Finely Tuned Submicroporous Thin-Film Molecular Sieve Membranes for Highly Efficient Fluid Separations

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Polymeric membranes with increasingly high permselective performances are gaining a significant role in lowering the energy burden and improving the environmental sustainability of complex chemical separations. However, commercial deployment of newly designed materials with promising intrinsic properties for fluid separations has been stalled by challenges associated with fabrication and scale up of low-cost, high performance *defect-free* thin-film composite (TFC) membranes. Here, a facile method to fabricate the next generation TFC membranes using a bridged-bicyclic triptycene tetra-acyl chloride (Trip) building block with a large fraction of finely tuned structural *submicroporosity* (pore size < 4 Å) is demonstrated. The TFCs exhibit superb potential for removal of small (~ 200 g mol⁻¹) organic micro-contaminants from organic solvent streams by showing both improved rejection and permeance in organic systems compared to current state-of-the-art commercial membranes. The TFCs also display unprecedented properties for desalination applications with performance located far above the current water permeance/sodium chloride rejection trendline. The strategy of using highly

contorted triptycene building blocks with well-defined interconnected internal free volume elements establishes a scalable, generalized approach to fabricate highly selective, submicroporous TFC membranes for a wide variety of challenging energy-intensive fluid separations.

Current large-scale unit operation processes for fluid separations are primarily based on thermal principles and account for ~10-15% of the world's total energy consumption.^[1] This massive energy penalty for purification of liquid and gaseous feed stocks provides a high impact opportunity for alternative processes. Membrane technology is emerging as one of the most promising energy efficient separation processes in the chemical separation industry. Its continued growth can be attributed to lower energy requirements translating to lower capital and operating cost as well as significantly reduced environmental impact compared to conventional thermal separation processes. Additionally, membrane technology offers the advantages of continuous process operation, modular design, and small system footprint and is predicted to be a main contributor to global energy- and carbon-reduction initiatives in the coming decades.^[2]

In 2008, the global membrane market was valued at ~12 billion USD with a compound annual growth rate (CAGR) of ~10%.^[3] Reverse osmosis (RO) and nanofiltration (NF) membranes contribute significantly to the total global membrane sales with the majority of products comprising of variations of thin-film composite (TFC) membranes made by interfacial polymerization. Such highly crosslinked aromatic submicroporous (*i.e.*, pore size < 4 Å)^[4] polyamide TFC membranes — pioneered by John Cadotte — revolutionized the desalination industry due to their unprecedented combination of high water flux and salt rejection.^[5–8] Surprisingly, despite their immense commercial success for *aqueous* RO and NF applications, the IP membrane formation process has not been implemented in other large-scale fluid separation processes, especially organic solvent nanofiltration (OSN) and gas separations.^[9–11] Polymers of intrinsic microporosity (PIMs) are an emerging group of solution processible amorphous microporous materials (pore size < 20 Å) gaining significant attention in membrane-based separations due to their ability to transcend the conventional permeability/selectivity trade-off relationships.^[12–15] Such materials exhibit exceptionally high free volumes as a result of inefficient chain packing by architectural designs using highly rigid and contorted

spirobisindane-, triptycene-, ethanoanthracene-, and Tröger's base-building blocks.^[13,16–21] To date, technical challenges associated with fabricating defect-free, inexpensive, thin-film composite membranes as well as the inability to achieve low molecular weight cut-offs (MWCOs) have severely limited the industrial use of PIM-based and similar membrane materials. For example, Cook et al. demonstrated successful dip-coating of several ladder polymers (PIM-1, PIM-7, PIM-8) on crosslinked polyetherimide (Ultem 1000) and polyacrylonitrile porous supports with thicknesses of $\sim 100 - 300$ nm.^[22] The membranes showed reasonable solvent permeances (PIM-1 displayed methanol permeance of 2.5 LMH/bar) but suffered from moderate solute rejections translating to high MWCOs in the range of 500–800 g mol⁻¹ for OSN applications. For small solutes such as 300 g mol⁻¹ polystyrene, PIM-1 exhibited only a rejection of < 5% in methanol.

Thin-film fabrication using in-situ interfacial polymerization (IP) offers a promising alternative method to produce highly crosslinked, reproducible, ultrathin PIM-derived membranes employing an industrially scalable, low-cost, roll-to-roll process.^[8,23–26] Early reports demonstrated that IP-based *polyarylate* TFCs can be successfully produced from PIM-motifs, e.g. spirobisindane-derived biscatechol sodium salts reacted with trimesoylchloride (TMC) proposed for use in OSN.^[27] Similar to the work reported for dip-coated ladder PIMs^[22], the resulting membranes demonstrated high organic solvent permeances due to their microporous texture but exhibited only moderate organic solute rejections (*i.e.*, moderate solute cut-off), thereby limiting their potential for commercial OSN applications. Interestingly, water permeance and salt rejection properties of the polyarylate-based TFCs have not been reported to date.

Triptycene, a member of the iptycene family, has been established as a remarkable PIM building block for ladder PIMs and PIM-polyimides (PIM-PIs) as gas separation membrane materials owing to its rigid and 3D paddlewheel-like structure with uniformly structured internal fractional free volume (IFV), making it an excellent candidate monomer material to synthesize

TFCs by IP.^[16,28–34] Ren et al.^[33] reported semi-aromatic co-polyamide membranes of triptycene hexaacyl chloride (TPA) and TMC reacted with piperazine (PIP) by interfacial polymerization for RO and OSN applications. An increase in the content of the triptycene moiety in the co-polymer boosted water permeance but also resulted in unacceptable loss in salt and organic solute rejections. For example, a membrane made from 80% TPA and 20% TMC reacted with PIP (TPA-80) exhibited poor NaCl and MgSO₄ rejections of 10.5 and 38.5%, respectively.

Figure 1. Characterization of interfacially polymerized polymers. (a) Reaction scheme for the synthesis of crosslinked aromatic polyamide using MPD and triptycene-1,3,6,8-tetraacetyl chloride (Trip) monomers with internal free volume (IFV) trapped within chain repeat units, (b) MPDTMC and, (c) MPDTrip energy-minimized amorphous cells. The Connolly surface area of MPDTMC is estimated as 1900 Å² and that of MPDTrip as 4700 Å² with MPDTrip exhibiting improved IFV interconnectivity. Grey/blue isosurfaces represent the accessible free volume at a probe radius of 1 Å, (d) sorption behavior using CO₂ BET measurements at 273 K up to 1 bar for MPDTMC and MPDTrip powders. Inset denotes pore size distributions for MPDTMC and MPDTrip powders obtained from CO₂ isotherms at 273 K employing the non-local density functional theory (NLDFT), (e) XRD spectra of MPDTMC and MPDTrip powders with average d-spacing obtained using Bragg's law.

Herein, we report the successful fabrication of highly permeable *and* selective interfacially polymerized *fully aromatic polyamide* thin-film composite membranes using a novel bridged-bicyclic triptycene-based tetra-acetyl chloride (Trip) PIM-type building block with *m*-phenylene diamine (MPD). The TFC membranes showed exceptional performance with potential for a wide range of energy intensive fluid separations, including brackish water RO, organic NF and H₂/CO₂ gas separation. The superb performance of the newly developed membranes resulted from the dominant fraction of finely tuned *submicropores* (average pores < 4 Å) in the selective, strongly hydrogen-bonded polyamide layer.

Figure 1a shows the reaction scheme of the triptycene-1,3,6,8-tetraacetyl chloride (Trip) monomer with MPD to fabricate a fully aromatic, highly crosslinked network polyamide (polyaramid). The 3D structure of the triptycene moiety, comprising of a [2,2,2]-tricyclic ring system with three benzene groups fused at 120°, entraps permanent intramolecular free volume (IFV) when compared to the traditional commercially used planar trimesoyl chloride moiety. Molecular dynamics simulations (**Figure 1b and 1c**) demonstrated that the substitution of the TMC with the sterically hindered triptycene moiety permitted a significant increase of the polymer fractional free volume (from ~14 to 24%) and higher interconnectivity between the free volume units. Accessible surface area and pore size distributions of MPDTMC and MPDTrip polymer powders were probed using CO₂ sorption at 273 K which displayed about two-fold increase in accessible surface area (from 49 to 92 m² g⁻¹) for MPDTrip (**Figure 1d**) while maintaining a dominant fraction of submicropores (**Figure S6a-b**). Isosteric heat of

adsorption (**Figure S6d**) displayed minimal variation (approximately between 30-40 kJ mol⁻¹) between the two systems. This confirmed the improvement of the accessible surface area in MPDTrip resulted from the geometry of the triptycene building block rather than its improved interaction with the acidic and quadrupolar CO₂ gas.^[35,36] However, it is important to note that the accessible surface areas obtained here using both bulk network polyamides were significantly lower than the surface areas of linear and network PIMs previously reported.^[15,37] Classical polymers of intrinsic microporosity with BET surface areas (calculated using N₂ sorption isotherms) of ~ 800 m² g⁻¹, such as PIM-1 and KAUST-PI-1, contain a bimodal pore size distribution containing a large fraction of micropores (~7–20 Å) with embedded ultramicropores (< 7 Å).^[38] Here, both materials displayed BET surface areas of < 50 m² g⁻¹ obtained from N₂ adsorption isotherms at 77 K (**Figures S7**). **Figure 1e** compares the XRD spectra of these two highly microporous PIMs with MPDTRIP and MPDTMC — both MPD-based polymers show an amorphous structure as indicated by their broad diffraction spectra. Furthermore, the average chain d-spacing (calculated by Bragg's law) indicates submicroporous structural characteristics for both MPDTrip (d = 3.90 Å) and MPDTMC (d = 3.6 Å), whereas traditional microporous polymers, PIM-1 and KAUST-PI-1, display main d-spacings of 9.8 and 8.3 Å, respectively, with much smaller shoulder values around 4.0 and 5.3 Å. This *qualitative* trend was supported by calculated pore size distributions based on non-local density functional theory (NLDFT) applied to CO₂ adsorption at 273 K which also indicated pores of < 4 Å in the MPDTrip and MPDTMC polyamides (**Figure S6a-b**). Based on this analysis, MPDTrip *cannot* be classified as a typical high BET surface area polymer of intrinsic microporosity. However, the sterically contorted Trip building block in MPDTrip induced enhanced free volume with finely tuned, slightly increased submicropore size (3.9 Å) compared to its more conventional counterpart MPDTMC (3.6 Å), resulting in significantly boosted liquid permeances while maintaining excellent solute rejections, as discussed below. Thermogravimetric analysis of MPDTrip powder (**Figure S8**) demonstrated excellent thermal

stability up to 300 °C, comparable to aromatic MPDTMC polyamide, implying potential to develop high-performance TFC membranes with chemical and thermal stability for high-temperature applications.

Table S1 summarizes the conditions for membrane preparation and their physical properties discussed in this work. All membrane types were characterized by FTIR spectroscopy (**Figure S9**) to confirm the formation of polyamide layers.

Figure 2. Imaging of interfacially polymerized TFC membranes. (a) Cross-section SEM image of a defect-free MPD Trip-100 membrane highlighting structural features, (b) high magnification SEM image of MPD Trip-100 TFC emphasizing the selective layer and support/selective layer interface, (c) SEM top surface images of the TFCs. Samples produced

using an organic solution temperature of 20 °C show two distinct top layer structures as highlighted by insets i-iv, (d) 3D visualizations of the MPDTMC-20 and MPDTrip-20 surfaces using AFM, (e) Ellipsometry images highlighting the variance in surface morphology over larger sample areas, *i.e.*, 4x4 mm for MPDTMC-20 and MPDTrip-20.

Figure 2a and **Figure S11** show a similar ridge-and-valley structure for the MPDTrip TFCs as commonly observed for conventional MPDTMC network polymers.^[39–41] **Figure 2b** displays the loose, highly heterogeneous structure of the top surface of the TFC membranes that is composed of large voids trapped within thin polyamide layers.^[42] Membranes fabricated at 20 °C exhibit partial surface coverage (based on multiple sample images estimated to be less than 5% of the total surface area) by powder-like network polymer features on the top of the ridge-and-valley assemblies (**Figure 2c** sections i-iv), which have been previously observed for membranes made by the IP process and were postulated to have negligible effects on transport properties.^[43–47] On both the micron- (AFM characterization, **Figure 2d**, and **Figure S12-13**) and millimeter scales (*via* ellipsometry, **Figures 2e** and **S14**) MPDTrip-20 displayed higher surface roughness compared to MPDTMC-20 (**Table S2**). Thickness estimations (**Table S3**) using ellipsometry indicated on average *thicker* MPDTrip layers compared to MPDTMC membranes.

Separation of high value solutes and environmentally harmful compounds dissolved in organic media by organic solvent nanofiltration (OSN) is a membrane process with significant industrial potential. However, currently very few membranes are suitable for OSN application due to insufficient solvent permeance and/or solute rejection.^[48,49] In our study, the substitution of TMC with the bulkier, more sterically hindered Trip monomer significantly enhanced water and organic solvent permeance, as shown in **Table S6** (in good qualitative agreement with enhanced submicroporous free volume described above). The replacement of TMC with Trip boosted the water permeance from 3.4 to 9.2 LMH/bar (~170% increase). In a series of aliphatic alcohols, methanol permeance exhibited an increase of 80% from 4.8 to 9.1 LMH/bar and more significant permeance enhancements were observed for ethanol from 1.0 to 2.4 LMH/bar

(~140% increase), and isopropanol permeance even soared from 0.05 to 0.36 LMH/bar (~600% increase). Meanwhile, polar aprotic solvents exhibited even larger permeance enhancements of ~1700% for acetone and methyl ethyl ketone (MEK), and ~2900% for tetrahydrofuran (THF) in MPDTrip TFCs compared to their MPDTMC counterparts (Table S6).

Figure 3. Liquid separation properties of the TFC membranes. (a) Rejection of various dyes through fabricated TFCs in methanol; SO = Sudan Orange ($M_w = 216$ g mol⁻¹); CR = Chrysoidine G ($M_w = 249$ g mol⁻¹); DR = Disperse Red ($M_w = 314$ g mol⁻¹); BB = Brilliant Blue R ($M_w = 826$ g mol⁻¹). Comparative data for microporous TFCs (PAR-TTSBI/PI and PAR-BHPF/PI) obtained from Jimenez-Solomon et al.^[27], (b) rejection of selected solutes through fabricated TFCs in water. Comparative data for microporous TFCs obtained from Kandambeth et al.^[50] (M-TpBD) and Agarwal et al.^[51] (TB-OH and TB-OH CS), (c) permeance of methanol vs. selectivity for small solutes (210 - 320 g mol⁻¹) for state-of-the-art TFCs. Comparative data were obtained from the literature^[27,52–59] with details shown in Table S12, (d) sodium chloride rejection comparison of the MPDTrip-20 TFC membrane fabricated in this study with state-of-the-art desalination membranes. Comparative data were obtained from the literature^[33,60–65] with details listed in Table S14.

At a high relative pressure of 0.95, the water vapor sorption of bulk powders revealed 30% increased water uptake (from 13 to 17.4 mmol g⁻¹) in the MPDTrip polymer compared to MPDTMC, as shown in **Figures S17-S18**. Meanwhile, MPDTrip methanol uptake decreased by 25% (7.7 to 5.8 mmol g⁻¹) compared to MPDTMC. Hence, the 170% and 80% increases for MPDTrip-20 in water and methanol permeance, respectively, were most likely due to enhanced diffusivity of the solvents through the higher free volume MPDTrip membranes.

Both in-house fabricated TFCs demonstrated excellent rejection for small dyes in methanol (as shown in **Figure 3a**) with MWCOs of ~ 200 g mol⁻¹. Substitution of TMC with Trip improved methanol permeance while maintaining high rejection for even the small Sudan Orange G dye (SO - Mw = 216 g mol⁻¹) — for example, MPDTrip-20 showed ~80% increased methanol permeance from 4.8 to 8.7 LMH bar⁻¹ with a high rejection of 99.1 ± 0.6%. Interestingly, the average rejection of MPDTrip-20 for the largest dye in this series, Brilliant Blue R (Mw = 826 g mol⁻¹), was slightly lower (98 ± 1.3%), which could be due to adsorption of some dye on the membrane surface (**Table S7**).

The high dye rejection was sustained when methanol was substituted with ethanol or isopropanol as the solvent phase (**Table S8-S10**). This can potentially be explained by the increased proportion of interconnected size-selective *submicroporous* regions in the MPDTrip polymer (as observed with NLDFT and XRD pore size characterization) which can be finely tuned to improve solvent permeance while maintaining size selectivity. These results are particularly interesting compared to state-of-the-art polyarylate microporous TFC membranes previously reported which exhibit low rejection (<< 90%) for solutes < 300 g mol⁻¹.^[27] An identical high rejection trend was maintained when solute rejection was measured in aqueous systems (**Figure 3b**). Both in-house membranes exhibited excellent and comparable solute rejections (MWCO ~200 g mol⁻¹) with MPDTrip TFCs demonstrating 180% improved water permeance compared to MPDTMC. Comparably, previous attempts to analyze the feasibility of microporous materials for aqueous separations demonstrated improved permeance but coupled

with significant losses in solute rejection and MWCO as shown for Tröger's base PIMs (TB-OH and TB-OH CS) and covalent organic-framework-based membranes (M-TpBD) in **Figure 3b**.^[50,51] The ability to couple high permeance with high rejection truly differentiates the MPDTrip TFCs in this study to previous approaches which resulted in permeance gains with significant rejection losses for liquid separations^[27,50–59] and fills a consistently reiterated need in the chemical industry.^[48,49,66,67]

Filtration performance of MPDTrip-20 TFCs with methanol was further evaluated *via* the permeance/selectivity trade-off (displayed in **Figure 3c**) in comparison to state-of-the-art TFC membranes. Clearly, MPDTrip polyamide membranes *significantly* exceeded the selectivity performance of recently reported ultrathin MPDTMC nanofilms (< 10 nm) synthesized on cadmium hydroxide nanostrands supports while matching their permeance.^[52] Furthermore, MPDTrip-20 TFC showed enhanced permselectivity compared to MOF-integrated TFC polyamides as well as previously fabricated high-free-volume thin-film polyarylates (intended for organic nanofiltration applications) that currently remain the most successful efforts to introduce kinked building blocks in the interfacial polymerization membrane fabrication process.^[27,68]

MPDTrip membranes also displayed excellent stability and separation performance in water/salt separations, specifically for brackish water purification (**Figure 3d**). MPDTrip-20 showed high sodium chloride rejection of ~96% with water permeance of 9.2 LMH/bar. In comparison, commercial Dow Filmtec NF270 nanofiltration and recently fabricated Turing-structured polyamide membranes exhibit similar water permeance of ~10 and ~12.5 LMH/bar, respectively, but with very low sodium chloride rejections of ~30 and ~50%, respectively (**Figure 3d**).^[62,65] As expected for a more size-selective defect-free membrane, MPDTrip demonstrated exceptional permeance/rejection performance for a series of divalent salts, as shown in **Table S13**. Long-term continuous performance over a period of 100 h of MPDTrip

demonstrated excellent stability of water permeance (~ 10 LMH bar⁻¹) and NaCl rejection of 96% (**Figure S23**).

In preliminary studies for potential gas separation applications, MPDTrip-100 TFCs demonstrated 4-fold increase in H₂ permeance (56 vs. 14 GPU) compared to the tighter MPDTMC-100 membrane coupled with a drop in H₂/CO₂ selectivity from ~ 26 to 9 (**Table S15-S16**). However, the MPDTrip-100 TFC membrane displayed about 2-3 times higher H₂ permeance with equivalent selectivity of ~ 9 compared to the best previously reported state-of-the-art hydrogen/carbon dioxide separation membranes (**Table S17**).^[28,69–72] The enhanced performance of crosslinked submicroporous MPDTrip TFC membranes demonstrates the extraordinary potential of applying a triptycene building block combined with interfacial polymerization to fabricate highly selective and permeable polyamide TFC membranes across water, organic solvent, and gas systems.

Experimental Section

Membrane Fabrication: The synthesis and characterization of the novel triptycene-1,3,6,8-tetraacyl chloride (Trip) is described in detail in Section 1.5 of the Supporting Information. Membranes were fabricated using interfacial polymerization with methods similar to ones mentioned elsewhere.^[23,61] Sepro PAN-350 coupons (11.5 x 15.5 cm) were first immersed in tap water for 24 h followed by 1 h in deionized (DI) water. Thereafter, 2 wt vol%⁻¹ of MPD was dissolved in DIW and 0.0038 mol dm⁻³ of organic monomer — trimesoyl chloride (TMC) or triptycene-1,3,6,8-tetraacetyl chloride (Trip) — was dissolved in toluene. The organic solution was heated at the required temperature for 30 min, *i.e.*, 20 °C for liquid separation membranes or 100 °C for gas separation membranes. The porous support was immersed in the aqueous phase for 5 min, followed by passing through a rubber roller. It was then fixed in a Teflon frame, and the organic phase was poured over the top surface. The reaction time was set at 300 s, and then the sample was washed with toluene and *iso*-propanol three times, respectively. Finally,

the membrane was dried at room temperature for 48 h before testing. The sample designation is defined by i) monomer type, e.g., MPDTMC or MPDTrip, and ii) temperature of the organic phase, e.g. "-20" and "-100" for 20 and 100 °C, respectively. Data from at least three samples were collected for all liquid and gas permeation tests.

Permeation experiments: The permeation properties of pure solvent and methanol/dye as well as aqueous PEG feeds (Section 1.2 Supporting Information) were determined using a dead-end filtration system operated at a feed pressure of 15.5 bar. Brackish water flux and salt rejections were measured using a cross-flow system operated at 15.5 bar. The pure-gas permeation properties of the membranes were carried out with a constant pressure/variable volume set-up at a feed and permeate pressure of 7.9 bar and 1 bar, respectively. All experiments were performed at 23 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest: The authors have no financial/commercial Conflict of Interest.

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Table of Contents

ToC text

Novel pressure-driven thin-film composite membranes containing entrapped structural submicroporosity (pore size $< 4 \text{ \AA}$) exhibit superb performance for removal of small solutes from aqueous or organic solutions. The membranes potentially lower the energy burden and improve the environmental sustainability of chemical separations that are currently based on thermal principles and account for $\sim 10\text{-}15\%$ of the world's total energy consumption.

ToC figure

ToC keyword

Submicroporous thin-film composite membrane