

10. Supramolecular Membranes for Liquid Separation

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ABSTRACT

To minimize the cost and energy consumption of liquid separations, there is a widespread research interest in developing new emerging materials, such as supramolecular materials. Supramolecular materials with non-covalent interactions and dynamic bonds show robust and reversible physicochemical properties and have advantages for liquid separations due to their easy synthesis by simply mixing appropriate counterparts, fascinating reversibility of the ensembles, and diverse functionalities. Molecular recognition driven self-assembly plays a key role in the fabrication of supramolecular aggregates and networks through cross-linking and block copolymerization. Block copolymers prohibit degradation or depolymerization of supramolecular structures under various physicochemical and biological conditions. Water-based supramolecular membranes that are sustainable in harsh conditions and effective in contaminants removal have attained many attractions. Polyelectrolytes are the other suitable precursors for the preparation of supramolecular materials. Self-healing and stimuli-responsiveness are also discussed as the novel features of these materials with diverse applications, such as membranes and adsorbents. Finally, the main challenges and perspectives in the fabrication of supramolecularmembranes are represented.

10.1. Introduction

Water and energy are two key resources and become increasingly important due to the exponential population growth and the depletion of fossil fuels. Lack of access for clean and safe drinking water is a critical challenge for billions of people, especially in Africa^{1,2}. Moreover, water and energy are linked together, and production of freshwater requires huge energy¹⁻⁵. Membrane technology for water and wastewater treatment has received great attention due to its advantages, such as less use of chemicals, low energy demand, easy scale-up and low operating and maintenance costs⁶. Current membrane-based technologies, e.g., reverse osmosis (RO) and nanofiltration (NF) have lower energy consumption over conventional thermal processes (e.g., multi-effect distillation) due to no phase change of the former. However, researchers are continuing to search for ways to further minimize the energy consumption of water purification by developing advanced membranes with high permeability and selectivity and long durability⁷.

Supramolecular materials are generally formed by assembling of small units via noncovalent interactions, such as Van der Waals forces, hydrogen bonding, host-guest interaction, π - π stacking, and metallic coordination or ionic attractions⁸⁻¹⁰. They show reversible physiochemical properties and stimuli-response, and hence have found many applications, especially in nanotechnology, transport systems, biomedical membranes and separation and purification of high value compounds^{7, 10, 11}. Moreover, robust noncovalent materials with three-dimensionally (3D) ordered nanostructures are potential candidates for separation membranes due to their high adaptivity, reversibility, recyclability and ease fabrication via self-assembly¹².

Block copolymers of definite constructions¹³⁻¹⁸, polyelectrolytes with opposite charges^{19, 20}, and water-based supramolecular materials^{12, 21-23} are examples of mostly used materials for supramolecular membranes in the forms of hollow fiber, porous films or dense coatings^{7, 11}. The pore sizes of the supramolecular membranes are mainly in the range between

ultrafiltration (UF, 2-100 nm)^{15, 16, 21, 24-26} and NF (1-2 nm)^{18, 20, 22, 27-33}. However, researchers have also investigated other nanostructures with designed nanopores and functionalities to expand the applications of supramolecular membranes¹¹.

In this chapter, we first discuss the advantages and disadvantages of supramolecular membranes for liquid separations. Then, supramolecular chemistry in terms of possible supramolecular interactions, such as hydrogen bonding, host-guest interaction, molecular recognition and self-assembly are introduced. Next, the fabrication strategies of different types of supramolecular membranes, including block copolymer membranes, water-based supramolecular membranes, and stimuli-responsive membranes are discussed. Their diverse applications, such as UF, NF, RO and forward osmosis (FO) are also reviewed. Finally, conclusions and perspectives on supramolecular membranes are presented.

10.2. Advantages and Disadvantages of Supramolecular Membranes

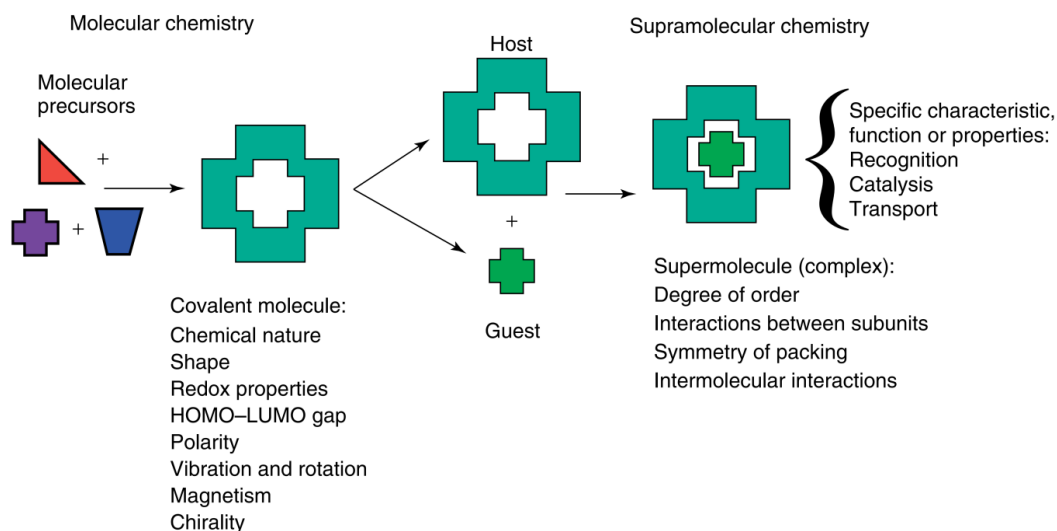
The development of supramolecular and dynamic chemistry for the fabrication of functional devices by noncovalent interactions and dynamic bonds provides some advantages. First, the target molecules can be easily prepared by simply mixing appropriate counterparts, such as hydrogen bond donors with acceptors. In addition, the reversibility of the ensembles provides a unique advantage in developing stimuli responsive functional materials³⁴. Block copolymers are important precursors for the synthesis of supramolecular membranes due to their advantages, such as versatile morphologies, narrower pore size distributions and high porosity, and being available with narrow molecular weight distribution in large amounts and at reasonable costs³⁵.

The main challenge in the preparation of supramolecular membranes is the lack of efficient fabrication methods²¹. Another challenge is the design and synthesis of high-performance membranes³⁶. Large-scale and economical production of supramolecular membranes is also challenging due to the high cost of the starting materials. Other challenges in supramolecular

membranes include the difficulty in tuning the membrane pore size²⁷, relatively high material costs, low processability of the system and low membrane stabilities¹⁴.

10.3. Supramolecular Chemistry

Supramolecular chemistry is related to “chemistry beyond the molecule”, “the chemistry of the noncovalent bonds”, and even “Lego chemistry”³⁷. Molecules of supramolecular materials interact with each other simply by diverse noncovalent interactions, which are weaker (2-300 kJ·mol⁻¹) than most covalent bonds (150-450 kJ·mol⁻¹). Lehn first defined the host-guest mechanism in which the large host molecule possessing convergent binding sites (*e.g.*, Lewis basic donor atoms, hydrogen-bond donors, *etc.*) act as a central hole, or cavity for the guest which possesses divergent binding sites (*e.g.*, a spherical, Lewis acidic metal cation, or hydrogen bond-accepting halide anion) and may be a monatomic cation, a simple inorganic anion, an ion pair, or a more sophisticated molecule (*e.g.*, a hormone, pheromone, or neurotransmitter) as shown in **Figure 10.1**³⁷. The recent supramolecular chemistry focuses on the interactions between molecules, underpins a wide variety of chemistry and materials science impinging on molecular host-guest chemistry, solid-state host-guest chemistry, crystal engineering and the understanding and control of the molecular solid state (including crystal structure calculation), supramolecular devices, self-assembly and self-organization, soft materials, nanochemistry and nanotechnology, complex matter, and biological chemistry³⁷.



[Figure 10.1. Components of traditional supramolecular “host-guest” chemistry.^{37]}

10.3.1. Supramolecular Interactions

Supramolecular materials are constructed by additive and cooperative noncovalent interactions. These interactions include a wide range of directional/non-directional attractive or repulsive forces as listed briefly in **Table 10.1**³⁸. Directional forces are capable of generating well-designed geometries via spatial control of interacting species, while non-directional interactions can act in relative distances of interacting partners affecting the orientations of molecular species³⁷⁻³⁹.

Table 10.1. Supramolecular interaction types, properties and examples.

Supramolecular interactions	Directionality	Bond energies (kJ·mol ⁻¹)	Examples
Reversible covalent bonds	Directional	150–450	Crosslinking of cysteine with sulfur–sulfur bonds
Ion-ion	Nondirectional	100–350	NaCl
Van der Waals	Nondirectional	<5	Inclusion compounds
π-π interactions	Directional	2–50	Benzene (edge-to-face) DNA (face-to-face)
Cation-π and anion-π interactions	Directional	5–80	+N(CH ₃) ₄ ⁺ (toluene)

Ion-dipole	Slightly directional	50–200	Na ⁺ crown ether complex
Dipole-dipole	Slightly directional	5–50	–C≡N groups
Hydrogen bonds	Directional	4–120	Carboxylic acid dimer
Closed-shell metal-metal	Nondirectional	5–60	Argentophilic (Ag · · · Ag)
Coordination bonds	Directional	100–300	M-pyridine
Halogen bonds	Directional	10–50	Sulfur–iodine complex

Although supramolecular structures are typically held by noncovalent interactions, some changes in the structure of a supramolecular assembly can also be affected by covalent bonds that are easily broken and formed under relatively mild conditions. A well-known example is the crosslinking of cysteine residues caused by the formation of sulfur–sulfur bonds (disulfides) that affect the tertiary structure of proteins⁴⁰.

Ion-ion and Van der Waals interactions have high strength and nondirectional nature. Molecules considered “soft” exhibit the most pronounced Van der Waals interactions, which are particularly important in a condensed phase (*e.g.*, solid state) where solvent effects are eliminated³⁹. However, introduction of formal positive and negative charges into molecular species (*e.g.*, macrocycle) can lead to the formation of directional effects in supramolecular associations (*e.g.*, host-guest systems)^{41, 42}. π - π interactions also play a role in determining the assembly of biological molecules, with the sequence-dependent structure of DNA being a prominent example⁴³. Benzene, a major component of the organic chemistry, has been found in at least three possible structures for the benzene dimer, namely, offset parallel, T-shaped edge-to-face, and tilted-T structure⁴⁴. Interactions between a cation or anion to π -electrons result in the formation of cation- π and anion- π interactions, such as the strong binding of alkali-metal cations (*e.g.*, Na⁺) to simple aromatics⁴⁵. These interactions are supposed to have electrostatic nature and contain a component of polarization. Sometimes, electrostatic

interaction between an ion and a neutral molecule forms ion-dipole and dipole-dipole interactions with a dipole or two molecules with dipoles, respectively, from intermediate to weak strength. The solvation of metal cations (*e.g.*, hydration) is caused by ion-dipole interactions, while interactions between highly polar molecules (*e.g.*, nitriles) are caused by dipole-dipole interactions⁴⁶.

The hydrogen bond is the most important anisotropic interaction which exhibits a relatively strong and highly directional nature⁴⁷. The strength of hydrogen bonds varies from “weak” or “nonconventional” ($2\text{--}20\text{ kJ}\cdot\text{mol}^{-1}$) for weak electronegative atoms (A and B) like $\text{C}\text{--}\text{H}\cdots\text{O}$, to a “strong” bond ($20\text{--}40\text{ kJ}\cdot\text{mol}^{-1}$), *e.g.*, $\text{N}\text{--}\text{H}\cdots\text{O}$ bond³⁹. Interaction between closed-shell metal cations, coordination bonds with intermediate strength and reversible dynamic nature³⁸, halogen bonds⁴⁸ and hydrophobic effects^{37, 49} are other reversible interactions that play important roles in the creation of supramolecular materials.

10.3.2. Host-guest Chemistry and Molecular Recognition

In host-guest chemistry, a clathrate compound holds two or more components together without any ordinary chemical union but through complete enclosure of one set of molecules in a suitable structure formed by another⁵⁰. The host is a large entity with convergent binding sites (*e.g.*, Lewis basic donor atom, and hydrogen bond donors), and the guest (*e.g.*, a simple inorganic anion, monoatomic cation, or a biomolecule) possesses divergent sites (*e.g.*, spherical and Lewis acidic metal cation)⁵¹. The hosts can be classified into intramolecular cavities (*e.g.*, cavitands) and extramolecular cavities (*e.g.*, clathrands) based on topological relationships between hosts and guests. Host-guest compounds can be classified depending upon supramolecular interactions between host and guest as being in a complex^{37, 49}.

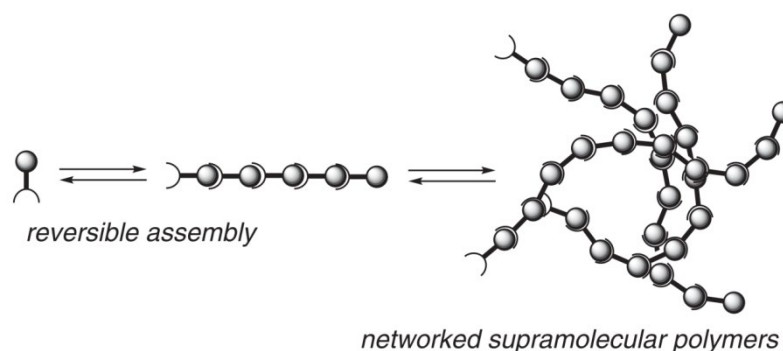
Molecular recognition is complementary to host-guest chemistry and supramolecular synthesis, and it is the way that molecules select and bind each other in a structurally well-defined pattern⁵². The two molecules associate each other when functional groups of one

molecule complement the other, leading to the share of noncovalent information such as the lock-and-key mechanism⁵³. Supramolecular chemistry is highly concentrated on the lock-and-key chemistry.

10.3.3. Molecular Recognition-directed Self-assembly

Self-sorting of small supramolecular building blocks during the self-assembly process can create large, complex structures without any elaborate synthetic procedures and is commonly observed in different elements of the origin of life⁵⁴. Diverse noncovalent interactions varying in type and strength, ranging from very weak dipole-dipole interactions to very strong metal-ligand or ion-ion interactions with reversible response to external factors, such as temperature, pH, concentration, and the polarity of the medium allow precise control of the self-assembly process. Formation of supramolecular materials is different from conventional synthesis methods that are based on irreversible covalent bonding, because the supramolecular is an equilibrating structure in a balance between enthalpy and entropy and evaluation of the minimum thermodynamic state is required⁵⁵.

Molecular recognition and self-assembly play significant roles informing supramolecular aggregates and networks in solution and in the solid state, respectively³⁸. Supramolecular crosslinking and supramolecular block copolymerization are two methods to prepare supramolecular materials⁵⁶. As shown in **Figure10.2**, supramolecular polymerization initiates with molecular associations between the monomers bearing complementary binding sites form oligomers in a thermodynamically reversible process, and average dynamic properties can be estimated based on the association constant of each connection site⁵⁶. Then, the formed oligomers associate with each other to form entangled polymers with 3D networked structures. Of particular note, the prepared supramolecular polymers can exhibit similar physical properties to conventional polymers if interchain interactions between supramolecular polymeric chains are dominant.



[Figure 10.2. Scheme of reversible associations between monomers to form supramolecular polymers.^{56]}

10.4. Fabrication of Supramolecular Membranes

10.4.1. Block Copolymer Based Supramolecular Membranes

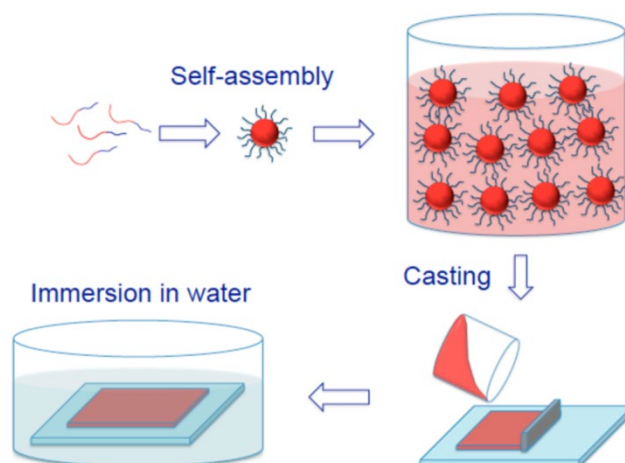
Supramolecular block copolymers containing two or more chemically distinct polymeric blocks have recently emerged as a promising candidate for a variety of applications, such as membrane separation, template formation and lithography techniques^{6, 25, 57-64} due to their advantages of both supramolecular polymers and block copolymers⁶⁵. Their features prevent them from degradation or depolymerization of main-chain polymers under variable physicochemical and biological conditions, while exhibiting the special features of supramolecular structures through interchain non-covalent interactions⁶¹⁻⁶⁴. Furthermore, supramolecular block copolymers can self-assemble into flexible hierarchical nanostructures at all scales and dimensions in solution⁶⁴.

Block copolymers can be synthesized precisely via highly controlled living polymerization techniques, including ionic polymerization (cationic⁶⁶, anionic⁶⁷, group transfer⁶⁸), atom-transfer radical polymerization⁶⁹, reversible deactivation radical polymerization⁷⁰, nitroxide-mediated polymerization⁷¹, chain growth polycondensation⁷², metal-catalyzed olefin metathesis⁷³, and

ring-opening metathesis polymerization⁷⁴. And then, supramolecular copolymers can be formed by proper interactions, such as metal-ligand coordination and/or hydrogen bonding⁷⁵.

The prepared block copolymers can be used to fabricate membranes. For instances, Vriezokolk *et al.* synthesized a nanostructured supramolecular material by self-assembly of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) copolymers and poly(acrylic acid) (PAA) homopolymer, and then coated the synthesized supramolecular material on top of a substrate²⁴. The blocks could self-assemble into cylinders, while PAA was located in the core of the cylinders. Nanopores were then created after selectively removing PAA component. A drawback of this method is scale up of spin-coating, which could be replaced by dip-coating if the solvent evaporation rate could be controlled appropriately. Another problem is intrusion of the supramolecular solution into the porous support layer, leading to pore-blockage and decreased permeability.

Historically, block copolymers have been used to fabricate the support layers of UF or RO membranes⁷⁶. As depicted in **Figure 10.3**, a combined process, first self-assembly and then nonsolvent-induced phase separation (NIPS), is considered as the most promising technology for scalable production of block polymer based membranes³⁵. Amphiphilic block copolymers have received more attention because the chemically incompatible, but covalently linked hydrophobic and hydrophilic segments can drive the organization of the macromolecules into supramolecular structures⁷⁷.



[**Figure 10.3.** Schematic of block copolymer self-assembly and nonsolvent-induced phase separation procedures (SNIPS process).^{35]}

10.4.2. Water-based Supramolecular Membranes

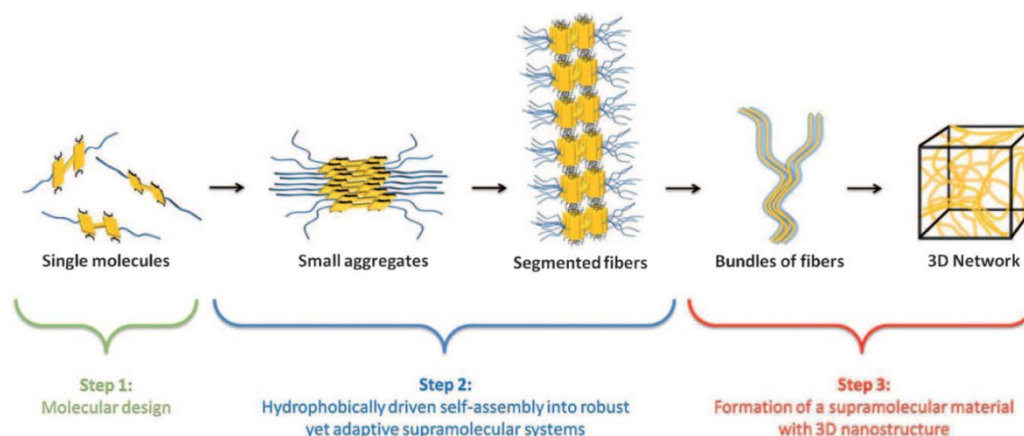
A variety of supramolecular systems like self-complementary molecular structural units⁷⁸, supramolecular polymers of self-assembled calixarenes⁷⁹, robust self-assembled dimmers⁸⁰ and oligomers⁸¹ have been prepared by noncovalent hydrogen-bond interactions due to their specific features such as adaptivity¹⁰, ease of fabrication, recyclability, multifunctionality, stimuli-responsiveness, and self-healingness^{8, 82-86}. The novel organization in nanoscale gives them advanced functions that cannot be achieved in conventional systems⁸⁷. However, these robust yet adaptive materials are not applicable in polar solvents, like water due to the low stability, poor robustness and relative weakness of noncovalent interactions⁸⁸. Furthermore, supramolecular materials are usually prepared in non-polar solvents without moisture, and have low mechanical stability due to weak external physical forces holding them together⁸⁹.

Water as a green solvent has attracted special attention in supramolecular chemistry^{6, 21, 88, 89}. In nature, many chemical synthesis and reaction processes are performed in aqueous environment. Hence, application of water as a solvent has received interest recently^{6, 21, 88, 89} because water is cheap, safe and universally available solvent used in biocompatible materials, such as artificial tissues⁹⁰. Moreover, strong solvophobic (*i.e.*, hydrophobic) effects

of water makes it easy to create highly robust noncovalent materials, such as protein folding resulted aggregates, substrate adhesion, and membrane constitution as the aggregation of hydrophobic moieties can decrease energy at water/hydrophobic interface⁹¹.

The main host–guest interaction mechanism constituted by hydrogen bond donors, such as amide -NH with an acceptor, *e.g.*, a carbonyl C=O can be easily devised for self-assembly of supramolecular materials⁹². The strength of the covalent and noncovalent bonds are in the order of 100–400 and 5–50 kJ·mol⁻¹, respectively³⁷. Thus, creation of water stable systems with strong noncovalent interactions is a challenge as they become energetically almost insignificant in water⁹³. To create a water-based supramolecular system, hydrophobic/electrostatic interactions are required⁹⁴. Capito *et al.* employed self-assembly to prepare membranes by both hydrophobic and electrostatic interactions of peptide amphiphile and polyelectrolyte in aqueous media⁹⁵.

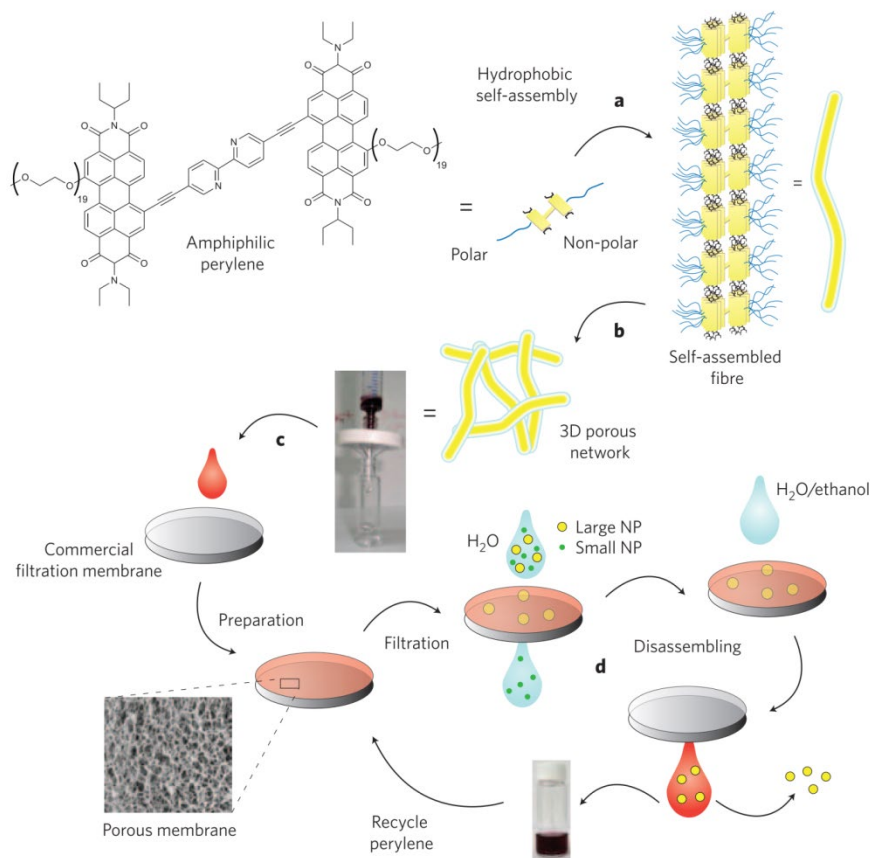
From Kreig's review on supramolecular materials, there are three main steps (see **Figure 10.4**) to prepare such materials, including (1) selection of molecular construction units, (2) self-assembly of constructing units into 1D nanofibers, and (3) gelation of 1D nanofiber structure to afford 3D supramolecular materials¹². They also used amphiphile PP2b to simply prepare water-based nanoporous supramolecular membranes in a single step and achieved efficient separation of gold nanoparticles of 5 nm with a H₂O flux of 110 LMH/bar²¹.



[Figure 10.4.Steps to prepare supramolecular gel-phase materials. Step 1 is to select molecular construction units. Step 2 is to construct self-assembly units into 1D nanofibers.

Step 3 is to produce gel-phase supramolecular materials.^{12]}

Beginn *et al.* prepared porous membranes using poly[2-ethyl-hexyl methacrylate-co-2-diethylaminoethyl methacrylate-cross-1,4-butane diol dimethacrylate]. The resultant membranes had cylindrical pores with a diameter of 6–15 nm and displayed an anion/cation selectivity of >100 by gel template leaching⁹⁶. In another study, Lu *et al.* cast the methanol solution of supramolecular nanoarrays on the polyethersulfone (PES), and the prepared NF membrane exhibited high rejection rates towards organic contaminant dyes and As(III) without compromising water flux²⁸. Rybtchinski *et al.* successfully synthesized amphiphilic perylene-graft-poly(ethylene oxide) building blocks. These supramolecules self-assembled into fibers in aqueous solution, which were subsequently used to fabricate 3D networks and/or free-standing membranes. The resultant recyclable membranes were evaluated in pressure-driven separation applications, such as separations of gold metal nanoparticles, heavy metals, drugs and organic molecules from the aqueous medium (see **Figure 10.5**)^{21, 22, 89}.

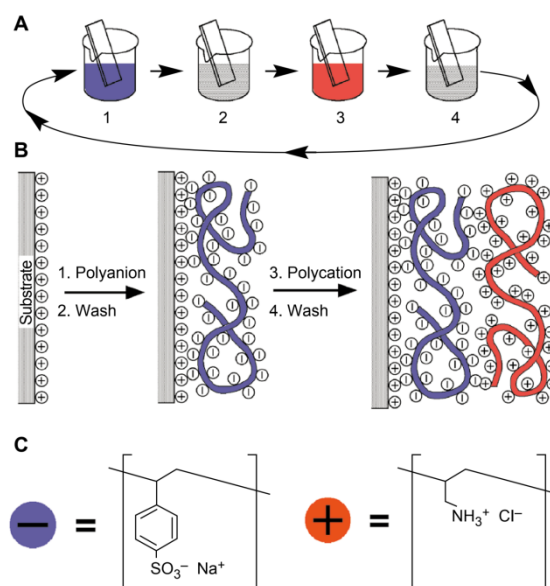


[Figure 10.5. Procedures of supramolecular recycle membranes preparation and uses in pressure-driven separation process. (a) Hydrophobic self-assembly of amphiphilic perylene into fibers. (b) Self-assembled fibers into 3D porous networks. (c) Porous membranes formed from the deposition of supramolecular networks into commercial filtration membrane. (d) Size-selective filtration process of porous membranes.^{89]}

10.4.3. Polyelectrolyte-based membranes

Polyelectrolytes are polymer chains with weak/strong cationic/anionic charges along their backbone. Poly(methacrylic acid) (PMAA) is an example of a weak polyelectrolyte with pH-dependent dissociation and charging, whereas poly(styrene sulfonate) (PSS) is a strong polyelectrolyte⁹⁷. Self-assembled polyelectrolyte membranes are prepared via electrostatic interactions between oppositely charged groups, and can represent the features of the polyelectrolyte materials such as the aggregation, pH dependency in solution and strong salt

properties^{6, 98}. A widely applied synthetic approach for polyelectrolyte membranes is the repeat layer-by-layer (LBL) deposition of polycations and polyanions on a beaker as shown in **Figure 10.6**⁹⁹.



[Figure 10.6. Schematic of layer-by-layer deposition to form polyelectrolyte membranes. (A) Film deposition process using polycations and polyanions. (B) Simplified adsorption steps of molecules. (C) Chemical structures of poly(styrene sulfonate) and poly(allylamine hydrochloride).^{99]}

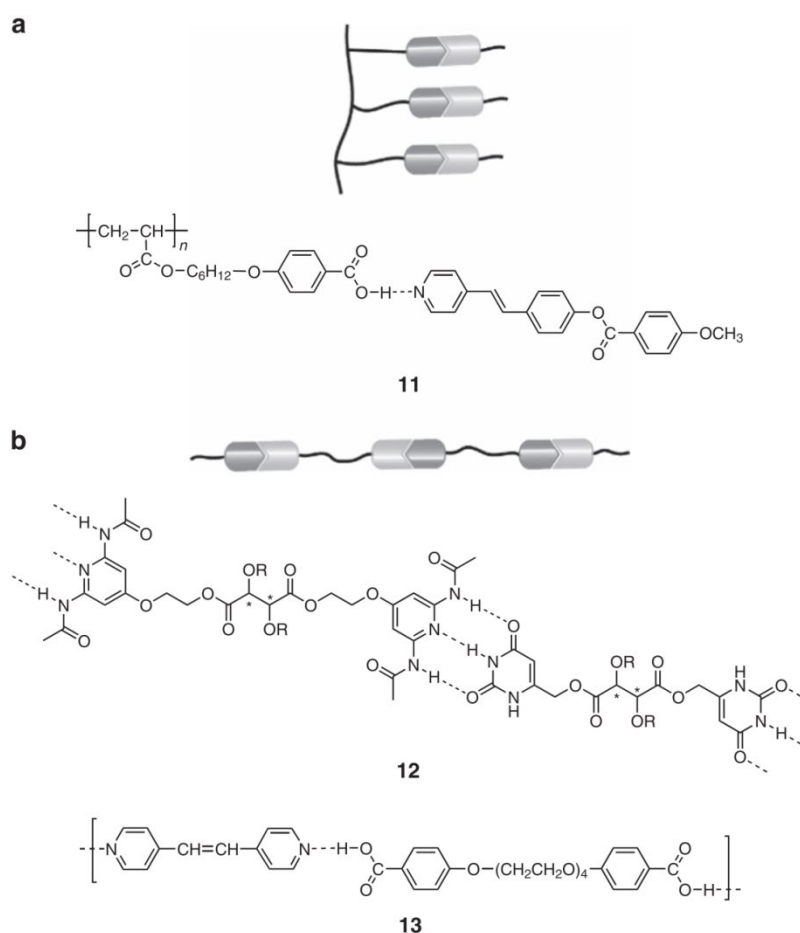
LBL assembly can be done through a variety of chemical interactions, including electrostatic interactions, coordination chemistry^{100, 101}, chemical crosslinking¹⁰², hydrophobic interactions¹⁰³, hydrogen bonding^{13, 103}, and metal-ligand interaction^{104, 105}. Metal-ligand interactions can be used in LBL assembly, or metallo-supramolecular polyelectrolyte polymers can be induced¹⁰⁶⁻¹⁰⁸. The latter case leads to the preparation of charged metallo-supramolecular polymers by difunctional coordination with metal ions¹⁰⁹.

Free-standing polyelectrolytes which are usually prepared by dissolving the substrates or scarifying layers between film and substrate are reportedly prone to damage, therefore a porous substrate such as polyethylene terephthalate, porous alumina, polystyrene, polycarbonate, hydrolyzed polyacrylonitrile, cellulose acetate, PES and polyamide with high

flux and good mechanical stability is preferred in the preparation of composite polyelectrolyte membranes^{11, 110}.

10.4.4. Liquid Crystal-based Membranes

Liquid-crystalline (LC) polymers have a wide range of applications in energy and environment fields, and have been successfully used in membranes¹¹¹. The concept of supramolecular chemistry is used to prepare hydrogen-bonded LC polymers with the LC moieties along backbone (main-chain), side-chain or within network^{17, 111-116}. The side-chain LC polymers were prepared by complexation of the pendant benzoic acid moieties with stilbazoles (see **Figure 10.7a**)¹¹¹ and then others reported preparation of polysiloxane-based^{117, 118} and polyacrylate-based^{16, 119} side-chain LC polymers. Main-chain supramolecular LC polymers can be prepared by creation of hydrogen bonds between two complementary bi-functional components (see **Figure 10.7b**)¹¹¹.



[Figure 10.7.Schematic representation of molecular structures. (a) Supramolecular side-chain LC polymers. (b) Supramolecular main-chain LC polymers.^{111]}

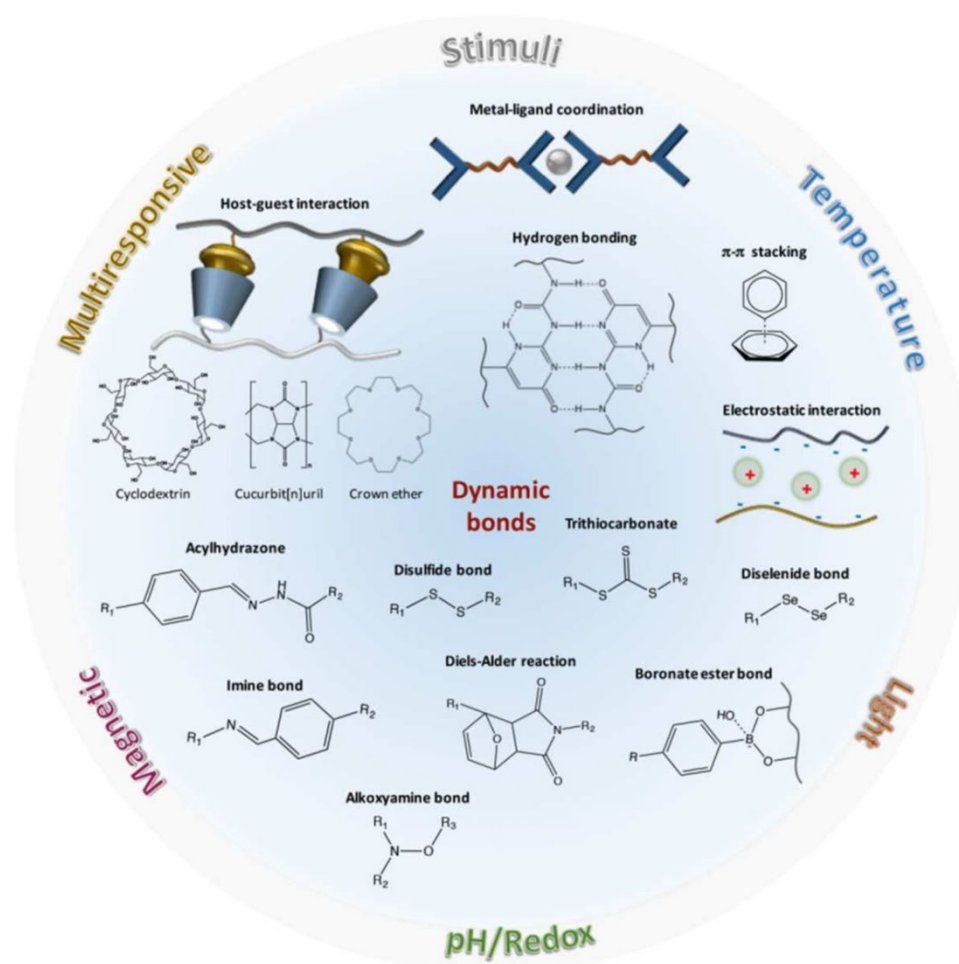
LC polymeric materials are an important category of high flux membrane materials²⁷⁻³⁰. The LC networks with diverse morphologies like lamellar, columnar, and bicontinuous arrays have been reported (see **Figure 10.7**)¹¹¹. It is observed that polymeric chains can align themselves in a direction parallel to molecular displacement to utilize the positioning of nanotubes in direction similar to the molecular displacement¹¹.

Zhou *et al.* developed in-situ polymerization of lyotropic (*i.e.*, amphiphilic) LC assemblies to prepare size-selective NF membranes with tailored functional pores of 1-2 nm¹²⁰. This process fixes the ionic head-groups at the hydrophilic/hydrophobic interface to produce open, ion-lined, aqueous domains¹²¹. A polymerizable inverted hexagonal (H_{II})¹²² phase and the type-II

bicontinuous cubic phases¹²³ could be inverted to a NF membrane media having well-defined concentric water pores with diameters in the range of 1-5 nm.

10.4.5. Stimuli-responsive Supramolecular Membranes

Commercially available filtration membranes have "static" structures while, some polymers are stimuli responsive¹². Responsive membranes are a class of materials that can change their structures and properties sharply in response to environmental stimuli. In order to prepare stimuli responsive membranes, it is required to provide weaker interactions between host and guest molecules and high affinity to form inclusion compounds¹²⁴. Different factors like temperature, light, magnetic field and etc. have been utilized for creation of responsive structures (see **Figure 10.8**)¹²⁵.



[**Figure 10.8.**Dynamic bonds utilized for stimuli responsive polymers.¹²⁵]

Self-healing is a consequence of preparation of materials with reversible noncovalent connections and can provide many benefits to facilitated remote-control self-healing properties upon crack/failure, restoring the properties of the pristine material, and extending the life-cycle of the products^{125, 126}. These self-healing stimuli-responsive materials can be synthesized by introducing reversible bonds in the form of crosslinked points or bi-functional building blocks¹²⁵. These materials can be easily broken and reformed under relatively mild physicochemical conditions/stimuli followed by microphase separation, gel-sol transition, volume/shape change, or photo-chromic responses¹²⁷.

Stimuli-responsive materials have received attention for preparation of self-healing membranes^{11, 16, 18}. Clodt *et al.* prepared high flux, pH and temperature responsive supramolecular membranes by modifying the surface with pH-responsive polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) and grafting thermal responsive poly (N-isopropyl acrylamide)¹⁶. One specific characteristic of these membranes is their ability to close and open their pores by lowering or increasing the pH, respectively.

In another study, Nunes *et al.* prepared mono-dispersed asymmetric pH-responsive nano-channels/membranes with tailorable order and density¹⁸. The prepared polymeric nano-channels had sub-10 nm diameters and cylindrical pores with 400 nm lengths by self-assembly of metal-block copolymer complexes, followed by NIPS. The main features of the fabricated membranes are their narrow pore size distribution and high porosity, leading to higher selectivity compared with commercial nanofiltration membranes with broader pore size distribution¹⁸.

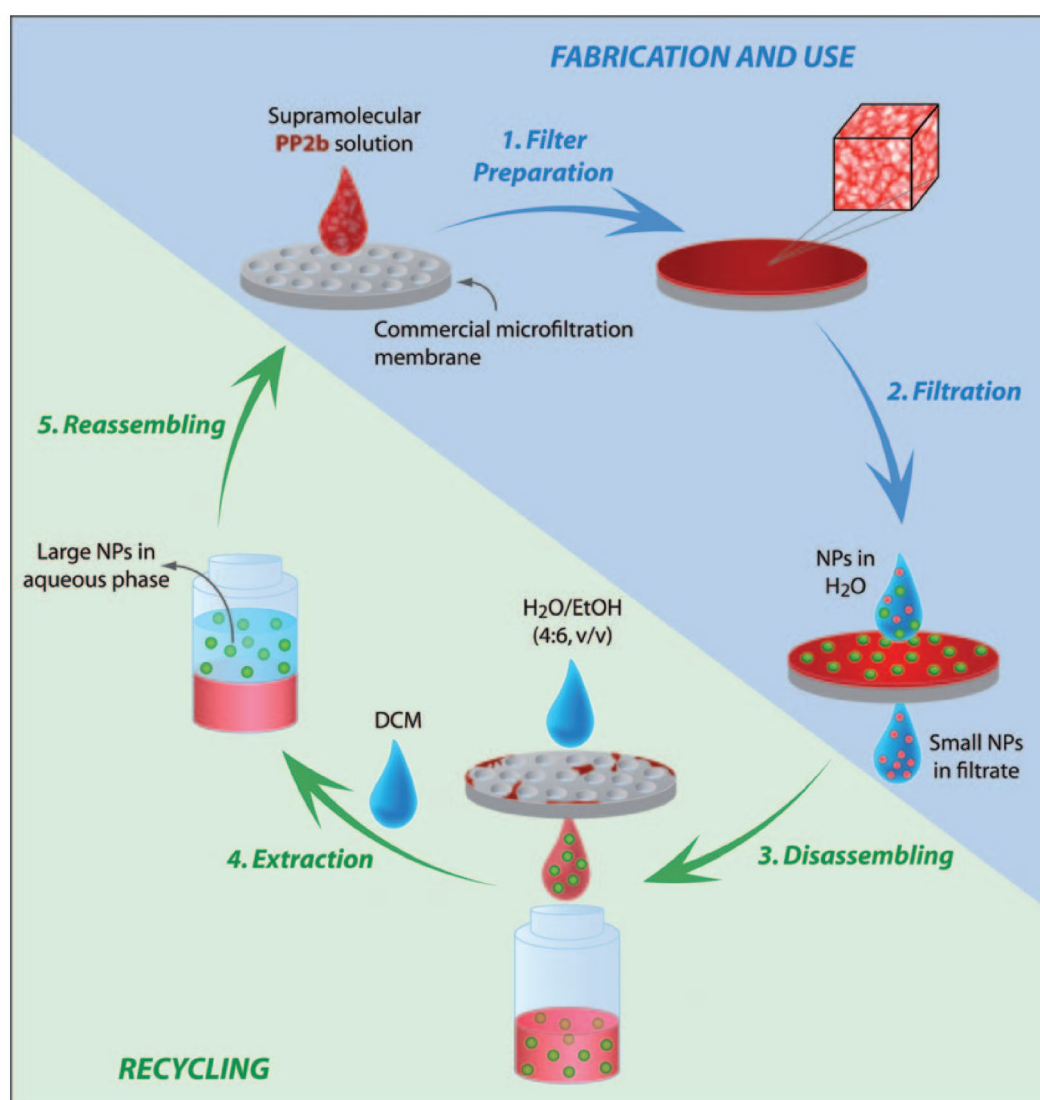
10.5 Liquid Separation Applications

10.5.1 Ultrafiltration

Typically, UF membranes have pore sizes between 2-100 nm²⁶ with applications of removing colloid particles and macromolecules^{128, 129}. Krieg *et al.* synthesized an amphiphilic precursor

and deposited it on a cellulose acetate support via filtration, affording supramolecular UF membranes with a fibrous top layer²¹. The fabricated membranes showed excellent mechanical stability and good separation performance for various nanoparticles (*i.e.*, gold NPs) according to the size difference.

Furthermore, they can easily disassemble the supramolecular membrane by washing with H₂O/EtOH. After extracting with DCM, the recovered materials can be redeposited on the substrate (see **Figure 10.9**)¹². This 'green' process thus opens a new avenue for the development of environmentally friendly UF membranes^{11, 21, 26}.



[Figure 10.9. Schematic illustration of fabrication, use, and recycling of supramolecular membranes.^{12]}

10.5.2. Nanofiltration

Supramolecular membranes have also been prepared for NF. An early work done by Lu *et al.* reported the use of supramolecular structures in NF membranes for efficiently removing organic dye and As(III) from water²⁸. They developed a noncovalent porous membrane that can maintain its integrity and pore size under high transmembrane pressures.

In fact, it is somehow difficult to prepare defect free membranes with a pore size below 5 nm²⁷. The main issue in the shift from UF to NF is the sharp decrease in the membrane flux according to the Hagen–Poiseuille’s equation:

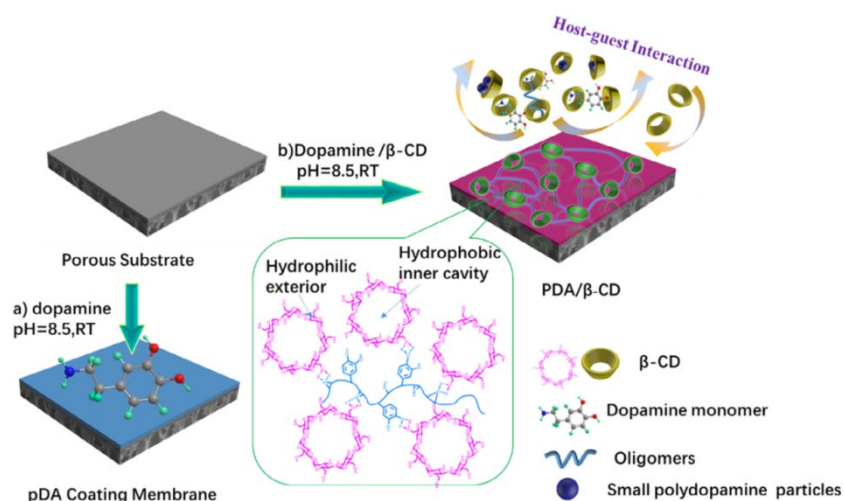
$$\frac{dv}{dt} = (\pi R^4 \Delta p) / (8 \eta L) \quad (9.1)$$

where, Δp , η and L represent the pressure difference, viscosity and membrane thickness respectively. To achieve high water permeability, Yu *et al.* combined self-assembly of AB/AC block copolymer blends with nonsolvent-induced phase separation and successfully fabricated a highly porous membrane with a pore diameter as small as 1.5 nm, achieving H₂O flux ten times higher than the permeance of commercial nanofiltration membranes and quantitative rejection of solutes with molecular weights >600 g·mol⁻¹²⁷.

Another approach to fabricate supramolecular NF membranes is LBL deposition of polyelectrolytes with different charges on a support. Hong *et al.* prepared high-flux PSS/poly(diallyldimethylammonium chloride) NF membranes with high charge density²⁰. The resultant membrane could reject 98% phosphate from a chloride/phosphate mixture with a solution flux of 2.4 m³/m²·day at 4.8 bar.

Supramolecular chemistry is also applied for preparation of organic solvent nanofiltration (OSN) membranes, that is a developing sustainable technology to simultaneously purify organic solvents and recycle nano-scale molecules^{130, 131}. Zhang *et al.* incorporated inherent

nano-cavity biocompatible β -cyclodextrin (β -CD) as powerful molecular hosts and mussel-inspired polydopamine (pDA) as the building blocks, and combined the host-guest interactions and hydrogen-bonds to prepare OSN membranes with honeycomb microstructures via one-step “green” process (see **Figure 10.10**)³³. β -CDs have the inherent cavity (6.0–6.5 Å) and therefore are suitable for creating transporting channels for organic solvent molecules¹³²⁻¹³⁴. The guest monomers/oligomers/pDA nanoparticles were captured by the β -CD/pDA layer, preventing the formation of pDA aggregates and creating nonselective voids during the self-assembly.



[**Figure 10.10.** Schematic illustration of pDA/ β -CD OSN membrane preparation via one step green process.³³]

10.5.3. Reverse Osmosis

RO membranes have been widely used for seawater desalination. They generally have a top selective layer, a microporous polysulfone support layer and a non-woven fabric layer for mechanical stability¹⁹. The top layer with supramolecular structures can be constructed by layer-by-layer depositing ¹³⁵polymer precursors with complementary interactions (e.g., electrostatic, hydrogen bonding or covalent bonding)^{136, 137}. Raval *et al.* prepared thermally-crosslinked PE multilayers as effective desalination RO membranes with an excellent ion rejection rate of 99.8% but a reduced water flux¹³⁸. Electrostatic interactions of poly(acrylic

acid) and poly(allylamine hydrochloride) enabled the preparation of non-covalently attached supramolecular multilayer¹³⁹ and can be further stabilized via crosslinking reaction between the carboxylic acid and amine groups^{140, 141}. Toutianoush *et al.* also reported the preparation of polyvinylamine/polyvinylsulfate-based ultrathin top layer for desalination of aqueous salt solutions and seawater by RO¹⁴², achieving completely rejections to MgCl₂ and MgSO₄ and enhanced rejection rates to NaCl (from 84 to 96% at 5 bar) and Na₂SO₄ (from 93.5 to 98.5% at 40 bar), respectively.

10.5.4. Forward Osmosis

A motivating application for supramolecular materials is recently emerged to wastewater treatment by FO¹⁴³. Currently, FO still faces some critical challenges, such as concentration polarization, membrane fouling, reverse solute diffusion, and lack of cost-effective techniques to recycle the solute. Recently, supramolecular materials have been used as physical crosslinkers to develop graphene oxide-based FO membranes by a pressure-assisted self-assembly method¹⁴⁴. The graphene oxide rejection layer of the FO membrane was intercalated by a supramolecular star polymer consisting of quaternary poly (2-(dimethylamino)ethyl methacrylate) and negatively charged blue lemon polyoxometalate. The prepared 2D FO membranes crosslinked by the supramolecular star polymer showed higher water flux and better fouling resistance than traditional TFC membranes. Li *et al.* ionically bonded water-soluble hollow cup-like macrocyclic molecules, sulfthiacalix[4]arene (STCAss) and sulfocalix[4]arene (SCA) into the polyamide network to engineer molecular-sieving TFN membranes for organic solvent FO¹⁴⁵. Introducing STCAss and SCA into the polyamide network not only increased the free volume, but also reduced the thickness of the TFN layers.

10.5.5. Other Applications

Owing to the outstanding and unrivaled features, the separation applications of supramolecular membranes have gone beyond UF, NF, RO, and FO. For instance, they have also been

employed in antifouling and antibiofouling membranes^{30, 146}, to recover heavy and precious metals from wastewater¹⁴⁷. Other advanced applications include chlorine resistance membranes³¹, self-healing functionalized poly(ether sulfone) membranes for osmotic power generation¹⁴⁸, anion/cation selective membranes¹⁴⁹, and self-assembled polyelectrolyte membranes for pervaporation^{150, 151}.

10.6. Conclusions

Supramolecular membranes with high permeability and selectivity, and/or unique reversible properties have been of great interest for liquid separations. These materials show reversible physiochemical properties and advantages for liquid separation due to their diverse non-covalent interactions and dynamic bonds, such as Van der Waals forces, hydrogen bonding, host-guest interaction, π - π stacking, and metallic coordination or ionic attractions. To sum up, the target supramolecules can be prepared by simply mixing appropriate counterparts, such as hydrogen bond donors with acceptors. Another advantage is the reversibility of the ensembles which provides an unmistakable advantage when preparing stimuli responsive functional materials³⁴. Block copolymers are the most important precursors for the synthesis of supramolecular based membranes due to their advantages like versatile morphology, narrower pore size distribution and high porosity, and being available with narrow molecular weight dispersity and at reasonable cost, where scaling-up is not a problem³⁵.

Molecular recognition driven self-sorting of small supramolecular building blocks can create large, complex structures of supramolecular aggregates and networks in solution and in the solid state, respectively, without any complicated synthetic procedures. Supramolecular crosslinking and supramolecular block copolymerization are two methods to prepare polymeric supramolecular materials. Moreover, self-healing and stimuli-responsiveness in supramolecular membranes owing to their reversible noncovalent connections can assist in the case of crack/failure, restoring the properties of the pristine material because they can be

easily broken and reformed under relatively mild physicochemical conditions/stimuli followed by microphase separation, sol-gel transition, volume/shape change, or photo-chromic responses.

Having the advantages of both supramolecular polymers and block copolymers helps them to prohibit from degradation or depolymerization under variable physicochemical and biological conditions while exhibiting the specific features of supramolecular structures through interchain non-covalent interactions. Because most of the robust and adaptive supramolecular materials are not applicable in polar solvents (e.g., water) due to the low stability, poor robustness and relative weakness of noncovalent interactions, water-based supramolecular membranes sustainable in harsh conditions and effective in purification of water from heavy metals and organic molecules have attained many attractions. Furthermore, polyelectrolytes with weak/strong cationic/anionic along their backbone have been incorporated in the fabrication of defect-free multilayer membranes with tunable properties via LBL assembly.

The main challenge in this field is the lack of fabrication strategies and advanced techniques, which hinder the production of these membrane materials²¹. Another challenge is to find appropriate 2D and polymeric materials for phase-inversion or coating/etching technique to prepare high-performance membranes, although researchers have tried to use porous frameworks, biomimetic and block-copolymers to prepare these nanoporous membranes³⁶. Large scale and economical production of the fabricated membranes are also challenging due to the high-cost starting materials in the production of the low-cost high-performance NF membranes, and this may be solved by innovative and modern techniques, such as 3D printing and molecular electrophoretic gating over membrane surface to control pore size development for high-performance NF membranes¹⁵²⁻¹⁵⁵. Another issue in the production of NF membranes from self-assembled block copolymers is to reduce the pore size to sub 5 nm without any post-treatment²⁷. Liquid crystal-based membranes have also been used in the filtration of large molecules which would be encountered in UF applications. However, the main

challenge is the high cost of starting materials and low processability when compared with conventional UF and NF membranes¹⁴.

To conclude, supramolecular chemistry has received considerable attention in liquid separations, meanwhile there are many open areas for researchers to explore the different aspects of supramolecular materials.

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