

## Video Article

# Layer-by-layer Synthesis and Transfer of Freestanding Conjugated Microporous Polymer Nanomembranes

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## Abstract

CMP as large surface area materials have attracted growing interest recently, due to their high variability in the incorporation of functional groups in combination with their outstanding thermal and chemical stability, and low densities. However, their insoluble nature causes problems in their processing since usually applied techniques such as spin coating are not available. Especially for membrane applications, where the processing of CMP as thin films is desirable, the processing problems have hindered their commercial application.

Here we describe the interfacial synthesis of CMP thin films on functionalized substrates via molecular layer-by-layer (l-b-l) synthesis. This process allows the preparation of films with desired thickness and composition and even desired composition gradients.

The use of sacrificial supports allows the preparation of freestanding membranes by dissolution of the support after the synthesis. To handle such ultra-thin freestanding membranes the protection with sacrificial coatings showed great promise, to avoid rupture of the nanomembranes. To transfer the nanomembranes to the desired substrate, the coated membranes are upfloated at the air-liquid interface and then transferred via dip coating.

## Video Link

The video component of this article can be found at <https://www.jove.com/video/53324/>

## Introduction

The preparation of ultra-thin polymer membranes is of high interest for applications in gas separation and nanofiltration. Challenges in the synthesis are represented by (a) the control of the membrane thickness and the homogeneity and (b) transfer of such fragile membranes. To overcome challenge (a), molecular layer-by-layer synthesis<sup>1</sup> has shown great promise in controlling the thickness and homogeneity of thin films grown at the solid-liquid interface.<sup>2,3</sup> Controlling the number of layers linearly controls the film thickness. The l-b-l method has been successfully used to fabricate surface mounted metal organic frameworks (SURMOFs),<sup>4-7</sup> also the synthesis of thin polymer films via l-b-l reaction of polymer chains was demonstrated.<sup>8</sup> The challenge (b) concerns the handling of these ultra-thin membranes. To avoid rupture or wrinkling of the nanomembranes sacrificial supports of coatings have shown great promise.<sup>9</sup>

Here we will present a detailed protocol for synthesis of conjugated microporous polymer (CMP)<sup>10-13</sup> thin films through sequential addition of the molecular building blocks, with desired thickness and composition. The preparation of free-standing CMP nanomembranes is achieved by using a sacrificial support. To handle and transfer the CMP nanomembranes to other supports we will describe a simple protocol to protect the membranes with sacrificial coatings and their upfloating to the liquid air interface and subsequent transfer using dip-coating.

## Protocol

### 1. Synthesis of CMP Thin Films through Sequential Addition

1. Self-assembled monolayer (SAM) functionalization of gold on mica.
  1. Prepare 1 mM solution of 11-thioacetyl-undecane acid-propargyl amide<sup>14</sup> in ethanol (SAM-solution). Mix using ultrasonic bath till solution is clear. Protect the bottle from light using aluminum foil.
  2. Obtain gold coated mica wafer under argon. After withdrawal from the storage container immerse the mica wafer directly to the SAM-solution for 18 hr.

3. Take the prepared Au-mica wafer out of the SAM-solution, rinse with ethanol and dry under nitrogen stream. Afterwards store the substrate protected from light and under inert gas.
2. Precursor solutions.
  1. Weigh 18.64 mg Cu-catalyst (Tetrakis(acetonitrile)copper(I)hexafluoro-phosphate), 20.83 mg tetraphenylmethane (TPM)-alkyne and 24.22 mg TPM-azide and fill each component into a separate Schlenk flask. See **Figure 1** for TPM-alkyne and TPM-azide, the synthesis is described in Reference<sup>15</sup>. Evacuate and refill with inert gas (N<sub>2</sub> or argon) 3 times.
  2. Add 25 ml water-free tetrahydrofuran (THF) to each Schlenk flask. Protect the flasks with TPM-azide and TPM-alkyne from light using aluminum foil.
3. Prepare apparatus for CMP fabrication.
 

Note: The synthesis apparatus is shown in **Figure 2**.

  1. Use a 250 ml one neck round bottom flask. Fill in 130 ml THF. Put the prepared substrate coated with alkyne terminated SAM in the sample compartment. Use a sample holder, so that the substrate is standing upright.
  2. Connect the apparatus to the Schlenk line via the junction on top of the reflux cooler.
  3. Evacuate and ventilate with inert gas 3 times.
4. Sequential addition under inert conditions.
  1. Set the heater to 90 °C and wait till the THF is refluxing.
  2. Let out THF from the sample compartment over the outlet at the bottom of the sample compartment. Close the outlet.
  3. Give 1 ml of the prepared TPM-azide solution and 0.5 ml of the Cu(I) catalyst solution to the sample compartment via the screw cap with septum. Use a syringe with a hollow needle to transfer the solutions sequentially from the Schlenk flask to the reaction apparatus. Note: The sequence has no influence to the reaction.
  4. Wait approximately 30 min.
  5. Let out the reaction solution over the outlet at the bottom of the sample compartment. Close the outlet and collect the condensed THF for rinsing the sample. Wait approximately 30 min.
  6. Let out the rinsing solution over the outlet at the bottom of the sample compartment. Close the outlet.
  7. Give 1 ml of the prepared TPM-alkyne solution and 0.5 ml of the Cu(I) catalyst solution to the sample compartment via the screw cap with septum. Use a syringe with a hollow needle to transfer the solutions sequentially from the Schlenk flask to the reaction apparatus. Note: The sequence has no influence to the reaction.
  8. Wait approximately 30 min.
  9. Let out the reaction solution over the outlet at the bottom of the sample compartment. Close the outlet and collect the condensed THF for rinsing the sample. Wait approximately 30 min.
  10. Repeat steps 1.4.3 to 1.4.9 until the desired amount of layers is reached. Note: One layer is approximately 1 nm thick.
  11. Take out the CMP-coated mica substrate, rinse it with THF, ethanol and dry it under nitrogen stream.

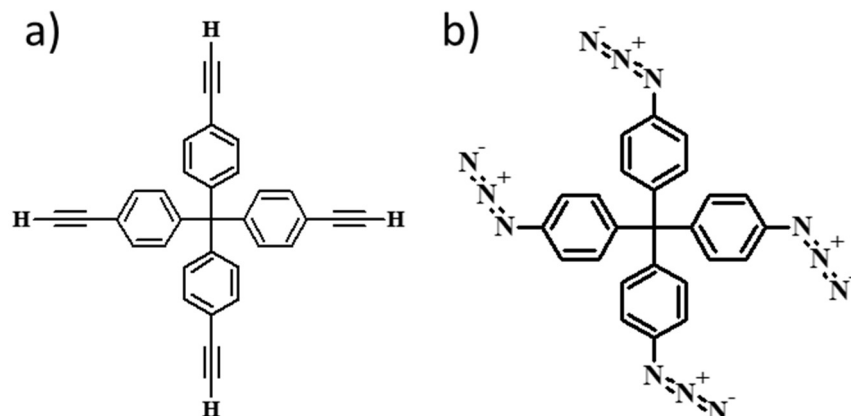
## 2. Transfer of CMP Nanomembranes

1. Poly(methyl methacrylate) (PMMA) solution.
  1. Prepare a solution of 4% (wt) PMMA (M 996 kDa) in ethyl acetate. Dissolve the PMMA using ultrasonic bath till the solution is clear.
2. Spin coating of PMMA solution.
  1. Set the spin coater to ramp time 10 sec from 0 to 4,000 rpm, holding time 40 sec and ramp time 10 sec from 4,000 to 0 rpm.
  2. Place the CMP coated mica substrate on the spin coater and put the PMMA solution on the wafer till it is completely covered. Start the spin coater.
  3. After spin coating is completed, put the sample for 5 min on a heating plate at 90 °C.
  4. Cut off 1 mm from each edge of the coated mica substrate. Use a scissor to cut the edges.
3. Transfer of PMMA coated CMP nanomembrane.
  1. Prepare solution of I<sub>2</sub>/KI/H<sub>2</sub>O (1:4:40 <sub>m/m/m</sub>) and of KI/H<sub>2</sub>O (1:10 <sub>m/m</sub>).
  2. Fill the I<sub>2</sub>/KI/H<sub>2</sub>O solution in a 150 ml crystallizing dish and fill the KI/H<sub>2</sub>O solution in a 100 ml crystallizing dish. Put the PMMA coated CMP gold on mica substrate, with mica in contact to solution, on top of the I<sub>2</sub>/KI/H<sub>2</sub>O solution. Be careful that it does not sink. Wait at least 5 min.
  3. Put the PMMA coated CMP gold mica substrate from the I<sub>2</sub>/KI/H<sub>2</sub>O solution on top of the KI/H<sub>2</sub>O solution, with mica in contact to solution. Be careful that it does not sink. Wait at least 5 min.
  4. Fill distilled water in a 250 ml crystallizing dish. Strip off the PMMA/CMP/gold film from the mica. Do this by slightly immersing the substrate, beginning from one edge, in distilled water. Hold the substrate so that the mica is pointing to the water. Note: The procedure is shown in **Figure 3**.
  5. Dip-coat the PMMA/CMP/gold on the silicon wafer. Do this by approaching the PMMA/CMP/gold slowly with the wafer until it touches edge of the swimming PMMA/CMP/gold membrane. Pull out the silicon wafer slowly, once the Si-wafer is in contact with the PMMA/CMP/gold membrane.
  6. Strip the PMMA/CMP/gold film off from the silicon wafer. Do this by slightly immersing the substrate, beginning from one edge, in the I<sub>2</sub>/KI/H<sub>2</sub>O solution. Wait 15 min.
  7. After the gold is completely etched, transfer the PMMA/CMP membrane to water via the silicon wafer. Wait 15 min.
  8. Repeat step 2.3.7 three times to wash the membrane with water.
  9. Transfer the washed PMMA/CMP membrane to the desired substrate, e.g., a microscope slide or a gold coated silicon wafer, via the method mentioned in step 2.3.5. Let the PMMA/CMP substrate dry in air for at least 2 hr.
4. Dissolution of PMMA.

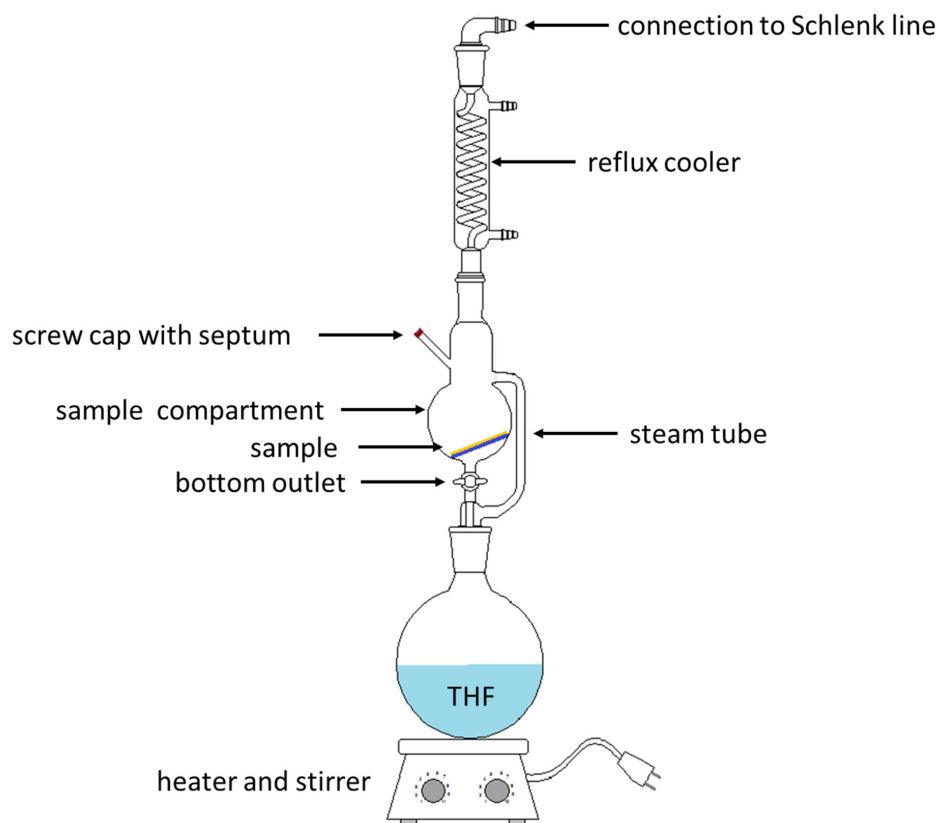
1. Put the PMMA/CMP substrate in acetone. Wait 30 min. Take out the substrate and rinse it with acetone.
2. Repeat step 2.4.1 three times.
3. Let the CMP substrate dry for at least 2 hr.

## Representative Results

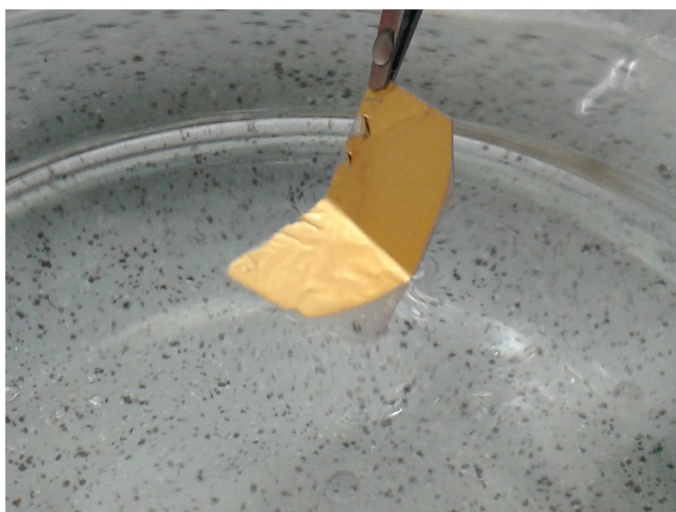
The membranes are characterized by infrared reflection absorption spectroscopy (IRRAS).<sup>16</sup> **Figure 4** shows IRRAS-spectra from a CMP-membrane transferred to a gold wafer. Typical bands from the vibrations of the aromatic backbone are at  $1,605\text{ cm}^{-1}$ ,  $1,515\text{ cm}^{-1}$  and  $1,412\text{ cm}^{-1}$ . Unreacted alkyne and azide groups can be observed by characteristic bands at  $2,125\text{ cm}^{-1}$  and  $1,227\text{ cm}^{-1}$ . **Figure 5** shows a scanning electron microscopy (SEM) image. The freestanding membrane is clearly visible.



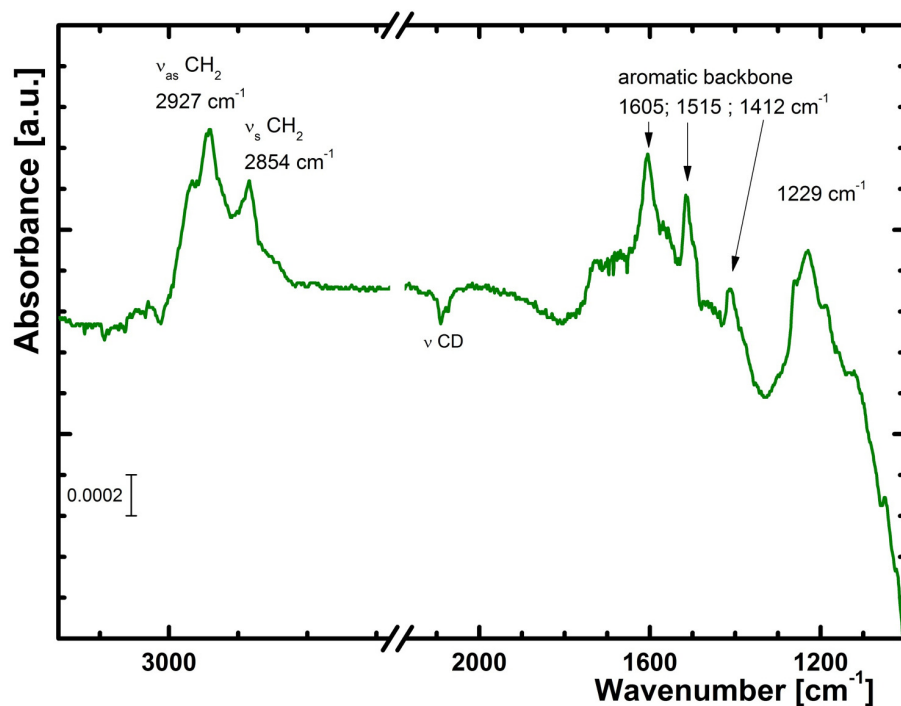
**Figure 1. Molecular building blocks.** Molecular structures of (A) TPM-alkyne and (B) TPM-azide. [Please click here to view a larger version of this figure.](#)



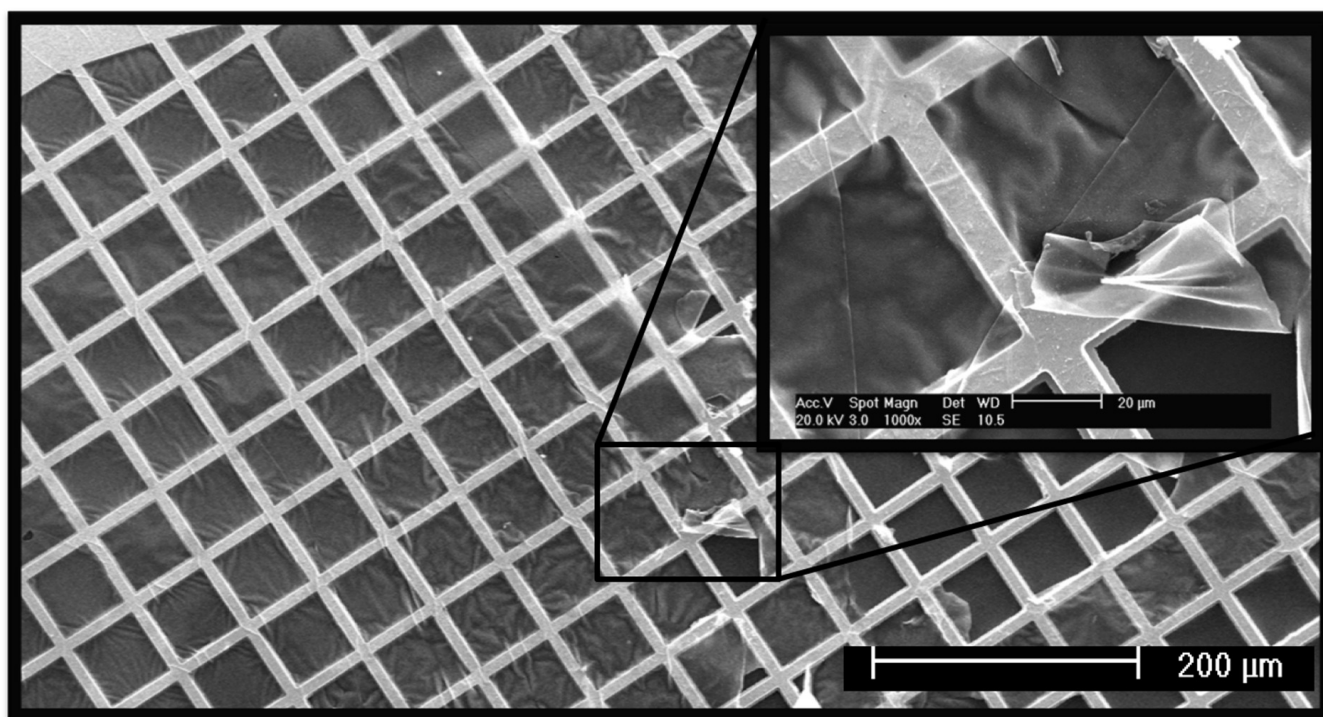
**Figure 2. Reaction apparatus.** Set up for the layer-by-layer synthesis of the CMP thin-films. The apparatus consists of a one neck round bottom flask as reservoir for the THF, the steam tube to lead the THF vapor to the reflux cooler. The THF condensates are collected in the sample compartment. The chemicals can be inserted over the screw cap with a septum. The sample compartment is emptied via the bottom outlet. [Please click here to view a larger version of this figure.](#)



**Figure 3. Removing mica.** The PMMA/CMP membrane is starting to detach from the edge of the mica-substrate. Half of the PMMA/CMP is floating on top of the water, the other half is still attached to the mica substrate. [Please click here to view a larger version of this figure.](#)



**Figure 4. IRRA-spectra.** IRRA-spectra from a CMP-membrane transferred to a gold-wafer. The bands from the vibrations of the aromatic backbone at 1,605, 1,515 and 1,412  $\text{cm}^{-1}$  are characteristic for the CMP-membrane. The CD vibration is due to the background used. [Please click here to view a larger version of this figure.](#)



**Figure 5. SEM-image.** SEM-Image of the CMP-membrane. The freestanding membrane is nicely shown. (Reprinted with permission from Lindemann, P. *et al. Chem. Mater.* **26**, 7189 - 7193. Copyright 2014 American Chemical Society.) [Please click here to view a larger version of this figure.](#)



## Discussion

For the synthesis of the CMP-film the solution of the catalyst has to be fresh. A broken catalyst (*i.e.*, oxidized) is indicated by a blue coloration of the solution. The fresh solution is colorless.

A crucial point is to cut the edges of the mica substrate after spin coating PMMA. Also defects in the substrate should be cut, *i.e.*, each spot where the PMMA can come in contact with the mica substrate, because of a missing gold layer. Otherwise the gold layer cannot be stripped off from the mica substrate easily. Also concerning the detachment of the gold layer from the mica substrate, after the detachment started on one edge or corner, one should continue on this edge till the gold layer is completely detached.

During the transfer of the PMMA/CMP membranes with a silicon wafer, *e.g.*, from the water bath to the iodine solution or from the iodine solution to water, it is important that the membrane doesn't dry. Once the membrane dries on the Si-wafer, it is almost impossible to detach it again.

After dissolving the PMMA, each rinsing step should be performed cautiously; an overlapped edge from the membrane can lead to a removing of the membrane from the substrate.

At the moment the size of the samples is limited by the size of the sample compartment. The thickness of the fabricated CMP films is limited by the reaction time because each cycle needs around 2 hr. For a less labor intensive synthesis the reaction apparatus could be modified by adding a syphon; as a result the sample compartment will be emptied automatically, comparable to a Soxhlet extractor.

Our technique combines the processing of ultrathin conjugated microporous polymer films and the use of a sacrificial substrate to obtain CMP nanomembranes. The synthesis of CMP nanomembranes was yet not possible because of the low processability of powder CMP.

In comparison to other techniques, for example the production of SURMOFs<sup>7</sup>, we achieved a reduction on the amount of solvent used. Especially the rinsing step in case of SURMOF production has a high consumption of solvent, in this case, due to the use of refluxing THF, we could decrease the consumption of THF drastically.

We expect that the presented method will find application in gas and liquid phase separation because of the possibilities to fine-tune the selectivity and permeance by the control over pore size and chemical affinity. In addition, modular synthesis of CMP materials from functional building blocks suitable for other applications, such as catalysis, sensing, or organic electronics, could also benefit from the described processing method.

## Disclosures

The authors have nothing to disclose.

## Acknowledgements

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