

# Synthesis of Sub-10 nm Two-Dimensional Covalent Organic Thin Film with Sharp Molecular Sieving Nanofiltration

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Supporting Information Placeholder

**ABSTRACT:** We demonstrated here a novel and facile synthesis of two-dimensional (2D) covalent organic thin film with pore size around 1.5 nm using a planar, amphiphilic and substituted heptacyclic truxene based triamine and a simple dialdehyde as building blocks by dynamic imine bond formation at the air/water interface using Langmuir-Blodgett (LB) method. Optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), all unanimously showed the formation of large, molecularly thin and free standing membrane that can be easily transferred on different substrate surfaces. The 2D membrane supported on a porous polysulfone showed a rejection rate of 64% and 71% for NaCl and MgSO<sub>4</sub> respectively, and a clear molecular sieving at molecular size around 1.3 nm, which demonstrated a great potential in the application of pretreatment of seawater desalination and separation of organic molecules.

**Keywords:** *Two dimension (2D) Membranes; Separation; Nanofiltration; Langmuir-Blodgett; Imine bond.*

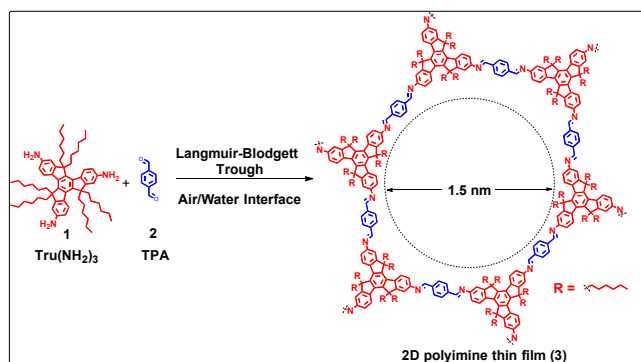
Two-dimensional (2D) porous polymers have great potential in membrane applications because they can be used as building blocks to prepare ultra-thin and thus ultra-permeable membranes for gas/liquid separations. Compared to other porous materials such as metal organic frameworks they may have better chemical stability and higher mechanical strength. Their physical properties can be very different from that of the bulk which may also open potential applications in sensing, electrochemistry, coatings, biotechnology, catalysis, organic photovoltaic devices, energy storage, gas storage and semiconductors.<sup>1-12</sup>

Ideally, two-dimensional polymer (2DP) should be atomically or molecularly thin with long range internal order or periodicity along the two orthogonal directions in order to obtain both high flux and high selectivity.<sup>13-14</sup> However, synthesis of such perfect structure is still an elusive goal. There are many reports on the synthesis of 2DP by “top-down” approach such as topochemical polymerization using (4+4) cycloaddition reactions in the presence of UV irradiation followed by exfoliation of monolayers from polymerized crystals,<sup>15-17</sup> nano-sheets generated from covalent organic frameworks (COFs)<sup>18-20</sup> as well as metal-organic frameworks (MOFs).<sup>21-22</sup> One of the drawbacks of “top-down” exfoliation approach is a generation of few layers of nano-sheets with varying thickness and limited lateral dimension. On the other hand, few examples of “bottom-up” approach using covalent and

coordination chemistry<sup>23-26</sup> to synthesize 2DPs are reported, but none of them have made in films with enough dimension to report their separation performance.

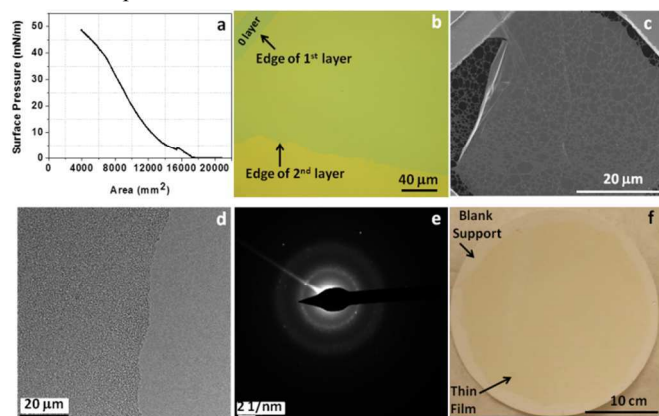
Herein we report the synthesis and separation performance of a 2DP made from two aromatic building blocks, hexa-alkylated truxene based triamine [**Tru**(NH<sub>2</sub>)<sub>3</sub>] (**1**) and terephthalaldehyde (**TPA**) (**2**) at air/water interface using a Langmuir Blodgett method. Truxene is a very useful building block due to its extraordinary solubility, thermal stability and simplicity with which it can be modified. An enormous variety of truxene derivatives has been developed and found applications in optics, transistors, organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), molecular resistors and lasers.<sup>27</sup> Incorporation of such optical and electronic active scaffold into 2DP synthesis could help in the future development of novel photo and electro active thin film. The imine bond formed between the two precursors could be an important linkage in membrane applications.<sup>28</sup> Imine bonds are well-known to form reversibly (“dynamically”), enabling a self-correction mechanism by which molecular entities can be formed under thermodynamic control. This mechanism has been used as a powerful tool to prepare various well-defined molecular architectures from discrete molecular building blocks to complex assemblies such as covalent organic frameworks, porous materials, molecular knots, polymers, and novel macrocycles, etc.<sup>29-33</sup> However, to the best of our knowledge, there is only one report so far for the synthesis of 2DP through Langmuir-Blodgett method using imine bonding.<sup>31</sup>

The truxene 2DP membrane was synthesized according to scheme 1. Truxene has a planar heptacyclic polyarene structure with three -CH<sub>2</sub>- “clips” added to rigidify the structure and keep the four phenyl rings coplanar. Six hexyl chains are attached to truxene to form monomer **1** through a synthesis route showed in Scheme S1, (SI), which makes the molecule amphiphilic in nature. It is expected that the hydrophobic hexyl chains can help to prevent truxene from dispersing into the aqueous solution, and hence help to form a thin layer at the air/water interface. The two monomers are polymerized through the Schiff base reaction in A<sub>3</sub>+B<sub>2</sub> fashion to form a continuous thin film. From the density functional theory (DFT) calculation (Figure S4 and S5, SI), the pore size of the film is estimated to be around 1.5 nm and the thickness of a monolayer is between 0.85 and 1.7 nm based on two different arrangement of monomer **1**. The pore size is in the nanofiltration (NF) region which can find extensive applications, for example, pretreatment of seawater to remove divalent ions and separation of organic molecules.



**Scheme 1. Synthesis of 2D polyimine thin film 3 (ideal structure) using triamine 1 and dialdehyde 2 at the air/water interface.**

The surface pressure-area isotherm is an important indicator of how the monomers are packed at the interface. Figure 1a shows the pressure-area isotherm when the two monomers are dispersed at the air/water interface before polymerization. It shows that the surface pressure increases smoothly when the surface area is decreased. There is no clear phase transition<sup>34</sup> from gaseous to liquid or to solid state to be observed, but a steep step is observed at around 7 mN/m which indicates a compact layer is formed at this surface pressure.

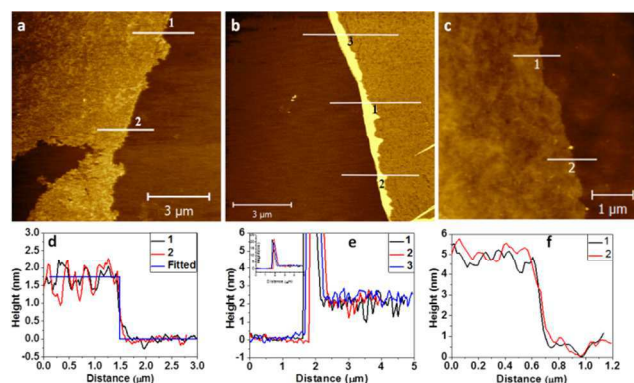


**Figure 1.** (a) pressure-area isotherm, (b) optical microscopy image of the truxene 2DP film 3 on SiO<sub>2</sub>/Si surface, (c) SEM image of 2DP film 3 on TEM grid, (d) HR-TEM image of 2DP film 3 on TEM grid, (e) SAED diffraction image, (f) Digital picture of 2DP film 3 deposited on a porous polysulfone support.

The polymerization is initiated by carefully introducing a catalyst, trifluoroacetic acid, into the solution. The obtained film can be transferred to different support surfaces by the Langmuir-Schaefer (LS) method. Multilayers can be obtained by repeating the transfer process. An optimal surface pressure for polymerization was found around 10 mN/m, which gives a compact film with few layers that will be discussed in more details in the next paragraph. The films synthesized at this optimum condition were transferred to different supports for detail microscopic observations and the results are shown in Figure 1b-1f. Figure 1b shows the optical microscopy image of the membrane transferred on a SiO<sub>2</sub>/Si wafer surface. An apparent color contrast between a bare substrate and evident edges of the film helps in identifying the number of layers. Regions that have no film, single layer and two layers can be easily distinguished in Figure 1b. In each region the color is very uniform, indicating a continuous film with uniform thickness. Figure 1c show the SEM image of the film transferred to a TEM grid. SEM imaging supported a film-like morphology. The holy carbon of TEM grid present underneath can be clearly seen.

This indicates that the film obtained is noticeably thin. Near the edge some ruptures and rolling up in the film are observed, which is occurred mainly during the transfer and drying process. High-resolution TEM imaging (Figure 1d) further supported a continuous film like morphology with an evident edge of the film. As shown in (Figure S2, SI), the 2DP membrane is nearly transparent under electron beam. Selected area electron diffraction (SAED, Figure 1e) revealed a bright ring, indicative of some ordered structure within the amorphous film. Interatomic spacing (*d*-spacing) calculated from the diffraction ring is found to 0.292 nm. The membranes used for filtration studies were deposited on polysulfone support, which is shown in Figure 1f. Again, a clear color contrast can be observed to differentiate the thin film from the blank support.

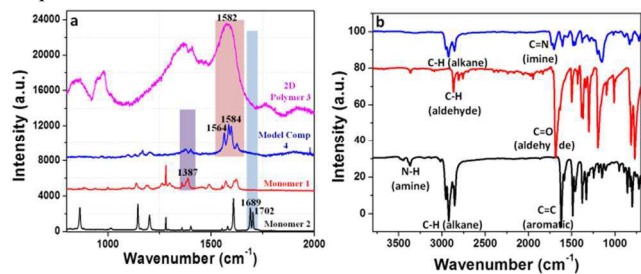
The membrane thickness was measured by AFM in tapping-mode. Figure 2 shows the height profiles of the films prepared at surface pressure of 0.5, 2, and 10 mN/m. The average film thicknesses are around 1.7, 2.3 and 4.7 nm, respectively. The film roughness is around 1 nm. The height profiles measured from different samples are very consistent, indicating the procedure is very reproducible. The average film thickness at 0.5 mN/m is close to the thickness of monolayer estimated from the DFT calculation. The films in all three cases appear continuous without pinholes. However, the selectivities of the first two membranes were found very low during the filtration tests, which implies that these membranes are not compact enough. To improve the performance, the third membrane was polymerized at 10 mN/m, slightly higher than the steep step found in the pressure-area isotherm. Presumably, this surface pressure should be high enough to keep contraction of the film during polymerization while from the other hand should be small enough to allow the monomers to have sufficient lateral mobility to undergo the substantial structural rearrangements that are required to form a bond. The AFM image in Figure 2c as well as the microscopic images in Figure 1 clearly showed that the membrane prepared at this surface pressure is compact. From the membrane thickness, the membrane is 2~3 molecular layers in this case.



**Figure 2.** AFM topography image and height profile of the truxene 2DP thin film after polymerizing at surface pressure of 0.5 mN/m (a, d), 2 mN/m (b, e) and 10 mN/m (c, f). Different curves in each height profile are measured from different samples that were made in the same conditions. Height thickness is calculated from Gwyddion software. Figure 2e shows that the thickness at the edge is very high, which should be due to accumulation of the film that can be seen from the AFM image. A complete height profile is shown in the insert.

To elucidate the internal chemical structure, ten layers of the truxene 2DP thin film (3) were deposited on a silicon wafer and was characterized by confocal Raman spectroscopy. Figure 3a shows a comparison of Raman spectra of monomers 1, 2, model compound 4 (Figure S12, SI) and 2DP (3). In the spectrum of

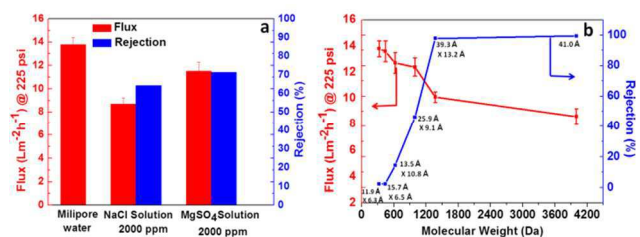
monomer **2**, Raman bands at 1689 and 1702  $\text{cm}^{-1}$  are typical of aldehyde stretching vibrations<sup>31</sup>. These characteristic signals are absent in the case of a model compound and 2DP thin film **3**. On the other hand, Raman signal at 1387  $\text{cm}^{-1}$  corresponds to the stretching vibrations of phenyl ring and amine functional group. Such wagging vibrations of amine group are absent in Raman spectrum of model compound **4**. New Raman bands at 1564 and 1584  $\text{cm}^{-1}$  in the spectrum of model compound **4** corresponds to C=N stretching vibrations of newly formed imine bond. Similarly, Raman stretching signal at 1582  $\text{cm}^{-1}$  in the spectrum of 2DP thin film (**3**) relates to the C=N of imine linkage in the polymer. Therefore, the results obtained from Raman spectroscopy confirms the distinctive imine linked structure present in 2DP thin film (**3**). Internal structure of thin film was further correlated by FTIR spectrum using synthesised bulk polymer material. Figure 3b shows a FTIR spectra of monomer **1** (black) having a stretching frequency at 3444–3369, 2954–2853, and 1620  $\text{cm}^{-1}$  corresponds to N-H, C-H, and C=C of amine, alkyl, and phenyl ring respectively. Monomer **2** (red) indicates a characteristic stretching vibration at 2866  $\text{cm}^{-1}$  of C-H (aldehyde) and 1684  $\text{cm}^{-1}$  corresponds to a carbonyl group. The FT-IR spectra of bulk polymer (blue) indicate almost complete consumption of the starting materials on the basis of the disappearance of the N-H stretching bands of **1** (3444–3369  $\text{cm}^{-1}$ ) and the carbonyl stretching bands of **2** (1684  $\text{cm}^{-1}$ ). Moreover, a new signal appeared at a frequency of 1728 and 1704  $\text{cm}^{-1}$  belongs to C=N stretching of imine bond<sup>35</sup> along with C-H stretching at 2954–2854 of alkyl chain. To further confirm the consumption of starting material, <sup>13</sup>C cross polarization magic angle spinning (CP-MAS) solid-state NMR spectrum of bulk polymeric material was recorded (Figure S13, SI). It shows a characteristic signals at 155.18 ppm which signifies the C=N carbon of newly formed imine bond and at 56.29 ppm corresponds to the carbon bridging the two aromatic rings of truxene. There is no prominent signal from the carbonyl carbon of aldehyde observed between 170–210 ppm. Hydrophobicity of the 2DP thin film is analyzed by water contact angle experiment. (Figure S3, SI) shows a contact angle of 55.9° for bare silicon wafer and 79.1° for thin film coated silicon wafer, which confirms the hydrophobic nature of the material.



**Figure 3.** (a) Raman spectra of monomer **2** (black), **1** (red), model compound **4** (blue) and 2DP thin film **3** (magenta), (b) FTIR spectra of monomer **1** (black), **2** (red) and bulk polymer **3** (blue).

The 2DP membrane prepared at the surface pressure of 10 mN/m and transferred (Figure S1, SI) on a porous polysulfone support was used for membrane studies. As the pore size is in the nanofiltration region, the membrane was tested first for water desalination of mono- and bi-valent salts and the results are shown in Figure 4a. Nanofiltration membranes typically cannot remove mono-valent salts like NaCl, but can remove bi-valent and tri-valent salts to some extent, and hence nanofiltration membranes can be used in pretreatment of seawater desalination<sup>36</sup>. As shown in Figure 4a, the membrane showed a pure water flux of around 13.8 LMH despite of the high hydrophobicity generated by the long alkyl chain, and a salt rejection of 64.27 % and 71.34 % with a slight decline in water flux (8.7 and 11.5 LMH) were achieved

for NaCl and  $\text{MgSO}_4$  solutions, respectively. Figure 4b shows the separation performance for organic molecules. Different molecular size organic molecules were chosen as probe, such as Methyl orange (MO) (MW 327.33), Rhodamine B (RB) (MW 442.55), Bromothymol blue (BB) (MW 624.38), Reactive Black 5 (RB) (MW 991.82), Direct Red 80 (DR) (MW 1373.07), and PEG (MW 4000). From Figure 4b, the cut-off molecular weight at 90% rejection rate is estimated to be around 1400 amu with a water flux around 10 LMH at 225 psi. However, the rejection rate should be explained more accurately from the molecular size. The molecular size is estimated from their molecular structure using Material Studio® (Figure S6 and Table S1, SI). For molecules with different dimension size, it is expected that the effective molecular size for transport is mainly determined by the smallest projection size. For example, the size of Direct Red 80 along the long chain is around 39.3 Å, while the size along the side chain is around 13.2 Å, so the effective molecular size should be around 13.2 Å. A clear molecular sieving effect can be observed. Small molecules such as methyl orange and Rhodamine B can pass the membrane easily with almost no retention, while big molecules such as Direct Red 80 and PEG were blocked almost completely. The cut-off molecular size is around 1.3 nm, which is very close to the membrane pore size estimated from the DFT calculation. The control experimental results in Table S2 and S3 in SI showed that the bare polysulfone support has almost no rejection for all the studied salts and dyes, and the water flux is more than 100 times higher than the 2DP membrane. Hence, it confirms that the separation is achieved mainly by the 2DP membrane.



**Figure 4.** (a) Pure and salt-water flux and rejection rate of the Truxene 2DP thin film, (b) Flux and rejection performance of the truxene 2DP thin film for Methyl orange (MO) (MW 327.33), Rhodamine B (RB) (MW 442.55), Bromothymol blue (BB) (MW 624.38), Reactive Black 5 (RB) MW 991.82), Direct Red 80 (DR) (MW 1373.07), and PEG (MW 4000).

In conclusion, we have successfully synthesized a free-standing, large area and imine bonded 2DP thin film at the air/water interface using the Langmuir-Blodgett method. The film thickness can be varied by changing the surface pressure for polymerization. At a surface pressure slightly higher than the pressure to form a compact packing as measured from the pressure-area isotherm, a compact membrane with thickness around 2–3 molecular layers was successfully obtained. The thin film morphology is confirmed by optical microscopy, SEM, TEM, and height analysis by AFM. The internal structure of the film was ascertained directly by confocal Raman spectroscopy and relatively by FTIR. The membrane structure is in general amorphous, but the dynamic imine chemistry did help to form a certain degree of short-range order. The membrane was found to be hydrophobic in nature. Filtration studies showed that the membrane has good salt rejection for both monovalent and divalent salts, and a clear molecular sieving for large organic molecules. The cut-off molecular size is around 1.3 nm, which is close to the predicted membrane pore size. The method present in this work can serve as a general approach to prepare 2DP membranes.

## ASSOCIATED CONTENT

### Supporting Information

Materials; membrane fabrication; separation test; characterization; geometry estimation; NMR of intermediate compounds. The Supporting Information is available free of charge on the ACS Publications website.

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### Notes

The authors declare no competing financial interests.

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