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Solvent-resistant Triazine-Piperazine Linked Porous Covalent Organic Polymer Thin-film Nanofiltration Membrane

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ABSTRACT

We present the fabrication of a novel porous covalent organic triazine-piperazine based membrane (CTP membrane) for solvent nanofiltration. The porous CTP skin layer grows on the top surface of polyacrylonitrile (PAN) support in presence of *N, N*-diisopropylethylamine (DIPEA) in the water/heptane interfacial reaction. The CTP skin layer membrane showed solvent-resistant property to a wide range of common solvents such as DMF, DMSO, and NMP; the stability of the composite membrane is limited by the PAN support. Chemical bonding and elemental analyses confirm the incorporation and linking of the triazine and piperazine components in the nanofilms skeleton. Electron microscopic image analysis demonstrates that the CTP skin layer nicely covers the PAN support and has porous and crumple morphology. The membrane exhibits excellent NF properties as demonstrated by the selective dye rejection and salt rejection experiment. The CTP membrane showed dye rejection (Reactive black-5; MW 992 g mol⁻¹) and salt rejection (Na₂SO₄) 96.7%, and 91.3%, respectively. The membrane comprised a stable porous robust structure, large surface area, well-defined pore topology, and solvent durability coupled with the zeta potential. All of these cooperatively benefits to achieve superior performances in separation, reusability with high permeance, leading to state of the art performance in the NF application.

Keywords: Nanofiltration; interfacial reaction; nanofilms; skin layer; solvent-resistant

1. Introduction

During the last two decades, nanofiltration became an integral element of separation technology aiding the separation of small molecules and multivalent ions from solvent streams. [1-3] Nanofiltration in organic solvent systems is an emerging field with a number of large industrial applications. [1, 2, 4] Typical nanofiltration membranes have a molecular weight cut-off between 200 and 1000 putting them between ultrafiltration and reverse osmosis (RO) with a lower operating pressure range than RO membranes.[2, 5, 6]

The majority of today's NF membranes are thin-film composite membranes made by interfacial polymerization.[3, 7-11] The selective layer grows as an attached layer on the porous support through the proper selection of monomers, additives and a combination of immiscible solvents.[12, 13] The performance of the TFC membranes depends on the chemistry of the reacting monomers, additives, and promoters; concentrations of the reactants and the nature of support membrane is of importance. Trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD) are preferred monomers to form TFC membranes at the interface of water/hydrocarbon.[3, 13] Several others linear alkane amines like ethylenediamine, 1,6-diaminohexane, diethylenetriamine, polyethyleneimine, tetraethylenepentamine and cyclic amine were used to tune TFC membrane.[14-16] Different piperazine derivatives are also important monomers for nanofiltration membrane manufacturing.[17] Isomeric biphenyl tetraacyl chloride was also used to prepare TFC membranes by interfacial polymerization.[18] The polyamide TFC membranes fabricated with acyl chloride based monomers suffer from a certain instability of the amide bond and lack of robustness.[19] This limitation is a motivation to create more stable membranes and in this context polyamine linked membranes are especially promising.[14] Cyanuric chloride

(CC) was used to prepare polyamine TFC membrane through the reaction with various alkane or aromatic amines.[14, 20]

To enhance and tune the performance of composite nanofiltration membranes several strategies have been used to enhance porosity, stability and to compose more open structures. Silica nanoparticles have been grafted to the polypiperazine-amide TFC NF membrane and showed enhanced water flux and divalent ions rejection.[21] A TiO_2 loaded TFC NF membrane has been developed via interfacial polymerization and showed enhanced flux and bivalent ions rejections.[22, 23] Karan *et al.* tuned the polyamide TFC film to a ultrathin level of 10 nm thickness through the use of a sacrificial layer of cadmium hydroxide nanostrands and membrane showed extremely high flux combined with good separation.[7] Liliana *et al.* developed new ultrathin TFC membrane on a cross-linked PAN support which showed excellent solvent stability.[10, 11] Recently, a polyamine composite membrane with cyanuric chloride as one monomer has been fabricated and realized open pore structure and good NF property at high pH.[14] Very recently, Sarath *et al.* developed self-standing porous covalent organic framework membranes (COMs) which were made from typical crystalline polymers with uniformly arranged ordered pore channels and showed high flux for organic solvents and separation performances.[24]

Porous covalent organic polymers (COPs) are supposed to be promising membrane materials but growing COPs as a continuous porous skin layer is challenging.[24] The structural linkers should be reactive enough and flexible or semi-rigid to produce continuous porous skin layers. Principally, covalent bonds in the porous COPs matrices are stable to provide a robust structure with a pH tolerance higher or comparable to the conventional polyamide TFC membranes.[20] It was reported that cyanuric chloride and piperazine generated robust, chemically, and thermally

stable a porous COP structure with large surface area and well-defined pores of 1.3 nm.[25-27] The cyanuric acid and piperazine react in presence of DIPEA and all three chlorine atoms of the cyanuric chloride experienced nucleophilic substitution in the temperature range 273-353 K.[25, 26, 28, 29]

Herein, we describe the synthesis of porous CTP skin layer on the PAN support in presence of DIPEA by interfacial polymerization using water and heptane as solvents for the reactants. The CTP skin layer is crumpled leading to a large surface area. The free-standing CTP film obtained by dissolving the PAN support exhibited a robust, solvent resistant porous structure with high porosity. The bonding analysis and elemental composition suggested the regular integration of the piperazine and triazine moieties. The stable covalent bonding, the robust, well-defined pore topology, solvent durability, chemical and thermal stability promoted the CTP membrane as a promising candidate for NF applications as demonstrated by the selective dye and salt rejection experiments.

2. Materials and methods

2.1. Materials

The Polyacrylonitrile (PAN) support membrane was supplied by the GMT Membrantechnik GmbH; Germany. Structural monomers such as cyanuric chloride (Reagent Plus, 99%), piperazine (Reagent Plus, 99%), and the organic proton scavenger N, N-diisopropylethylamine (DIPEA) were purchased from Sigma-Aldrich. Solvents such as *n*-heptane, N, N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-Methyl-2-pyrrolidone (NMP), methanol (MeOH) and ethanol (EtOH) were purchased from Sigma-Aldrich. Dyes including Reactive Black 5 (RB 5; MW. 991.82 g mol⁻¹), naphthalene blue black (NBB; MW 617.49 g mol⁻¹), methyl orange (MO; MW 327.33 g mol⁻¹) and inorganic salts including NaCl, NaNO₃,

Na_3PO_4 , Na_2SO_4 , MgCl_2 , MgSO_4 , and K_2SO_4 were purchased from Sigma-Aldrich. All of these chemicals were used without further purification.

2.2. Synthesis of the porous CTP membrane

The covalent organic triazine-piperazine linked porous polymer skin layer on the PAN support was developed by interfacial polymerization. In a typical process, 200 mg piperazine (2.32 mmol) was dissolved in 20 mL deionized water, then 400 μL of DIPEA was added and thoroughly homogenized. Then, this solution was poured on a Teflon-framed PAN support and allowed to saturate the PAN support for 10 min. Excess water droplets from the top surface of the PAN support were then removed by the air flow. The piperazine impregnated PAN membrane was then fixed in the Teflon-frame again. The cyanuric chloride solution (17 mg, 0.092 mmol) in 20 mL heptane was poured on the top surface of PAN support; the interfacial polymerization reaction took place for 40 s under cover. After the 40s the membrane was washed with pure *n*-heptane. Finally, the membrane was placed inside the oven at 353 K for 4 h to complete polymerization and crosslinking.

2.3. Free-standing CTP nanofilm

The CTP/PAN composite membrane described above was immersed in DMF for 24 h. The PAN support dissolved and the transparent nanofilm floated on the DMF surface as shown in the photographic images Fig. 8a-b. The CTP Nanofilm is insoluble in common solvents (water, methanol, ethanol and acetone) and some special solvents such as DMF, DMSO and NMP. The floated nanofilm has a sufficient stability that allows a transfer to a circled wire loop as shown in the photographic image Fig. 8b.

2.4. Characterization techniques

Transmission electron microscopy (TEM) images were taken on an FEI Tecnai twin microscope operated at 120 kV. The free-standing nanofilm was transferred to methanol. Then, it was transferred to the 400-mesh copper TEM grid, and the solvent evaporated, leaving the sample deposited on the TEM grid. Scanning electron microscopy (SEM) images were obtained from an FEI Nova Nano630 SEM, and an FEI Helios NanoLab™ 600 DualBeam operated at 10 kV. The rotation frequency was set to 5 kHz. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 smart FTIR spectrometer (Thermo Scientific, USA) equipped with a smart OMNI transmission ranging from 4000 cm^{-1} to 400 cm^{-1} at room temperature. NMR experiments were carried out in a Bruker Avance III 900 MHz spectrometer equipped with a triple-resonance 3.2 mm Bruker MAS probe (BrukerBioSpin, Rheinstetten, Germany). The ^{13}C CP MAS NMR spectra were recorded at room temperature using 900 MHz solid state NMR spectrometer at a resonance frequency of 226.38 MHz using a CP program from Bruker standard library. The contact time of cross-polarization (CP) was optimized to 3 ms, employing ramp100 for variable amplitude CP. To achieve high signal to noise ratio, the spectra were recorded by collecting 24 k scans with a recycle delay time of 5s. To differentiate between the real NMR peaks from side band effect signals the spectra were under 18 kHz and 20 kHz pinning rate. Bruker Topspin 3.0 software was used for data collection and spectral analysis. CHN elemental analysis was carried out on a Flash 2000 organic elemental analyser (Thermo Scientific, USA). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a thermal analyser TG 209 (Netzsch), under N_2 flow (20 mL/min). The surface wetting ability of the PAN support and the PT membrane was evaluated based on the dynamic water contact angle analysis. The measurement was performed using a Kruss drop shape analyzer-DSA100

(Hamburg, Germany) with a monochrome interline CCD camera at ambient condition. All the membranes were dried prior to the measurement, and a drop of water (5.0 μL) was deposited on the membrane surface using the sessile drop method. The contact angle was estimated using a circle fitting method by the drop shape analysis software. Average values of contact angles are presented from the three measurements of the each membrane.

The zeta potential was estimated by measuring the streaming potential using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria) equipped with a Clamping Cell. A pair of the membranes was fixed in the measuring cell with a flow channel gap adjusted to 100 μm , and Ag/AgCl electrodes were used to measure the streaming potential. Prior to use, the membrane was saturated for at least 24 h in the 10 mmol NaCl aqueous solution. The 10 mmol NaCl aqueous solution was used as a background electrolyte, and 0.1M HCl and 0.1M NaOH was used to adjust pH. The streaming potential was measured as a function of pressure in the pH range from 3 to 8. The zeta potential was calculated using the Helmholtz-Smoluchowski equation.[30, 31]

4.5. Nanofiltration performance

All NF experiments were carried out in a dead-end filtration system pressurized by nitrogen with an effective membrane area of 12.6 cm^2 and the pressure of NF experiment was 4 bar. Permeates was collected in a certain time interval and the flux (F) was estimated based on the following equation;

$$F = \frac{V}{A \cdot t \cdot \Delta p} \dots\dots\dots 1$$

Where, V is the volume of the permeate (L), A is the effective membrane area (m^2), t is the time (h) of permeate collection and Δp is the trans-membrane pressure (bar).

Rejection (R) of the membrane was calculated using the following equation.

$$R (\%) = \left(1 - \frac{C_p}{C_{AFS}}\right) \times 100 \dots\dots\dots 2$$

Where C_p and C_{AFS} are the concentration of permeate, and averaged concentration of the feed and retentate solution, respectively.

To demonstrate the dye rejection performance, different dyes solution in water and methanol of 10 ppm concentration has been chosen as the feed solution. Dye concentrations were determined with a UV-VIS (Perkin Elmer Lambda 1050) spectrophotometer. The rejection of the dyes was calculated based on the equation 2.

The membrane salt rejection was measured for different inorganic salts in aqueous solutions with the concentrations 100, 167, 250 and 500 mg/L. Salt concentration was determined by conductivity measurements (XL20, Accumet Excel, Fisher Scientific).

3. Results and discussion

The synthesis pathway of the triazine-piperazine linked porous COP material as proposed in Fig. 1(a-c) and the scheme for the fabrication of porous CTP skin layer on the surface of the PAN support is depicted in Fig 1d. The nucleophilic reaction of cyanuric chloride with piperazine composed the porous COP material in presence of an organic proton scavenger.[25, 28, 32] The polyacrylonitrile (PAN) membrane was employed as a support owing to its robustness, mechanical, chemical and thermal stability. Furthermore, its high porosity and hydrophilic nature promoted excellent water penetration, uniform spreading and good surface coverage.[33, 34] A polyester non-woven support gives additional mechanical stability. The cyanuric chloride solution in heptane was poured on the water-wet surface of the PAN support. The two immiscible liquids (water/heptane) created a well-defined interface. The nucleophilic substitution

Fig. 1. (a) The nucleophilic substitution of chlorine atoms of cyanuric chloride; (b) formation triazine-piperazine linked porous COPs network; (c) nonporous materials formed in absence of proton capture or in presence of strong inorganic base and (d) Schematic representation for the fabrication of CTP membrane on the surface of PAN support and free-standing CTP nanofilm.

of chlorine atoms of cyanuric chloride and successive polycondensation of triazine moieties with piperazine composed the porous network.[25, 26] The N, N-diisopropylethylamine captures the protons formed by the reaction.[27-29] During the progress of reaction, the piperazine molecules diffuse through the pores of the support membrane (act as a reservoir) to the interface and react with the cyanuric chloride to form the porous COP skin layer on top of the PAN support.[7] The CTP film grows in the interface into the organic phase and piperazine continuously diffuse to the interface to progress the reaction.[13, 35, 36] Earlier reports, which describe the formation of composite membranes by the interfacial reaction of cyanuric chloride with different amines, used a strong inorganic base like NaOH as the reaction promoter. The strong inorganic base acts a hydroxide donor which promoted to partially hydroxylation of the cyanuric chloride and led to generate the polymer membrane as reported.[14, 20] DIPEA on the other hand, acts as a typical proton acceptor and does not hydrolyze the cyanuric chloride. Also, the very low water solubility of heptane restricted diffusion of water into the heptane phase diminished the hydrolysis of cyanuric chloride molecules.[37] The fast interfacial reaction might increase the local temperature in the heptane layer as proposed by Karan et al.[7] who suggests, that Rayleigh-Bénard convection might lead to the crumpled membrane structure.[38] Due to the fast reaction, the film formation is kinetically controlled, which favors a porous amorphous structure. The surface CTP nanofilm was separated from the PAN support though dissolution of the PAN in DMF leading to a floating film on the DMF surface as shown in the Fig.7a-b. The free-standing nanofilm is insoluble, stable and robust and it was successfully transferred to a wire ring.

The SEM image analysis aided to investigate the surface morphology and cross-section of the studied membranes. Fig. 2 shows the SEM images of the PAN support, the CTP membrane attached to the PAN support and the free-standing nanofilm. The PAN support membrane

showed a smooth porous surface with pores of approximately 50 to 70 nm diameter (Fig. 2a). The surface of the CTP film attached to the PAN support and also the free-standing nanofilm showed a rough and crumpled structure. Thus, the CTP nanofilm retained its structural stability even after treatment with DMF. The cross-section image of the CTP/PAN composite membrane exhibits a well-defined polymer film formed on the top surface of the PAN support with a thickness of about 50 nm. TEM images of the free-standing CTP nanofilm are given in Fig. 3a-b. The TEM image at low magnification (Fig. 3 a) shows a continuous structure. But some dark spots or lines were observed. In the high-resolution TEM images, as shown in Fig. 3 b, low-electron-density spots (pores) throughout the sample with an average size > 1.0 nm were observed.

Fig. 2. FE-SEM images (a) of the PAN support membrane, FE-SEM images (b, c) and cross-section (d) images of the CTP/PAN composite membrane, FE-SEM images (e, f) of the free-standing nanofilm.

This is in agreement with the microporosity observed for the free-standing CTP nanofilm generated through the linkage of the triazine and piperazine components depicted schematically in Fig. 1.

Fig. 3. (a) TEM image; (b) HRTEM image of the free-standing CTP nanofilm and (c) TGA analysis of the free-standing CTP nanofilm; (p) and (q) bulk material synthesized without proton scavenger.

The thermogravimetric analysis of the bulk material and the free-standing membrane is shown in Fig. 3c. The experiment was performed up to 1050 K at a ramping rate of 10 K min⁻¹ under N₂ atmosphere. The bulk material, synthesized without the proton acceptor, showed poor thermal stability, as it started to decompose at 373 K and steadily continued its decomposition up to 773 K. The free-standing nanofilm, on the other hand, showed very good thermal stability, because it sustained its structural stability up to 560 K before it started to decompose continuously up to 970 K.

Fig. 4p shows the nitrogen physisorption isotherm of the nanofilm. The obtained sorption isotherm is a typical type I curve as defined by the IUPAC.[39] The material showed the gas uptake at a low relative pressure (P/P_0) up to 0.14, indicating the presence of microporosity in the material.[32] The gradual increase of uptake suggested the presence of mesoporosity in the material. The steep increase in nitrogen uptake was observed at a

relative pressure from 0.9 to 1.0 implying the existence of large mesopores.[32] The linking of the monomer constituents cyanuric chloride and piperazine generates a microporous skeleton, whereas interparticle gaps might be responsible for the mesoporous nature.[27, 40] The isotherm gives the BET surface area of $30 \text{ m}^2/\text{g}$ and a Langmuir surface area of $45 \text{ m}^2/\text{g}$, whereas the bulk material synthesized without proton scavenger exhibited a negligible surface area of approximately $3.2 \text{ m}^2/\text{g}$, thus representing a nonporous nature. The NLDFT (non-linear density functional theory) was used to calculate the pore size distribution; majority of the pores were found to be micropores with size around 1.42 nm , in addition to the mesopores having a broad range of size.

Fig. 4. (p) N_2 sorption isotherms of the free-standing nanofilm measured at 77 K (adsorption: filled circles and desorption: empty circles). The pore size distribution of the film using NLDFT is shown in the inset; (q) FTIR spectroscopy of the bulk CTP material (a), free-standing CTP nanofilm (b) cyanuric chloride (c) and piperazine (d).

Successful fabrication of the porous CTP film through the covalent linking of the monomers was confirmed using FTIR spectroscopy. Fig. 4q shows the FTIR spectra for the free-standing nanofilm, the bulk CTP material, cyanuric chloride, and piperazine. The free-standing nanofilm has been chosen for the spectral study because this film provided better

information compared to PAN attached film and thus helps to provide clear and exact bonding information. The spectra of the bulk CTP material was used to compare and confirm the spectral data of the CTP membrane. Several strong vibrational bands were observed in the region from 1200 to 1600 cm^{-1} , representing typical stretching modes of CN heterocycles.[27] The characteristic bending mode bands of the triazine unit of cyanuric chloride was observed at approximately 800 cm^{-1} in both cases, bulk porous CTP material, and the CTP membrane.[27] The bands observed at approximately 2918 and 2855 cm^{-1} corresponded to asymmetric and symmetric stretching modes of the CH_2 group of the piperazine component, Thereby indicating the linking of the piperazine component in the CTP membrane network.[27] The absence of bands, 590-720 cm^{-1} and 1310-1410 cm^{-1} due to the O-H bending frequency of the out of the plane and in the plane, indicated the absence of Ar-OH bond in the CTP skeleton.[41] Disappearance of the stretching vibrational bands around 850 cm^{-1} corresponding to the C-Cl bond of the cyanuric chloride affirmed the complete substitution of the three chloride atoms cyanuric chloride with piperazine in the synthesized porous CTP membrane.[25-27]

The ^{13}C NMR spectroscopy for the free standing film was used to analyze the structure of the porous CTP network as shown in Fig. 5. In the extended polymer skeleton piperazine and triazine units are alternatively linked, and at the terminal of the polymer network, the CH_2 group of the piperazine has a different chemical environment as shown schematically in Fig. 5a. The ^{13}C NMR spectrum contains one well-resolved peak at around 165.73 ppm and other three peaks in the aliphatic region at around 43.67, 36.33 and 29.96 ppm.[26, 42-44] The observed weak peaks at 200 ppm and 90 ppm denoted the side bands.[45] The intense chemical shift band at

43.67 ppm is attributed to the aliphatic CH₂ group of the interior piperazine signifying the extended

Fig. 5. (a) Schematic representation of chemical structure of CTP membrane with peak labelling for (a) ¹³C Solid-State MAS NMR spectra, (b) ¹H Solid-State MAS NMR in the CTP network, (c) possibility of phenolic hydroxyl formation (d) ¹³C Solid-State MAS NMR spectra of the free-standing CTP nanofilm and (e) ¹H Solid-State MAS NMR spectra of the free-standing CTP nanofilm.

network, whereas other two shoulder peaks (weak) around 36.33 and 29.96 ppm to CH₂ group of the terminal piperazine.[32] The peak observed at 165.73 ppm indicated the presence of the

tertiary carbon of the triazine moiety present in cyanuric chloride, and three carbons of the triazine component are equivalent in the CTP network (Fig. 5a).[26, 27] Hence, the NMR spectrum confirmed the presence of triazine and piperazine components in the CTP networks. The absence of any other peaks in the down filled region (instead of 165.73 ppm) imply the existence of only one type of tertiary carbon in the linked network, thereby further affirming all three C-Cl bonds participated in the nucleophilic substitution through the formation of C-N bonds in the porous CTP skeleton.[26, 27]

The ^1H -NMR spectroscopy was further used to validate the chemical structure of the CTP skeleton. In the ^1H -NMR spectra, peaks were observed at 4.12, 2.44, 1.73, 1.48 and 1.08 ppm as shown in Fig. 5 (e). The assignment of protons in the proposed CTP network are shown schematically in Fig. 5b and c. The peak at 4.12 ppm was assigned to the interior proton of the CH_2 group of the piperazine, whereas the 2.44 ppm and 1.73 ppm and 1.48 ppm peaks were attributed to the terminal CH_2 group of piperazine..[28, 29, 46] The band at 1.09 ppm signifies the terminal $-\text{NH}$ proton of the piperazine moiety.[32, 46] The absence of a ^1H -NMR signal of the Ar-OH proton confirms that all C-Cl bonds of cyanuric chloride were linked to the piperazine resulting into $-\text{C}-\text{N}$ bonds through nucleophilic substitution leading to the CTP network as shown in Fig. 5c.

The CHN analysis was used to estimate elemental compositions of the free-standing nanofilm. The CTP membrane has 35.35 wt.%, 53.50 wt.%, 5.12 wt.% nitrogen, carbon, and hydrogen, respectively, whereas the bulk porous CTP material shows the respective composition 41.57 wt.%, 50.97 wt.% and 5.98 wt.%. The estimated results are in close agreement with the theoretical values 41.17 wt.%, 52.94 wt.%, 5.88 wt.% nitrogen, carbon, and hydrogen, respectively.[27, 44]

The water contact angle and dynamic water contact angle measurement has been used to investigate the water wettability and water penetration property for both, the PAN support and the CTP membrane attached to the PAN support as shown in Fig. 6a-c.

Fig. 6. (a) Contact Angle measurement of the PAN support; (b) Contact Angle measurement of the CTP membrane attached to the PAN support; (c) Dynamic contact angle measurement for PAN support (p) and the CTP membrane attached to the PAN support (q) and (d) zeta potential of the PAN support (p) and the CTP membrane attached to the PAN support (q).

The PAN support membrane showed a dynamic contact angle from 42° to 32° within 28 s [Fig. 6c (p)], whereas the contact angle of the CTP decreased from 76° to 62° during the same time.

[Fig. 6b (q)]. The results clearly show that both membranes are hydrophilic in nature as the contact angle shows a dynamic of water penetration.[47]

Fig. 6d shows the zeta potential of the PAN support and the CTP membrane attached to the PAN support in the pH range from 3 to 8. The PAN support membrane showed a negative zeta potential in the entire pH range though the membrane does not have any charged groups. This characteristic nature for the PAN membrane is possibly due ascribed to the adsorption of electrolyte anions onto its surface.[48, 49] The CTP membrane showed positive zeta potential at lower pH < 4, whereas at higher pH > 4 zeta potential was negative. At low pH, the surface nitrogen sites were protonated. The isoelectric point (IEP) of the CTP membrane is around 4.4. At high pH, the quaternary nitrogen sites were deprotonated, coupled with adsorption of some electrolyte anions.[50]

The salts rejection performance and corresponding flux of the porous CTP membrane are shown in Fig. 7 and Table 1. The CTP membrane attached to the PAN support was chosen as the standard membrane. Aqueous solutions of salts with different anions and charges, such as Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , and different cations and charges, such as Na^+ , K^+ , and Mg^{2+} were used. The membrane showed a rejection of 38.9 % for NaCl at 100 mg/L concentration, but with increasing concentration, the rejection decreased to 15.2 % (500 mg/L). The NaNO_3 showed rejections of about 48.6% at a concentration of 100 mg/L. The Na_3PO_4 was experienced higher rejection of 77.85% compare to the NaCl and NaNO_3 . The sulfate based salts, such as Na_2SO_4 and K_2SO_4 showed the highest rejection (> 91%) at 100 mg/L, compare to the other studied salts. The charge effect of the cations was also studied; monovalent Na^+ based salts showed higher rejection (NaCl; 38.9%, and Na_2SO_4 ; 91%) compare to the divalent Mg^{2+} based salts (MgCl_2 ; 21.02% and MgSO_4 ; 52.34%). The several factors of the CTP membrane plays a crucial role in the rejection;

The CTP membrane possesses negative zeta potential in the studied salts solution (pH 6-7). The negative charge, uniform narrow pores, and high porosity of the CTP membrane play the vital role in the rejection.[51] The small monovalent anions like Cl^- and NO_3^- showed lower rejection

Fig. 7. The plot of salt rejection of the porous CTP membrane in aqueous solution of the different salts at various concentrations.

than the multivalent anions such as SO_4^{2-} and PO_4^{3-} . This is because PO_4^{3-} and SO_4^{2-} are the larger size and greater negative charge, and thus experienced more repulsion from the CPT membrane. Hence, restricted for passing through the narrow pores.[50, 51] The support PAN membrane itself showed little rejection due to the large pores (50-70 nm) which allowed to easy pass of the anions. Fig. 8d schematically shows that the CTP membrane restricted to pass the salts, while it allowed the water molecules to pass. The observed trend of the rejection of the anions as follows; $\text{Cl}^- < \text{NO}_3^- < \text{PO}_4^{3-} < \text{SO}_4^{2-}$ and order of the rejection for the different cations

Table 1: Salt rejection and Flux of the CTP membrane.

Entry	Salts	Rejection (%)	Flux ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)
1	NaCl	38.9	9.1
2	NaNO ₃	48.6	8.2
3	Na ₃ PO ₄	77.9	7.8
4	Na ₂ SO ₄	91.3	10.8
5	MgCl ₂	21.0	8.1
6	MgSO ₄	52.4	8.1
7	K ₂ SO ₄	89.9	8.25

based on the same anions; $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$. The cations with greater positive charge attracted more towards the membrane and formed a skin layer on the CTP membrane which preferably allows passing anion, and thus reduced the rejection.[51, 52] Again, increasing concentration of the salts solution favor to form screen layer on the membrane and reduced rejection was expected.[51, 52] The CTP membrane retained high flux of 7.76 - 10.82 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, because of the high porosity, and assembly of thin-films skin layer.

The dyes rejection performance and flux of the porous CTP membrane are given in Fig. 9 and Table 2. The CTP membrane attached to the PAN support was employed for the dye rejection study. The PAN support membrane showed low methyl orange rejection of 17.7% in water, whereas a marginal increase of rejection to 20% in methanol was observed. The CTP membrane showed methyl orange rejection of 42% in water with a little increase of rejection of 47.1% in

Fig.8. Photographic images (a) free-standing CTP membrane; (b) transferred to a wire loop; (c) dyes rejection results as given from the left side; Reactive Black 5 in water (retentate (ia), permeate(ib)), (ii) Reactive Black 5 in methanol (retentate (iia), permeate (iib)), (iii) Naphthalene Blue Black (retentate (iia), permeate (iib)), (iv) Methyl Orange (retentate (iva), permeate (ivb)) and scheme for the nanofiltration for dyes and salts in the CTP membrane.

methanol. The CTP membrane showed excellent rejection of the reactive black 5 and naphthalene blue black in the water and methanol solutions, more than 97%, and 84%, respectively (Fig. 9 and Table 2). Furthermore, the rejection performance of the CTP membrane at higher dye concentration (20 ppm) showed almost similar results as shown in Table S1 (Supplementary Information). The membrane showed rejection vary from 97% to 98% at 20 ppm concentration in both solvents, methanol, and water (Supplementary Information). The CTP membrane comprised a rough and crumpled structure. So, CTP membrane layer has some sort of defects which effects the rejection performances. This is the possible reason behind from the complete rejection of dye molecules. The photographic images of the feed, retentate, and

Fig. 9. The plot of different dyes rejection of the CTP membrane (a) Reactive Black 5 in water, (b) Reactive Black 5 in methanol, (c) Naphthalene Blue Black in methanol and (d) Methyl Orange in methanol.

permeate of the different dyes have been shown in Fig. 8c. The support PAN has the high water flux of $150 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, but the CTP membrane attached to the PAN showed a decreased flux of $7.5\text{--}11.3 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. The decrease of flux of the CTP membrane due to the presence of narrow pores, and assembly of the skin layer on the PAN support. The selected dyes, such as methyl orange, reactive black 5, and naphthalene blue black are negatively charged. In the operative

Table 2: Dyes rejection performances of the CTP membrane

Membrane	Dyes and Molecular Weight (MW: gmol^{-1})	Solvents	Flux ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Rejection (%)
PAN	Methyl orange (MO: 327)	Water	150	17.7
CTP/PAN Support	Methyl orange (MO: 327)	Water	9.49	42.0
CTP/PAN Support	Reactive black-5 (RB-5: 992)	Water	7.45	96.1
CTP/PAN Support	Naphthalene blue black (NBB: 616)	Water	8.23	84.0
CTP/PAN Support	Methyl orange (MO: 327)	Methanol	11.23	47.1
CTP/PAN Support	Reactive black-5 (RB-5: 992)	Methanol	10.56	96.7
CTP/PAN Support	Naphthalene blue black (NBB: 616)	Methanol	10.34	83.0

condition of the dyes rejection, the membrane acts as negatively charged due to the neutral pH of the dyes solution. Thus, all dyes experienced repulsion from the CTP membrane, and narrow pores topology also restricted the passing of the dyes. The PAN membrane although negatively charges but it showed little rejection because dye molecules simply pass through the large pores (50-70 nm). The CTP membrane showed long-term solvent durability and as for demonstration, we used water and methanol as the solvent as shown in Figure S2 (Supplementary Information).

Table 3: Comparison of rejections of dye molecules of different types of membranes reported in the literature with synthesized CTP membrane.

Membrane	Solvent	Conc ⁿ (ppm)	Dyes	Flux	Rejection (%)	Ref.
TFC on PA/Cellulose	DMF	35	Amino black	1.4	92	[53]
TFC/Cross-linked PAN	DMF	35	Rose Bengal	0.75	95	[10]
TFC/Cross-linked PAN	DMF	35	Methyl Orange	1.70	30	[10]
MPD-10%-MPD-0.1% (Alumina Support)	Methanol	20	Napthalene brown	2.34- 52.00	95.5- 99.9	[7]
MPD-10%-MPD-0.1% (Alumina Support)	Methanol	20	Acid Fuchsin	2.05- 51.84	96.2- 99.9	[7]
MPD-4%-MPD-0.1% (XP84 Support)	Methanol	20	Napthalene brown	3.87- 18.62	98.1- 99.9	[7]
PIP-0.1% (XP84 Support)	Methanol	20	Napthalene brown	1.27	98.2	[7]
TA/CuII 10 modified PAN	Water	10	Methyl Orange	52	65	[54]
TA/CuII 10 modified PAN	Water	10	Protoporphyrin IX disodium salt	52	97	[54]
TFPDHF-2D COF	Methanol	10	Amino Black	40	20	[55]
TFPDHF-2D COF	Methanol	10	Reactive Black	40	90	[55]
TFPDHF-2D COF	Methanol	10	Reactive Green	46	99.4	[55]
PAN – Pebax® 1657 1% 3 min 2% TDI	I-propanol	5	Brilliant blue	0.1	95±3	[56]
XPAN – Pebax® 1657 1% 3 min 2% TDI	DMF	10	Brilliant blue	1.0	95±5	[56]
PAN-H/PPy IPA (7.5%)	THF-DMF	70	Rose Bengal	0.03- 4.11	71-99	[57]
CTP/PAN Support	Methanol	10	Reactive black-5	10.56	97	This work
CTP/PAN Support	Water	10	Reactive black-5	7.45	96	This work
CTP/PAN Support	Methanol	20	Reactive black-5	9.75	98	This work
CTP/PAN Support	Water	20	Reactive black-5	7.06	98	This work

The CTP membrane showed higher flux for the methanol compared to the water due to lower viscosity of the methanol than the water. The separation performance of the CTP membrane was studied using different dye molecules with different molecular weights and sizes. The resultant rejections of the dye molecules based on the molecular weight in two different solvents methanol and water as shown in Figure S1 (supplementary information). The membrane showed almost similar results in both solvents (water and methanol). A S-shaped rejection graph with molecular weight was obtained thereby indicating that the rejections of the dye molecules due to the size exclusion and/or electrostatic repulsion. The molecular-weight-cutoff (MWCO) of the membrane was found to be 992 gmoI⁻¹.

Table 3 lists comparative results of the separation performances of the studied membrane with the reported membrane in the literature.[7, 10, 53-57] The comparison table showed that different concentration of dyes solution was used to study the membrane separation performances. The varieties of the concentration of the dyes solution were selected due to the solubility and agglomeration issue of the dyes in different solvents. However, our CTP membrane showed comparable rejection performances compared to the wide variety of reported membrane in the literature.

4. Conclusions

We have designed and synthesized novel porous covalent organic triazine-piperazine based thin film membrane from the commercially available relatively inexpensive starting materials. The membrane skin layer has been developed on top of the PAN support. The instability of the interface due to the rise of local temperature during first-rate interfacial polymerization reaction of the monomers created the crumple skin layer. Covalent linking of the monomers and extended networks generated the microporosity. The structure formation has been investigated and supported by use of different techniques. The porous and thinfilm nature of the CTP membrane provided the large surface area, and covalent bonding offers well-defined pore topology with excellent solvent stability and robustness. The NF property of the membrane has been evaluated based on the selective dyes and salts rejection experiment. The high porosity, well-defined pore

topology, and of the CTP membrane facilitates to deserve excellent separation performances, thereby making it a promising candidate in the NF applications. This strategy may be useful to develop other porous COPs NF membranes varying the support and monomers.

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References

- [1] J. Luo, Y. Wan, Effects of pH and salt on nanofiltration—a critical review, *J. Membr. Sci.*, 438 (2013) 18-28.
- [2] 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.
- [3] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, 83 (1993) 81-150.
- [4] P. Silva, L. Peeva, A. Livingston, Nanofiltration in organic solvents, *Adv. Membr. Technol. Appl.*, (2008) 451-467.
- [5] B. Yuan, X. Wu, Y. Chen, J. Huang, H. Luo, S. Deng, Adsorption of CO₂, CH₄, and N₂ on ordered mesoporous carbon: approach for greenhouse gases capture and biogas upgrading, *Environ. Sci. Technol.*, 47 (2013) 5474-5480.
- [6] A. Zhang, R. Ma, Y. Xie, B. Xu, S. Xia, N. Gao, Preparation polyamide nanofiltration membrane by interfacial polymerization, *Desalin. Water Treat.*, 37 (2012) 238-243.
- [7] S. Karan, Z. Jiang, A.G. Livingston, Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation, *Science*, 348 (2015) 1347-1351.
- [8] X. Li, Y. Cao, H. Yu, G. Kang, X. Jie, Z. Liu, Q. Yuan, A novel composite nanofiltration membrane prepared with PHGH and TMC by interfacial polymerization, *J. Membr. Sci.*, 466 (2014) 82-91.
- [9] J. Zhao, Y. Su, X. He, X. Zhao, Y. Li, R. Zhang, Z. Jiang, Dopamine composite nanofiltration membranes prepared by self-polymerization and interfacial polymerization, *J. Membr. Sci.*, 465 (2014) 41-48.

- [10] L. Pérez-Manríquez, J. Aburabi'e, P. Neelakanda, K.-V. Peinemann, Cross-linked PAN-based thin-film composite membranes for non-aqueous nanofiltration, *React. Funct. Polym.*, 86 (2015) 243-247.
- [11] L. Pérez-Manríquez, A.R. Behzad, K.V. Peinemann, Sub-6 nm Thin Cross-Linked Dopamine Films with High Pressure Stability for Organic Solvent Nanofiltration, *Macromol. Mater. Eng.*, (2016).
- [12] B. Tang, C. Zou, P. Wu, Study on a novel polyester composite nanofiltration membrane by interfacial polymerization. II. The role of lithium bromide in the performance and formation of composite membrane, *J. Membr. Sci.*, 365 (2010) 276-285.
- [13] W.J. Lau, A.F. Ismail, N. Misdan, M.A. Kassim, A recent progress in thin film composite membrane: a review, *Desalination*, 287 (2012) 190-199.
- [14] K.P. Lee, G. Bargeman, R. de Rooij, A.J. Kemperman, N.E. Benes, Interfacial polymerization of cyanuric chloride and monomeric amines: pH resistant thin film composite polyamine nanofiltration membranes, *J. Membr. Sci.*, 523 (2017) 487-496.
- [15] N. Saha, S. Joshi, Performance evaluation of thin film composite polyamide nanofiltration membrane with variation in monomer type, *J. Membr. Sci.*, 342 (2009) 60-69.
- [16] P. Buch, D.J. Mohan, A. Reddy, Preparation, characterization and chlorine stability of aromatic-cycloaliphatic polyamide thin film composite membranes, *J. Membr. Sci.*, 309 (2008) 36-44.
- [17] W. Lihong, L. Deling, L. Cheng, L. Zhang, C. Huanlin, Preparation of thin film composite nanofiltration membrane by interfacial polymerization with 3, 5-diaminobenzoylpiperazine and trimesoyl chloride, *Chin. J. Chem. Eng.*, 19 (2011) 262-266.
- [18] L. Li, S. Zhang, X. Zhang, G. Zheng, Polyamide thin film composite membranes prepared from isomeric biphenyl tetraacyl chloride and m-phenylenediamine, *J. Membr. Sci.*, 315 (2008) 20-27.
- [19] C. Yao, R. Burford, A. Fane, C. Fell, R. McDonogh, Hydrolysis and other phenomena affecting structure and performance of polyamide 6 membrane, *J. Appl. Polym. Sci.*, 34 (1987) 2399-2408.
- [20] K.P. Lee, J. Zheng, G. Bargeman, A.J. Kemperman, N.E. Benes, pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation, *J. Membr. Sci.*, 478 (2015) 75-84.
- [21] D. Hu, Z.-L. Xu, C. Chen, Polypiperazine-amide nanofiltration membrane containing silica nanoparticles prepared by interfacial polymerization, *Desalination*, 301 (2012) 75-81.
- [22] Q. Wang, G.-s. Zhang, Z.-s. Li, S. Deng, H. Chen, P. Wang, Preparation and properties of polyamide/titania composite nanofiltration membrane by interfacial polymerization, *Desalination*, 352 (2014) 38-44.

- [23] H.S. Lee, S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film nanofiltration membranes containing TiO₂ nanoparticles, *Desalination*, 219 (2008) 48-56.
- [24] S. Kandambeth, B.P. Biswal, H.D. Chaudhari, K.C. Rout, H. Kunjattu, S. Mitra, S. Karak, A. Das, R. Mukherjee, U.K. Kharul, Selective Molecular Sieving in Self-Standing Porous Covalent-Organic-Framework Membranes, *Adv. Mater.*, (2016).
- [25] H. Zhao, Z. Jin, H. Su, X. Jing, F. Sun, G. Zhu, Targeted synthesis of a 2D ordered porous organic framework for drug release, *Chem. Commun.*, 47 (2011) 6389-6391.
- [26] H.A. Patel, F. Karadas, A. Canlier, J. Park, E. Deniz, Y. Jung, M. Atilhan, C.T. Yavuz, High capacity carbon dioxide adsorption by inexpensive covalent organic polymers, *J. Mater. Chem.*, 22 (2012) 8431-8437.
- [27] S.K. Das, X. Wang, M.M. Ostwal, Y. Zhao, Y. Han, Z. Lai, Highly stable porous covalent triazine–piperazine linked nanoflower as a feasible adsorbent for flue gas CO₂ capture, *Chem. Eng. Sci.*, 145 (2016) 21-30.
- [28] P. De Hoog, P. Gamez, W.L. Driessen, J. Reedijk, New polydentate and polynucleating N-donor ligands from amines and 2, 4, 6-trichloro-1, 3, 5-triazine, *Tetrahedron Lett.*, 43 (2002) 6783-6786.
- [29] A. Chouai, E.E. Simanek, Kilogram-scale synthesis of a second-generation dendrimer based on 1, 3, 5-triazine using green and industrially compatible methods with a single chromatographic step, *J. Org. Chem.*, 73 (2008) 2357-2366.
- [30] A. Szymczyk, P. Fievet, M. Mullet, J. Reggiani, J. Pagetti, Comparison of two electrokinetic methods—electroosmosis and streaming potential—to determine the zeta-potential of plane ceramic membranes, *J. Membr. Sci.*, 143 (1998) 189-195.
- [31] R.J. Hunter, *Zeta potential in colloid science: principles and applications*, Academic press, 2013.
- [32] H.A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan, C.T. Yavuz, Highly Stable Nanoporous Sulfur-Bridged Covalent Organic Polymers for Carbon Dioxide Removal, *Adv. Funct. Mater.*, 23 (2013) 2270-2276.
- [33] J. Wang, Z. Yue, J.S. Ince, J. Economy, Preparation of nanofiltration membranes from polyacrylonitrile ultrafiltration membranes, *J. Membr. Sci.*, 286 (2006) 333-341.
- [34] M. Kumar, R. Shevate, R. Hilke, K.-V. Peinemann, Novel adsorptive ultrafiltration membranes derived from polyvinyltetrazole-co-polyacrylonitrile for Cu (II) ions removal, *Chem. Eng. J.*, 301 (2016) 306-314.
- [35] V. Freger, Nanoscale heterogeneity of polyamide membranes formed by interfacial polymerization, *Langmuir*, 19 (2003) 4791-4797.
- [36] W. Xie, G.M. Geise, B.D. Freeman, H.-S. Lee, G. Byun, J.E. McGrath, Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and a new disulfonated diamine, *J. Membr. Sci.*, 403 (2012) 152-161.

- [37] L.J. Kirschenbaum, B. Ruekberg, A Correlation of the Solubility of Water in Hydrocarbons as a Function of Temperature Based on the Corresponding Vapor Pressure of Pure Water, *Chem. Sci.*, (2013) 1-9.
- [38] S.J. Vanhook, M.F. Schatz, J. Swift, W. McCormick, H.L. Swinney, Long-wavelength surface-tension-driven Bénard convection: experiment and theory, *J. Fluid Mech.*, 345 (1997) 45-78.
- [39] P.B. Balbuena, K.E. Gubbins, Theoretical interpretation of adsorption behavior of simple fluids in slit pores, in: *Langmuir*, 1993, pp. 1801-1814.
- [40] S.K. Das, M.K. Bhunia, M.M. Seikh, S. Dutta, A. Bhaumik, Highly porous Co (II)-salicylate metal-organic framework: synthesis, characterization and magnetic properties, *Dalton Trans.*, 40 (2011) 2932-2939.
- [41] J. Coates, Interpretation of infrared spectra, a practical approach, *Encyclopedia of analytical chemistry*, (2006) 1-23.
- [42] M.G. Schwab, B. Fassbender, H.W. Spiess, A. Thomas, X. Feng, K. Mullen, Catalyst-free preparation of melamine-based microporous polymer networks through Schiff base chemistry, *J. Am. Chem. Soc.*, 131 (2009) 7216-7217.
- [43] B.V. Lotsch, M. Döblinger, J. Sehnert, L. Seyfarth, J. Senker, O. Oeckler, W. Schnick, Unmasking Melon by a Complementary Approach Employing Electron Diffraction, Solid-State NMR Spectroscopy, and Theoretical Calculations—Structural Characterization of a Carbon Nitride Polymer, *Chem. Eur. J.*, 13 (2007) 4969-4980.
- [44] M.K. Bhunia, S.K. Das, P. Pachfule, R. Banerjee, A. Bhaumik, Nitrogen-rich porous covalent imine network (CIN) material as an efficient catalytic support for C–C coupling reactions, *Dalton Trans.*, 41 (2012) 1304-1311.
- [45] S. Yoo, J.D. Lunn, S. Gonzalez, J.A. Ristic, E.E. Simanek, D.F. Shantz, Engineering nanospaces: OMS/dendrimer hybrids possessing controllable chemistry and porosity, *Chem. Mater.*, 18 (2006) 2935-2942.
- [46] L.-L. Lai, H.-C. Hsu, S.-J. Hsu, K.-L. Cheng, A Convenient Synthesis of Triazine-Based Dendrons and Dendrimers via a Convergent Approach and a Study of Their Interactions with Tetrafluorobenzoquinone, *Synthesis*, 2010 (2010) 3576-3582.
- [47] M. Mänttari, A. Pihlajamäki, M. Nyström, Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH, *J. Membr. Sci.*, 280 (2006) 311-320.
- [48] D. Musale, A. Kumar, G. Pleizier, Formation and characterization of poly (acrylonitrile)/chitosan composite ultrafiltration membranes, *J. Membr. Sci.*, 154 (1999) 163-173.
- [49] T. Jimbo, M. Higa, N. Minoura, A. Tanioka, Surface characterization of poly (acrylonitrile) membranes graft-polymerized with ionic monomers as revealed by ζ potential measurement, *Macromolecules*, 31 (1998) 1277-1284.

- [50] S. Verissimo, K.-V. Peinemann, J. Bordado, Influence of the diamine structure on the nanofiltration performance, surface morphology and surface charge of the composite polyamide membranes, *J. Membr. Sci.*, 279 (2006) 266-275.
- [51] G.T. Ballet, A. Hafiane, M. Dhahbi, Influence of operating conditions on the retention of phosphate in water by nanofiltration, *J. Membr. Sci.*, 290 (2007) 164-172.
- [52] G.T. Ballet, L. Gzara, A. Hafiane, M. Dhahbi, Transport coefficients and cadmium salt rejection in nanofiltration membrane, *Desalination*, 167 (2004) 369-376.
- [53] M.H. Abdellah, L. Pérez-Manríquez, T. Puspasari, C.A. Scholes, S.E. Kentish, K.-V. Peinemann, A catechin/cellulose composite membrane for organic solvent nanofiltration, *J. Membr. Sci.*, 567 (2018) 139-145.
- [54] T. Chakrabarty, L. Pérez-Manríquez, P. Neelakanda, K.-V. Peinemann, Bioinspired tannic acid-copper complexes as selective coating for nanofiltration membranes, *Sep. Purif. Technol.*, 184 (2017) 188-194.
- [55] D.B. Shinde, G. Sheng, X. Li, M. Ostwal, A.-H. Emwas, K.-W. Huang, Z. Lai, Crystalline 2D Covalent Organic Framework Membranes for High-Flux Organic Solvent Nanofiltration, *J. Am. Chem. Soc.*, 140 (2018) 14342-14349.
- [56] J. Aburabie, K.-V. Peinemann, Crosslinked poly (ether block amide) composite membranes for organic solvent nanofiltration applications, *J. Membr. Sci.*, 523 (2017) 264-272.
- [57] X. Li, P. Vandezande, I.F. Vankelecom, Polypyrrole modified solvent resistant nanofiltration membranes, *J. Membr. Sci.*, 320 (2008) 143-150.

GRAPHICAL ABSTRACT

Solvent-resistant Triazine-Piperazine Linked Porous Covalent Organic Polymer Thin-film Nanofiltration Membrane

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Highlights

- Porous covalent triazine-piperazine based nanofiltration membrane was prepared.
- Membrane skin layer was grown on the top of PAN through the interfacial polymerization.
- Membrane was resistant to a wide range of solvents; DMF, DMSO, and NMP.
- The NF properties were evaluated by the dye rejection and salt rejection experiments.