Polytriazole membranes with ultrathin tunable selective layer for crude oil fractionation

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Abstract The design of materials and their manufacture into membranes that can handle industrial conditions and separate complex non-aqueous mixtures are challenging. We report a versatile strategy to fabricate polytriazole membranes with 10 nm thin selective layers containing subnanometer channels for the separation of hydrocarbons. The process involves the use of the classical non-solvent induced phase separation method and thermal crosslinking. The membrane selectivity can be tuned to the lower end of the typical nanofiltration range (200 to 1000 g mol⁻¹). The polytriazole membrane can enrich up to 80-95 % of the hydrocarbon content with less than 10 carbon atoms (140 g mol⁻¹). These membranes preferentially separate paraffin over aromatic components, making them suitable for integration in hybrid distillation systems for crude oil fractionation.

One-Sentence Summary: Crosslinked polytriazole nanofiltration polymeric membranes for crude oil fractionation

Separation processes are essential in the chemical, pharmaceutical, and petrochemical industries and are widely used to purify solvents and chemicals, solvent exchange, catalyst recycle and recovery (1). Conventional separation techniques such as distillation, adsorption, evaporation, and extraction are energy-intensive. These separations represent up to 40–70% of both capital and operating costs (2).
Membrane technology is considered sustainable due to its low carbon footprint, small spatial requirements, and a lack of phase transition in most cases. Organic solvent nanofiltration (OSN) could more broadly replace traditional separation processes (3) if better membranes address the requirements of chemical, pharmaceutical, and petrochemical processes (4). For that, the membranes should combine easy processability with stability in a wide range of organic solvents and pH. They should be mechanically and thermally stable to reduce the physical aging since many processes in the chemical, pharmaceutical, and petrochemical separations take place at 60–90 °C or even higher temperature ranges (5-7). Although inorganic materials might have higher thermal and solvent stability, they have limitations, such as high cost, low mechanical properties, and difficult scale-up (8).

Polymeric membranes are less expensive than most inorganic ones, easy to process and integrate in large-scale modules. However, only a few classes of polymeric materials, such as poly(dimethylsiloxane) and polyimide, are being industrially used for nanofiltration of non-aqueous solutions. Polybenzimidazole, poly(ether ether ketone) (PEEK), and polymers with intrinsic microporosity (PIM) are under evaluation (9-11). Swelling effects, when exposed to harsh environments, affect the separation performance in many cases. Recently, a series of PIM-like polymers was reported that show attractive crude oil separations (12). This is a challenging separation and more materials are needed to handle the industrial conditions and successfully separate complex mixtures (13). Overcoming the permeability and selectivity trade-off, particularly in industries like crude oil refining (5, 13) without considerable membrane aging is a difficult task.

We report a simple strategy to fabricate polytriazole asymmetric membranes with ultrathin selective layers by combining the classical non-solvent induced phase separation (NIPS) method and thermal crosslinking. The resulting membranes were tested with highly challenging liquid feeds containing high-boiling polar aprotic solvents used to extract aromatic fractions from refinery streams, and separately tested with one of the most complex mixtures like those present in crude oil. We chose polytriazole with pendant hydroxyl (OH) groups (PTA-OH, Fig. 1A, characterized in Figs. S1-S3(14) as membrane material because it can easily be synthesized in large quantity with good mechanical properties and has a high thermal and thermal-oxidative stability. Additionally, the pendant OH groups make this polymer versatile in terms of crosslinking or modification (14). The membrane formation first involves the dissolution of the polytriazole polymer in the solvents (N-methyl-2-pyrrolidone (NMP) or N,N′-dimethylformamide (DMF)), followed by solution casting and immersion in water. To induce the crosslinking reaction, we simply treated the polytriazole membranes at 300°C for 1h, 2h and 3h, and at 325°C for 1h and 2h, in a furnace under an air environment. The resulting crosslinked membranes are stable in organic solvents, in strong acids (hydrochloric acid 37% (HCl) and sulfuric acid 98% (H2SO4)) and base (sodium hydroxide 2M (NaOH)) (Fig. S4). A PTA (without OH) membrane treated at 325°C for 2h dissolved in tetrahydrofuran, indicating that the the OH functionalization is relevant for the crosslinking reaction.

We propose that the PTA-OH thermal crosslinking leads to the structure depicted in Fig. 1A. To confirm it, we applied Fourier Transform Infrared (FTIR) spectroscopy, high-resolution Solid-State Nuclear Magnetic Resonance (SS-NMR), Dynamic Nuclear Polarization (DNP) coupled with multinuclear 2D (1H, 13C, 17O, 15N) spectroscopy, and Electron Paramagnetic Resonance (EPR) spectroscopy. The spectra are shown in Figs. 1B-D and Figs. S5-S11.
FTIR (Fig. S5) did not show significant change, besides a slight decrease of the broad peak characteristic of OH, indicating that OH remains part of the network. An indication of the crosslinked structure is given by Electron Paramagnetic Resonance (EPR, Fig. S6). While no signal is seen for PTA, the signal characteristic of delocalized electrons for PTA-OH increases as the reaction time for polyoxadiazole to PTA-OH increases. An intenser signal is observed as the membranes are thermally treated, suggesting an increase in carbon conjugation as previously observed in other network forming systems (15). Clearer evidence for the crosslinked structure proposed in Fig. 1 was obtained by SS-NMR and DNP.

The $^{13}$C cross-polarization magic-angle spinning (CP-MAS) for the pristine PTA-OH shows the aromatic carbons (Ar) in the region 129-134 ppm, two peaks at 158 and 154 ppm corresponding to chemical shifts for the C – O bond (labeled $a$) and the carbon in the triazole ring (labeled $b$) respectively and a peak at 115 ppm (labeled $c$) (Fig. S7A). For the crosslinked membrane treated at 325°C for 2h a new peak appeared at 155 ppm (labeled $e$), and additional peaks in the range of 117 - 119 ppm (labeled $e$), which are associated with the formation of the crosslinked network (Fig. S7B). To confirm the findings from CP-MAS data, we used heteronuclear correlation spectroscopy (HETCOR). Fig. 1B compares the 2D $^1$H-$^{13}$C and 2D $^{13}$C-$^{13}$C spectra. We used the 2D $^{13}$C-$^{13}$C mixing with proton-driven spin-diffusion (PDS) and applying phase-alternated-recoupling-irradiation-schemes (PARIS) for 120 ms (CP). This technique provides high resolution and all broad signals can be resolved. In addition to the carbon atoms correlations for the pristine PTA-OH, clear new correlations peaks are presented for the thermally treated membrane at 155, 117, and 119 ppm corresponding to the crosslinked network formation. Moreover, a correlation between carbons participating in the crosslinking and the purely aromatic ones at 129 ppm was detected, indicating that the two carbons are in close physical proximity. A new OH proton was confirmed for the thermally treated membranes by the presence of a new signal at 2.4 ppm in the $^1$H MAS NMR spectrum (Fig. S8A). Additionally, the 2D $^1$H-$^1$H double quantum/single quantum displays an extra correlation outside the diagonal between OH and aromatic protons for the thermally treated membranes (Figs. S8B and S8C).

We distinguished two sets of oxygen coordinations (labeled $O_1$ and $O_2$) for the thermally treated sample demonstrated by $^{17}$O DNP spectroscopy, which offers very high sensitivity, without using isotopically enhanced samples (Fig. 1C Fig. S9). $O_1$ corresponds to uncrosslinked sites and $O_2$ to those crosslinked labeled as 2 in Fig. 1A. We also consider a third possibility labeled 3 in Fig. 1A, but its signal would overlap with the others. The successful acquisition of $^{17}$O DNP allows us to collect the multidimensional correlation spectroscopy. A major challenge for this analysis has been so far the low natural isotopic (NA=0.038%) and quadrupolar nature of $^{17}$O nuclei (I=5/2), which lead to an excessive spectrum line broadening. However, a significant improvement to the application of DNP MAS NMR to $^{17}$O has been possible by using the PRESTO polarization transfer technique combined with quadrupolar a Carr-Purcell-Meiboom-Gill (QCPMG) experiment. This enabled us the detection of $^{17}$O sites. Fig. S10 shows that the $^{17}$O signal of the PTA-OH sample is mostly correlated with OH protons signals, whereas for the thermally treated sample, it is clear that the two different $^{17}$O sites are connected with $^1$H signal of OH and aromatic in agreement with the expected shifts. At the same time, the $^{15}$N CP-MAS and the $^{15}$N-$^1$H CP-MAS HETCOR of the thermally treated membranes reveal a distribution of new signals in the range of 380-390 ppm attributed to the nitrogen atoms named N$_4$, N$_5$ (Fig. 1D Fig. S11).
Fig. S12 indicates that by heating a non previously treated PTA-OH membrane only a slight weight decrease (<4%) is observed in the range of 275 - 400°C. For previously treated samples (325°C for 2h) the weight decrease goes down to 1.5 %. PTA (without OH) membranes do not have any loss in this temperature range. This confirms that any reaction in the 275 - 400°C range should involve the OH groups, however with a very low degree of elimination of OH or other groups. TGA analysis coupled with mass spectrometry (TGA-MS) (Fig. S12C) confirmed the low weight loss in this temperature range and indicated that species being eliminated have a mass corresponding to the size of water molecules.

In summary, the spectroscopic and thermal analysis characterizations support the structure proposed in Fig. 1A.

After the thermal crosslinking, the membranes maintain their flexibility (Fig. S4). Flexibility and minimal plastic deformation are important in pressure-driven membrane applications to ensure that the membrane performance would be maintained for a long time (5, 6). The mechanical properties were quantitatively evaluated by dynamic mechanical analysis. The tensile strength and Young's moduli were measured from stress-strain experiments. All membranes exhibited similar stress-strain behavior, but the crosslinked ones have higher values of stress and Young’s modulus (Fig. S13). The creep recovery measurement indicates how much the membranes would irreversibly deform under pressure (Fig. S13F). The crosslinked membranes have less pronounced creep, implying that they are less susceptible to irreversible deformation (16).

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to investigate the morphology of the membranes before and after crosslinking. We compared the SEM images of PTA-OH membranes prepared by the NIPS process from casting solutions in NMP and DMF. In both cases, the untreated membranes have high pore density, but those prepared with NMP have slightly smaller pores and lower porosity seen in surface (Fig. S14) and cross-sectional images (Fig. 2 and Fig. S15). As a consequence, the water permeance is higher for the membranes prepared with DMF (90 L h m⁻² bar⁻¹) compared with those using NMP (60 L h m⁻² bar⁻¹), while the molecular weight cutoff is 25 kg mol⁻¹ and 10 kg mol⁻¹, respectively. The SEM images reveal that the thermal treatment induces a relaxation of the surface polymer layer, closing the pores, and forming an ultrathin dense layer on the top of the membrane (Fig. 2). This denser layer can be better seen by TEM (Fig. 2E-G, S16 and S17). What appears to be scattered pinholes on the surface can be still identified in the D300-2h membrane (Fig. S14A), but membranes treated at higher temperatures have a defect-free surface. The TEM image of a D300-1h membrane in Fig. S16A shows pores partially closed while the dense layer is being formed. Membranes cast from NMP are pinhole-free even when treated at 300°C. Their dense layer is smoother and thinner. The wavy morphology of the denser layer of membranes cast from DMF originates due to the larger pores of the pristine membranes. Although the polytriazole Tg is above 350°C (Fig. S12D), the polymer chain mobility close to the surface can be higher than in the bulk as reported for other glassy systems (17) and leads to the formation of the dense ultrathin skin closing the pores. The thickness of this layer is not fully homogeneous, being thinner where the pores originally were. Membranes cast from solutions in DMF with higher polymer concentration have a smoother morphology (Fig. S17), since the pores initially formed are also smaller, and less chain reptation is required to form the dense layer. The membrane porosity and smoothness of the formed dense layer depend on the casting solution viscosity, which is higher in NMP than in DMF and increases as the polymer concentration increases (Fig. S18). Fig. 2G shows the nodular
The crosssection SEM images (Fig. 2) reveal a highly porous structure below the ultrathin dense layer, which is retained even after the thermal treatment. Open interconnected pores are also observed between larger cavities (Fig. 2c) facilitating the permeant transport. We assume that the stability of the porous sublayer to collapse is favored by the high glass transition ($T_g$) in the bulk of the polytriazole (above 350°C), due to preexistent $\pi-\pi$ interactions which minimize the rearrangement of the polymer chains during the crosslinking.
The stability of the crosslinked PTA-OH membranes and their morphology constituted by an ultrathin dense layer built on an asymmetric porous structure make them specially attractive for challenging applications in the chemical and petrochemical industry with a perspective of high selectivity aligned to low transport resistance. We first investigated the performance of the membranes for the filtration of solutions in polar (DMF) and apolar (toluene) solvents. This had the objective of confirming that the membrane integrity is maintained in a separation medium frequently used for chemical separations and gave us an overall evaluation of the membrane properties in terms of permeance and selectivity. The ultimate challenge for the membranes was testing them for crude oil fractionation. Fig. S19A shows how the permeance of different solvents varies with the inverse of their viscosity for D300-3h membranes. The linearity indicates that the transport follows Hagen-Poiseuille law and the separation is size-selective. Plots considering Hansen solubility parameters and molecular diameters (Fig. S19C-E), which have fitted well other nanofiltration systems (18) with a stronger solution-diffusion component for the transport, led to a poor correlation. No compaction was observed when testing with DMF, seen by a linear correlation of flux and pressure (Fig. S19E). The DMF permeance through D325-1h membranes remained constant in tests up to 70h (Fig. S20A) and practically recovered the starting permeance values when sequential tests in temperatures up to 90°C and back to 30°C (Fig. S20B) were performed. The rejection of methyl orange (MO) was high and stable (Fig. 20C). The permeances of membranes prepared from casting solutions in NMP and DMF under similar conditions were compared (Fig. S21). The MO size (molecular weight = 327 g mol⁻¹) is close to the membrane molecular weight cut-off (MWCO) measured at 30 and 65°C, with the rejection improving when the crosslinking temperature increases from 300 to 325°C (Fig. S21E, S21F). While the DMF permeance is higher for membranes prepared by casting from solutions in DMF and thermally treated for 1 to 2h, as the crosslinking reaction time increases, to 3h, the differences in performance practically disappear. When the filtration temperature was increased to 90°C, the MWCO of membranes N300-3h increased to 585 g mol⁻¹, the size of acid fuchsin. The increase of permeance of more than 2-fold by increasing the temperature from 30 to 90°C is due to a decrease of DMF viscosity (19) and also to some swelling of membranes crosslinked at milder conditions.

The DMF permeances of N300-3h membranes are at least 20 times higher than the values reported for state-of-the-art integrally asymmetric membranes at high temperature (10, 20) and comparable or even higher than those of the state-of-the-art thin-film composite membranes (Table S1) (10, 12, 21-38).

The membranes were then tested for the filtration of highly apolar systems like hydrocarbon solutions in toluene. The rejection of hexaphenylbenzene (Mw=534.7 g mol⁻¹) by N300-3h membranes is presented in Fig. S22A. Fig. 22B shows the separation of a mixture of three hydrocarbons, methylnaphthalene, 1,3-diisopropylbenzene, and pristane, dissolved in toluene, by a N325-1h. Similar rejection (60%) was obtained for the linear saturated hydrocarbon (268 g mol⁻¹) and the 1,3-diisopropylbenzene (162 g mol⁻¹), while methylnaphthalene (142.2 g mol⁻¹) was concentrated in the permeate side (Fig. 22B). The results indicate the potential of the polytriazole membranes to discriminate among different classes and sizes.

The main goal of this work is the development of membranes for the hydrocarbon fractionation. We then evaluated the performance of the membranes to fractionate dilute crude oil,
a feed closer to the real industrial feedstock. Based on the previous selectivity and permeance results, N300-1h, N300-3h and N325-1h membranes were selected for evaluating their performance in fractionating a 1:40 (volume ratio) solution of Arabian extra light crude oil (39 > API > 30 (American Petroleum Institute gravity)) in toluene. Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) was used as the analytical method for the feed and permeate compositions. Fig. 3 and Fig. S23 show the separation results and the permeances connected to the experiments conducted at 30 and 65°C.

Fig. 3A-C shows the gray spectra of the diluted crude oil feed and the colored permeate spectra corresponding to the permeates of N300-1h, N300-3h, N325-1h, which are clear solutions (Fig. 3D). The spectra maxima corresponding to the fraction with highest abundance shifts from 400 to 350 and 300 g mol⁻¹, indicating that by choosing the right treatment conditions we can tune the properties of the selective layer and the separation. The N325-1h membrane leads to the enrichment of the lowest molecular weight fraction. The permeate has a higher ratio of components with a carbon number between 18 to 25, associated with kerosene fuel. The permeances during crude oil separation are in the range of 1.9 – 2.5 L m⁻² h⁻¹ bar⁻¹ at 30°C, whereas at 65°C, the permeances increase almost 2 fold to 3.3 and 6 L m⁻² h⁻¹ bar⁻¹ (Fig. 3F and S23D). The permeance values are 10 to 300-fold higher than recently reported systems, which show enrichment in the permeate of molecules with a molecular weight around 170 g mol⁻¹ (12). In addition, when we permeated the crude oil mixture for 72h through the membrane, no significant decrease in permeance was observed (Fig. S23D).

We further evaluated the potential of N300-1h membranes for the fractionation of pure Arabian superlight crude oil (50 > API > 39) without prior dilution. The filtration experiments were carried out at 90 °C to 150°C to decrease the oil viscosity and avoid pore blocking. GC-MS was used to analyze the components in the permeates. A standardized C₇-C₄₀ normal-saturated alkanes solution was utilized as reference to roughly correlate the GC retention times with the normal alkanes carbon numbers (Fig. 4 and Fig. S24). Fig. 4B shows the broad size distribution of the crude oil used as feed for the experiments leading to the permeates in Fig. 4A and 4C.

A highly effective enrichment of up to 80-95 % in hydrocarbons with carbon numbers lower than C₁₀ (molecular weight around 140 g mol⁻¹) was detected in the permeate (Fig. 4A), whereas the hydrocarbons between C₁₀-C₁₅ were in the range of 7 - 15%. Molecules with carbon numbers in the range of C₁₅-C₂₀ and higher than C₂₀ were only 4% and less than 1%, respectively.

A comprehensive two dimensional gas chromatography GCxGC data is shown in Fig. S25. These results complement the observations in Fig. 4 and S24, demonstrating that the membranes can discriminate between hydrocarbons of different sizes and discriminate between paraffins and aromatics as well. Low molecular weight hydrocarbons are of high potential usages as blending components for gasolines or lubricate base oils. By increasing the filtration temperature to 120 °C, the polytriazole membrane led to a fraction 95 % enriched in smaller hydrocarbons (carbon numbers below C₁₅ corresponding to molecular weight around 180 g/mol), whereas the hydrocarbons between C₁₅-C₂₀ were only in the range of 3 - 4%. Fig. S25 indicates that paraffins and alkylbenzenes are the preferential compounds in the permeate at 90°C. Therefore, these data suggest that the polytriazole membranes could be integrated into a hybrid distillation system to fractionate crude oil.
The crude oil is a complex mixture. The effective separation of small molecules by the membrane can be supported by a cluster formation between different components, which facilitates only the permeation of small molecules and molecules that are not generating aggregates, like linear hydrocarbons. Furthermore, the solvents – membrane interactions and different diffusion and sorption mechanisms of each component in the crude oil can also contribute to the selection between the paraffin/aromatics (12). The results obtained for hydrocarbons separation show that moving from rather simple binary mixtures to dilute complex mixture, which has thousands of different components, the advantages for the membrane could be preserved with a similar molecular weight cutoff range.

In addition, the possibility of tuning the membranes separations properties by controlling the crosslinking conditions opens new perspectives of fractionation procedures. For example, using as feed a 1:1 mixture of Arabian superlight oil (39 > API > 30) to toluene (volume ratio) instead of 1:40 to toluene, and a D300-1h membrane, which has a thin layer with looser structure than the most crosslinked ones, it is possible to separate the larger molecules in the first stage, such as asphaltene. This is demonstrated by the lighter color of the permeate and by the FT-ICR-MS spectra (Fig. 4C) with lighter but still broad distribution of the masses. The permeate obtained in the first stage was utilized as feed in the second stage using the more crosslinked D325-1h membrane with a tighter layer. The GC chromatogram shows that more than 90% of the hydrocarbons with carbon numbers below C10 were concentrated in the permeate side (Fig. 4D).

The results reported here show that by rationally selecting the polymer structure and combining the classical NIPS method with thermally crosslinking, it is possible to obtain promising membranes for a highly challenging chemical separation: the fractionation of crude oil. The versatility of the polytriazole in terms of processability and crosslinking allows obtaining polymeric membranes with a tailored selective layer using a method that is easy to scale up. The tunable selectivity and permeances of the ultrathin polytriazole layer make these membranes suitable to be integrated into a cascade system for a specific range of hydrocarbons separation. High thermal stability permits testing a wide feed mixture in different conditions, suggesting that the polytriazole membranes can be integrated into hybrid membrane configurations for energy-efficient crude oil fractionation.
References and Notes


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Author contributions:

Conceptualization: SC, SN
Methodology and investigation: SC (design, membrane preparation, SEM, separation performance), VM (mechanical properties, TEM, DSC), GF (separation performance), WZ (FT-ICR MS and GC-MS), EAH (NMR), AHE (EPR), MA (TGA-MS)
Funding acquisition and supervision: SN
Writing – original draft: SC, SN
Writing – review & editing: SC, SN

Competing interests: The authors declare no competing interests. SC, VM, and SN are inventors on a patent application US 63/174,376 recently submitted by KAUST.

Data and materials availability: All data are available in the manuscript or the supplementary material.

Supplementary Materials
Materials and Methods
Figs. S1 to S25
Table 1

Fig. 1. Structure and characterization of thermally crosslinking membranes. (A) Structure of PTA-OH and the proposed crosslinked network. (B) 2D $^1$H-$^{13}$C heteronuclear correlation (HETCOR) and $^{13}$C-$^{13}$C (with proton driven spin-diffusion (PDS)) NMR spectra of the pristine PTA-OH (blue) and of the membrane treated at 325°C for 2h (red). The peaks indicated by letters are assigned to the carbon atoms in the structures depicted in (A). (C) $^{17}$O PRESTO-QCPMG DNP spectra of pristine (blue) and treated samples (red). (D) $^1$H-$^{15}$N CP-MAS HETCOR spectra of pristine (blue) and treated samples (red).

Fig. 2. Morphology of membranes cast from 16 wt% PTA-OH solutions in DMF. (A-C) Cross-sectional SEM images of membranes treated at 300°C for 3h (D300-3h). (D-G) TEM cross-sectional images (D) Untreated PTA-OH membrane. (E) D325-1h membrane (inset: higher magnification of the selective layer). (F and G) Selective layer of a D325-2h membrane.

Fig. 3. Polytriazole membrane performance with dilute crude oil as feed. (A-C) FT-ICR MS spectra of the feed and permeate in experiments conducted at 30°C with 1:40 (volume ratio)
Arabian super light crude oil to toluene mixtures, using thermally treated membranes cast from 16% PTA-OH solutions in NMP (N300-1h, N300-3h and N325-1h). (D) Photographs of permeate, feed, and retentate after filtrations at 65°C. (E) Double bond equivalent vs. carbon number for the feed and the permeate using a N325-1h membrane. (F) Permeance of dilute crude oil solutions at 30°C and 65°C using a N300-3h membrane.

**Fig. 4. Crude-oil separation by polytriazole membranes** (A) Gas chromatograms of crude oil fractions in different temperatures: 90°C, 120°C, and 150°C. The inset photograph shows the permeate obtained at 90°C. (B) FT-ICR MS spectra of the Arabian superlight crude oil. Inset photograph of the crude oil feed. (C) FT-ICR MS spectra of the retentate and permeate in experiments conducted at 30°C with 1:1 (volume ratio) Arabian extra light crude oil to toluene mixtures, using a D300-1h membrane. The inset photograph of the retentate and permeate. (D) Gas chromatograms of the permeate obtained at 90°C using a D325-1h membrane and as feed the permeate depicted in (C). Inset photograph of the feed permeate and retentate.

**Fig. 1**

**Fig. 2**
Fig. 3
Fig. 4

A

B

C

D

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Supplementary Materials for

Polytriazole membranes with ultrathin tunable selective layer for crude oil fractionation

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This PDF file includes:

Materials and Methods

Figs. S1-S25

Table S1
1. Materials and Methods

Materials

Polyphosphoric acid 84% (PPA) and 4,4’-(hexafluoroisopropylidene) bis(benzoic acid) were purchased from Alfa Aesar, hydrazinium sulfate from VWR chemicals, 4-aminophenol, aniline, N-methyl-2-pyrrolidone (NMP), N,N’-dimethylformamide (DMF) (99.8%), C7-C40 saturated alkanes standard and all the other reagents were obtained from Sigma-Aldrich.

Methods

Polymer synthesis

The polytriazoles with hydroxyl groups (PTA-OH) and without (PTA) were synthesized in the lab by a two steps polycondensation reaction. The first step consists of the synthesis of a polyoxadiazole (POD) precursor, adapting a procedure reported before. First, 650 g of PPA and 60 g of 4,4’-(hexafluoroisopropylidene) bis(benzoic acid) were mixed in a 2000 mL three necks flask. The mixture was stirred at 90 °C under nitrogen until a homogeneous solution was formed, then 24 g of hydrazinium sulfate was added. The mixture was heated at 167 °C for 2-2.5 hours. The resulting highly viscous POD solution was precipitated in water and neutralized with 1 M NaOH. 55 g POD were then dissolved in 365 mL NMP at 90 °C under nitrogen in a 2000 mL three necks flask. When a homogeneous solution was obtained, approx. 2.2 g of PPA and 40 g of 4-aminophenol were added, and reaction mixture was heated to 195 °C for 72 h. The resulting brown-colored solution was precipitated in a large amount of distilled water and washed several times with hot water and methanol to remove the unreacted 4-aminophenol. A similar procedure was used to prepare polytriazole without OH groups, but instead of 4-aminophenol, aniline was used. The polymers were purified by re-precipitation from NMP three times. The PTA-OH synthesized and used in this work was 98% functionalized, as confirmed by NMR characterization.
Membrane preparation

The polytriazole membranes were prepared by non-solvent-induced phase separation (NIPS). 16 wt% polytriazole solutions in N-methyl-2-pyrrolidone (NMP) or N,N'-dimethylformamide (DMF) were cast on a glass plate using a doctor blade with 200 μm gap. The polymer membranes were obtained by immersing the glass plate into a distillate water bath. The membranes were washed with distillate water for 72 h to eliminate any remaining solvent and freeze-dried. To crosslink the polytriazole membranes by thermal treatment, we used a Lindberg/Blue M™ 1200°C Split-Hinge Tube Furnaces. The furnace heating rate was set at 5°C per minute. The obtained integral asymmetric membranes were thermally treated in the furnace under an air atmosphere at 120°C for 30 min before continuing the treatment to 300°C for 1h, 2h, and 3h, and to 325°C for 1h and 2h.

The PTA-OH membranes are referred to as N- or D- depending on the solvent used for casting. The temperature and time of thermal treatment are then indicated. For example, D-300-2h is a membrane cast from solutions in DMF, submitted to thermal treatment at 300°C for 2h.

Molecular weight characterization

Gel permeation chromatography (GPC) was used to analyze the molecular weight of the synthesized polytriazole. The GPC system was equipped with an Agilent refractive index detector, and DMF was used as a mobile phase at 45°C. Molecular weight was determined from a calibration curve obtained using polystyrene standards.

Spectroscopic characterization

The chemical changes during thermal treatment were evaluated by spectroscopic methods.

*Fourier Transform Infrared (FTIR) spectroscopy* was performed on a Nicolet 6700 FT-IR System. 16 scans with a spectral resolution of 4 cm⁻¹ were recorded for each FTIR spectrum.

*Electron Paramagnetic Resonance (EPR)*

Continuous-wave Bruker EMX PLUS spectrometer operation at x-band (BrukerBioSpin, Rheinstetten, Germany) was used to record all EPR spectra at room temperature. The spectrometer is equipped with standard high Q resonator ER4122SHQE for high sensitivity CW-EPR and
operating at (9.384688) GHz. All spectra were recorded under the same conditions by collecting 5 scans with 25 dB microwave attenuation with 5 G modulation amplitude and 100 kHz modulation frequency. Bruker Xenon software (Bruker BioSpin, Rheinstetten, Germany) was used for data collection, and origin software was used for plotting the spectra.

**Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy**

One-dimensional $^1$H MAS and $^{13}$C CP/MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 or 600 MHz resonance frequencies for $^1$H. Experiments at 400 MHz employed a conventional double-resonance 4 mm CP/MAS probe, while experiments at 600 MHz utilized a 2.5 mm double-resonance probe. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane. For $^{13}$C CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time of typically 2 ms, and finally, the acquisition of the $^{13}$C signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the $^1$H nuclei, and the number of scans ranged between 10000 and 20000 for $^{13}$C and was 32 for $^1$H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

Two-dimensional $^1$H-$^1$H double-quantum (DQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double resonance 3.2 mm CP/MAS probe, according to the following general scheme: excitation of DQ coherences, $t_1$ evolution, z-filter, and detection. The spectra were recorded in a rotor synchronized fashion in $t_1$ by setting the $t_1$ increment equal to one rotor period (45.45 µs). One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in $w_1$ was achieved using the States-TPPI method. A MAS frequency of 22 kHz was used. The 90° proton pulse length was 2.5 µs, while a recycle delay of 5 s was used. A total of 128 $t_1$ increments with 128 scans per each increment were recorded. The DQ frequency in the $w_1$ dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons and correlates in the $w_2$ dimension with the two corresponding proton resonances.
2D $^1$H–$^{13}$C heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer using a 2.5 mm MAS probe. The experiments were performed according to the following scheme: $90^\circ$ proton pulse, $t_1$ evolution period, CP to $^{13}$C, and detection of the $^{13}$C magnetization under TPPM decoupling. For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, while the $^{13}$C channel RF field was matched to obtain an optimal signal. A total of $64 t_1$ increments with 2000 scans each were collected. The sample spinning frequency was 15 kHz. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere to lead to correlations only between pairs of attached $^1$H–$^{13}$C spins (C–H directly bonded).

2D $^{13}$C–$^{13}$C spectra were recorded using a 2 s recycle delay, 10 ms (F2) and 1.3 ms (F1) acquisition time, and an accumulation of 256 scans (both CP and DE). $^{13}$C–$^{13}$C mixing was achieved through proton-driven spin-diffusion (PDSd) using phase-alternated-recoupling-irradiation-schemes (PARIS) for 120 ms (CP) or 200 ms (DE) mixing. 70 kHz SPINAL64 1H decoupling was applied during both direct and indirect dimensions.

**Dynamic Nuclear Polarization NMR spectroscopy (DNP).**

For the DNP experiments, samples were prepared by incipient wetness impregnation of polymeric membranes with radical TEKPol solutions. The solutions consisted of 16 mM TEKPol (TEKPol, MW= 905 g/mol) in 1,1,2,2-tetrachloroethane (TCE). TEKPol was dried under a high vacuum (10−4 mbar), and the solvent was stirred over calcium hydride and then distilled in the vacuum. The compound was finely ground in a mortar and pestle prior to the preparation of DNP experiments. In a typical experiment, 15 mg of the polymeric samples were impregnated with the appropriate volume of 16 mM solution of TEKPol (nTEKPol = 0.5 - 1.2 μmol/sample) and packed into a 3.2 mm o.d. sapphire rotor capped with a Teflon plug. The packed samples were immediately inserted into the pre-cooled DNP probe for experiments.

The data were acquired on a 263 GHz/400 MHz Avance III Bruker DNP solid-state NMR spectrometer equipped with a 3.2 mm Bruker triple resonance low temperature magic angle spinning (LTMAS) probe and the experiments were performed at ca. 100 K with a 263 GHz gyrotron. The sweep coil of the main magnetic field was set for the microwave irradiation occurring at the $1H$ positive enhancement maximum of the TEKPol biradical. For the $^{15}$N CP-
MAS DNP experiments, the acquisition parameters included a 3 s repetition delay and a 1H π/2 pulse length of 2.3 μs to afford 100 kHz 1H decoupling using the SPINAL 64 method. The contact time was typically 4 ms for the cross-polarization experiments. The MAS frequency varied between 8 and 12 kHz. The 2D ¹H–¹⁵N HETCOR spectra were acquired with 2048 scans per t₁ increment, 96 individual increments, and a contact time of 4 ms. DUMBO-1 homonuclear 1H decoupling was applied, and the proton chemical shifts were corrected by applying a scaling factor of 0.57.

¹⁷O PRESTO-QCPMG experiments were performed under MAS at 10 kHz with 160 μs (2 rotor periods) of dipolar recoupling. The ¹⁷O central-transition selective 90 and 180° pulses lasted 5 and 10 μs, respectively. The spikelet separation was set to 1.25 kHz, and 40k scans were acquired with a 4 s recycle delay.

The ¹⁷O{¹H} PRESTO-QCPMG HETCOR experiments were acquired using the same conditions as the 1D spectra with 3000 scans per t₁ increment. Frequency-switched Lee–Goldberg homonuclear decoupling was applied during t₁ to improve the resolution in the ¹H dimension, and the States-TPPI method was used for phase-sensitive detection.

**Thermal, morphological, and mechanical characterization**

The thermogravimetric analysis (TGA) was performed on a TGA Q50, TA Instrument, under air atmosphere from 25 to 800 °C, with a heating rate of 10 °C min⁻¹. The analysis of evolved gases during the membrane crosslinking was conducted for selected samples on a thermal analyzer (STA, NETZSCH STA TG/DSC 449 F1 Jupiter®) coupled with a mass spectrometer. The samples were in this case heated in a nitrogen atmosphere with a flow rate of 70 mL/min. The sample was placed in a standard alumina crucible. For the analysis of the evolved gases, a NETZSCH Aeolos® QMS 403 mass spectrometer was connected via a heated capillary to the heated adapter head of the thermal analyzer outlet. The temperature of the connections and the MS inlet was set to 250°C. The sample was measured in the temperature range from 25 to 325°C at a heating rate of 5 °C /min and kept isothermally for 1 h.

The glass transition temperature (T_g) of the hydroxy-polytriazole was measured by differential scanning calorimetry (DSC) on a TA DSC250 instrument, with a heating rate of 10°C min⁻¹.
The morphology of pristine and thermally treated membranes were investigated by Scanning Electron Microscopy (SEM) on a Nova Nano microscope, using a 3-5 kV voltage and a working distance of 3-5 mm. The morphology was also studied by Transmission Electron Microscopy (TEM). Initially, the films were embedded in epoxy resin at 60 °C, and then ultrathin sections (70 nm) were cut using an ultramicrotome (Leica EM UC6). The membranes were imaged on a Titan CT (FEI company) microscope operating at 300 kV after they were stained with ruthenium oxide.

The membrane mechanical characterization was performed on a TA Instruments Q850 Dynamic Mechanical Analyzer in tensile mode. Rectangular samples (15x5 mm) were cut from the membranes with 70–80 μm thickness. The stress-strain curves were recorded using a force ramp of 0.1 N/m, at 25 °C. Five samples were tested for each membrane. The ultimate tensile properties are calculated as the average of stress and strain at break. A strain–recovery analysis was performed by subjecting membranes to a stress of 1 MPa for 20 min, followed by a recovery period of 80 min with removed stress. The applied stress level was chosen to ensure that the creep measurements remained in the linear viscoelastic deformation regime of the stress-strain curve, and it is comparable to the 5 bar pressure used for flux measurements. A small preload force of 0.01 N was applied to keep the sample right in the recovery regime.

The crystallinity and the d-spacing of the membranes were investigated using a Bruker D8 Advance diffractometer with Cu-Kα radiation source at 40 kV and 40 mV. The diffraction data were measured in the range of 5°–60°.

Membrane performance

The membranes performances were investigating in a dead-end cell, using a membrane area of 0.95 cm² and at pressures between 2 to 5 bar. The water permeance measurements of the membranes prepared in DMF and NMP were performed at room temperature. The solvent permeance was evaluated using equation 1:

\[ J = \frac{Q}{AA\Delta P} \]  \hspace{1cm} (1)

where \( Q \) is the permeation rate (L h⁻¹), \( A \) is the active filtration area (m²), and \( \Delta P \) is the pressure (bar).
The performances in various polar and non-polar organic solvents were evaluated at room temperature using 3 different membranes. The solvents were tested consecutively following the sequence: methanol, ethanol, acetone, hexane, heptane, toluene, and tetrahydrofuran.

The thermal treated membranes performances in DMF were consecutively measured at different temperatures, from 30 to 90℃, using an active membrane area of 0.95 cm² at pressures of 2-5 bar. Before the measurements, the membranes were immersed in DMF for 30 minutes and then transferred in water before being mounted in the filtration cell. The membranes performances were reported as an average of 3 different measurements. The long-time stability in DMF was performed by direct heating the dead-end cell at 65℃. The permeances were measured for approximately 67 h. The DMF flux at 30 and 65℃ as a function of pressure was measured by consecutively increase the pressure from 2 to 10 bar. For each pressure, the flux was measured for at least 2h.

The rejection in DMF was investigated by filtrating methyl orange (MO, Mw=327 g mol⁻¹) and acid fuchsin (AF, Mw=585 g mol⁻¹). The concentration of the dyes in DMF was between 10 to 50 ppm. The rejection experiments were performed between 2 h and 4 h, discarding at least 10 mL before collecting the samples for analysis. The rejection (R) was evaluated using equation 2:

\[
R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}
\]

where \(C_p\) is the solute concentration in the permeates, and \(C_f\) is the solute concentrations in the feed. UV spectrometer (NanoDrop 2000c) was used to evaluate the separation of the dye molecules.

The hydrocarbon rejection using binary mixture was investigated by dissolving hexaphenylbenzene (Mw=534.7 g mol⁻¹) in toluene at a concentration of 100 ppm. UV spectrometer (NanoDrop 2000c) and equation 2 were used to evaluate the separation. The filtration was performed under 5 bar for 20h. For measuring multi-components rejection, methylnaphthalene, 1,3-diisopropylbenzene, and pristane were dissolved in toluene in a ratio of 1 / 99 mol % of hydrocarbons/toluene. Gas chromatography was used to test the separation performance. The filtration was performed under 5 bar for 48h. The binary and multicomponent mixture experiments were carried out at 30℃. The fractionation of dilute crude oil was investigated by consecutively heating at 30 and 65℃. The Arabian extra light crude oil was diluted
in toluene in a volume ratio of 1:40. To measure the permeance during the experiments, we collected samples at different intervals (4h to 10h). The initial feed volume was 200 mL, and the total volume permeated was between 20 to 80 mL. The permeation experiment (consecutively permeating at 30 and 65°C) was carried out for approximately 100 h. The feed and the permeances were analyzed using FT-ICR MS. The filtration experiments with pure Arabian super light crude oil were performed by consecutively heating at 90, 120, and 150°C under 15 bar. The area of the membranes for this experiment was between 0.95 and 3.14 cm². Different fractions were collected every 24 or 48h. The initial feed volume was 50 or 100 mL, and the total volume permeated was between 10 to 17 mL. The permeation experiment (consecutively permeating at 90, 120, and 150°C) was carried out for approximately 10 days. This experiment was confirmed using 3 different membranes. For the experiments with crude oil (dilute Arabian extra light crude crude oil and pure Arabian super light crude oil), vials with rubber septum were connected to the permeate side tube to diminish the evaporation of the lighter components from the permeance. The building pressure within the vials was equalized by the aid of a needle. The permeates obtained using pure Arabian super light crude oil as feed were investigated using the GC. To identify the components in the permeates a standardized C7-C40 saturated alkanes solution in hexane was used. The enrichment of the hydrocarbons in the permeance was calculated by integrating the GS peaks below C10, in the range of C10-C15 and C15-C20, and higher than C20. The crude oil fractionation experiment was performed starting with a 1:1 feed mixture of Arabian extra light toluene. For this experiment, we used membranes with 0.95 cm². The initial feed mixture was 70 mL, and in the first stage, we collected 36 mL. For the second step, the collected amount in the first step was utilized as feed, and we permeated 10 mL out of this.

The gas chromatography-mass spectrometry (GC MS) was performed on an Agilent 7890A GC with both flame ionization detector (FID) and quadrupole mass spectrometer (Agilent 5975C MSD) via a three-way splitter. 2µL of the permeated oil sample was injected into the split/splitless inlet under 300 °C. The split ratio of 10:1 was employed. The sample was further separated on a HP-5MS column (30 m x 250 µm x 0.25 µm with Agilent part number 19091S-433) with the flow rate of 3 mL/min. The oven was kept at 40°C for 1 minute and increased to 250°C with a rate of 2°C/min. The elutes were separated into 2 flows, for FID and MSD separately, after the column separation. The MSD peaks were used for structural elucidation, and FID signals were used for
quantitative analysis. The GC was calibrated with C7-C40 n-alkanes. The calculation of carbon number distribution is roughly based on the retention times of individual normal alkane standards.

The oils were further characterized on a Bruker SolariX XR 9.4 Tesla Fourier-transform ion cyclotron resonance mass spectrometer (FT ICR MS, BRUKER DALTONIK GmbH, Bremen, Germany) with an atmospheric pressure photoionization ionization (APPI) source. The instrument was first calibrated with low molecular weight polystyrene beforehand. The samples were diluted in toluene and directly infused into the ionization sources by a syringe pump with a flow rate of 10 μL/min. The APPI source was operated with a nebulizer pressure of 2.5bar, vaporizer temperature of 400 °C, dry gas flow of 4.0L/min, and dry temperature of 220 °C. Each data set was acquired with 8 Megawords sizes by accumulating 300 scans in the mass range of 150-1200 Da. The FT ICR MS spectra were further treated by the Bruker DataAnalysis V4.5 software; only the peaks with S/N higher than 5 were considered for following chemical formula assignment. The chemical formula assignment was performed with Composer software (Sierra Analytics, Modesto, CA, USA). Giving an error range of ±0.5ppm, the most probable elemental composition of each monoisotopic mass peak was calculated according to the determined accurate mass within the chemical formula range of C1-H100H1-200N0-3O0-3S0-3. The resulting chemical formulas were further sorted into different compound classes, such as radical hydrocarbon ions (HC), protonated hydrocarbon ions (HC [H]), radical ions of hydrocarbons with one S atom (S), and so forth. Then, the iso-abundance plot was used to display the distribution of certain compound classes in terms of carbon number, double bond equivalent number, and abundance.

The GC×GC-TOF/MS analysis was performed using an Agilent 7890B gas chromatography system (Agilent Technologies, Wilmington, Delaware), equipped with a Zoex ZX1 cryogenic thermal modulator (Zoex Corporation, Houston, Texas) and a Jeol TOF MS (AccuTOF GCx-plus, JEOL, Japan). The GC×GC system was consisted of a normal (non-polar x mid-polar) two-dimensional column configuration. The first-dimension column was a 30 m nonpolar HP-5MS UI capillary column (5%-Phenyl-methylpolysiloxane) with an internal diameter of 0.25 mm and a stationary-phase film thickness of 0.25 μm. The second-dimension was a 1m mid polar BPX-50 capillary column (50% Phenyl Polysilphenylene-siloxane) with an internal diameter of 0.1 mm and a film thickness of 0.1 μm. Helium (99.999%) was used as the carrier gas with a constant flow rate of 0.8 mL min⁻¹. The GC × GC-TOF/MS injector temperature was maintained at 300 °C with a split ratio of 150:1. The oven temperature was initially maintained at 80 °C for 1 min, and then...
ramped to 325 °C at a rate of 2 °C min⁻¹. The modulation period was 6 s with pulse time 0.350 ms. The mass spectrometer was operated in electron ionization (EI+) mode at 70 eV. The transfer line and ion source temperatures were kept constant at 250 °C. The detector voltage of TOF was 2500 Volts and data were acquired at a rate of 50 Hz. Mass spectra were obtained from m/z 50 to 450. The 2D data were processed and displayed using the GC ImageTM VersionTM 2.9 software (Lincoln NE, USA). The NIST/EPA/NIH EI Mass Spectral Library 2.3 version was used to confirm the identification.

![Fig. S1. GPC analysis of PTA-OH.](image_url)
**Fig. S2.** NMR characterization of non-functionalized PTA in solution. (A) $^1$H NMR and (B) $^{13}$C NMR.
Fig. S3. NMR characterization of PTA-OH in solution. (A) $^1$H NMR and (B) $^{13}$C NMR.
**Fig. S4.** Solvent stability test. Photographs of thermally treated PTA-OH immersed in DMF, acids, and base conditions for more than 3 months. Demonstration of the flexibility of the treated membranes.

**Fig. S5.** FTIR spectra. Untreated membranes (PTA-OH) and membranes treated at different temperatures and times.
Fig. S6. EPR spectra. (A, C) PTA-OH and (B) PTA obtained by reacting polyoxadiazole at 195°C with (A, C) aminophenol or (B) aniline. Reaction times: (A) 24, 48, 72h, (B) 48h and (C) 24h. (C) PTA-OH was further treated at 300 and 325°C for 1 to 3h.
Fig. S7. $^{13}$C solid-state NMR (CP MAS) spectra. (A) untreated PTA-OH membranes and (B) treated at 325°C for 2h (D325-2h).
**Fig. S8.** $^1$H solid-state and 2D $^1$H-$^1$H quantum NMR spectra. (A) $^1$H solid-state MAS NMR and (B) 2D $^1$H-$^1$H double quantum/single quantum spectra of untreated PTA-OH membranes (blue line) and of D325-2h membranes.
Fig. S9. $^1$H MAS DNP SENS (100 K, 400 MHz / 263 GHz). (A) untreated PTA-OH and (B) D325-2h membrane in a 16 mM TEKPol solution in 1,1,2,2-tetrachloethane (TCE). The recycle delay was 3 s, and the MAS frequency was 8 kHz ($\varepsilon = $ DNP enhancement factor). The sample was stored in its rotor at -4°C. Red line represents the spectra without any microwave irradiation (16 scans), while the black line shows the experiment under microwave irradiation (16 scans).
Fig. S10. $^{17}$O-{1H} PRESTO-QCPMG HETCOR DNP spectra. (A) untreated PTA-OH and (B) treated membrane at 325°C for 2h (D325-2h).
Fig. S11. 1D $^1$H–$^{15}$N cross-polarization magic-angle spinning (MAS) DNP SENS spectra. (A) untreated and (B) treated membrane in a 16 mM TEKPol solution in 1,1,2,2-tetrachloroethane (TCE).
**Fig. S12.** Thermal analysis of PTA and PTA-OH membranes. Membranes prepared without or with treatment at different temperatures and time: (A) weight loss as a function of temperature and (B) corresponding curves derivative; (C) TGA-MS data for a PTA-OH sample heated to 325 °C, under a heating rate of 5 °C min⁻¹. After reaching the temperature, the sample was kept under this condition for 1 h. (D) DSC, second heating curve.
**Fig. S13.** Mechanical properties of the membranes before and after the thermal treatment. (A) Young’s modulus, (B) yield stress, (C) ultimate stress, (D) ultimate strain, and (E) toughness, (F) creep-recovery curves.
Fig. S14. SEM images of membrane surfaces. PTA-OH membranes cast from solutions in (A) DMF and (B) NMP without and with thermal treatment.

Fig. S15. SEM images of membrane cross-sections. PTA-OH membranes cast from solutions in (A) DMF and (B) NMP without and with thermal treatment.
**Fig. S16.** TEM images of ultramicrotomed membranes. PTA-OH membranes cast from solutions in (A) DMF and (B) NMP after thermal treatment.

**Fig. S17.** TEM images of ultramicrotomed membranes. Membranes treated at 325°C for 2h, which were obtained starting from (A) 16 wt% and (B) 18 wt% PTA-OH solutions in DMF.
**Fig. S18.** Rheology of the membrane casting solutions. Viscosity of solutions of 16 and 18 wt% PTA-OH versus shear rate.
**Fig. S19.** Organic solvent permeances through D300-3h membranes. (A) Permeances of different solvents as a function of the inverse of their viscosities. (B, C, D) Solvent permeances correlated with Hansen solubility parameters, as a function of the inverse of their viscosity, multiplied by the inverse of the molecular diameters and Hansen solubility parameters. (B) total (δ), (C) polar (δ_p) and (D) H-bonding (δ_H) contributions. Units: δ, MPa^{1/2}, η, mPa s, and d, nm; (E) DMF flux as a function of pressure.
Fig. S20. Performance stability for D325-1h membranes. (A) Permeance as a function of time. (B) Performance in sequential changes of temperature. (C) Methyl Orange (MO) rejection in sequential temperature changes (absorbances of the permeates collected at 30, 65 and 90°C, feed and retentate).

Fig. S21. Filtration of MO solutions in DMF at different temperatures. Permeances of membranes cast from PTA-OH solutions in NMP (orange) or DMF (green) treated under different conditions: (A) N300-2h and D300-2h (B) N300-3h and D300-3h, (C) N325-1h and D325-1h (D) N325-2h and D325-2h. (E) MO rejection as a function of temperature for D300-2h, D300-3h, D325-1h, D325-2h membranes. (F) MO rejection as a function of temperature for analogous membranes cast from solutions in NMP; AF rejection for N300-3h.
Fig. S22. Membrane separation performances using hydrocarbons solutions in toluene. (A) UV-Viz spectra of feed (hexaphenylbenzene solution) and permeate using N300-3h membranes. (B) Rejection of multicomponent hydrocarbons using N325-1h membranes.
Fig. S23. Dilute crude-oil separation using ultrathin PTA-OH membranes. (A, B, C) FT-ICR MS spectra of the feed and permeates filtered at 65°C using N300-1h, N300-3h and N325-1h membranes. The feed consists of Arabian light 1:40 (volume ratio) crude oil:toluene. (D) Permeance of dilute crude oil solutions at 30°C and 65°C using N325-1h membranes.
**Fig. S24.** Gas chromatograms of different crude oil permeate fractions. Fractions collected after filtration with N300-1h membranes at 90°C, 120°C, and 150°C, respectively, compared to those of C7-C40 normal-alkanes standard solutions in hexane. The inset photographs show the permeate obtained at each filtration temperature.

**Fig. S25.** Two-dimensional (2D) gas chromatogram (GCxGC). Permeate obtained using a N300-1h membrane after filtration of crude oil at 90°C. Paraffins and isoparaffins are preferentially concentrated. Light alkylbenzenes hydrocarbons were also detected.
Table S1. Summary of ultrathin polytriazole membranes performance.

<table>
<thead>
<tr>
<th>Membrane (Material)</th>
<th>Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Solute</th>
<th>MW (g mol⁻¹)</th>
<th>Rejection (%)</th>
<th>Ref.</th>
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<td>DMF (T) toluene</td>
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<tr>
<td>D300-3h (PTA-OH)</td>
<td>21 (30°C) 10</td>
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<td>93 (DMF)</td>
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<tr>
<td>N300-3h (PTA-OH)</td>
<td>21 (30°C) 36 (65°C) 48 (90°C)</td>
<td>Methyl orange</td>
<td>327</td>
<td>90</td>
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<td>Commercial Membranes</td>
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<td>Solute</td>
<td>MW (g mol⁻¹)</td>
<td>Rejection (%)</td>
<td>Ref.</td>
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<tr>
<td>Polyarylate/ PI support</td>
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<td>crystal violet</td>
<td>408</td>
<td>99 (MeOH)</td>
<td>(29)</td>
</tr>
<tr>
<td>PA/PI support or alumina</td>
<td>0.18</td>
<td>Methyl orange</td>
<td>327</td>
<td>97.7 (MeOH)</td>
<td>(30)</td>
</tr>
<tr>
<td>PA/PI support or alumina</td>
<td>0.1</td>
<td>Methyl orange</td>
<td>327</td>
<td>96.8 (MeOH)</td>
<td>(30)</td>
</tr>
<tr>
<td>PA/PI support or alumina</td>
<td>3.45</td>
<td>Methyl orange</td>
<td>327</td>
<td>98.9 (MeOH)</td>
<td>(30)</td>
</tr>
<tr>
<td>PA</td>
<td>8 (30°C) 10 (60°C) 12 (90°C)</td>
<td>PS oligomers</td>
<td>600</td>
<td>90</td>
<td>(31)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD-based</td>
<td>1.6</td>
<td>Methyl orange</td>
<td>327</td>
<td>93 (MeOH)</td>
<td>(32)</td>
</tr>
<tr>
<td></td>
<td>CD-based</td>
<td>Trianglamine/ PAN support</td>
<td>Spirocyclic polymers</td>
<td>COF</td>
<td>COF</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
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<td>-----</td>
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</tr>
<tr>
<td></td>
<td>1</td>
<td>19.8</td>
<td>0.1-07</td>
<td>7.8</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Methyl orange</td>
<td>Polystyrene, dilute hydrocarbons, crude oil</td>
<td>Sudan black B</td>
<td>Sudan black B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>327</td>
<td>335</td>
<td>456</td>
<td>456</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95.7 (EtOH)</td>
<td>&gt;90 (toluene)</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(33)</td>
<td>(12)</td>
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</table>

PI = polyimide, PA = polyamide, PDMS = polydimethylsiloxane, PBI = polybenzimidazole, PEEK = polyetheretherketone, COF = covalent organic framework, CD = cyclodextrin, PAN = polyacrylonitrile