

# PhD Thesis Cédric Van Goethem – Extended abstract

## 'Preparation and characterization of novel thin-film nanocomposite and asymmetric nanofiltration membranes'

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### 1. Summary

Nanofiltration (NF) and solvent resistant NF (SRNF) have the potential to provide an energy efficient and easily scalable alternative separation technique for many separation problems with industrial and societal relevance. For (SR)NF to fully live up to this promise, membranes with enhanced separation performance and stability have to be developed. In this work, novel Metal-Organic Framework (MOF)-based Thin-Film Nanocomposite (TFN) membranes and a crosslinking strategy for PVDF were developed to provide a solution to both problems.

In the first part, an innovative approach to allow better control over MOF-based TFN membranes termed Evaporation controlled Filler Positioning (EFP) was designed. EFP-based membranes showed >3-fold increase in permeance without deteriorating salt retention, and this requiring the use of up to 80x less MOF compared to comparable literature. Similar to what is commonly observed in literature, characterization revealed very little MOF particles actually embedded in the membrane. This discrepancy was investigated using advanced characterization which allowed us for the first time to demonstrate that fillers can degrade during TFN membrane preparation. This knowledge was then integrated to form a scalable synthesis method for MOF-based TFN membranes using acid stable MOF fillers. This ultimately allowed the preparation of TFN membranes with a >8-fold increase in permeance in SRNF.

In the second part, a one-pot crosslinking strategy for PVDF membranes was developed and patented. After detailed physicochemical characterization of the implications of crosslinking, the application of this material in harsh separations was tested. Crosslinked PVDF was shown to be stable in extreme pH (up to 5 M HCl or NaOH), solvents and combinations thereof. Based on this material, a scalable diafiltration-based process was developed to allow the purification of tailored (MOF) nanoparticles that are becoming increasingly important to many technologic innovations.

### 2. Problem addressed

Climate change caused by the increasing atmospheric concentration of greenhouse gases is a worldwide problem resulting in a warmer climate with more extreme conditions. Separations typically account for about 50% of the industrial energy consumption and can represent up to 15% of the total energy consumption in industrialized countries. Improving the energy efficiency of separation processes can thus have an immense impact.<sup>1</sup>

Membrane technology-based separations promise up to 90% lower energy consumption compared to traditional separation processes such as distillation.<sup>1</sup> Especially (solvent resistant) nanofiltration (NF) and reverse osmosis (RO) that are able to retain small organic molecules (< 1000 Da) and ions are interesting to replace conventional separation techniques.<sup>2</sup> Membrane material development over the past years has focused tremendously on the development of membranes that combine a low molecular weight cut-off (MWCO) with ultra-high permeance.<sup>3</sup> Whereas such properties are to some extent useful for the concentration of a dilute solute, most separation problems concern the true separation of two similar size molecules. To accomplish this, a very sharp MWCO is which none of the current generation commercially available membranes has. Preferably, this MWCO should be easily shifted.

Membrane stability in harsh conditions is an additional issue, especially for polymeric membranes. These harsh conditions include solvents, extreme acidic or alkaline pH, high temperatures and combinations thereof. Process examples include high temperature homogeneous catalyst recovery from a solvent-based reaction mixture<sup>4</sup> or the purification of pharmaceutical waste streams composed of solvent/water mixtures at non-neutral pH<sup>5</sup>.

### 3. State of the art

The current state-of-the-art membranes for NF and RO are polyamide (PA)-based thin-film composite (TFC) membranes.<sup>6</sup> A porous support layer prepared via phase inversion is impregnated with an aqueous solution of a diamine-type monomer, before being covered with an immiscible organic solution containing an acid chloride-type monomer. At the interface, the diamine diffuses into the organic layer and reacts to form the PA. This reaction is self-limiting as the diffusion of the two reactants towards each other is limited by the growing film which results in a thin yet dense toplayer.

Jeong et al. (2007) proposed composite TFC-membranes with filler particles embedded into the toplayer, so-called thin-film nanocomposite (TFN) membranes, in analogy with mixed matrix membranes (MMM).<sup>7</sup> Since this first report, a huge number of publications has been published regarding the use of different fillers and fabrication methods for TFN membranes. Although it has been shown numerous times that fillers can introduce molecular sieving properties to MMMs,<sup>8</sup> this has so far not been shown to occur in the same way in TFN membranes. The fact that achieving a high volume fraction of filler inside such a TFN membrane without creating defects is very challenging, is probably the biggest cause for the lack of molecular sieving properties in addition to the lack of true MWCO determination of synthesized membranes.<sup>9</sup>

PA is known to have limited chemical stability in certain environments.<sup>10</sup> (SR)NF in harsh conditions thus relies predominantly on integrally skinned asymmetric (ISA)-type membranes prepared from high-performance polymers such as polysulfone (PSf) or polyimide (PI) for application in respectively non-neutral pH or solvents. Recent years has seen the development of many promising novel membrane materials with excellent stability such as poly(ether ether ketone)<sup>11</sup>, cyanuric acid-based polyamines<sup>10,12</sup>, polyoxindole<sup>13</sup>, etc. Very little materials however combine excellent stability, stability in solvent-non-neutral pH combinations and a sufficiently low MWCO with a scalable membrane manufacturing strategy.

### 4. Key scientific and technological innovations

#### Thin-Film Nanocomposite (TFN) membranes

- **Evaporation controlled Filler positioning (EFP)** was developed as a novel strategy for the preparation of TFN membranes. The two step-process allows independent control and optimization of filler positioning and interfacial polymerization (IP). >3-fold increase in permeance was realized without loss of NaCl-retention and this using an extremely low filler loading of only 0.005 wt% (80x less compared to literature).
- The **locally harsh conditions during IP were for the first time shown to be able to degrade fillers** in TFN membrane preparation. This filler stability issue was then demonstrated to be able to explain the commonly observed paradox for TFN membranes of large performance increases but little evidence for the incorporation of a significant filler fraction.
- EFP was transformed from a tedious, non-scalable technique to an **elegant and scalable technique using spray-coating**. Spray-coating based TFN membranes with acid-stable MOF fillers were applied in SRNF and resulted in EtOH permeance increases >8-fold without loss of retention for a 479 g.mol<sup>-1</sup> solute.

#### Crosslinking of PVDF as a versatile, ultrastable membrane material

- An optimized **procedure for the crosslinking of PVDF NF membranes was developed and patented** based on a one-pot simultaneous dehydrofluorination and diamine-based Michael addition reaction.
- Crosslinked PVDF membranes were shown to be **extremely resilient in harsh conditions**:
  - Extreme pH: no loss of retention was observed for crosslinked PVDF NF membranes in extreme acidic or alkaline pH (respectively 5 M HCl or NaOH)
  - Solvents: Crosslinked PVDF was found to be stable in a wide range of solvents. Drying and solvent activation were established as excellent tools to push respectively membrane retention and permeance to levels comparable with state-of-the-art membranes.
  - Solvent/extreme pH combinations: Recovery and purification of MOF nanoparticles using diafiltration with crosslinked PVDF membranes was demonstrated as a proof for crosslinked PVDF stability in combinations of solvents with acids/bases.

## 5. Results

Membrane technology has grown tremendously over the past decades, replacing and supplementing conventional separation techniques such as distillation, chromatography, adsorption, absorption, etc. This growth was only possible because of the continuous development of novel membrane materials, membrane types, modules and processes. Many separation processes, ranging from small volume niche applications to huge-scale separations, are however still dependent on energy-intensive traditional separation processes because membrane technology cannot yet provide an industrially applicable and competitive alternative. Different technological issues are at the origin of this, such as too low permeance, stability issues, module design, etc.

This work is divided into two main parts. In part one, high performance Metal-Organic Framework (MOF)-based Thin-Film Nanocomposite (TFN) membranes were developed through the design of novel synthesis procedures and careful analysis of the role of the MOF in TFN membranes. In part two, the stability issue that membranes face in harsh conditions was tackled through the development of a novel membrane material, crosslinked PVDF. Both the physicochemical changes during the crosslinking as well as its applicability in various conditions were studied.

The chapter numbers below refer to respective chapter in the PhD-thesis.

### 5.1. Thin-Film Nanocomposite (TFN) membranes

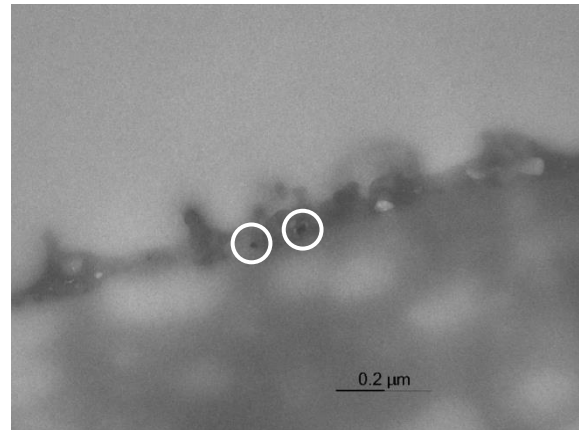
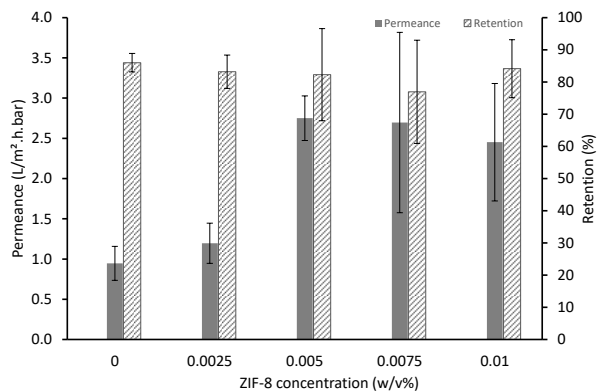
The preparation of TFN membranes is almost identical to that for TFC membranes (*vide supra*). Filler particles are added to either the aqueous or organic phase (with the latter the most common practice) of the interfacial polymerization (IP).<sup>14</sup> While conceptually simple, this approach suffers from several drawbacks. (i) The organic phase of IP is usually an apolar organic solvent such as hexane, heptane or toluene. The low dielectric constant of such solvents implies that the dispersion of nanoparticles is often difficult.<sup>15</sup> Even strong sonication can often not prevent the formation of nanoparticle (np) aggregates. Such aggregates are a source for defect formation in the TFN-toplayer. The resulting non-selective permeation through these defects will result in the (often observed) higher permeance at the expense of a higher MWCO. (ii) Because the filler np's are dosed into one of two reagent-containing phases of the IP, their **incorporation is inherently coupled to the actual IP**. As a consequence, filler incorporation is a random process and cannot be controlled independently, **leading to low degrees of filler incorporation and large losses of (often expensive) filler**.

#### 5.1.1. Evaporation controlled Filler positioning (EFP)

To resolve the issues outlined above, a novel synthesis protocol aimed at providing better control over the incorporation of fillers in TFN membranes with the ultimate goal to maximise the benefits of filler incorporation was developed in chapter two. The **Evaporation controlled Filler Positioning (EFP) method** utilises solvent evaporation of a filler dispersion deposited on the support membrane as a tool to deposit a layer of filler at the interface prior to the IP.<sup>9</sup> As such, this splits the normal single step TFN membrane preparation into two separate stages: filler positioning and actual IP. Although more tedious, two separate steps allow for independent control and optimization.

EFP-membranes prepared using different loadings of the MOF ZIF-8 showed mixed results. At really high concentrations (not shown) increased water permeance compared to the reference TFC membrane was observed but this was accompanied by a reduced NaCl retention. In contrast, low ZIF-8 concentrations did result in the desired increased permeance without loss of NaCl retention (Figure 1, left). A spectacular **3-fold increase in H<sub>2</sub>O permeance was observed and this at filler loadings as low as 0.005 w/v%**. Literature reports of similar MOF-based TFN membranes require up to 80x higher MOF concentrations to reach the optimal result, illustrating the importance of repositioning the filler at the interface. Further physicochemical characterization of the EFP-membranes was performed to obtain a better understanding of the EFP-protocol, using amongst others TEM and XPS. Whereas XPS clearly indicated the presence of Zn in the EFP-TFN membranes, TEM imaging did not reveal the incorporation of particles with dimensions similar to the 150 nm-sized ZIF-8 particles used in the membrane preparation (Figure 1, right). Only a small amount of tiny particles were observed which could be degradation fragments of the ZIF-8 particles, but the exact origin of these fragments remained unclear. This

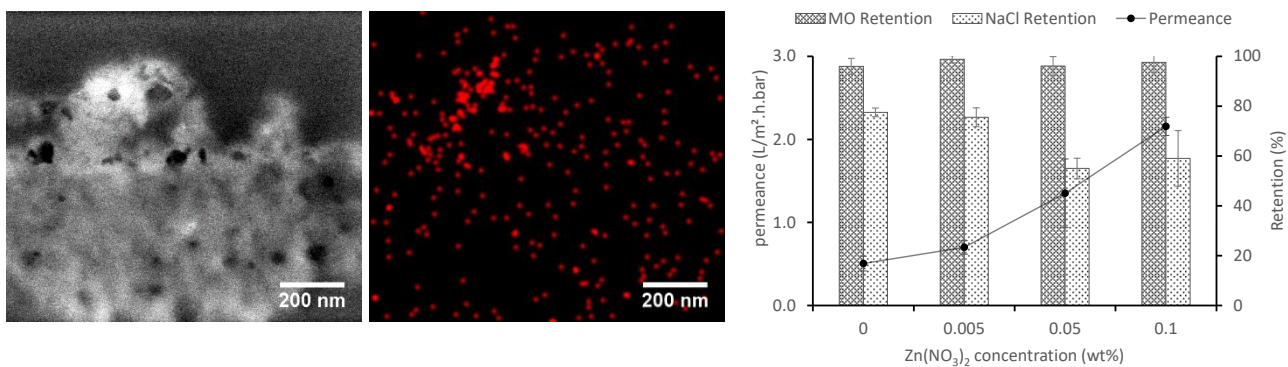
inconsistency between the observed amount of fillers incorporated in a TFN membrane and the membrane performance is often observed in literature and leaves questions regarding the exact functioning of TFN membranes. These formed the subject of chapter three (5.1.2).



**Figure 1.** (left) Water permeance and NaCl retention for EFP-based TFN membranes prepared using low concentrations of ZIF-8. (right) A representative TEM image of a ZIF-8 based TFN membrane showing no 150 nm ZIF-8 particles were incorporated in the toplayer. What could presumably be ZIF-8 degradation fragments is highlighted using white circles.

### 5.1.2. The role of MOFs in TFN membranes

Chapter two revealed **inconsistencies between the TFN membrane performance and the amount of filler incorporated**. These are also common in literature and do not fit the conventional paradigm that it is primarily the low-resistance pathways for solvent transport provided by the porous filler particles that control the final TFN membrane performance. As such, chapter three focused on gaining a more detailed understanding of the formation and functioning of TFN membranes. Advanced STEM-EDX imaging (collaboration with Prof. Sara Bals, UAntwerpen) of the EFP membranes revealed no ZIF-8 particles incorporated in the toplayer. Membranes prepared from high concentrations ZIF-8 revealed detectable concentrations of Zn, but not in the form of particles (Figure 2, left). This led to the **hypothesis that the acid sensitive ZIF-8 particles were partially degraded during the IP** as a consequence of the very fast and localized HCl that is formed as a by-product of the IP polycondensation reaction. This hypothesis was verified by testing the influence of Zn<sup>2+</sup> and 2-methylimidazole on regular IP. Especially the Zn<sup>2+</sup> was found to lead to similar permeance increases (Figure 2, right) indicating that indeed filler degradation could explain the combination of high-performance membranes with little filler incorporation. A second verification experiment was performed by adding a base (thus an acid quencher) to TFN membrane synthesis. XRD analysis confirmed that only in the presence of the acid quencher, the ZIF-8 particles retained crystallinity when incorporated into the TFN membrane.



**Figure 2.** (left) HAADF-STEM image and STEM-EDX Zn-mapping of a 0.1 wt% ZIF-8 based EFP membrane showing the presence of Zn in the mapping without observation of actual ZIF-8 particles in the HAADF-image. (right) Water permeance and NaCl/Methyl Orange (327 g.mol<sup>-1</sup>) retention for TFC membranes prepared in the presence of Zn(NO<sub>3</sub>)<sub>2</sub> illustrating the influence a Zn-salt can have on TFC membrane properties.

### 5.1.3. Spray-coating based preparation of TFN membranes

The findings of chapter 3 (5.1.2) combined with the inherent limitations of the EFP-protocol developed in chapter 2 (5.1.1), led to the **use of spray-coating as a technique to synthesize EFP-TFN membranes using the acid-stable MOF UiO-66** in chapter 4. After validation of the spray-coating, membranes prepared using various filler loadings were applied in SRNF. Up to >8-fold increase in permeance was realized without compromising the retention for the 479 g.mol<sup>-1</sup> Rhodamine B solute. The retention for the smaller Methyl Orange dye (327 g.mol<sup>-1</sup>) did decrease with increasing UiO-66 concentration leading to a **60 % increase in the separation factor of the two dye molecules**. This suggests the UiO-66 contributes to molecular sieving of the two dyes although the effect of possible ultra-small defects cannot be ruled out. Although UiO-66 is inherently more stable compared to the ZIF-8 used in 5.1.1., careful characterization was performed to confirm effective incorporation of the UiO-66 in the membrane. ADF-STEM imaging clearly revealed the incorporation of UiO-66 nanoparticles with the number of particles observed correlating with the concentration used during synthesis.

### 5.1.4. Impact of this work

The impact of the work presented in section 5.1 is twofold. On the one hand, the 3 publications (2 published<sup>9,16</sup>, 1 being finalized) **convey 2 important messages to the membrane community**: Section 5.1.2 was the **first reported published regarding the importance of using stable fillers to avoid degradation**. As such, this work can be considered as guiding the TFN-community into the selection of suitable fillers as well as in understanding the functioning of TFN membranes. The numerous citations of this work underline the importance of this message (37 citations, Web of Science on 15/04/2021). In addition, section 5.1.1 and 5.1.3 illustrate **the power of optimized synthesis procedures for TFN membranes** that consider the complexity of incorporating fillers in TFN membranes. We believe this work inspires other research groups to use and further develop this method as illustrated by the citation count (72 citations, Web of Science on 15/04/2021).

On the other hand, this work also has a **large impact on the continuation of our own research into TFN membranes** as two main issues remained for TFN membranes to achieve true molecular sieving. (i) Membranes prepared with high filler loadings were still prone to form filler aggregates or non-selective voids at the filler-polymer interface which compromises true molecular selectivity of the membranes. (ii) In addition, TFNs are in general prepared using tight PA as the surrounding polymer. This PA only allows passage of very small (solvent) molecules which downgrades the role of the filler to a low-resistivity pathway for solvent molecules instead of contributing to the molecular separation.

## 5.2. Crosslinked PVDF-based membranes

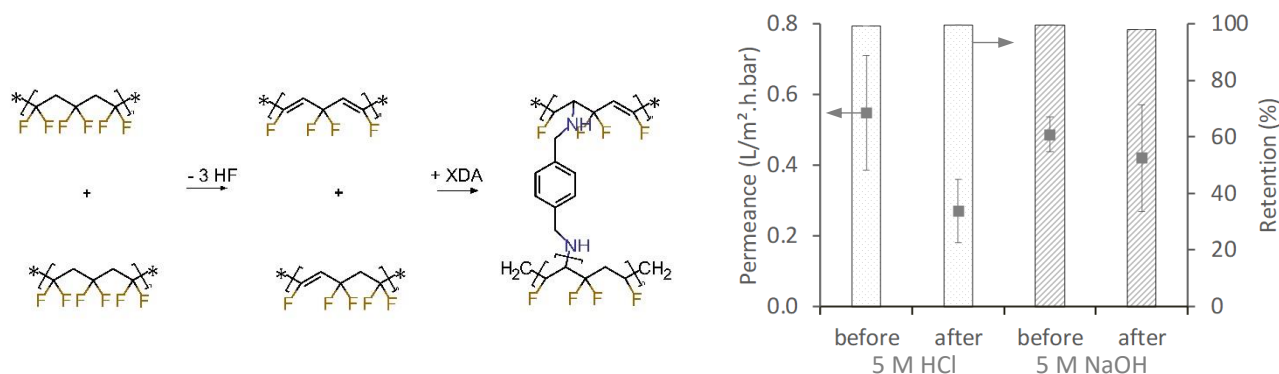
Although PA-based TFC membranes nowadays dominate the aqueous NF market because of their excellent performance, integrally skinned asymmetric (ISA)-type NF membranes dominate in areas where current TFC membranes fail due to the harsh conditions. Very little membrane materials can withstand harsh conditions such as solvents, extreme pH, high temperature or combinations thereof. In the second part of this work, a **PVDF crosslinking strategy was developed and patented (GB1801230.2) as an ultra-resilient membrane material for UF/NF in extreme conditions**.

### 5.2.1. Development of crosslinked PVDF and application in extreme pH NF

In chapter 5, a one-pot crosslinking reaction was developed based on a NaOH/MgO-based dehydrofluorination of the PVDF polymer chains combined with a diamine-based Michael addition reaction to form the crosslinks (Figure 3, left).<sup>17</sup> The physicochemical changes induced by this reaction were characterized in-depth by ATR-FTIR, SEM-EDX, XRD, TGA, DSC and DMA analysis. SEM-EDX elemental analysis and FTIR confirmed the crosslinking reaction to be successful with the degree of crosslinking increasing with increasing crosslinking time. This was further substantiated by DSC and XRD which revealed that the semicrystalline nature of PVDF was partially erased through the crosslinking as a result of the crosslinking changing the repeating  $-\text{[CH}_2\text{CF}_2\text{]}-$  units in the polymer chain. Filtration performance testing of crosslinked PVDF NF membranes revealed the crosslinking to result in a **MWCO reduction from 1000 to 327 Da. This can be attributed to the slight swelling of the membrane in the MeOH-based crosslinking solution and subsequent tighter network formation during**



**the crosslinking itself.** Optimal membrane performance was obtained after 24 h of crosslinking. The optimized membranes were then tested for their applicability in extreme pH NF. **No significant change in retention for RB (1017 g.mol<sup>-1</sup>) was observed after submersion for 5 days in 5 M HCl or NaOH** (Figure 3, right), something almost **no current industrial nor academic polymeric membrane is known to be stable in.**



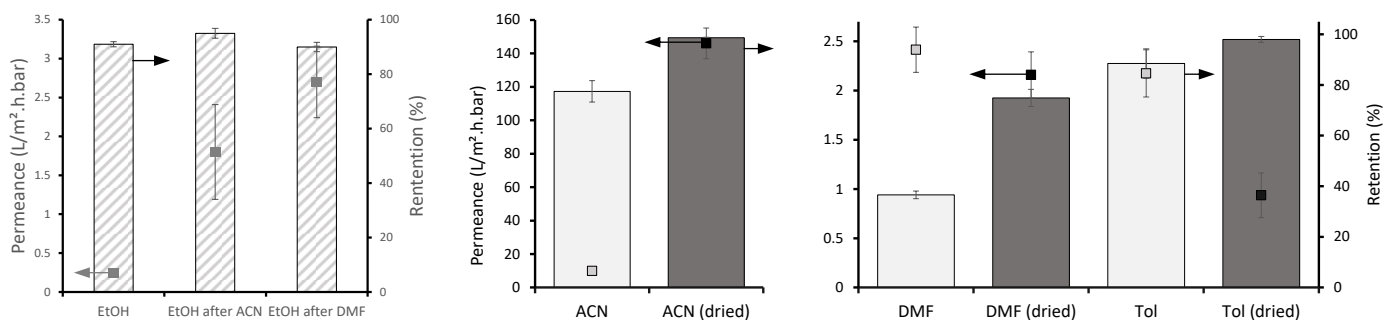
**Figure 3.** (left) The one-pot crosslinking reaction for PVDF consisting of the simultaneous NaOH/MgO-based dehydrofluorination and diamine-based Michael addition. (right) Water permeance and RB (1017 g.mol<sup>-1</sup>) retention before and after exposure of the crosslinked PVDF NF membranes to 5 M HCl or NaOH for 5 days.

### 5.2.2.Solvent resistant NF

The formation of a polymer network structure through the crosslinking of the PVDF-NF membranes should result in solvent stability and as such make the membranes suitable for application in SRNF. This was explored in chapter 6 through the sequential filtration of EtOH, *i*PrOH, ACN, DMF and toluene.<sup>18</sup> The crosslinked PVDF membranes however did not show good performance in either of the afore mentioned solvents. The crosslinked PVDF applied in the polar protic alcoholic solvents showed excellent retention (>90% for Rose Bengal, RB, 1017 g.mol<sup>-1</sup>) but permeances were very low. In contrast, the performance in polar aprotic or apolar solvents showed opposite results: good permeance but no satisfactory retention. A correlation between the permeance and different physico-chemical parameters (molar volume, Hildebrand parameter, dipole moment and viscosity) was investigated, showing permeance and reciprocal viscosity to give the strongest correlation ( $r^2 = 0.85$ ). This strong correlation agrees with previous research<sup>19-21</sup>. The correlation could not be further improved by the addition of any of the other aforementioned parameters.

**Further experiments however led to the observation of two interesting phenomena that provided a solution to the low permeance in polar protic solvents and the low retention in harsher solvents.** (i) **Solvent activation to improve permeance in polar protic solvents:** During the consecutive solvent filtrations, EtOH filtrations were repeated to observe possible permanent changes in the membrane performance. Retention only changed slightly (< 2.5 %), but a strong permeance increase was noticed after contact with ACN, and a really **drastic permeance increase by a factor of 11 was observed after DMF treatment** (Figure 4, left). The ACN and especially the DMF filtrations caused swelling of the membrane, which increased the polymer chain mobility. This swelling could then facilitate the removal of remaining reactants from the membrane, thereby freeing up pore volume. In addition, loosely crosslinked polymer chains can be leached out of the membrane matrix. Similar effects have been observed in literature for PA-TFC membranes<sup>22,23</sup>, where solvent activation increased membrane permeance without compromising retention. ATR-FTIR analysis did not reveal any significant chemical changes to the membranes after exposure to ACN or DMF but <sup>1</sup>H-NMR analysis of ACN/DMF after exposure to a crosslinked PVDF membrane confirmed the leaching out of less crosslinked polymer chains. After solvent activation, the performance of the crosslinked PVDF NF membranes was comparable to that of commercial and academic state-of-the-art crosslinked PI membranes with the major difference being the much better stability of crosslinked PVDF in harsh conditions. (ii) **Drying of the membranes to improve retention in polar aprotic / apolar solvents:** Accidentally, one batch of membranes was dried. Instead of throwing the membranes, the opportunity was taken to investigate the effect of drying on the membrane performance. **After drying, a striking increase in RB retention was observed in the filtration of RB from ACN, DMF and Toluene**

(Figure 4, right). Although this could be caused by pore collapse during drying, the fact that permeance was found to be decreased for DMF and Toluene but increased for ACN suggests another effect should be at the origin. ATR-FTIR and SEM-EDX elemental analysis revealed that the crosslinking degree increased upon drying which should lead to reduced swelling, hence explaining the improved retention. The increased crosslinking degree is hypothesized to originate from the drying bringing together free amine groups from crosslinker moieties that only reacted once.



**Figure 4.** (left) EtOH permeance and RB retention for a pristine crosslinked PVDF NF membrane and after filtration of ACN and DMF showing the solvent activation effect. (right) Permeance and RB retention for ACN, DMF and Toluene before and after drying.

### 5.2.3. Recovery and purification of MOF nanoparticles

Nanoparticles (np) are becoming increasingly important for a wide variety of applications, going from therapeutics<sup>24</sup> to catalysis<sup>25</sup> and incorporation in membranes<sup>26</sup>. At lab-scale, the separation steps in np synthesis are mostly performed using centrifugation, which is difficult to scale-up and to use in a continuous process. **Membranes offer a promising and easily scalable alternative, but its use is limited by the harsh conditions in which np's are prepared.** Indeed, these often include combinations of harsh solvents, extreme pH and high temperature.<sup>25</sup>

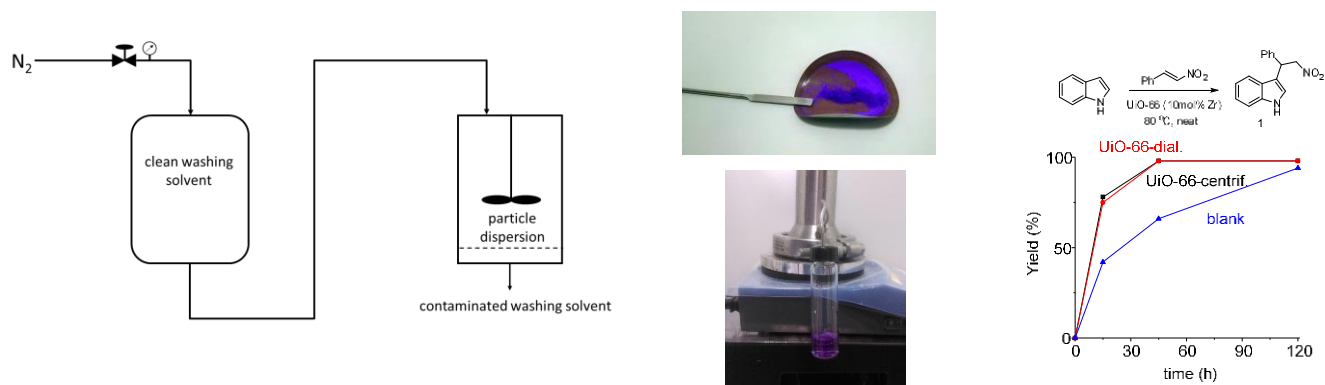
To resolve these issues, a lab-scale **diafiltration process using crosslinked PVDF membranes was developed** for the synthesis and purification of MOF nanoparticles (Figure 5, left).<sup>27</sup> The recovery and purification of 5 prototypical MOFs (ZIF-67, ZIF-8, UiO-66, HKUST-1 and MIL-53) was explored with synthesis conditions that varied from relatively simple room temperature synthesis in methanol<sup>28</sup>, to much harsher conditions such as the solvothermal synthesis of UiO-66 in a DMF/HCl mixture at 120 °C.<sup>25</sup>

Initially, the efficiency of the diafiltration towards the removal of unreacted reagents and retaining the np's was validated using UV-vis observation of the Co(NO<sub>3</sub>)<sub>x</sub>(Mim)<sub>y</sub> (x + y = 2) concentration in the permeate. The concentration of the Co-complex in the permeate was found to decrease exponentially with increasing diavolume and matched with the diafiltration model. **This predictability offers a key advantage in the production of np's as the removal of leftover reagents (which often influence the activity of the np's) can be easily and accurately controlled.**

After process validation, the applicability of the crosslinked PVDF-based diafiltration process in the recovery of several prototypical MOFs in a wide range of conditions was explored. **The crosslinked PVDF membranes were able to recover and purify the MOF np's, even from the very harsh DMF/HCl mixture.** Although the crystallographic structure of the MOF np's was not influenced by the diafiltration process (confirmed through XRD analysis), TEM image did reveal that in some cases, larger particles were formed than in comparable synthesis combined with centrifugation. Analysis of the conditions in which this occurred, quickly revealed that this occurs only for room temperature synthesis where Ostwald ripening can continue during the initial stages of the diafiltration. On the other hand, higher temperature solvothermal synthesis are quenched rapidly by the

addition of the room-temperature diafiltration solvent and thus did not show larger particle sizes compared to centrifugation.

As the final quality of the np's is only measured by their performance in real applications, UiO-66 nanoparticles prepared using either centrifugation or diafiltration were tested for their catalytic activity towards 2 reactions. In both the Friedel-Crafts alkylation of indole with an electron deficient alkene (Figure 5, right) as in the reaction between oxindole and benzaldehyde (not shown), the catalytic activity of both UiO-66 batches was not significantly different confirming the applicability of diafiltration.



**Figure 5.** (left) Schematic illustration of the lab-scale dead-end diafiltration setup. (middle, top) image illustrating the ease with which the MOF nanoparticles can be recovered from the membrane surface. (middle, bottom) image showing the purple permeate containing the  $\text{Co}(\text{NO}_3)_x(\text{Mim})_y$  ( $x + y = 2$ ) complex, but no ZIF-67 particles. (right) Comparison of the catalytic activity of UiO-66 prepared via diafiltration (red) and normal centrifugation (black).

#### 5.2.4. Impact of this work

Section 5.2.1, 5.2.2 and 5.2.3 showed that crosslinked PVDF is a versatile material with promising performance for different applications where very few other membranes types are applicable. This led to a **patent application (GB1801230.2) for the crosslinked PVDF membranes** and hence the further development of this class of membranes was not halted. The unique properties of crosslinked PVDF have since the development of the material sparked interest from both academic and industrial side. The development of crosslinked PVDF has generated impact on three levels.

(i) **Development of a scalable PVDF crosslinking strategy:** The crosslinking procedure developed and explored in the section 5.2.1-3 is expensive and lengthy. Careful assessment of the roles of the different chemicals involved allowed us to design a more elegant and scalable approach. This simplified protocol reduced the number of required chemicals from 4 to 2, is >3 times cheaper, >20 times faster and the crosslinking solution can be reused >4 times without significant changes in the crosslinking.<sup>29</sup>

(ii) **Scale-up of crosslinked PVDF membrane preparation:** The potential we see in crosslinked PVDF combined with the demand coming from several sources for trying crosslinked PVDF membranes, has pushed us to investigate upscaling of crosslinked PVDF. To accomplish this, **one FTE researcher is currently exploring the in-house role-to-role fabrication of UF and NF PVDF-based membranes using the group's Smartcoater 300. 30x300 cm membranes have already been prepared** and the properties of these role-to-role membranes have been validated experimentally to be identical to those obtained via lab-scale membrane preparation. In addition to in-house upscaling, the **crosslinking of already commercial PVDF membranes is currently being explored with an industry leading water technology provider to make its PVDF membranes more robust.**

(iii) **crosslinked PVDF in real applications**



## 6. References

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