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Thin porphyrin composite membranes with enhanced organic solvent transport

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Abstract

Extending the stability of polymeric membranes in organic solvents is important for applications in chemical and pharmaceutical industry. Thin-film composite membranes with enhanced solvent permeance are proposed, using porphyrin as a building block. Hybrid polyamide films are formed by interfacial polymerization of 5,10,15,20-(tetra-4-aminophenyl)porphyrin/m-phenylene diamine (MPD) mixtures with trimesoyl chloride. Porphyrin is a non-planar molecule, containing a heterocyclic tetrapyrrole unit. Its incorporation into a polyamide film leads to higher free volume than that of a standard polyamide film. Polyamide films derived from porphyrin and MPD amines with a fixed total amine concentration of 1 wt% and various porphyrin/MPD ratios were fabricated and characterized. The porphyrin/MPD polyamide film was complexed with Cu(II), due to the binding capacity of porphyrin to metal ions. By coupling scanning transmission electron microscopy (STEM) with electron energy-loss spectroscopy (EELS), Cu mapping was obtained, revealing the distribution of porphyrin in the interfacial polymerized layer. By using porphyrin as amine-functionalized monomer a membrane with thin selective

skin and enhanced solvent transport is obtained, with good dye selectivity in the nanofiltration range. For instance, an ultra-fast hexane permeance, 40-fold increased, was confirmed when using 0.5/0.5 porphyrin/MPD mixtures, instead of only MPD as amine monomer. A rejection of 94.2% Brilliant Blue R (826 g/mol) in methanol was measured.

Keywords

Organic solvent nanofiltration, solvent-resistant membrane, porphyrin, polyamide, thin-film composite membrane

Introduction

Organic solvent nanofiltration (OSN) has rapidly attracted worldwide attention in diverse industrial fields, including petrochemical, fine chemical, food, and pharmaceutical industries, which require an intensive and costly molecular separation and purification in organic solvent processes [1-11]. Distillation, evaporation, chromatography, crystallization and adsorption-desorption technologies are traditionally used for organic solvent separations. However, these technologies are energy intensive and may create additional organic waste streams. Compared to other methods, nanofiltration require simpler equipment, with reduced energy consumption, provides better separation performance and easier solvent recycling. Therefore, the technology is expected to become a greener and cheaper alternative solution for organic solvent separations. Despite having significant advantages, membrane-based processes are still less widespread in the industry than water-based separations. Membranes with better-tuned characteristic and higher stability in different solvents would change this scenario.

Various types of membranes have been investigated including ceramic, polymeric, and mixed-matrix [3]. Polymeric membranes are expected to be the most successful in industrial application, because of their low cost, good processability, and easy scale-up. However, the stability of polymeric membranes in organic solvents is a key issue, which hinders their application in more challenging chemical separations.

The development of robust polymeric membranes with excellent solvent separation performance has been intensively studied aiming at a breakthrough in organic solvent separations. The first organic solvent resistant membrane generation has been integrally skinned asymmetric, prepared by solution casting and phase inversion in water, followed by crosslinking. Membranes based on polyacrylonitrile (PAN) were among the first [12], followed by many reports on polyimides [13]. Polyimide exhibits good chemical and thermal stability and is easy to crosslink [14]. To increase the stability of membranes in organic solvents, different post-treatment methods, for example UV-curing of polysulfone membrane [15], and chemical crosslinking of polyacrylonitrile (PAN) [16], polybenzimidazole (PBI) [17], polyaniline [18], polyamide-imide [19], polyimide [20], polytriazole [21] and copolyazoles [22] have been used. High polymer concentration is required to form a dense selective skin for nanofiltration applications. However, this normally leads to low porosity and therefore low permeance.

Thin-film composite (TFC) membranes have been very successful in applications such as seawater desalination [23] and they have a large potential in the chemical industry as well, if the right chemistry is chosen. TFC membranes are fabricated by a two-step process including the formation of porous support, followed by the deposition of a thin selective layer. By having two separate processes, optimizations of the active layer and ultrafiltration support can be carried out independently with more flexibility to obtain high permeance membranes, without sacrificing selectivity. An important criterion for the development of active layers and porous supports for TFC membranes to be used in chemical processes is their high solvent resistance. Various types of active layers have been previously developed, such as crosslinked coatings of poly(ether block amide) (Pebax[®]) [24] and polyurethanes [25], direct polymerized polypyrrole [26], layer-by-layer deposited charged polyelectrolytes [27, 28], interfacially polymerized polyamide/poly(amide-co-ester) [29-34], cast and photo-crosslinked polyimide [35], and MOF thin films, prepared by interfacial synthesis [36]. The most commonly used method for the fabrication of thin selective layer is the interfacial polymerization. Modifications of polyamide thin selective layers have been previously investigated to further enhance the membrane permeance and selectivity in organic solvents. Reported modifications are the incorporation of fillers including metal-organic frameworks

(MOFs) [37, 38], functionalized SiO₂ [39], carbon nanotubes [40], cyclodextrins [41], and TiO₂ [42]. Furthermore, it has been demonstrated that the post-treatment of polyamide TFC membranes by solvent activation results in enhanced membrane performance [32]. A recent study published by Jimenez-Solomon et al. [43] reports a new approach to design polyarylester thin selective films with high separation performance in organic solvents, by manipulating the molecular structure of monomers. Non-planar phenol monomers including 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethylspirobisindane and 9,9-bis(4-hydroxyphenyl)fluorene provide higher microporosity and interconnectivity, resulting in an increase of solvent permeance. The methanol permeance of the membranes prepared with non-planar monomers reach a permeation of $8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is almost 10-fold higher than that of membranes prepared with planar monomers. Recently, covalent-organic-framework (COF) membranes with precise pore channels of 1 – 2 nm have been reported with ultra-fast permeation for polar solvents [44, 45]. However most of the reported solvent resistant nanofiltration membranes with fast polar solvent transport have very low nonpolar solvent permeation [32, 46]. The number of nanofiltration membranes, having high permeance for both polar and nonpolar solvents, remains limited. Membranes prepared by interfacial polymerization of cyclodextrin with terephthaloyl chloride [47] is a recent sample with high permeance for solvents of different polarities, such as methanol ($9.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and hexane ($3.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$).

In this study, a polyamide network was formed by interfacial polymerization of an amine functionalized porphyrin, 5,10,15,20-(tetra-4-aminophenyl)porphyrin, and m-phenylene diamine (MPD) with trimesoyl chloride (TMC). We chose porphyrin as building block for two different reasons. First, the non-planar structure of porphyrin is expected to enhance the free volume of the crosslinked polyamide network, resulting in high permeance. In addition, nonpolar solvents, such as benzene, toluene, hexane [48, 49], should have a high affinity for the heterocyclic tetrapyrrole core of the porphyrins, promoting their fast transport through the membrane.

Materials

Polyetherimide (PEI, Ultem™1000, Sabic), diethylene glycol (DEG, Sigma-Aldrich), and N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) were used, respectively, as polymer, pore forming agent, and solvent for preparation of PEI membrane support casting solution. 1,6-Hexanediamine (Sigma-Aldrich) was utilized as crosslinker for the PEI support. The polyamide film was synthesized by reacting trimesoyl chloride (TMC, Sigma-Aldrich) and two amine-functionalized monomers, 5,10,15,20-(tetra-4-aminophenyl)porphyrin (PorphyChem) and m-phenylene diamine (MPD, Sigma-Aldrich) (Fig. 1). Organic solvents including dimethyl sulfoxide (DMSO), dimethylformamide (DMF), n-hexane, methanol, acetone, and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. Sudan Blue II (350 g/mol) and Brilliant Blue R (826 g/mol) were supplied by Sigma-Aldrich and used as solutes in the rejection tests. Sodium dodecyl sulfate (SDS), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl) were purchased from Sigma-Aldrich and used as received. Polyester non-woven fabric sheet (TH100) was ordered from Hirose.

(a) (b)

Fig. 1. Three-dimensional molecular structure of amine monomers: (a) 5,10,15,20-(tetra-4-aminophenyl)porphyrin and (b) m-phenylene diamine (MPD).

Experimental

Preparation of crosslinked PEI porous supports

Asymmetric PEI membranes were prepared by phase inversion using 10.2/7.8/82 (w/w/w) PEI/DEG/NMP as casting solution. Briefly, a piece of non-woven fabric was attached to a glass plate. NMP was sprayed on the fabric to pre-wet the support, and the excess solvent was removed by a filter paper before casting the polymer solution. The polymer solution was spread on the pre-wetted fabric, using a 200 μm gap casting knife. The precipitation of the polymer film/fabric was conducted by immersing it in a water bath at room temperature. PEI membranes were obtained and kept in water for

one day to completely eliminate any solvent. Subsequently, the PEI membrane was immersed in a methanol solution, containing 10 wt% 1,6-hexanediamine for 24 h at room temperature to crosslink the imide groups of PEI. The crosslinked PEI membrane was washed with water to remove unreacted 1,6-hexanediamine. After crosslinking, the surface chemistry of the crosslinked membrane was compared with the pristine membrane by an attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The membranes were dried and the surface chemistry was analyzed using a Nicolet™ iS™10 FT-IR spectrometer (Thermo Scientific, USA).

Interfacial polymerization

Fig. 2. Schematic of interfacial polymerization between porphyrin and MPD in the aqueous phase and TMC in the organic phase.

Thin polyamide layers were prepared on the top of the crosslinked PEI membrane by interfacial polymerization. The polymerization reaction was performed at the interface between an aqueous phase containing amine-functionalized monomers and an organic phase containing acid chloride (Fig. 2). The aqueous solutions were prepared from porphyrin/MPD monomers at concentrations of 0/1, 0.25/0.75, and 0.5/0.5 (w/w) in a mixture of DMSO/water (25/75, w/w) containing concentrations of SDS varying from 1 to 4 (wt%). The organic solution contained 0.15 wt% TMC in hexane. All solutions were freshly prepared before use. Before the interfacial polymerization process, the crosslinked PEI support, initially wet with water, was immersed in a 25/75 (w/w) DMSO/water solution for 15 min. The support was fixed in a frame to expose only the side with smaller pores to the reaction. Subsequently, the crosslinked support was immersed in the aqueous (DMSO/water) solution containing the reactive amines for 2 min and pressed with a roller and filter paper to remove excess. The organic solution was then poured onto the support soaked with the amine solution for 1 min to form the polyamide film. The as-prepared polyamide

membrane was dried in air for 1.5 min and washed with DMF for 1 min to remove unreacted monomers. The membrane was rinsed with deionized (DI) water and stored in DI water at 4 °C.

Characterization

The membrane surface and cross-sectional morphology were imaged on a field-emission scanning electron microscope (FESEM), NovaTM NanoSEM 630 (FEI). All samples were freeze-dried to completely remove water while maintaining the structure. For cross-sectional imaging, the membranes were fractured in liquid nitrogen. Samples were immobilized on an aluminum stub using aluminum conductive tape and then coated with iridium (~ 3 nm thickness) before imaging.

The morphology of porphyrin/MPD polyamide films was imaged on a FEI Titan 80-300 ST transmission electron microscope (TEM), operating at 300 kV. The porphyrin/polyamide films were complexed with copper and imaged on an aberration corrected scanning transmission electron microscopy (AC-STEM) mode, coupled with electron energy-loss spectroscopy (EELS). In this way, the STEM-EELS spectrum image (SI) dataset was acquired to generate the Oxygen, Nitrogen, and Copper elemental maps. Self-standing thin polyamide films were fabricated by pouring 0.15 wt% TMC solution in hexane on a porphyrin/MPD in DMSO/water solution. The interfacial polymerization was performed at room temperature for 20 s. The resultant polyamide film was air dried for 1 min and washed with DI water several times. Subsequently, the film was transferred onto a copper grid and air-dried overnight before imaging. A Cu specific mapping was obtained. The Cu-complexed polyamide film was prepared by immersion of the polyamide film into an aqueous solution containing 100 mM CuSO₄ for 5 h at room temperature, followed by washing with deionized water to remove unreacted reagent and finally the film was transferred onto a copper grid and air dried before imaging.

UV-vis diffuse reflectance measurements of polyamide membrane selective layers were recorded using a UV-vis spectrophotometer equipped with a diffuse reflectance accessory (DRA) (Cary 5000, Varian).

Zetasizer Nano (Malvern) with a surface zeta potential cell was used to measure the zeta potential of polyamide membranes. A solution containing 100 ppm particles in DI water at pH 7.1 were used as suspended particle solutions for the surface zeta potential measurement.

X-ray diffraction (XRD) patterns of the pristine and porphyrin-modified freestanding films were recorded on a Bruker D8 Avance with Cu K α radiation.

Atomic force microscope (AFM, Agilent Technologies, model 5400 SPM) was used to determine the selective layer thickness. The samples were scanned in tapping mode in the air with a silicon AFM cantilever (Nanosensors) with a scanning range of 3 μm x 3 μm . AFM scanning was performed on the pristine (0/1 porphyrin/MPD, 4% SDS) and porphyrin-modified (0.5/0.5 porphyrin/MPD, 4% SDS) freestanding films sitting on smooth surface of silicon wafers. To obtain the freestanding films, polyamide TFC membranes were prepared using non-crosslinked PEI supports. Subsequently, the membranes were immersed in DMF to dissolve the supports and release freestanding polyamide films.

Water contact angles of freeze-dried polyamide TFC membranes were measured using a Krüss Easydrop (Krüss GmbH, Germany) at room temperature. The static contact angle measurement was conducted by advancing 2 μL of liquid (water or hexane) on the top surfaces of the membranes.

Lab-scale nanofiltration tests

The nanofiltration performance was evaluated at room temperature under a trans-membrane pressure of 2 bar, using a dead-end permeation cell with an effective membrane area of 3.1 cm^2 . Permeance and rejection values were determined to evaluate the membrane performance. The permeance tests were subsequently carried out in the following order: deionized water, methanol, acetone, THF, and hexane. Before each liquid permeation measurement, the membrane was stabilized under the sample testing

conditions for 20 – 30 min. Then, the permeate was collected for a period of 40 – 60 min. The permeance ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) of deionized water, methanol, acetone, THF, and hexane was determined by the following equation:

$$\text{Permeance} = \Delta V / (\Delta t A_{\text{eff}} \Delta P) \quad (1)$$

where ΔV (L) is the volume of liquid that has permeated through the membrane in a predetermined time Δt (h); A_{eff} is the effective membrane surface area (m^2); ΔP is the trans-membrane pressure (bar).

Sudan Blue II and Brilliant Blue R were used as model solutes for membrane selectivity characterization. The feed solution containing 20 ppm model solutes was added to the filtration cell, under stirring. A large feed volume (300 mL) was used for each rejection test to maintain the retentate volume at $> 95\%$ of the initial feed volume. The first 5 – 7 mL of the permeate was discarded, the subsequent 5 mL of the permeate was collected for the rejection analysis. The rejection of polyamide membranes was determined as a function of the solute concentration in the permeate (C_p) and the solute concentration in the retentate (C_r):

$$\text{Rejection} = (1 - C_p / C_r) \times 100\% \quad (2)$$

The solute concentration was determined by a NanoDrop 2000/2000C spectrophotometer (Thermo Fisher Scientific). The concentration of Sudan Blue II and Brilliant Blue R and Direct Red 80 in the testing solutions was calculated from the absorption values at their characteristic wavelength of 652 nm and 585 nm, respectively.

Results and discussion

A polyamide membrane for organic solvent nanofiltration should contain a dense crosslinked polyamide film and a solvent resistant porous support. To obtain a robust, thermally stable and highly organic-resistant support, PEI was used as casting material to fabricate porous PEI support (pristine PEI support), followed by crosslinking of the imide rings by 1,6-hexanediamine to form amide groups. The reaction was confirmed by ATR-FTIR. Fig. 3 shows the spectra of pristine and crosslinked PEI membranes. The characteristic peaks of polyetherimide at 1780 and 1720 cm^{-1} ($\text{C}=\text{O}$), and 1354 cm^{-1} ($\text{C}-\text{N}$) are observed in the pristine PEI membrane ATR-FTIR spectrum. In the ATR-FTIR spectrum of the crosslinked membrane, the appearance of new amide peaks at 1645 cm^{-1} ($\text{C}=\text{O}$), and 1543 cm^{-1} ($\text{C}-\text{N}$) and weak imide characteristic peaks confirms the success of the chemical cross-linking reaction.

Fig. 3. ATR-FTIR spectra of pristine PEI and cross-linked PEI membranes.

The support was then coated by a thin polyamide layer, obtained by interfacial polymerization, containing building blocks of porphyrin. The amine-functionalized porphyrin was covalently embedded, as part of the polyamide layer, during the polycondensation. For this purpose, the amine-functionalized porphyrin was mixed to MPD in aqueous monomer solution. The effect of the porphyrin/MPD concentration on the morphology, surface properties and separation performance of the resultant porphyrin/MPD polyamide membranes was investigated. 0/1, 0.25/0.75, and 0.5/0.5 (w/w) porphyrin/MPD solutions in 25/75 (w/w) DMSO/water with 4 wt% SDS were used as aqueous phases for interfacial polymerization. To eliminate the effect of SDS to the membrane performance in the comparison between the pristine and porphyrin modified membranes, all membranes were fabricated using the same SDS concentration (4 wt% SDS in the mixture of DMSO/water solution). The successful incorporation of porphyrin in the crosslinked polyamide matrix was confirmed by UV-vis diffuse reflectance spectroscopy and the change in color of polyamide membranes after interfacial polymerization. Fig. S1 displays UV-vis diffuse reflectance spectra of polyamide membranes with strong absorption peaks at 436 nm represented for porphyrin

absorption in membranes prepared from 0.25/0.75 and 0.5/0.5 porphyrin/MPD solutions. A larger porphyrin concentration in solution, and the consequent larger content of porphyrin in the polyamide film, is seen by the increased intensity of porphyrin absorption peak. The result is in good agreement with the change in color of membrane surfaces from white (0/1 porphyrin/MPD) to dark green (0.5/0.5 porphyrin/MPD), as shown in Fig. S1. It confirms that porphyrin was successfully incorporated into the polyamide film. FTIR was used to confirm the changes in chemical composition of films prepared from 0.5/0.5 porphyrin/MPD, compared to 0/1 porphyrin/MPD freestanding films (Fig. 4). The increased intensity of the characteristics peaks at 1650 and 1484 cm^{-1} (C=C vibrations) 1605 cm^{-1} (C=C stretching of pyrrole ring), 780 cm^{-1} (C-H out-of-plane deformations of the phenyl ring), 719 cm^{-1} (C-H trans out-of-plane bending of the phenyl ring) and the presence of new peaks at 1100 cm^{-1} (pyrrole stretching vibration) and 1390 cm^{-1} (C=N stretching vibration) are attributed to porphyrin.

Fig. 4. ATR-FTIR spectra of 0/1 porphyrin/MPD and 0.5/0.5 porphyrin/MPD freestanding films.

TEM was used to evaluate the morphology of membranes coated with a 0.25/0.75 porphyrin/MPD polyamide film. Fig. S2 shows bright field images of a 0.25/0.75 porphyrin/MPD polyamide film under sub-micron and sub-nano magnifications. A defect-free crumpled nodular polyamide film with elongated and doughnut-like structures can be seen from the TEM images. No crystalline structure is observed in the images indicating that porphyrin is not aggregated during 0.25/0.75 porphyrin/MPD polyamide film formation. The heterocyclic tetrapyrrole unit of porphyrin has a high binding capacity to transition metal ions to form porphyrin-metal ion complexes. Hence, a thin Cu(II)-complexed 0.25/0.75 porphyrin/MPD polyamide film was fabricated and examined by STEM-EELS technique. The characterization of the sample with STEM-EELS technique can provide high-resolution elemental mapping images that show the distribution of complexed Cu on porphyrin heterocyclic tetrapyrrole unit represented the dispersal of porphyrin on 0.25/0.75 porphyrin/MPD polyamide film. Fig. 5(a and d) show STEM image of Cu(II)-complexed 0/1 and 0.25/0.75 porphyrin/MPD polyamide films used for O, N and Cu maps. Fig. 5(b and

e) show Cu element mapping images of the films in which Cu is shown in blue color. In Fig. 5(c and f), red, green, and blue colors correspond to O, N, and Cu elements. No Cu is detected in the 0/1 porphyrin/MPD polyamide film (Fig. 5b), while Cu is evident and well dispersed in the 0.25/0.75 porphyrin/MPD polyamide film (Fig. 5e), without any aggregation, indicating the uniform distribution of porphyrin in the polyamide film.

Fig. 5. STEM image of (a) 0/1 porphyrin/MPD and (d) 0.25/0.75 porphyrin/MPD polyamide films. STEM-EELS elemental mapping, after complexation with Cu(II): (b and e) Cu mapping (blue), and (c and f) composite mapping of O (red), N (green), and Cu (blue) for 0/1 porphyrin/MPD and 0.25/0.75 porphyrin/MPD polyamide films, respectively.

Fig. 6. Surface (top row) and cross-section (bottom row) images of (a) 0/1 porphyrin/MPD, (b) 0.25/0.75 porphyrin/MPD, and (c) 0.5/0.5 porphyrin/MPD membranes.

Fig. 6 shows the selective layer and cross-sectional SEM morphology of the resultant membranes. The images in the top row show the complex crumpled nodular polyamide films, which cover the PEI support. Increasing the porphyrin concentration from 0 to 0.5 wt%, while keeping constant concentrations of 1 wt% total amine monomer and 4 wt% SDS in water, led to smoother and thinner polyamide films. The incorporation of porphyrin resulted in thinner polyamide films, as confirmed by the AFM analysis. The polyamide films were detached from the supports and transferred to silicon wafers. The topographical images and their thickness profiles are shown in Fig. 7. The AFM results confirm that thinner polyamide films were obtained with the introduction of porphyrin, compared to that of the pristine membrane.

Fig. 7. AFM topography images of (a) 0/1 porphyrin/MPD and (c) 0.25/0.75 porphyrin/MPD polyamide films and their respective profiles (b and d) of lines shown in topography images.

The hydrophilicity and organophilicity of 0/1 and 0.5/0.5 porphyrin/MPD membranes are illustrated in Fig. S3a. Compared to membranes prepared without porphyrin, those prepared with 0.5/0.5 porphyrin/MPD solutions have lower hexane contact angle, indicating higher organophilicity. This is due to the high affinity of porphyrin to nonpolar solvents. Interestingly, a 0.5/0.5 porphyrin/MPD membrane has also lower water contact angle than the one prepared without porphyrin. In Fig. S3, the FTIR spectrum of a polyamide film with high porphyrin concentration shows a more intense peak at 3280 cm^{-1} , which is the characteristics peak of N–H stretching. Compared to 0/1 porphyrin/MPD, 0.5/0.5 porphyrin/MPD membrane has less negatively charged surface (less negative zeta potential). FTIR and zeta potential results indicate the presence of high amount of –NH_2 , –NH= , –NH– groups on 0.5/0.5 porphyrin/MPD polyamide layer, which facilitates hydrogen bonding with water molecules.

The effect of porphyrin on the free volume of the polyamide film was evaluated, using XRD. The XRD patterns (Fig. S4) are broad, as characteristic of amorphous polymers. The angle corresponding to the maximum intensity gives an indication of the average distance between chain segments and therefore an estimation of the free volume. The maximum for the 0.5/0.5 porphyrin/MPD film shifted to a slightly lower angle (2θ), indicating a larger distance between segments in the crosslinked network of 0.5/0.5 porphyrin/MPD film compared to 0/1 porphyrin/MPD film. Hence, the selective layer of 0.5/0.5 porphyrin/MPD membrane would have slightly larger free volume than 0/1 porphyrin/MPD membrane.

Fig. 8. Permeance and Brilliant Blue R rejection of 0/1, 0.25/0.75, and 0.5/0.5 porphyrin/MPD membranes for water, methanol, and acetone filtrations.

Fig. 8(a, c, and e) and Fig. 9(a and c) compare water, methanol, and acetone, THF, and hexane permeance of membranes derived from different aqueous solutions containing 4 wt% SDS. The permeance increases with the porphyrin/MPD content in the thin films, according to the following sequence: $0/1 < 0.25/0 < 0.5/0.5$. The presence of porphyrin in the polyamide film decreases the contact angles both of water and

apolar organic solvents (Fig. S3a), and slightly increases free volume (Fig. S4). As a result, the permeance of porphyrin-modified membranes is higher. Furthermore, the modified porphyrin-modified polyamide layers are thinner (Fig. 6, cross-sectional images, and Fig. 7), also contributing to a lower resistance to the water transport. Compared to the non-modified polyamide membrane, those prepared from 0.25/0.75 and 0.5/0.5 porphyrin/MPD have 2 to 4-fold higher permeance of methanol, acetone, and THF. Interestingly, ultra-fast, 10 and 40-fold higher hexane permeance than that of unmodified membranes, was observed for those prepared from 0.25/0.75 and 0.5/0.5 porphyrin/MPD solutions. A reason for this exceptionally high hexane permeation is the high affinity of porphyrin to nonpolar solvents [48]. As shown in Fig. 8(b, d, and f) and Fig. 9 (b and d), the membrane selectivity slightly decreases for porphyrin-modified membranes, probable due to a less negatively charged surface, which reduces the electrostatic repulsion between the membrane surface and negatively charged dyes.

Fig. 9. Permeance and Sudan Blue II rejection of 0/1, 0.25/0.75, and 0.5/0.5 porphyrin/MPD membranes for THF and hexane filtrations.

SDS was used as surfactant to produce homogeneous porphyrin aqueous solutions. The SDS concentration is an important factor to change the structure and separation performance of polyamide films as discussed previously [50, 51]. Three types of 0.25/0.75 porphyrin/MPD membranes derived from three aqueous solutions, containing 1, 2, and 4 wt% SDS, were fabricated and characterized. The morphology of the three membranes is presented in Fig. 10.

Fig. 10. Surface (top row) and cross-section (bottom row) SEM images of 0.25/0.75 porphyrin/MPD membranes.

Fig. 11. (a) Permeance and (b) Brilliant Blue R rejection of 0.25/0.75 porphyrin/MPD membranes.

The surface morphology of the polyamide film has larger features with less crumbled nodules at higher SDS concentration. The thickness remains constant. The water and methanol permeance of 0.25/0.75 porphyrin/MPD membranes having 1% SDS, 2% SDS, and 4% SDS is compared in Fig. 11a. The membrane prepared from 0.25/0.75 porphyrin/MPD and 2% SDS exhibits a large increase in permeance, compared to that prepared with 1% SDS. However, a further increment of SDS concentration to 4 wt% did not lead to an additional increase of the permeance. SDS is an amphiphilic molecule and forms micelles in solutions when having a concentration above its critical micelle concentration (CMC). The CMC of SDS in water at room temperature is 8.2 mM (0.23%). Therefore, all aqueous solutions used in the interfacial polymerization are above CMC, containing SDS-porphyrin complexes and free SDS micelles. Free SDS micelles are small non-reactive agents, which are incorporated into the polyamide film, during interfacial polymerization. During the washing step, the free SDS micelles are probably removed from the polyamide film, and create free volume in the network. Hence, the polyamide membrane permeance increases by using higher SDS concentration. However, the result shows that by using 4% SDS only negligible improvement in the permeance is obtained. Membranes prepared with 4% SDS contain fewer nodules on the selective layer (Fig. 10c, top). Due to the increased free volume, the rejection is lower than when prepared with 2% SDS, as shown in Fig. 11b.

Fig. 12. (a) Pure solvent permeance of 0.25/0.75 porphyrin/MPD, 2% SDS membrane and (b) its rejection. Membrane photography after rejection tests in (a) water, methanol, and acetone and (b) THF and hexane.

The membranes prepared with 1% SDS have slightly lower selectivity than those prepared with 2% SDS membrane. The permeances of 0.25/0.75 porphyrin/MPD membranes with 2% SDS to water and various organic solvents are shown in Fig. 12a. The rejections of Brilliant Blue R and Sudan Blue II in different solvents are presented in Fig. 12b. A high permeance and a good selectivity in the nanofiltration range for water, polar and nonpolar organic solvents, and low dye fouling propensity were observed (Fig. 12 (c and

d)). Based on the performance data in Fig. 8, 9, 11 and 12, it can be concluded that membranes prepared from 0.25/0.75 porphyrin/MPD with 2% SDS would be the best choice for separation of solutions containing Brilliant Blue R. For separation of larger solutes, membranes prepared from 0.5/0.5 porphyrin/MPD with 4% SDS would be preferred.

Conclusion

We developed for the first time solvent resistant TFC nanofiltration membranes using porphyrin as amine-functionalized monomer for interfacial polymerization. The morphology, surface properties, and performance of the polyamide membranes are tunable by varying the ratio of porphyrin and MPD monomers in the aqueous solutions during the interfacial polymerization process. By increasing the porphyrin/MPD ratio from 0/0 to 0.5/0.5 the permeance was increased from 16.5, 6.7, 8.2, 1.2, and 0.7 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ to 48.4, 32.5, 36.3, 4.8, and 28.7 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for water, methanol, acetone, THF, and hexane, respectively. The membrane rejection decreased, following a trade-off, when the porphyrin/MPD ratio was increased. However, the enhanced liquid permeance is much more remarkable than the selectivity reduction at high porphyrin/MPD ratios. The porphyrin-modified polyamide membrane fabrication process is simple and reproducible using commercially available porous supports, indicating the scale-up feasibility of this work. Porphyrins with different functionalizations and analogous compounds are available in nature or as synthetic molecules and could be also explored membrane fabrication.

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Highlights

- Thin film composite membranes with porphyrin as building block
- Hexane permeance 10 to 40-fold higher than pristine polyamide membrane
- Brilliant Blue R rejection above 94 %

Accepted

Fig. 1.

Fig. 2.

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig.7

Fig. 8.

Fig. 9

Fig. 10

Fig. 11

Fig. 12