantum dots (GQDs) [132]. Another example is a lithium selective channel-like structure self-assembled by liquid-crystalline (LC) with crown ether derivatives, which demonstrates ion selectivity $Li^+/Na^+ = 10.35$ due to a strong interaction between Li^+ and crown ether [83]. However, the alignment, packing and general insertion strategies of these macrocycles into membrane matrices and transport mechanism of resulting membranes are still limited and need to be further investigated.

Prospective applications for nm to sub nm pore size membranes with uniform pore size distributions

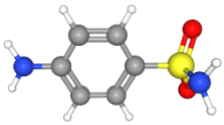
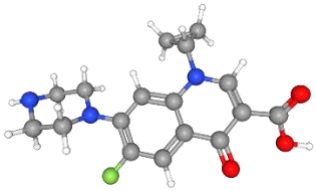
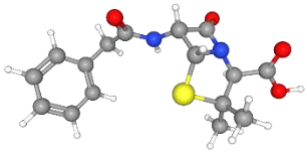
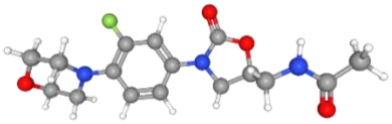
The following sub-sections describe anticipated applications of mono-disperse, nanometer-scale BBMs to refine or improve current technologies. As the development of bioinspired and biomimetic materials continues, we will be able to tailor the nanometer-pore geometries and assemble these porous components into membranes with enhanced performance [3]. BBMs with well-defined porous components and uniformity of pore size distribution will usher membranes into a new era, intensifying membrane productivity and achieving precise selectivity, both of which are challenges for current widely dispersed and uncontrolled porous membranes. Several potential applications will

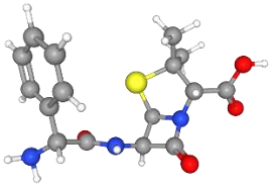
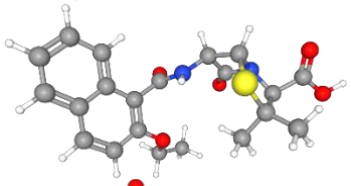
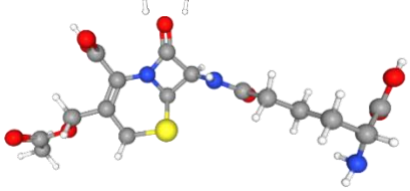
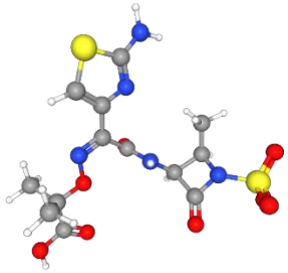
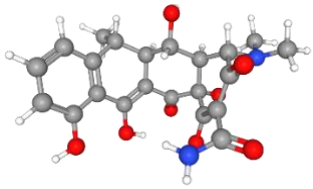
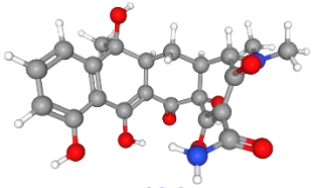
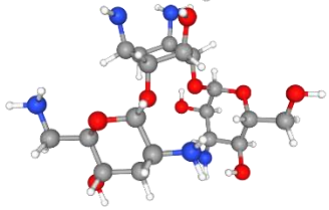
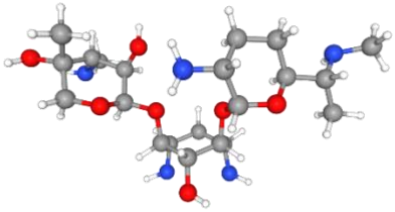
benefit from the exquisite selectivity of these BBMs, such as recovery of antibiotics, catalysts, and biomass components, which will be discussed along with organic acid purification and gas separations.

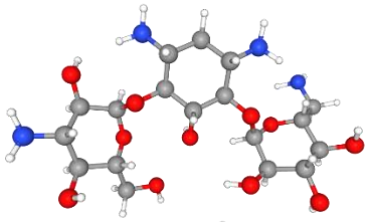
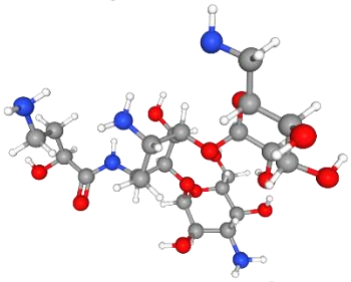
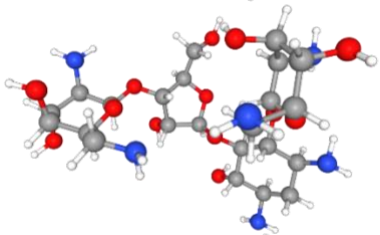
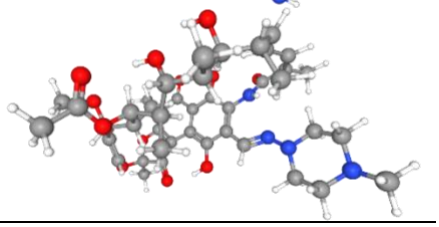
Antibiotic separations

Antibiotics, secondary metabolites produced by microorganisms, have been widely used to treat bacterial infections since the discovery of penicillin by Alexander Fleming in 1929. Antibiotics are one of the most commercially important bioproducts: their market size reached 39.8 billion USD in 2015 and is expected to reach 57.0 billion USD in 2024 [133]. Various production techniques can be applied to industrial antibiotic production, including fermentation [134], semi-synthetic methods [135], and synthetic routes [136]. We propose that filtration membranes with monodisperse nanometer scale pores could be used to enhance the process efficiency and economics of downstream processing of antibiotics. We illustrate this by taking industrial penicillin fermentation as an example. The typical process includes fermentation, biomass removal, solvent extraction, and antibiotic crystallization [137]. During the solvent extraction step, antibiotics are selectively extracted into the organic phase (commonly n-butyl acetate) [137]. However, one main challenge in the solvent extraction process is the formation of stable emulsions, caused by the fermentation byproducts (such as polysaccharides and proteins) that are not completely removed during the biomass removal step; these emulsions reduce the effectiveness of penicillin extraction into the organic phase [137-140]. A previous study showed improvements in the organic extraction yield because smaller amounts of the emulsion are produced when the fermentation media is filtered using ultrafiltration membranes with a tight (5 kDa) molecular weight cutoff [138]. Hence, we expect that filtration using membranes with a monodisperse, sub-nanometer pore size could remove byproducts while allowing the passage of antibiotics (typically 100 –1,000 Da, or physical dimensions between 0.6 – 1.2 nm, see **Table 3** for a detailed list) into the permeate, reducing emulsion formation in the organic extraction process and improving the antibiotic yield. In subsequent steps, antibiotics could be concentrated and separated using smaller pore size biomimetic membranes.

Table 3. Molecular estimations of common antibiotics for separations and recovery (300-1,000 Da)

Antibiotics	MW (Da)	Molecular Size (nm)*	Molecular Structures
Sulfonamides	127	0.66	
Ciprofloxacin	331	0.91	
Penicillin G	334	0.92	
Linezolid	337	0.92	

Ampicillin	349	0.93	
Nafcillin	415	0.98	
Cephalosporins	415	0.98	
Aztreonam	435	1.00	
Doxycycline	444	1.01	
Tetracycline	444	1.01	
Tobramycin	468	1.02	
Gentamicin	478	1.03	

Kanamycin	485	1.04	
Amikacin	586	1.10	
Neomycin	615	1.12	
Rifampin	823	1.24	

* Assume the antibiotic has a sphere shape to estimate the molecular size in diameter, $D = 0.132\ MW^{1/3}$ (nm). MW: Molecular weight in Dalton (Da) [141].

Organic acid separations

Organic acids, such as acetic, gluconic, amino and lactic acid, are widely used as food additives due to their low toxicity [142]. For instance, gluconic acid can be applied to improve beverage clarity [143], and lactic acid can be used as a pH control agent [144, 145]. These acids are also being proposed as bio-based building blocks for other industrially relevant chemicals [146, 147]. Organic acids can be produced commercially by several methods, including chemical oxidization, electrolytic oxidation, or fermentation [142]. Because the chemical oxidation process entails steps that are toxic to the environment, and because the electrolytic oxidation process is costly, fermentation processes are most widely used [142]. After organic acids are produced via fermentation, downstream processes such as isolation, purification, evaporation, and crystallization are needed to purify products. For the organic acid separation process, membrane separations can improve product purity [148-150]. Membranes with a monodisperse sub-nanometer pore size can be applied in two ways. High-molecular-weight organic acids can be concentrated using these membranes, while for low-molecular-weight organic acids, these membranes can be used to separate the acids from larger molecules present in the fermentation broth [149]. However, membrane design will need to account for the effects of fouling, concentration polarization and other practical challenges, such as compatibility of membranes with the operating conditions (high temperature, extreme pressures, aggressive organic solvents, and high concentrations of acid/base) [142, 151].

Based on their purity, lactic acids and amino acids are useful ingredients in food, pharmaceutical, and biological products [152]. Recovery, desalination and purification of amino acids and lactic acids can be accomplished using NF in a simple, economical process compared to chromatography, distillation and extraction [153]. It is an essential separation process to achieve monomer grade lactic acid enriched permeate and amino acid enriched retentate from the fermentation broth [154]. In addition, recovery and recycling of unconverted sugars from the fermentation broth could improve the economics of the overall process [153, 155]. Current NF membranes cannot efficiently achieve this separation due to the influence of the ionic compounds of sodium lactate/glucose on glucose retention [156]. Hence, recovery cannot proceed in a single stage owing to the challenging selectivity of the similarly sized glucose/lactate separation [152]. These inefficient and currently unachievable separations are likely a result of the poor selectivity resulting from the wide pore distribution of current NF membranes and the presence of charged species on the membranes. The similar molecular weight of undesired products and that of valuable components make separation impossible with current NF membranes or in a single stage. A uniform pore sized membrane would be a strong candidate to improve and facilitate the separation and recovery of sugar, lactic acid and amino acids.

Gas separations

The area of gas separations has been widely acknowledged as a potential beneficiary from improved membrane technology. Most gas separations are currently performed using energy-intensive processes such as distillation, although pressure-swing absorption is also used in some cases [102, 157, 158]. However, the design of sufficiently permeable and selective polymeric membranes has led to membrane processes for some separations, particularly in applications such as offshore natural gas production, in which space is at a premium [158]. In such polymeric membranes, the selectivity depends on both the diffusion coefficient (higher for small molecules) and the sorption coefficient (usually higher for more condensable molecules) for each gas in the mixture, with an increase in either resulting in greater permeation of that given component [102]. However, one major challenge is that membrane quality standards for successful gas separations are much stricter compared to other applications in terms of pore (free void) size distributions and defect-free intact selective layers. This problem arises from the fact that many of the critical target gas pairs to be separated have very narrow kinetic diameter gaps with respect to each other (**Table 4**) and, therefore, failure to achieve high quality membranes can lead to detrimental selectivity loses, particularly if only diffusion based (size dependent) separations are desired and/or possible. For example, diffusion coefficients for CH_4 vary over an order of magnitude in membrane pores in which diameters change by only one or two angstroms (3.5-5 Å) around the kinetic diameter of CH_4 (3.75 Å). This example illustrates the fundamental design principle of synthesizing membranes with uniform pores, the diameters of which fall in between the two kinetic diameters of gas pairs. This separation mechanism is well described by molecular sieving at sub-nanometer scales (**Fig. 4**). Concurrently, it implies that any nanoscopic pinholes over macroscopic membrane surface areas can be critical defects hindering successful gas separations. Presently, most practical gas separation membranes have adopted relatively thick (sub-micron) selective layers to avoid these issues, but this accommodation results in compromised membrane productivity.

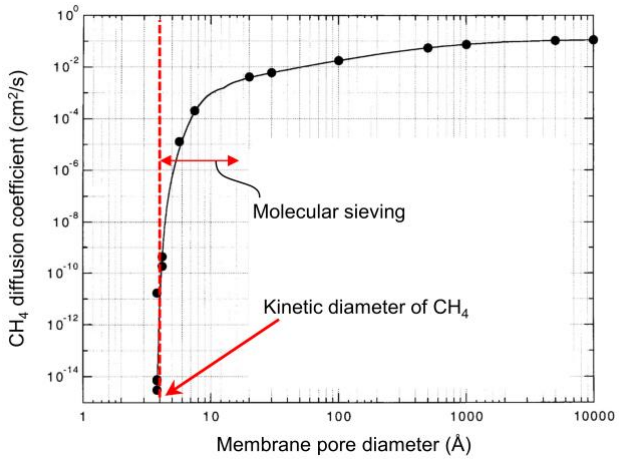


Fig. 4. Methane (CH_4) diffusion coefficient change in zeolite and ceramic membranes of characterized pore diameters. Order of magnitude change occurs over a small size range due to the molecular sieving effect [159]. Copyright 1996 Elsevier Ltd.

The two characteristic features of BBMs, unitary pore shapes and self-assembly, provide great avenues for rational solutions to above mentioned challenges of size-based separations. First, recent progress in biomimetic channel research have demonstrated achieving designed pore shapes within the size range spanning ~3 Å to ~1 nm even with sub-angstrom scale accuracy [2]. Also, established organic chemistry confers tunability of pore apertures to biomimetic artificial channels, especially in the kinetic diameter ranges of impactful gas pairs to be separated (**Table 4** and **Table S2**). Secondly, and importantly, self-assembly properties used for biomimetic membrane assembly in some case exhibits molecular self-repair properties that could be highly advantageous. Just beyond biomimetic membranes, uniform pore structures appear in a number of porous materials such as zeolites, zeolitic-imidazolate frameworks (ZIFs) or metal-organic frameworks (MOFs), and they have been adopted in the quest for effective gas separation membranes. These materials have shown substantial progress during the last few decades but still face challenges with defect-sealing and integration into MMMs [119]. For biomimetic membranes, self-repair driven by molecular self-assembly have been shown to be effective even at molecularly single layered membranes. For example, lipid-like amphiphilic peptoids exhibit lateral growth to form 2D membranes on the mica substrates, and *in situ* atomic force microscopy (AFM) images have revealed their self-repairing properties after mechanical defects were induced over the membranes (**Fig. 5**). Overall, these molecularly thin, self-repairable, and precisely sized-pore properties make biomimetic and bioinspired membranes a promising platform to explore for gas separation membranes while maximizing membrane productivity.

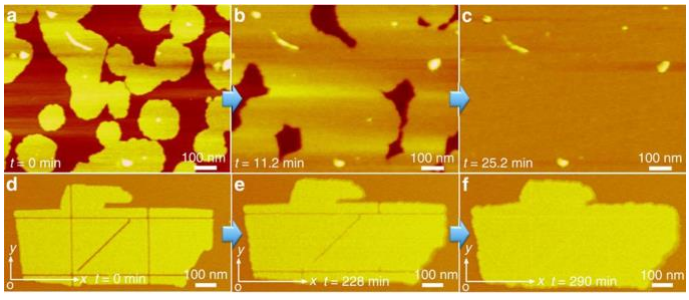


Fig. 5. Formation of self-assembled biomimetic peptoid membranes and their self-repairing properties. *In situ* AFM images of (a-c) heterogeneous lateral growth and formation of macroscopic peptoid membranes on mica substrate and (d-f) self-repairing peptoid membrane surface after mechanical scratches were induced on the surface [160]. Copyright 2016 Nature Publishing Group.

Gas separations are often conducted under conditions that could be considered challenging for polymeric membranes and thus BBMs as well. The required temperature for a separation depends on the component volatilities and required pressure: all species must remain in the vapor phase at the required pressure [157, 158], and the temperatures used tend to range from ambient to 250 °C. In addition to the required temperature stability, the membranes used for such separations would benefit from a narrow pore size distribution: differences in the kinetic diameters for species to be separated range from about 0.1 Angstroms (e.g. N_2 vs CH_4) [161] to 2.7 Angstroms (e.g. He vs CH_4) [23, 161], as shown in **Table 4**. Many such separations take place during natural gas processing, in which methane must be separated from contaminants such as CO_2, N_2, He, and light alkanes (C3+) [24, 158]. Organic vapor separations currently carried out by distillation (at a high energy cost), such as n-hexane/dimethylbutane [162] and p-xylene/o,m-xylene [163], are another promising application. Air separations (O_2/N_2) are another potential area of application for membrane processes, and polymeric membranes have been proposed for this purpose [157]. However, the proposed polymeric membranes are sufficiently selective and would benefit more from improved permeability than improved selectivity [157]

Table 4. Typical operating conditions for gas separations*

Gases	Kinetic diameters [Å]	Temperature [°C]	Pressure [bar]	Current Technology
CO_2/CH_4 [102, 158]	3.3/3.75	50	40	Amine absorption, Polymer membranes
N_2/C_{3+} hydrocarbons [102]	3.65/> 4	≤ 25	≤ 27	Polymer membranes
N_2/O_2 [157, 164]	3.65/3.46	25	0.1-10	Polymer membranes, Cryogenic fractionation, Pressure-swing adsorption (PSA)
Ethylene/ethane [161, 165, 166]	4.2/4.4	25-50	1-6	Distillation, Carbon molecular sieve, MOF, and polymer membranes (proposed)
CO_2/N_2 [102, 167]	3.3/3.65	25-50	0.1-10	Amine Absorption, Polymer membranes (proposed)
CO_2/H_2 [102, 168-170]	3.3/2.89	-20-300	≤ 21	PSA, polymer membranes (proposed)
N-butane/isobutene [171]	4.3/4.9	25-320	≤ 1	ZIF membranes (proposed)
N_2/CH_4 [24, 158, 172]	3.65/3.75	-10-20	14-70	Distillation, polymer membranes, PSA
N-hexane/dimethylbutane [162, 171]	4.3/6.2	25-200	≤ 1	Silicate and zeolite membranes (proposed)
p-xylene/o,m-xylene [163]	5.9/6.8	30-100	1	ZIF membranes (proposed)
He/CH_4 [23]	1/3.75	25	70-100	Distillation, PSA
He/N_2 [23]	1/3.65	25	70-100	Distillation, PSA

*Temperatures and pressures are given for a membrane process (current or proposed).

Homogeneous catalyst retention and recovery

Numerous reactions in bulk chemical, fine chemical, specialty chemical, and pharmaceutical synthesis require a catalyst, which can be either heterogeneous (e.g., a metal nanoparticle) or homogenous (e.g., an ion complex in solution) [21, 22]. Homogeneous catalysts are more advantageous because all catalytic sites are accessible to the dissolved reactants, and their selectivity is more tunable [21]. The recycling of homogeneous catalysts from reaction mixtures has been known to increase catalytic productivity. However, the lack of a method to separate or retain the catalyst from the product stream results in loss of catalyst. Quite often the catalysts used are expensive and contain rare metals, so it is important to recover them.

Typical methods for catalyst/product separations used in industry (such as distillation) are not recommended, since most homogenous catalysts are thermally sensitive and decompose at temperatures below 150 °C [21]. As a result, several methods are being studied and are beginning to be applied commercially. These are heterogenization, scavenging, biphasic solvents, and organic solvent nanofiltration [22]. Organic solvent nanofiltration (OSN) using membranes provides a relatively simple and low-energy method for catalyst recovery, although designing a highly selective membrane that can separate product from catalyst remains a challenge due to their similar size and to membrane incompatibility with the reaction conditions [173]. Membranes with precisely defined pore sizes and solvent-resistance could significantly improve OSN as a method for catalyst retention. The required size selectivity and operating conditions for such membranes are shown in **Table 5**.

Table 5. Separation conditions and molecule properties for homogeneous catalyst separations.

Reaction	Temperature [°C]	Pressure [bar]	Solvent	Product/ Catalyst Molecular weight [Da]	Estimated Product/ Catalyst Radii [Å]*	Catalyst
Styrene/iodobenzene Heck coupling [129]	60-160	30	THF	180/224	4/6	$Pd(OAc)_2(PPh_3)_2$
Hydroformylation of oct-1-ene [130]	70-90 (120-180)	25-50 (20-40)	$scCO_2$** (Water/ Decane)	144/665	4/8***	$Co_2(CO)_8$/ $Ph_2P(CH_2CH_2O)_nMe$
Iodobenzene/methyl acrylate Heck coupling [131]	80-110	8-30	DMF	162/224	4/6	$[Pd(OAc)_2]_n$/ dppp
Dimethyl itaconate hydrogenation [132]	35	10	Methanol	145/929	4/9***	Rh–EtDUPHOS
Methyl-2-acetamidoacrylate hydrogenation [132]	22-37	2-10	Methanol	160/723	4/8***	Ru–BINAP
Ring-closing metathesis of N-tosyldiallylamine [133]	35	45	Toluene	224/626	4**/8**	Hoveyda-Grubbs Catalyst® M72 (C627)

*Diameters are approximated using the assumption that all molecules are solid spheres, as has been done to estimate protein sizes [141].
**Supercritical carbon dioxide.
***For these species, density was unknown, so a density of 0.9 g/mL was used for small organic molecules and 1.8 g/mL for organometallic catalysts based on average values for the molecules with known density.

Organic solvent nanofiltration

Organic solvent nanofiltration (OSN) has emerged as a significant separation process for purification of liquid organic solvents from valuable products. OSN has application potential in many fields, such as the fine-chemical, pharmaceutical, and biochemical industries [174]. OSN is an economic and ecological alternative to thermal separations. The separation performance of these membranes is governed by factors such as the sieving effect and Donnan effects, as well as affinity effects [175]. However, current OSN membranes do not have the molecular specificity with uniform pore distributions to efficiently separate molecules of similar size. In addition, OSN membranes would need to remain stable and selective under challenging conditions. These conditions may include being chemically compatible with metallic catalysts (antimony, beryllium, and platinum group metals), solvents (supercritical CO_2, ionic liquids, and fluorous liquids), and the reactants and products (typically organic molecules), as well as remaining stable at elevated temperatures (40-120 °C [22]). The extreme process conditions rule out the options of using MPs or AWCs with structures dependent on hydrogen bonding. Temperature and solvent stable artificial channels would require precise pore sizes and would provide a significant improvement in OSN for catalysts. Membrane embedded with macrocycle molecules create a potential to improve solvent transport, shape selectivity and organic micropollutant removal [176, 177]. For example, the microporoisty of membrane was controlled by the polymerized β-cyclodextrin (β-CD), resulting in enhanced methanol transport (9.4 LMH/bar) and cylindrical/spherical molecule separation [127]. Nevertheless, in downstream chemical processes, selective removal of high-value alkyl-aromatics and chemical isomers is challenging and is required for precise molecular selectivity of membrane separation or absorption.

OSN is also gaining popularity in the vegetable oil refining process to remove hydratable phospholipids. Crude vegetable oils contain various minor substances such as phospholipids, coloring pigments, and fatty acids. Conventional methods of oil extraction and refining require large quantities of solvent that are undesirable due to their toxic chemical components and high energy consumption, as well as to the cost involved in recovery processes [175]. The molecular weight of triglycerides and phospholipids are roughly in the vicinity of 800 Da and 900 Da, which makes it difficult for them to be separated by a membrane [178]. The vegetable oil refining process involves degumming to remove the phospholipids. Traditionally, during oil processing, phospholipids form micelles in a non-aqueous environment, which micelles contain 10-30% of crude oil and 70-90% of hexane. Hence, phospholipids can be separated from triacylglycerol in the micelle stage by using appropriate membranes [179, 180]. Nevertheless, energy cost reductions and waste disposal are major concerns for oil refining processes, necessitating alternative methods that improve conventional processes [179]. We propose that monodisperse pore sized membranes would contribute to an efficient separation of valuable products and simplify the oil refining process without forming micelles to separate triglycerides, phospholipids and other minor undesired chemicals.

Nanofiltration in food processing

The use of NF in food processing industries has evolved from a novel approach into a reliable and economical separation system [181]. The majority of NF development started in the food, juice, dairy and milk processing industries, especially for whey protein valorization [182-184]. This is due mainly to its intermediate molecular weight cut off (200-1,000 Da), between that of UF and RO. The lower operating pressures compared to reverse osmosis and the unique selectivity of the membranes render NF a less energy-intensive and more eco-friendly option for downstream separations. NF has been applied by integration with other membrane processes throughout the milk and dairy processing steps: cheese making, whey protein concentration, fractionation of protein hydrolysates, waste stream purification, and effluent reclamation [181]. NF is widely viewed as an alternative to electrodialysis (ED) in food processing. The use of NF instead of ED has the advantage of simultaneous recovery, concentration and demineralization of whey products, in addition to lower operating costs and more permselectivity towards the undesirable monovalent salts (K^+, Cl^- or Na^+) [185]. However, current NF membranes exhibit a high permeability for monovalent salts such as NaCl, KCl but have a very low permeability for organic compounds such as lactose, proteins, and urea. NF can be effectively used for the permeation of a salt solution typical of that found in dairy UF permeate. The rejection behavior is a strong function of both charge interactions and solute size of the feed solution for charged NF and UF membranes [152].

Whey processing is a significant stage to purify, recover and concentrate nutritional and functional ingredients and by-products for the food industry [181]. Whey is the residual liquid of cheese and casein production. NF is used to deacidify whey produced by the addition of hydrochloric acid to milk in the production of casein [152]. The recovery and concentration of lactose-enriched streams and protein-enriched streams can add benefits to whey products [181]. Whey should be demineralized before it is processed for human or animal consumption. NF of whey is also carried out for lactose decalcification, deashing, and the removal of other salts [186]. Salt removal is important for preventing scaling and build-up on evaporators or heat exchangers. NF-membranes with molecular weight cut-off 200 to 1,000 have a high permeability for univalent salts (NaCl, KCl) but low permeability for organic compounds (lactose, proteins, urea etc.). Traditionally, several membrane separation modules are needed to purify and recover whey proteins, lactose, vitamins and nutrients [181]. It has been reported that a series of membranes with different MWCO (1 kDa, 3 kDa and 5 kDa) is required to achieve 100 % recovery of lactose in permeate [187]. We anticipate that the development of more selective separation membranes such as BBMs will contribute to high recovery and precise separation of lactose, as well as fractionalized protein products, and could simplify the multi-stage separation modules to a few stages, or even a single stage, in food processing.

Protective and breathable fabrics

Protective barrier materials and fabrics are designed to possess properties to exclude or detoxify toxic chemicals and biological threat including chemical warfare agents (CWAs), while allowing facile perspiration and efficient

heat loss from body [188, 189]. The protective fabrics should be breathable (a moisture vapor transport rate (MVTR) >1,500–2,000 g m^{-2} d^{-1}), preventive penetration to small molecules (~100-250 Da for CWAs such as soman and sarin), waterproof, flexible, lightweight, and durable[190]. However, traditional garment materials are non-porous polymers such as butyl rubber [191] or loaded with adsorbents for harmful chemicals [192], which suffer from low MVTR and leads to high discomfort and physiological burden on longer-term usage by military personnel and civilians [193].

Some approaches using functionalized MOFs to capture, degrade or target detoxification of the CWAs and prevent penetration with their high surface areas and adsorption capacities [194-196]. In addition, well-ordered nanomaterials and thin selective barriers are fabricated to be permselective to water vapor, toxic chemicals, and gases [197]. For example, GO-based membranes with the thickness of 0.7-1.2 nm are vapor permeable (3,900 g m^{-2} d^{-1}), selective to small gases (He, N_2 and C_2H_6) and adsorb CWA simulants (dimethyl methyl phosphonate, DMMP and 2-chloroethyl ethyl sulfide, CEES) via π- π interactions [198]. CNT membranes with organized sub-nm pores exhibit MVTR ~8,000 g m^{-2} d^{-1} and exclude charged dyes and nanoparticles of ~5 nm [92]. CNT membranes functionalized with responsive copolymers demonstrate MVTR > 4,000 g m^{-2} d^{-1} while hindering the permeation of nerve agent simulant (diethyl chlorophosphite, DCP) via the collapse of polymeric chains [199]. Nevertheless, large-scale of waterproof and protective porous materials for garments or clothes that allow vapor transport while excluding all chemical and biological threats and limiting water loss from body via size exclusion are area of investigation [190]. With the development of channels and porous materials, we could expect to create breathable and hydrophobic fabrics with tunable, uniform, and rigid pores, which simultaneously protect against harmful agents, enhance vapor transport, and prevent water permeation.

Ion/ion selectivity, recovery, and separations

REEs possess unique chemical properties and electronic configuration in energy storage, electronic devices, glass processing, fluorescent materials, and catalysis [200]. As the demand of the REEs has grown significantly, their disposal, separation, and recovery are of great importance. However, the purification of REE is a complicated process including several steps of solvent extraction and/or ion exchange due to the similar chemical properties in the aqueous solution [201]. In addition, to extract alkali metal ions from brine and seawater is also challenging due to the similar ionic radii and same valence [202].

Recent research has focused on synthesizing precise molecular sieving/channels to address challenges and limitations of solution-diffusion based membrane separations, including the selective transport between metal ions of the same valence and rejection of small molecules [13]. Biological ion channels are desirable for efficient separations, such as potassium channel with $K^+/Na^+ = 10^4$. Synthetic ion channels, macrocycles, and MOFs have emerged as promising materials to adsorb, chelate and transport ions through the defined cavities and interactions (**Table 2**). For example, MOF-embedded membranes with cavity of 3.4 Å demonstrate ion selectivity of Li^+/Rb^+ = 4.6, Li^+/K^+ = 2.2, and Li^+/Na^+ = 1.4. The lower ion selectivity of synthetic membranes than that of biological channels maybe due to some defects in the membranes or non-rigid pore structures [203]. Recapitulating the transport mechanism from biological channels and investigating optimized insertion method to incorporate porous materials or biological channels into BBMs or MMMs are attractive research opportunities in this area.

Conclusions and outlook

BBMs with uniformity of pore size distribution can achieve precise separations and narrow the solute rejection ranges. These advantages would allow us to expand applications of membranes in the precise size-based separation of species including antibiotics/fermentation broth biomass separations, gas separations, homogeneous catalysts/reaction product separation, and organic acid recovery. These monodisperse biomimetic membranes could also be utilized in organic solvent separation and food processing, where separations of similar molecular sized solutes need to be conducted. However, some of these separations would need to be performed under conditions in

which at least some existing membrane types are unstable (**Table 6**). Notably, gas and catalyst separations involve nonaqueous environments and high temperatures, making them unsuitable for MPs and possibly self-assembled AWCs whose structures rely on hydrogen bonding. However, owing to their precise and versatile pore sizes as well as well-order porous properties, MPs and their mimics may find applications in separating antibiotics and other organic molecules from other species in a fermentation broth. For challenging separations, mixed matrix membranes, porous and polymeric membranes, as well as MOF-nanosheet composite membranes, have been proposed to improve separation performance. In addition, BBMs containing CNTs or AWCs with a well-defined and mediated pore size geometry and distribution could also provide an alternative way to achieve superior selectivity and performance. The precise selectivity of such membranes could contribute to similarly-sized small molecule separations in a variety of industries, particularly separations including molecules with tiny size differences ($\leq$ 1 Å diameter difference) and when the desired components are at low feed concentration. Such applications provide an incentive for the development of biomimetic membranes and bioinspired channels as well as biomimetic strategies that can function under the harsher conditions required.

Table 6. Summary of separation types and requirements

Separation	Temperature [°C]	P [bar]	Solvent	Permeant Diameter [Å]	Size Difference between Separated Species [Å]
Gas separations [23, 102, 157, 164, 168-170]	25-300	< 1-100	None (gas phase)	1-6	0.1-3 (gas 1/ gas 2)
Homogeneous catalyst retention [173, 204, 205]	20-160	2-200	Organic, fluorous, or ionic liquids, supercritical CO_2	2-4	2-12 (catalyst/ reaction product)
Antibiotics [138]	4-15	0.5-5	Water	5-20	15-80 (antibiotics/ proteins)
Organic Acids [206]	25, 37	7-35	Water	3-9	7-12 (organic acids/ sugars)
Breathable protective fabrics (chemical and biological threats) [189]	37-200	<2	Water	2.8	3-6.5 (CWA stimulants/ vapor)
Ion/ion separation and REE separations [201]	25-1,000	0.5-30	Ionic liquid, water, or oil	0.76-2.9	0.02-0.2 (ion 1/ ion 2)

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References

[1] Y.-x. Shen, P.O. Saboe, I.T. Sines, M. Erbakan, M. Kumar, Biomimetic membranes: A review, J. Membr. Sci., 454 (2014) 359-381.
[2] R. Chowdhury, T. Ren, M. Shankla, K. Decker, M. Grisewood, J. Prabhakar, C. Baker, J.H. Golbeck, A. Aksimentiev, M. Kumar, PoreDesigner for tuning solute selectivity in a robust and highly permeable outer membrane pore, Nat. Commun., 9 (2018) 3661.
[3] Y.-M. Tu, W. Song, T. Ren, Y.-x. Shen, R. Chowdhury, P. Rajapaksha, T.E. Culp, L. Samineni, C. Lang, A. Thokkadam, Rapid fabrication of precise high-throughput filters from membrane protein nanosheets, Nature Materials, (2020) 1-8.
[4] W. Song, M. Kumar, Artificial water channels: toward and beyond desalination, Current Opinion in Chemical Engineering, 25 (2019) 9-17.
[5] I. Kocsis, Z. Sun, Y.M. Legrand, M. Barboiu, Artificial water channels—deconvolution of natural Aquaporins through synthetic design, npj Clean Water, 1 (2018) 1-11.
[6] L. Chen, W. Si, L. Zhang, G. Tang, Z.-T. Li, J.-L. Hou, Chiral selective transmembrane transport of amino acids through artificial channels, Journal of the American Chemical Society, 135 (2013) 2152-2155.
[7] R.H. Tunuguntla, R.Y. Henley, Y.-C. Yao, T.A. Pham, M. Wanunu, A. Noy, Enhanced water permeability and tunable ion selectivity in subnanometer carbon nanotube porins, Science, 357 (2017) 792-796.
[8] W. Song, Y.-M. Tu, H. Oh, L. Samineni, M. Kumar, Hierarchical optimization of high-performance biomimetic and bioinspired membranes, Langmuir, 35 (2018) 589-607.
[9] S.P. Nunes, P.Z. Culfaz-Emecen, G.Z. Ramon, T. Visser, G.H. Koops, W. Jin, M. Ulbricht, Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes, J. Membr. Sci., 598 (2020) 117761.
[10] C. Lang, D. Ye, W. Song, C. Yao, Y.-m. Tu, C. Capparelli, J.A. LaNasa, M.A. Hickner, E.W. Gomez, E.D. Gomez, Biomimetic separation of transport and matrix functions in lamellar block copolymer channel-based membranes, ACS nano, 13 (2019) 8292-8302.
[11] A. Noy, Carbon Nanotube Porins: A Versatile Synthetic Biomimetic Membrane Channel Platform, Biophysical Journal, 114 183a.
[12] H. Sun, Y. Li, S. Yu, J. Liu, Hierarchical self-assembly of proteins through rationally designed supramolecular interfaces, Frontiers in Bioengineering and Biotechnology, 8 (2020).
[13] C.J. Porter, J.R. Werber, M. Zhong, C.J. Wilson, M. Elimelech, Pathways and Challenges for Biomimetic Desalination Membranes with Sub-Nanometer Channels, ACS nano, (2020).
[14] T. Guo, K. Han, L. Heng, M. Cao, L. Jiang, Ordered porous structure hybrid films generated by breath figures for directional water penetration, RSC Advances, 5 (2015) 88471-88476.
[15] J.R. Hoffman, W.A. Phillip, 100th Anniversary of Macromolecular Science Viewpoint: Integrated Membrane Systems, ACS Macro Lett., 9 (2020) 1267-1279.
[16] R. Epsztein, R.M. DuChanois, C.L. Ritt, A. Noy, M. Elimelech, Towards single-species selectivity of membranes with subnanometre pores, Nature Nanotechnology, (2020) 1-11.
[17] H.B. Park, J. Kamcev, L.M. Robeson, M. Elimelech, B.D. Freeman, Maximizing the right stuff: The trade-off between membrane permeability and selectivity, Science, 356 (2017) eaab0530.
[18] W.R. Bowen, J.S. Welfoot, Modelling of membrane nanofiltration—pore size distribution effects, Chemical engineering science, 57 (2002) 1393-1407.
[19] W.R. Bowen, J.S. Welfoot, Modelling the performance of membrane nanofiltration—critical assessment and model development, Chemical Engineering Science, 57 (2002) 1121-1137.
[20] Y. Du, Y. Lv, W.-Z. Qiu, J. Wu, Z.-K. Xu, Nanofiltration membranes with narrowed pore size distribution via pore wall modification, Chemical Communications, 52 (2016) 8589-8592.
[21] D.J. Cole-Hamilton, Homogeneous catalysis--new approaches to catalyst separation, recovery, and recycling, Science, 299 (2003) 1702-1706.
[22] I.V. Gürsel, T. Noël, Q. Wang, V. Hessel, Separation/recycling methods for homogeneous transition metal catalysts in continuous flow, Green Chem., 17 (2015) 2012-2026.

[23] P. Hale, K. Lokhandwala, Helium recovery from gas streams, in, Google Patents, 2005.
[24] C.A. Scholes, G.W. Stevens, S.E. Kentish, Membrane gas separation applications in natural gas processing, Fuel, 96 (2012) 15-28.
[25] S.H. Dave, B.D. Keller, K. Golmer, J.C. Grossman, Six Degrees of Separation: Connecting Research with Users and Cost Analysis, Joule, 1 (2017) 410-415.
[26] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, Science, 333 (2011) 712-717.
[27] A. Al-Karaghouli, L.L. Kazmerski, Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes, Renewable and Sustainable Energy Reviews, 24 (2013) 343-356.
[28] J.T. Arena, J.C. Jain, C.L. Lopano, J.A. Hakala, T.V. Bartholomew, M.S. Mauter, N.S. Siefert, Management and dewatering of brines extracted from geologic carbon storage sites, International Journal of Greenhouse Gas Control, 63 (2017) 194-214.
[29] Q. Yang, Y. Su, C. Chi, C. Cherian, K. Huang, V. Kravets, F. Wang, J. Zhang, A. Pratt, A. Grigorenko, Ultrathin graphene-based membrane with precise molecular sieving and ultrafast solvent permeation, Nature materials, 16 (2017) 1198-1202.
[30] Y. Liang, Y. Zhu, C. Liu, K.-R. Lee, W.-S. Hung, Z. Wang, Y. Li, M. Elimelech, J. Jin, S. Lin, Polyamide nanofiltration membrane with highly uniform sub-nanometre pores for sub-1 Å precision separation, Nature Communications, 11 (2020) 1-9.
[31] N.J. Harris, P.J. Booth, Folding and stability of membrane transport proteins in vitro, Biochim. Biophys. Acta, 1818 (2012) 1055-1066.
[32] M.F. De Volder, S.H. Tawfick, R.H. Baughman, A.J. Hart, Carbon nanotubes: present and future commercial applications, Science, 339 (2013) 535-539.
[33] K. Aitola, K. Domanski, J.P. Correa-Baena, K. Sveinbjörnsson, M. Saliba, A. Abate, M. Grätzel, E. Kauppinen, E.M. Johansson, W. Tress, High temperature-stable perovskite solar cell based on low-cost carbon nanotube hole contact, Adv. Mater., 29 (2017) 1606398.
[34] K. Liew, Z. Lei, L. Zhang, Mechanical analysis of functionally graded carbon nanotube reinforced composites: a review, Composite Structures, 120 (2015) 90-97.
[35] L. Song, J. Zhang, L. Sun, F. Xu, F. Li, H. Zhang, X. Si, C. Jiao, Z. Li, S. Liu, Mesoporous metal–organic frameworks: design and applications, Energy Environ. Sci., 5 (2012) 7508-7520.
[36] A.J. Howarth, Y. Liu, P. Li, Z. Li, T.C. Wang, J.T. Hupp, O.K. Farha, Chemical, thermal and mechanical stabilities of metal–organic frameworks, Nature Reviews Materials, 1 (2016) 15018.
[37] J. Ren, H.W. Langmi, B.C. North, M. Mathe, Review on processing of metal–organic framework (MOF) materials towards system integration for hydrogen storage, IJER, 39 (2015) 607-620.
[38] M. Rungta, G.B. Wenz, C. Zhang, L. Xu, W. Qiu, J.S. Adams, W.J. Koros, Carbon molecular sieve structure development and membrane performance relationships, Carbon, 115 (2017) 237-248.
[39] I.S. Wood, P. Trayhurn, Glucose transporters (GLUT and SGLT): expanded families of sugar transport proteins, Br. J. Nutr., 89 (2007) 3-9.
[40] J.P. Morth, B.P. Pedersen, M.J. Buch-Pedersen, J.P. Andersen, B. Vilsen, M.G. Palmgren, P. Nissen, A structural overview of the plasma membrane Na+,K+-ATPase and H+-ATPase ion pumps, Nature Reviews Molecular Cell Biology, 12 (2010) 60.
[41] S. Mathivanan, H. Ji, R.J. Simpson, Exosomes: Extracellular organelles important in intercellular communication, J. Proteomics, 73 (2010) 1907-1920.
[42] M. Mittelbrunn, F. Sánchez-Madrid, Intercellular communication: diverse structures for exchange of genetic information, Nature Reviews Molecular Cell Biology, 13 (2012) 328.
[43] W. Busch, M.H. Saier, The Transporter Classification (TC) System, 2002, Critical Reviews in Biochemistry and Molecular Biology, 37 (2002) 287-337.
[44] C. Tang, Y. Zhao, R. Wang, C. Hélix-Nielsen, A. Fane, Desalination by biomimetic aquaporin membranes: Review of status and prospects, Desalination, 308 (2013) 34-40.

[45] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z, Proceedings of the National Academy of Sciences, 104 (2007) 20719-20724.
[46] M. Kumar, M.M. Payne, S.K. Poust, J.L. Zilles, Polymer-based biomimetic membranes for desalination, in: Biomimetic membranes for sensor and separation applications, Springer, 2011, pp. 43-62.
[47] D.A. Doyle, J.M. Cabral, R.A. Pfuetzner, A. Kuo, J.M. Gulbis, S.L. Cohen, B.T. Chait, R. MacKinnon, The structure of the potassium channel: molecular basis of K+ conduction and selectivity, Science, 280 (1998) 69-77.
[48] C.H. Nielsen, Biomimetic membranes for sensor and separation applications, Analytical and bioanalytical chemistry, 395 (2009) 697-718.
[49] M. Wang, Z. Wang, X. Wang, S. Wang, W. Ding, C. Gao, Layer-by-layer assembly of aquaporin Z-incorporated biomimetic membranes for water purification, Environ. Sci. Technol., 49 (2015) 3761-3768.
[50] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nature Reviews Materials, 1 (2016) 1-15.
[51] P. Agre, Aquaporin water channels (Nobel lecture), Angew. Chem. Int. Ed., 43 (2004) 4278-4290.
[52] S. Qi, R. Wang, G.K.M. Chaitra, J. Torres, X. Hu, A.G. Fane, Aquaporin-based biomimetic reverse osmosis membranes: Stability and long term performance, J. Membr. Sci., 508 (2016) 94-103.
[53] Y. Li, S. Qi, M. Tian, W. Widjajanti, R. Wang, Fabrication of aquaporin-based biomimetic membrane for seawater desalination, Desalination, 467 (2019) 103-112.
[54] Y. Zhao, C. Qiu, X. Li, A. Vararattanavech, W. Shen, J. Torres, C. Helix-Nielsen, R. Wang, X. Hu, A.G. Fane, Synthesis of robust and high-performance aquaporin-based biomimetic membranes by interfacial polymerization-membrane preparation and RO performance characterization, Journal of Membrane Science, 423 (2012) 422-428.
[55] C. Hannesschläger, T. Barta, C. Siligan, A. Horner, Quantification of water flux in vesicular systems, Scientific reports, 8 (2018) 1-8.
[56] M. Erbakan, Y.-x. Shen, M. Grzelakowski, P.J. Butler, M. Kumar, W.R. Curtis, Molecular cloning, overexpression and characterization of a novel water channel protein from Rhodobacter sphaeroides, PLoS One, 9 (2014) e86830.
[57] C. Tang, Z. Wang, I. Petrinić, A.G. Fane, C. Hélix-Nielsen, Biomimetic aquaporin membranes coming of age, Desalination, 368 (2015) 89-105.
[58] G.G. Privé, Detergents for the stabilization and crystallization of membrane proteins, Methods, 41 (2007) 388-397.
[59] S. Swamy-Mruthinti, V. Srinivas, J.E. Hansen, C.M. Rao, Thermal Stress Induced Aggregation of Aquaporin 0 (AQP0) and Protection by α-Crystallin via Its Chaperone Function, PLoS One, 8 (2013) e80404.
[60] A.G. Livingston, Z. Jiang, Proteins tailor pore geometry, Nature Materials, 19 (2020) 257-258.
[61] T. Ren, M. Erbakan, Y. Shen, E. Barbieri, P. Saboe, H. Feroz, H. Yan, S. McCuskey, J.F. Hall, A.B. Schantz, Membrane protein insertion into and compatibility with biomimetic membranes, Advanced Biosystems, 1 (2017) 1700053.
[62] Y.-x. Shen, W. Song, D.R. Barden, T. Ren, C. Lang, H. Feroz, C.B. Henderson, P.O. Saboe, D. Tsai, H. Yan, Achieving high permeability and enhanced selectivity for Angstrom-scale separations using artificial water channel membranes, Nature communications, 9 (2018) 2294.
[63] J. Shen, R. Ye, A. Romanies, A. Roy, F. Chen, C. Ren, Z. Liu, H. Zeng, An Aquafoldmer-Based Aquaporin-Like Synthetic Water Channel, Journal of the American Chemical Society, (2020).
[64] Y.-x. Shen, W. Si, M. Erbakan, K. Decker, R. De Zorzi, P.O. Saboe, Y.J. Kang, S. Majd, P.J. Butler, T. Walz, A. Aksimentiev, J.-l. Hou, M. Kumar, Highly permeable artificial water channels that can self-assemble into two-dimensional arrays, Proceedings of the National Academy of Sciences, 112 (2015) 9810.
[65] S.-P. Zheng, L.-B. Huang, Z. Sun, M. Barboiu, Self-assembled Artificial Ion-Channels toward Natural Selection of Functions, Angew. Chem., (2020).
[66] M. Barboiu, Artificial water channels - incipient innovative developments, Chemical Communications, 52 (2016) 5657-5665.

[67] W. Song, H. Joshi, R. Chowdhury, J.S. Najem, Y.-x. Shen, C. Lang, C.B. Henderson, Y.-M. Tu, M. Farell, M.E. Pitz, Artificial water channels enable fast and selective water permeation through water-wire networks, Nature Nanotechnology, (2019) 1-7.
[68] M.S. Kaucher, M. Peterca, A.E. Dulcey, A.J. Kim, S.A. Vinogradov, D.A. Hammer, P.A. Heiney, V. Percec, Selective Transport of Water Mediated by Porous Dendritic Dipeptides, Journal of the American Chemical Society, 129 (2007) 11698-11699.
[69] E. Licsandru, I. Kocsis, Y.-x. Shen, S. Murail, Y.-M. Legrand, A. van der Lee, D. Tsai, M. Baaden, M. Kumar, M. Barboiu, Salt-Excluding Artificial Water Channels Exhibiting Enhanced Dipolar Water and Proton Translocation, Journal of the American Chemical Society, 138 (2016) 5403-5409.
[70] J. Shen, J. Fan, R. Ye, N. Li, Y. Mu, H. Zeng, Polypyridine-Based Helical Amide Foldamer Channels: Rapid Transport of Water and Protons with High Ion Rejection, Angew. Chem. Int. Ed., (2020).
[71] W. Song, C. Lang, Y.-x. Shen, M. Kumar, Design considerations for artificial water channel–based membranes, Ann. Rev. Mater. Res., 48 (2018) 57-82.
[72] M. Di Vincenzo, A. Tiraferri, V.-E. Musteata, S. Chisca, R. Sougrat, L.-B. Huang, S.P. Nunes, M. Barboiu, Biomimetic artificial water channel membranes for enhanced desalination, Nature Nanotechnology, (2020) 1-7.
[73] F. Chen, J. Shen, N. Li, A. Roy, R. Ye, C. Ren, H. Zeng, Pyridine/Oxadiazole-Based Helical Foldamer Ion Channels with Exceptionally High K+/Na+ Selectivity, Angew. Chem. Int. Ed., 59 (2020) 1440-1444.
[74] M. Barboiu, Encapsulation versus self-aggregation toward highly selective artificial K+ channels, Acc. Chem. Res., 51 (2018) 2711-2718.
[75] G.W. Gokel, S. Negin, Synthetic ion channels: from pores to biological applications, Acc. Chem. Res., 46 (2013) 2824-2833.
[76] Z. Zhang, X. Huang, Y. Qian, W. Chen, L. Wen, L. Jiang, Engineering Smart Nanofluidic Systems for Artificial Ion Channels and Ion Pumps: From Single-Pore to Multichannel Membranes, Adv. Mater., 32 (2020) 1904351.
[77] Y.H. Li, S. Zheng, Y.M. Legrand, A. Gilles, A. Van der Lee, M. Barboiu, Structure-Driven Selection of Adaptive Transmembrane Na+ Carriers or K+ Channels, Angew. Chem. Int. Ed., 57 (2018) 10520-10524.
[78] V. Lakshmanan, S. Vijayan, A Review on Application of Crown Ethers in Separation of Rare Earths and Precious Metals, in: Extraction 2018, Springer, 2018, pp. 1913-1930.
[79] A. Fang, K. Kroenlein, D. Riccardi, A. Smolyanitsky, Highly mechanosensitive ion channels from graphene-embedded crown ethers, Nature Materials, 18 (2019) 76-81.
[80] J.A. Mould, H.-C. Li, C.S. Dudlak, J.D. Lear, A. Pekosz, R.A. Lamb, L.H. Pinto, Mechanism for proton conduction of the M2 ion channel of influenza A virus, J. Biol. Chem., 275 (2000) 8592-8599.
[81] P.H. Schlesinger, R. Ferdani, J. Liu, J. Pajewska, R. Pajewski, M. Saito, H. Shabany, G.W. Gokel, SCMTR: a chloride-selective, membrane-anchored peptide channel that exhibits voltage gating, Journal of the American Chemical Society, 124 (2002) 1848-1849.
[82] B.P. Benke, P. Aich, Y. Kim, K.L. Kim, M.R. Rohman, S. Hong, I.-C. Hwang, E.H. Lee, J.H. Roh, K. Kim, Iodide-selective synthetic ion channels based on shape-persistent organic cages, Journal of the American Chemical Society, 139 (2017) 7432-7435.
[83] Y. Luo, N. Marets, T. Kato, Selective lithium ion recognition in self-assembled columnar liquid crystals based on a lithium receptor, Chemical science, 9 (2018) 608-616.
[84] C. Lang, W. Li, Z. Dong, X. Zhang, F. Yang, B. Yang, X. Deng, C. Zhang, J. Xu, J. Liu, Biomimetic transmembrane channels with high stability and transporting efficiency from helically folded macromolecules, Angew. Chem. Int. Ed., 55 (2016) 9723-9727.
[85] C. Lang, X. Deng, F. Yang, B. Yang, W. Wang, S. Qi, X. Zhang, C. Zhang, Z. Dong, J. Liu, Highly Selective Artificial Potassium Ion Channels Constructed from Pore-Containing Helical Oligomers, Angew. Chem. Int. Ed., 56 (2017) 12668-12671.
[86] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, Science, 312 (2006) 1034-1037.
[87] A. Noy, H.G. Park, F. Fornasiero, J.K. Holt, C.P. Grigoropoulos, O. Bakajin, Nanofluidics in carbon nanotubes, Nano today, 2 (2007) 22-29.

[88] Y. Kim, H. Muramatsu, T. Hayashi, M. Endo, M. Terrones, M. Dresselhaus, Thermal stability and structural changes of double-walled carbon nanotubes by heat treatment, Chemical Physics Letters, 398 (2004) 87-92.
[89] K. Metenier, S. Bonnamy, F. Beguin, C. Journet, P. Bernier, M.L. de La Chapelle, O. Chauvet, S. Lefrant, Coalescence of single-walled carbon nanotubes and formation of multi-walled carbon nanotubes under high-temperature treatments, Carbon, 40 (2002) 1765-1773.
[90] R.H. Baughman, A.A. Zakhidov, W.A. De Heer, Carbon nanotubes--the route toward applications, Science, 297 (2002) 787-792.
[91] T. Yamada, T. Namai, K. Hata, D.N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, S. Iijima, Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts, Nature nanotechnology, 1 (2006) 131.
[92] N. Bui, E.R. Meshot, S. Kim, J. Peña, P.W. Gibson, K.J. Wu, F. Fornasiero, Ultrabreathable and Protective Membranes with Sub-5 nm Carbon Nanotube Pores, Adv. Mater., 28 (2016) 5871-5877.
[93] F. Fornasiero, H.G. Park, J.K. Holt, M. Stadermann, C.P. Grigoropoulos, A. Noy, O. Bakajin, Ion exclusion by sub-2-nm carbon nanotube pores, Proceedings of the National Academy of Sciences, 105 (2008) 17250-17255.
[94] O. Beckstein, K. Tai, M.S. Sansom, Not ions alone: barriers to ion permeation in nanopores and channels, Journal of the American Chemical Society, 126 (2004) 14694-14695.
[95] R. Rao, C.L. Pint, A.E. Islam, R.S. Weatherup, S. Hofmann, E.R. Meshot, F. Wu, C. Zhou, N. Dee, P.B. Amama, Carbon nanotubes and related nanomaterials: critical advances and challenges for synthesis toward mainstream commercial applications, ACS nano, 12 (2018) 11756-11784.
[96] M.L. Jue, S.F. Buchsbaum, C. Chen, S.J. Park, E.R. Meshot, K.J.J. Wu, F. Fornasiero, Ultra-Permeable Single-Walled Carbon Nanotube Membranes with Exceptional Performance at Scale, Advanced Science, (2020) 2001670.
[97] R.L. McGinnis, K. Reimund, J. Ren, L. Xia, M.R. Chowdhury, X. Sun, M. Abril, J.D. Moon, M.M. Merrick, J. Park, Large-scale polymeric carbon nanotube membranes with sub–1.27-nm pores, Sci. Adv., 4 (2018) e1700938.
[98] N.S. Bobbitt, M.L. Mendonca, A.J. Howarth, T. Islamoglu, J.T. Hupp, O.K. Farha, R.Q. Snurr, Metal–organic frameworks for the removal of toxic industrial chemicals and chemical warfare agents, Chemical Society Reviews, 46 (2017) 3357-3385.
[99] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The chemistry and applications of metal-organic frameworks, Science, 341 (2013).
[100] B. Li, H.M. Wen, Y. Cui, W. Zhou, G. Qian, B. Chen, Emerging multifunctional metal–organic framework materials, Adv. Mater., 28 (2016) 8819-8860.
[101] M. Drobek, J.-H. Kim, M. Bechelany, C. Vallicari, A. Julbe, S.S. Kim, MOF-based membrane encapsulated ZnO nanowires for enhanced gas sensor selectivity, ACS Applied Materials & Interfaces, 8 (2016) 8323-8328.
[102] R.W. Baker, B.T. Low, Gas separation membrane materials: a perspective, Macromolecules, 47 (2014) 6999-7013.
[103] L. Wang, Y. Han, X. Feng, J. Zhou, P. Qi, B. Wang, Metal–organic frameworks for energy storage: Batteries and supercapacitors, Coord. Chem. Rev., 307 (2016) 361-381.
[104] L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Metal–organic frameworks for heterogeneous basic catalysis, Chem. Rev., 117 (2017) 8129-8176.
[105] C.A. Trickett, A. Helal, B.A. Al-Maythalony, Z.H. Yamani, K.E. Cordova, O.M. Yaghi, The chemistry of metal–organic frameworks for CO 2 capture, regeneration and conversion, Nature Reviews Materials, 2 (2017) 1-16.
[106] J. Lu, H. Zhang, J. Hou, X. Li, X. Hu, Y. Hu, C.D. Easton, Q. Li, C. Sun, A.W. Thornton, Efficient metal ion sieving in rectifying subnanochannels enabled by metal–organic frameworks, Nature Materials, (2020) 1-8.
[107] J.E. Mondloch, M.J. Katz, W.C. Isley III, P. Ghosh, P. Liao, W. Bury, G.W. Wagner, M.G. Hall, J.B. DeCoste, G.W. Peterson, Destruction of chemical warfare agents using metal–organic frameworks, Nature materials, 14 (2015) 512.
[108] J. Zhao, D.T. Lee, R.W. Yaga, M.G. Hall, H.F. Barton, I.R. Woodward, C.J. Oldham, H.J. Walls, G.W. Peterson, G.N. Parsons, Ultra-Fast Degradation of Chemical Warfare Agents Using MOF–Nanofiber Kebabs, Angew. Chem. Int. Ed., 55 (2016) 13224-13228.

[109] Y. Li, L.H. Wee, J.A. Martens, I.F. Vankelecom, Interfacial synthesis of ZIF-8 membranes with improved nanofiltration performance, J. Membr. Sci., 523 (2017) 561-566.
[110] S. Basu, M. Maes, A. Cano-Odena, L. Alaerts, D.E. De Vos, I.F. Vankelecom, Solvent resistant nanofiltration (SRNF) membranes based on metal-organic frameworks, J. Membr. Sci., 344 (2009) 190-198.
[111] S. Rojas, T. Baati, L. Njim, L. Manchego, F. Neffati, N. Abdeljelil, S. Saguem, C. Serre, M.F. Najjar, A. Zakhama, Metal–organic frameworks as efficient oral detoxifying agents, Journal of the American Chemical Society, 140 (2018) 9581-9586.
[112] M.X. Wu, Y.W. Yang, Metal–organic framework (MOF)-based drug/cargo delivery and cancer therapy, Adv. Mater., 29 (2017) 1606134.
[113] Y. Huang, M. Zhao, S. Han, Z. Lai, J. Yang, C. Tan, Q. Ma, Q. Lu, J. Chen, X. Zhang, Growth of au nanoparticles on 2D metalloporphyrinic metal-organic framework nanosheets used as biomimetic catalysts for cascade reactions, Adv. Mater., 29 (2017) 1700102.
[114] R. Wang, D. Jin, Y. Zhang, S. Wang, J. Lang, X. Yan, L. Zhang, Engineering metal organic framework derived 3D nanostructures for high performance hybrid supercapacitors, Journal of Materials Chemistry A, 5 (2017) 292-302.
[115] Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, Metal-organic framework nanosheets as building blocks for molecular sieving membranes, Science, 346 (2014) 1356-1359.
[116] Y. Peng, Y. Li, Y. Ban, W. Yang, Two-Dimensional Metal–Organic Framework Nanosheets for Membrane-Based Gas Separation, Angew. Chem. Int. Ed., 56 (2017) 9757-9761.
[117] T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F.X.L. i Xamena, J. Gascon, Metal–organic framework nanosheets in polymer composite materials for gas separation, Nature materials, 14 (2015) 48.
[118] K. Shen, L. Zhang, X. Chen, L. Liu, D. Zhang, Y. Han, J. Chen, J. Long, R. Luque, Y. Li, Ordered macro-microporous metal-organic framework single crystals, Science, 359 (2018) 206-210.
[119] X. Ma, Y. Chai, P. Li, B. Wang, Metal–Organic Framework Films and Their Potential Applications in Environmental Pollution Control, Acc. Chem. Res., 52 (2019) 1461-1470.
[120] A.F. Ismail, L. David, A review on the latest development of carbon membranes for gas separation, J. Membr. Sci., 193 (2001) 1-18.
[121] A.R. Mohamed, M. Mohammadi, G.N. Darzi, Preparation of carbon molecular sieve from lignocellulosic biomass: A review, Renewable and Sustainable Energy Reviews, 14 (2010) 1591-1599.
[122] J. Wang, J. Zhu, Y. Zhang, J. Liu, B. Van der Bruggen, Nanoscale tailor-made membranes for precise and rapid molecular sieve separation, Nanoscale, 9 (2017) 2942-2957.
[123] C. Zhang, W.J. Koros, Ultraselective carbon molecular sieve membranes with tailored synergistic sorption selective properties, Adv. Mater., 29 (2017) 1701631.
[124] M. Xue, Y. Yang, X. Chi, Z. Zhang, F. Huang, Pillararenes, a new class of macrocycles for supramolecular chemistry, Acc. Chem. Res., 45 (2012) 1294-1308.
[125] M. Hiraoka, Crown ethers and analogous compounds, Elsevier, 2016.
[126] F. Perret, A.W. Coleman, Biochemistry of anionic calix [n] arenes, Chemical communications, 47 (2011) 7303-7319.
[127] L.F. Villalobos, T. Huang, K.V. Peinemann, Cyclodextrin films with fast solvent transport and shape-selective permeability, Adv. Mater., 29 (2017) 1606641.
[128] U. Akiba, D. Minaki, J.-i. Anzai, Host-guest chemistry in layer-by-layer assemblies containing calix [n] arenes and cucurbit [n] urils: A review, Polymers, 10 (2018) 130.
[129] Q. He, G.I. Vargas-Zúñiga, S.H. Kim, S.K. Kim, J.L. Sessler, Macrocycles as ion pair receptors, Chem. Rev., 119 (2019) 9753-9835.
[130] Y. Zhou, K. Jie, R. Zhao, F. Huang, Supramolecular-Macrocycle-Based Crystalline Organic Materials, Adv. Mater., (2019) 1904824.
[131] E.M. Driggers, S.P. Hale, J. Lee, N.K. Terrett, The exploration of macrocycles for drug discovery—an underexploited structural class, Nature Reviews Drug Discovery, 7 (2008) 608-624.
[132] J. Xue, J. Shen, R. Zhang, F. Wang, S. Liang, X. You, Q. Yu, Y. Hao, Y. Su, Z. Jiang, High-flux nanofiltration membranes prepared with β-cyclodextrin and graphene quantum dots, J. Membr. Sci., 612 (2020) 118465.

[133] G.V. Research, Antibiotics Market Size To Reach $57.0 Billion By 2024, (2016).
[134] S. Sánchez, A. Chávez, A. Forero, Y. García-Huante, A. Romero, M. Sánchez, D. Rocha, B. Sánchez, M. Ávalos, S. Guzmán-Trampe, R. Rodríguez-Sanoja, E. Langley, B. Ruiz, Carbon source regulation of antibiotic production, The Journal Of Antibiotics, 63 (2010) 442.
[135] J. Kennedy, Mutasynthesis, chemobiosynthesis, and back to semi-synthesis: combining synthetic chemistry and biosynthetic engineering for diversifying natural products, Nat. Prod. Rep., 25 (2008) 25-34.
[136] J. Bérdy, Thoughts and facts about antibiotics: Where we are now and where we are heading, The Journal Of Antibiotics, 65 (2012) 385.
[137] S.Z. Li, X.Y. Li, Z.F. Cui, D.Z. Wang, Application of ultrafiltration to improve the extraction of antibiotics, Sep. Purif. Technol., 34 (2004) 115-123.
[138] L. Tessier, P. Bouchard, M. Rahni, Separation and purification of benzylpenicillin produced by fermentation using coupled ultrafiltration and nanofiltration technologies, J. Biotechnol., 116 (2005) 79-89.
[139] A.M.B. Alves, A. Morão, J.P. Cardoso, Isolation of antibiotics from industrial fermentation broths using membrane technology, Desalination, 148 (2002) 181-186.
[140] Y. He, G. Chen, Z. Ji, S. Li, Combined UF–NF membrane system for filtering erythromycin fermentation broth and concentrating the filtrate to improve the downstream efficiency, Sep. Purif. Technol., 66 (2009) 390-396.
[141] H.P. Erickson, Size and shape of protein molecules at the nanometer level determined by sedimentation, gel filtration, and electron microscopy, Biol. Proced. Online, 11 (2009) 32.
[142] P. Pal, R. Kumar, S. Banerjee, Manufacture of gluconic acid: A review towards process intensification for green production, Chemical Engineering and Processing: Process Intensification, 104 (2016) 160-171.
[143] P.O. Saboe, C.E. Lubner, N.S. McCool, N.M. Vargas-Barbosa, H. Yan, S. Chan, B. Ferlez, G.C. Bazan, J.H. Golbeck, M. Kumar, Two-Dimensional Protein Crystals for Solar Energy Conversion, Adv. Mater., 26 (2014) 7064-7069.
[144] M.C. Duke, A. Lim, S.C.d. Luz, L. Nielsen, Lactic acid enrichment with inorganic nanofiltration and molecular sieving membranes by pervaporation, Food Bioprod. Process., 86 (2008) 290-295.
[145] U.S.F.a.D.A.F. International Food Information Council (IFIC), Overview of Food Ingredients, Additives & Colors, (2010).
[146] B. Xiong, T.L. Richard, M. Kumar, Integrated acidogenic digestion and carboxylic acid separation by nanofiltration membranes for the lignocellulosic carboxylate platform, J. Membr. Sci., 489 (2015) 275-283.
[147] M.T. Agler, B.A. Wrenn, S.H. Zinder, L.T. Angenent, Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform, Trends Biotechnol., 29 (2011) 70-78.
[148] E. Połom, D. Szaniawska, Rejection of lactic acid solutions by dynamically formed nanofiltration membranes using a statistical design method, Desalination, 198 (2006) 208-214.
[149] A. Bouchoux, H.R.-d. Balmann, F. Lutin, Nanofiltration of glucose and sodium lactate solutions: Variations of retention between single- and mixed-solute solutions, J. Membr. Sci., 258 (2005) 123-132.
[150] P. Pal, J. Sikder, S. Roy, L. Giorno, Process intensification in lactic acid production: A review of membrane based processes, Chemical Engineering and Processing: Process Intensification, 48 (2009) 1549-1559.
[151] P. Saboe, M. Kumar, Adv. Mater., (2014).
[152] K. Nath, H.K. Dave, T.M. Patel, Revisiting the recent applications of nanofiltration in food processing industries: Progress and prognosis, Trends Food Sci. Technol., 73 (2018) 12-24.
[153] B. Vyas, P. Ray, Preparation of nanofiltration membranes and relating surface chemistry with potential and topography: Application in separation and desalting of amino acids, Desalination, 362 (2015) 104-116.
[154] D. Pleissner, R. Schneider, J. Venus, T. Koch, Separation of lactic acid and recovery of salt-ions from fermentation broth, J. Chem. Technol. Biotechnol., 92 (2017) 504-511.
[155] C. Rodrigues, L. Vandenberghe, A. Woiciechowski, J. de Oliveira, L. Letti, C. Soccol, Production and application of lactic Acid, in: Current Developments in Biotechnology and Bioengineering, Elsevier, 2017, pp. 543-556.
[156] C. Umpuch, S. Galier, S. Kanchanatawee, H. Roux-de Balmann, Nanofiltration as a purification step in production process of organic acids: Selectivity improvement by addition of an inorganic salt, Process Biochem., 45 (2010) 1763-1768.

[157] R.W. Baker, Future directions of membrane gas separation technology, Ind. Eng. Chem. Res., 41 (2002) 1393-1411.
[158] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, Ind. Eng. Chem. Res., 47 (2008) 2109-2121.
[159] M. Rao, S. Sircar, Performance and pore characterization of nanoporous carbon membranes for gas separation, Journal of Membrane Science, 110 (1996) 109-118.
[160] H. Jin, F. Jiao, M.D. Daily, Y. Chen, F. Yan, Y.-H. Ding, X. Zhang, E.J. Robertson, M.D. Baer, C.-L. Chen, Highly stable and self-repairing membrane-mimetic 2D nanomaterials assembled from lipid-like peptoids, Nat. Commun., 7 (2016) 1-8.
[161] S. Aguado, G.r. Bergeret, C. Daniel, D. Farrusseng, Absolute molecular sieve separation of ethylene/ethane mixtures with silver zeolite A, Journal of the American Chemical Society, 134 (2012) 14635-14637.
[162] H.H. Funke, A.M. Argo, J.L. Falconer, R.D. Noble, Separations of cyclic, branched, and linear hydrocarbon mixtures through silicalite membranes, Ind. Eng. Chem. Res., 36 (1997) 137-143.
[163] T. Matsufuji, N. Nishiyama, M. Matsukata, K. Ueyama, Separation of butane and xylene isomers with MFI-type zeolitic membrane synthesized by a vapor-phase transport method, J. Membr. Sci., 178 (2000) 25-34.
[164] S. Matson, W. Ward, S. Kimura, W. Browall, Membrane oxygen enrichment: II. Economic assessment, J. Membr. Sci., 29 (1986) 79-96.
[165] H. Bux, C. Chmelik, R. Krishna, J. Caro, Ethene/ethane separation by the MOF membrane ZIF-8: molecular correlation of permeation, adsorption, diffusion, J. Membr. Sci., 369 (2011) 284-289.
[166] M. Rungta, C. Zhang, W.J. Koros, L. Xu, Membrane-based ethylene/ethane separation: The upper bound and beyond, AIChE Journal, 59 (2013) 3475-3489.
[167] T.C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: an opportunity for membranes, J. Membr. Sci., 359 (2010) 126-139.
[168] H. Lin, E. Van Wagner, B.D. Freeman, L.G. Toy, R.P. Gupta, Plasticization-enhanced hydrogen purification using polymeric membranes, Science, 311 (2006) 639-642.
[169] D.R. Pesiri, B. Jorgensen, R.C. Dye, Thermal optimization of polybenzimidazole meniscus membranes for the separation of hydrogen, methane, and carbon dioxide, J. Membr. Sci., 218 (2003) 11-18.
[170] K.A. Berchtold, R.P. Singh, J.S. Young, K.W. Dudeck, Polybenzimidazole composite membranes for high temperature synthesis gas separations, J. Membr. Sci., 415 (2012) 265-270.
[171] Z. Vroon, K. Keizer, M. Gilde, H. Verweij, A. Burggraaf, Transport properties of alkanes through ceramic thin zeolite MFI membranes, J. Membr. Sci., 113 (1996) 293-300.
[172] K.A. Lokhandwala, I. Pinnau, Z. He, K.D. Amo, A.R. DaCosta, J.G. Wijmans, R.W. Baker, Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deployment, J. Membr. Sci., 346 (2010) 270-279.
[173] L. Peeva, J. Arbour, A. Livingston, On the potential of organic solvent nanofiltration in continuous heck coupling reactions, Organic Process Research & Development, 17 (2013) 967-975.
[174] P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A.G. Livingston, Molecular separation with organic solvent nanofiltration: a critical review, Chem. Rev., 114 (2014) 10735-10806.
[175] M. Priske, M. Lazar, C. Schnitzer, G. Baumgarten, Recent applications of organic solvent nanofiltration, Chem. Ing. Tech., 88 (2016) 39-49.
[176] T. Huang, T. Puspasari, S.P. Nunes, K.V. Peinemann, Ultrathin 2D-layered cyclodextrin membranes for high-performance organic solvent nanofiltration, Adv. Funct. Mater., 30 (2020) 1906797.
[177] Z. Wang, S. Guo, B. Zhang, J. Fang, L. Zhu, Interfacially crosslinked β-cyclodextrin polymer composite porous membranes for fast removal of organic micropollutants from water by flow-through adsorption, J. Hazard. Mater., 384 (2020) 121187.
[178] L. Firman, N.A. Ochoa, J. Marchese, C. Pagliero, Simultaneous improvement in solvent permeability and deacidification of soybean oil by nanofiltration, J. Food Sci. Technol., 54 (2017) 398-407.
[179] J.J. Torres, J.T. Arana, N.A. Ochoa, J. Marchese, C. Pagliero, Biodiesel purification using polymeric nanofiltration composite membranes highly resistant to harsh conditions, Chemical Engineering & Technology, 41 (2018) 253-260.

[180] G.M. Shi, M.H.D.A. Farahani, J.Y. Liu, T.-S. Chung, Separation of vegetable oil compounds and solvent recovery using commercial organic solvent nanofiltration membranes, J. Membr. Sci., (2019) 117202.
[181] S. Ganju, P.R. Gogate, A review on approaches for efficient recovery of whey proteins from dairy industry effluents, J. Food Eng., 215 (2017) 84-96.
[182] M. Cheryan, Membrane technology in the vegetable oil industry, Membrane Technology, 2005 (2005) 5-7.
[183] M.A. Mehaia, M. Cheryan, Lactic acid from acid whey permeate in a membrane recycle bioreactor, Enzyme and microbial technology, 8 (1986) 289-292.
[184] M. Cheryan, J.R. Alvarez, Food and beverage industry applications, in: Membrane Science and Technology, Elsevier, 1995, pp. 415-465.
[185] G. Rice, S. Kentish, V. Vivekanand, A. O'Connor, G. Stevens, A. Barber, Membrane-Based Dairy Separation: A Comparison of Nanofiltration and Electrodialysis, Developments in Chemical Engineering and Mineral Processing, 13 (2005) 43-54.
[186] K. Werth, P. Kaupenjohann, M. Knierbein, M. Skiborowski, Solvent recovery and deacidification by organic solvent nanofiltration: Experimental investigation and mass transfer modeling, J. Membr. Sci., 528 (2017) 369-380.
[187] A. Chollangi, M.M. Hossain, Separation of proteins and lactose from dairy wastewater, Chemical Engineering and Processing: Process Intensification, 46 (2007) 398-404.
[188] S.L. Bartelt-Hunt, D.R. Knappe, M.A. Barlaz, A review of chemical warfare agent simulants for the study of environmental behavior, Crit. Rev. Environ. Sci. Technol., 38 (2008) 112-136.
[189] K. Ganesan, S. Raza, R. Vijayaraghavan, Chemical warfare agents, Journal of pharmacy and bioallied sciences, 2 (2010) 166.
[190] A.R. Tehrani-Bagha, Waterproof breathable layers–a review, Advances in colloid and interface science, 268 (2019) 114-135.
[191] V. Dubey, S. Maiti, N. Rao, A. Gupta, Study of permeation of bis (2-chloroethyl) sulfide through elastomer membranes, Polymer—Plastics Technology and Engineering, 36 (1997) 445-460.
[192] R. Ramaseshan, S. Sundarrajan, Y. Liu, R. Barhate, N.L. Lala, S. Ramakrishna, Functionalized polymer nanofibre membranes for protection from chemical warfare stimulants, Nanotechnology, 17 (2006) 2947.
[193] M. Rother, J. Barmettler, A. Reichmuth, J.V. Araujo, C. Rytka, O. Glaied, U. Pieles, N. Bruns, Self-sealing and puncture resistant breathable membranes for water-evaporation applications, Adv. Mater., 27 (2015) 6620-6624.
[194] A. Phadatare, B. Kandasubramanian, Metal Organic Framework Functionalized Fabrics for Detoxification of Chemical Warfare Agents, Ind. Eng. Chem. Res., 59 (2019) 569-586.
[195] G.W. Peterson, A.X. Lu, M.G. Hall, M.A. Browe, T. Tovar, T.H. Epps III, MOFwich: Sandwiched Metal–Organic Framework-Containing Mixed Matrix Composites for Chemical Warfare Agent Removal, ACS applied materials & interfaces, 10 (2018) 6820-6824.
[196] B. Picard, I. Chataigner, J. Maddaluno, J. Legros, Introduction to chemical warfare agents, relevant simulants and modern neutralisation methods, Org. Biomol. Chem., 17 (2019) 6528-6537.
[197] Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, Rapid water permeation through carbon nanomembranes with sub-nanometer channels, ACS nano, 12 (2018) 4695-4701.
[198] C. Peng, Z. Iqbal, K.K. Sirkar, G.W. Peterson, Graphene Oxide-Based Membrane as a Protective Barrier against Toxic Vapors and Gases, ACS Applied Materials & Interfaces, 12 (2020) 11094-11103.
[199] Y. Li, C. Chen, E.R. Meshot, S.F. Buchsbaum, M. Herbert, R. Zhu, O. Kulikov, B. McDonald, N.T. Bui, M.L. Jue, Autonomously Responsive Membranes for Chemical Warfare Protection, Adv. Funct. Mater., (2020) 2000258.
[200] V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, Geoscience Frontiers, 10 (2019) 1285-1303.
[201] N. Swain, S. Mishra, A review on the recovery and separation of rare earths and transition metals from secondary resources, Journal of cleaner production, 220 (2019) 884-898.
[202] M.R. Landsman, R. Sujanani, S.H. Brodfuehrer, C.M. Cooper, A.G. Darr, R.J. Davis, K. Kim, S. Kum, L.K. Nalley, S.M. Nomaan, Water Treatment: Are Membranes the Panacea?, Annual Review of Chemical and Biomolecular Engineering, 11 (2020) 559-585.

[203] H. Zhang, J. Hou, Y. Hu, P. Wang, R. Ou, L. Jiang, J.Z. Liu, B.D. Freeman, A.J. Hill, H. Wang, Ultrafast selective transport of alkali metal ions in metal organic frameworks with subnanometer pores, Sci. Adv., 4 (2018) eaaq0066.
[204] D. Nair, J.T. Scarpello, I.F. Vankelecom, L.M.F. Dos Santos, L.S. White, R.J. Kloetzing, T. Welton, A.G. Livingston, Increased catalytic productivity for nanofiltration-coupled Heck reactions using highly stable catalyst systems, Green Chem., 4 (2002) 319-324.
[205] D. Wu, J. Zhang, Y. Wang, J. Jiang, Z. Jin, Aqueous/organic biphasic hydroformylation of 1-octene catalyzed by Co2 (CO) 8/Ph2P (CH2CH2O) nMe, Appl. Organomet. Chem., 26 (2012) 718-721.
[206] Y.H. Cho, H.D. Lee, H.B. Park, Integrated membrane processes for separation and purification of organic acid from a biomass fermentation process, Ind. Eng. Chem. Res., 51 (2012) 10207-10219.