Synthesis of Ultrathin Two-Dimensional Covalent Organic Thin Film with Sharp Molecular Sieving Nanofiltration

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Abstract: We demonstrated here a novel and facile synthesis of two-dimensional (2D) covalent organic hydrophobic thin film using planar, amphiphilic and substituted heptacyclic truxene based triamine and simple dialdehyde as building blocks by dynamic imine bond formation at the air/water interface using Langmuir-Blodgett (LB) method. Obtained thin film is characterized by optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), which unanimously exhibited the formation of large, molecularly thin and free standing sheet-like morphology covered all over the substrate. Internal structural at the molecular level of the imine bond formation in the obtained thin film was directly confirmed by confocal Raman spectroscopy and indirectly confirmed by FTIR of the bulk material synthesized using identical monomers in solution phase. The thin film formed tested further for nanofilteration and shows reasonable rejection performance.

Two-dimensional porous polymers (2DP) have great potentials 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

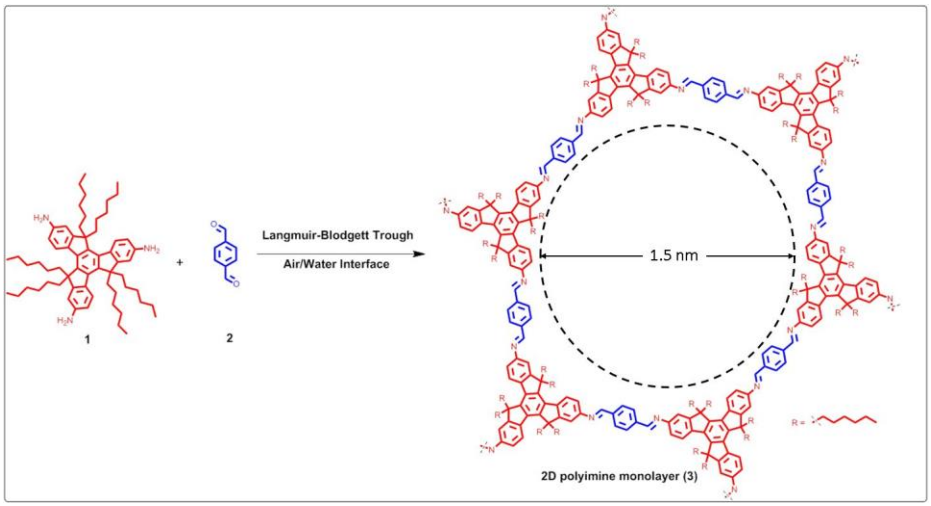
properties can be very different from that of the bulk which may also open potential applications in sensing, electrochemistry, coatings, biotechnology, catalysis, organic photovoltaic devices, energy storage, gas storage and semiconductors.[1-12]

Ideally, 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.[13-15] 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,[16-18] nano-sheets generated from covalent organic frameworks (COFs)[19-22] as well as metal-organic frameworks (MOFs).[23-25] 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[26-34] 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$_2$)$_3$**] (**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 resists and lasers.[35] 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 is an important linkage in membrane

applications. Most high performance membranes for water desalination and gas separations are imine polymers.[36] Imine bond has a well-known feature called "dynamic imine chemistry", which enables a self-correction mechanism to form molecular structures under better thermodynamic controls. 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.[37-39] However, to the best of our knowledge, there is only one report so far for the synthesis of 2DPs using imine bonding.[40]

The truxene 2DP membrane was synthesized according to scheme 1. Turxene has a planar heptacyclic polyarene structure with three $–CH_2–$ "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 S2 (SI), which makes the molecule amphiphilic in nature. It is expected that at the air/water interface, the hydrophobic hexyl chains will be pointing upwards towards the air while the heptacyclic aromatic rings will stay on the surface affixed by three hydrophilic amino groups towards the water phase, and therefore a thin layer is formed at the interface. The two monomers are polymerized through the Schiff base reaction in A_3+B_2 fashion to form a continuous thin film. From the density functional theory (DFT) calculation (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** (Figure 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 air/water interface.

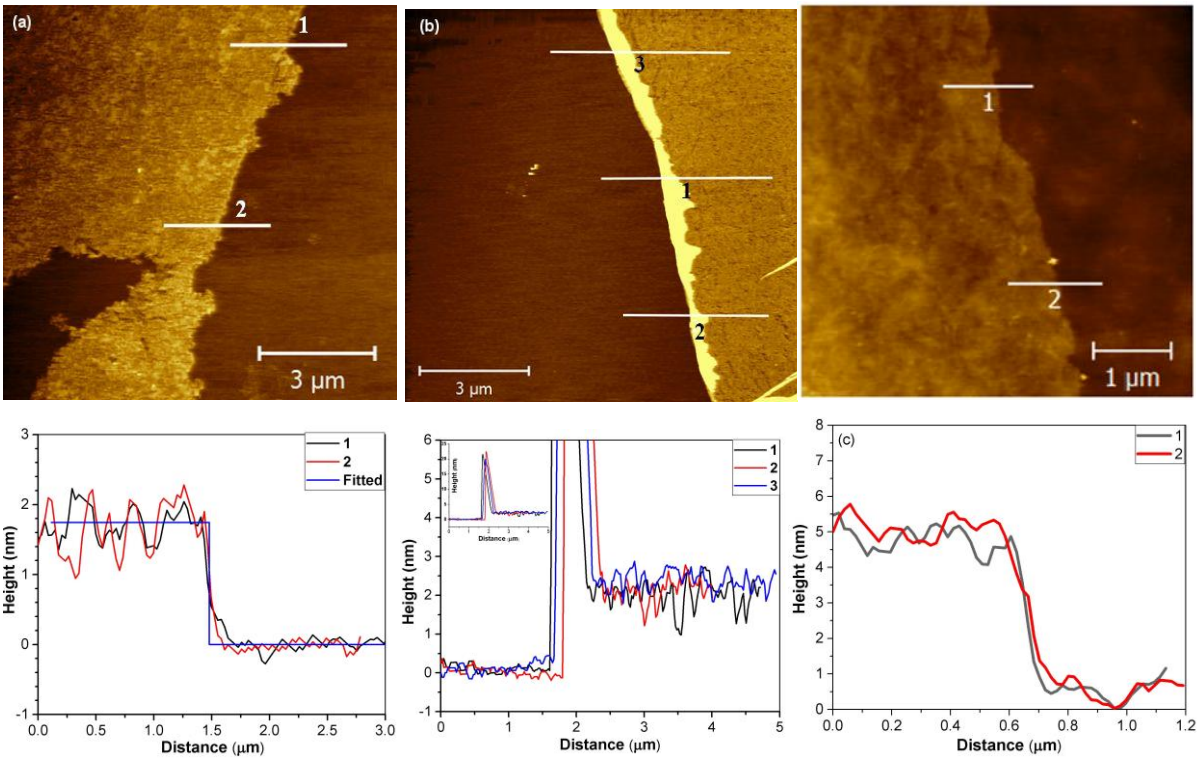


Figure 1. AFM topography image and height profile of the turxene 2DP thin film after polymerizing (a) 12.5, (b) 25 and (c) 50 µl of monomer solution respectively. Height thickness is calculated from Gwyddion software. (Inset in figure 2b shows a complete height profile graph, thickness at the edge is more may be due to accumulation of thin film).

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