# Supporting Information

# for

# Visualizing and Monitoring Interfacial Polymerization by Aggregation-Induced Emission

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**Contents**

## Experimental Procedures

### 1. Chemicals and materials

Tetrakis(4-aminophenyl)ethylene (TAPE, > 97%) was purchased from Shanghai Tensus Biotechnology Co., Ltd.. Trimesoyl Chloride (TMC, > 99%) was obtained from Qingdao Benzo New Materials Co., Ltd. and it was kept in vacuum chamber against hydrolyzing. 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][$BF_4$], 99%) was commercially provided by Dibai Chemical Technology Co., Ltd.. Evens Blue (Mw 960.8) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd.. Anhydrous solvents, including *n*-hexane, methanol, ethanol, N-methyl pyrrolidone, and 1,4-dioxane were used as received from Sinopharm Chemical Reagent Co., Ltd. without further purification. Deionized water (18.2 MΩ) was generated by an ELGA system. Anodic aluminum oxidation film (AAO, pore size 0.2 μm and diameter ϕ47 mm) was acquired from GE Healthcare UK Ltd.. Microfiltration membranes of polyethersulfone (PES) and Nylon (pore size 0.22 μm and diameter ϕ47 mm) were bought from Haiyan Corporation and washed in ethanol overnight before use.

### 2. Synthesis of cross-linked ultrathin polyamide film

Cross-linked polyamide films were synthesized by one-step interfacial polymerization reaction between TAPE and TMC as follow. Firstly, TAPE powder (0.0377 g, 96 mmol) was added to ionic liquid, [Bmim][$BF_4$] of 1.0 mL and then treated with ultrasound for 20 min at room temperature to result an orange transparent solution. TMC (0.1590 g, 0.60 mol) was dissolved into *n*-hexane to prepare 100 mL of solution. Secondly, a sample of TAPE solution (400 μL) was spread on a glass plate of 10 $cm^2$ by a doctor blade with a gap width of 200 μm. Next, the plate was horizontally immersed into a reaction chamber containing of 5.0 mL of TMC solution. Fast interfacial condensation reaction occurred at the interface between [Bmim][$BF_4$] and *n*-hexane and then generated a cross-linked polyamide film. The plate was taken out after 10 min of polymerization. The formed TAPE-TMC polyamide film was successively washed in hexane, N-methyl pyrrolidone, ethanol, and water. Freestanding polyamide films were obtained for further characterization or application supported with many substrates, *e.g.* silicon wafer, quartz plate, microfiltration membranes.

## 3. Fluorescence measurement

Photoluminescence (PL) spectra were recorded on the Shimadzu RF-5301PC fluorescence spectrometer at 298 K. A sample of 2.0 mL solution was added into a quartz cuvette to measure the PL spectra. The excitation wavelength was 400 nm for measuring the PL intensity of 50 μM TAPE dissolved in 1,4-dioxane/water or [Bmim][$BF_4$]/water solution with different water contents. The light slit was 3/5 nm. All solutions were freshly prepared and stabilized for 20 min before test. PL spectra of TAPE in [Bmim][$BF_4$] with different concentrations were also measured, and excitation light of 420 nm and slit of 3/5 nm were used to obtain stable and repeatable PL intensity. A simple of lab-made cuvette holder was designed, in which the cuvette was placed at fixed position, and a slit of 2 mm width was additionally installed at the light emission path. Thus, the detected emission signal was from excited solution at specific location in cuvette. When a certain volume of TAPE solution (400 μL) and TMC solution (1000 μL) were added into the cuvette in sequence, the obtained PL spectra only recorded the emission of TAPE solution underneath the interface between [Bmim][$BF_4$] and hexane. Here the PL spectra of TAPE with different concentrations were measured and the interfacial interference was eliminated by adjusting the position of the interface between [Bmim][$BF_4$] and hexane. The PL intensity of TAPE solution at 503 nm was recorded continuously during the interfacial polymerization. The time interval was 0.02 s per point in the first 5 min to capture fast intensity change and then was 0.5 s per point for long-time observation. All used solutions were freshly prepared against moisture adsorption.

## 4. Characterization

Attenuated total reflection-Fourier transform infrared spectrometer (Thermo Fisher scientific LLC Nicolet 6700) was used to analyze the chemical structures of TAPE-TMC polyamide films. Surface elemental composition was detected by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha). The film samples were supported by PES microfiltration membrane and completely dried in vacuum oven before test. UV-vis absorption spectra of the polyamide films were collected using Shimadzu UV-2450 spectrometer with integrating sphere accessory ISR-240. Fluorescent microscopy (Nikon Ti-V) was used to observe the films and capture fluorescence images. Powder X-ray diffraction (PXRD) was conducted with Rigaku D/Max-2550PC using monochromated Cu/Kα (λ 0.154 nm). Surface water wettability was evaluated by water contact angle (WCA) measured with

DropMeter A-200 system. Here TAPE-TMC polyamide films were deposited on piranha solution-treated silicon wafers. TGA analysis was performed using a TA instrument Q-50 TGA thermal analyzer under purging nitrogen gas atmosphere at a flow rate of 60 mL/min. Dried film sample of 3.6 mg was sealed in Pt cell and heated from 10 °C to 1000 °C to study the polymer degradation.

## 5. Morphology profiles of the polyamide film

The synthesized polyamide freestanding films were transferred on PES substrate and dried at atmosphere. The samples were cut into small pieces and treated by Pt sputtering for 30 s before surface observation. Some samples were frozen in liquid nitrogen and then were broken to obtain clear cross profiles. Surface and cross-sectional morphologies were observed by field emission scanning electron microscope (FESEM, Hitachi S-4800) at 3 kV.

## 6. Thickness measurement

Silicon wafer was chosen as support of TAPE-TMC polyamide films for thickness determination by spectrometer ellipsometer (J.A.Woollam M-2000. Measured spectra were fitted with “absorbing film” analysis mode. The determined values of film thickness were reliable when the value was below 200 nm. Scanning probe microscope (SPM, VECCO MultiMode) and stylus profilometer (Bruker Dektak XT) were also applied to measure the polyamide films. They could accurately survey the vertical height differential between film surface and silicon wafer. The measurement was repeated three times at least per point.

## 7. Organic solvent nanofiltration and dye separation

TAPE-TMC polyamide films synthesized at the free interface between [Bmim][$BF_4$] and hexane were deposited on Nylon microfiltration substrates by vacuum-assisted filtration. Then the composite membrane was installed into Millipore membrane pool for organic solvent nanofiltration. Effective membrane filtration area was 2.84 $cm^2$. Applying 0.2 MPa pressure from nitrogen gas, the Evens Blue in methanol was separated by the composite membrane. The solution permeate was collected per 20 min and recorded its volume. Dye concentration was detected through examining UV-vis absorbance at specific wavelength before and after separation.

## 8. Computational methods

Geometry optimization of molecule was performed for the ground state ($S_0$) by the density function theory at the level of B3LYP/6-31G* with Gaussian 09 software package.[1] Structure simulation of the cross-linked TAPE-TMC polyamide was conducted with LAMMPS software. The simulation cell consists of a cube box containing 240 TAPE and 320 TMC molecules, and PCFF force field was applied to these molecules. Continuous calculation of bonding process transformed these molecules to polymer in simulation cell, and after 21 steps annealing the final cross-linked structure was obtained. Further detailed analysis of atom coordinates provided the backbone visualization and the void distribution of polymer network.

## Supporting Figures and tables

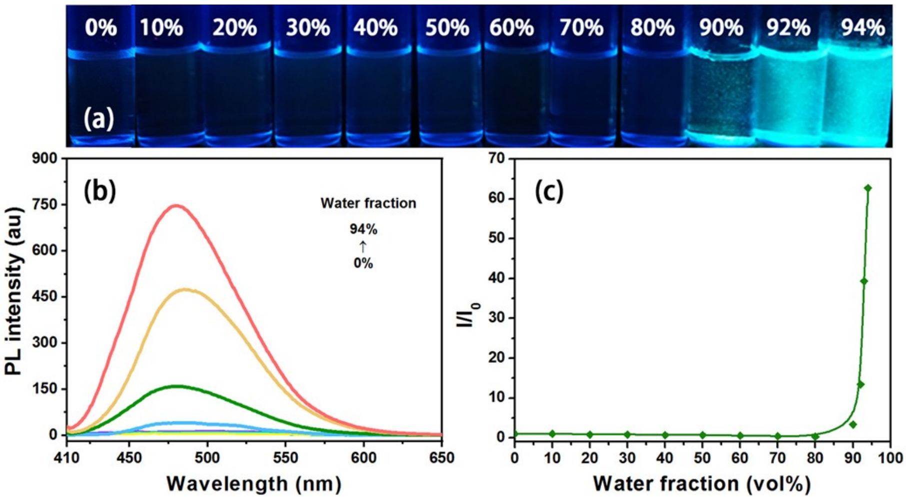


**Fig. S1** AIE properties of TAPE. (a) Digital photographs of TAPE in 1,4-dioxane/water mixtures with various water fractions, $f_w$. (b) Photoluminescence (PL) spectra of the TAPE solutions and (c) the peak PL intensity versus increased $f_w$.

**Table S1** Viscosity of several imidazolium ionic liquids at room temperature.[2]

| Ionic liquid | Phase | Temperature (K) | Viscosity (Pa·s) |
|---|---|---|---|
| [Emim][$BF_4$] | Liquid | 293.85 | 0.0434± 0.0047 |
| [Bmim][$BF_4$] | Liquid | 293.85 | 0.142 ± 0.0077 |
| [Hmim][$BF_4$] | Liquid | 293.15 | 0.286 ± 0.017 |
| [Bmim][$NTf_2$] | Liquid | 293.15 | 0.0627 ± 0.004 |

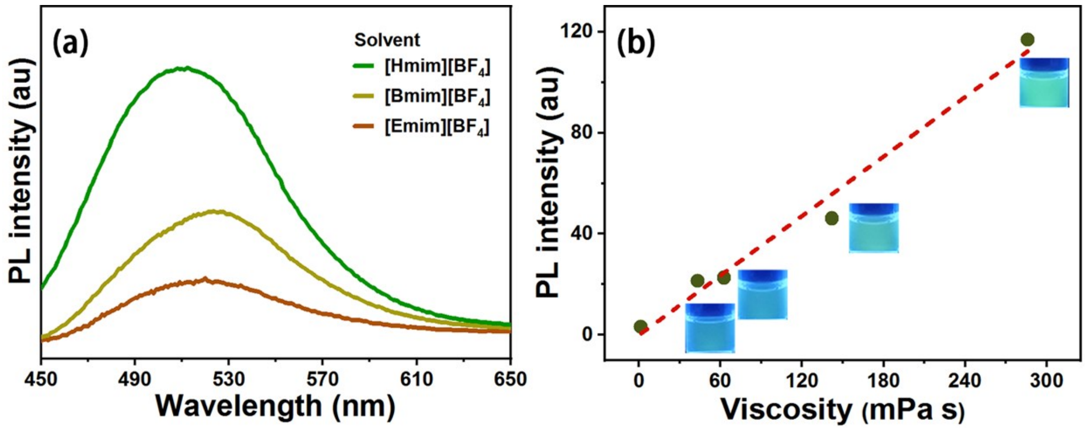


**Fig. S2** PL intensity of TAPE solved in different ionic liquids. (a) PL spectra of TAPE solutions of $5\times10^{-5}$ M. (b) The peak PL intensity versus solvent viscosity. It is obvious that the PL intensity increases linearly with the viscosity of imidazolium ionic liquids due to high thermal-movement restriction.

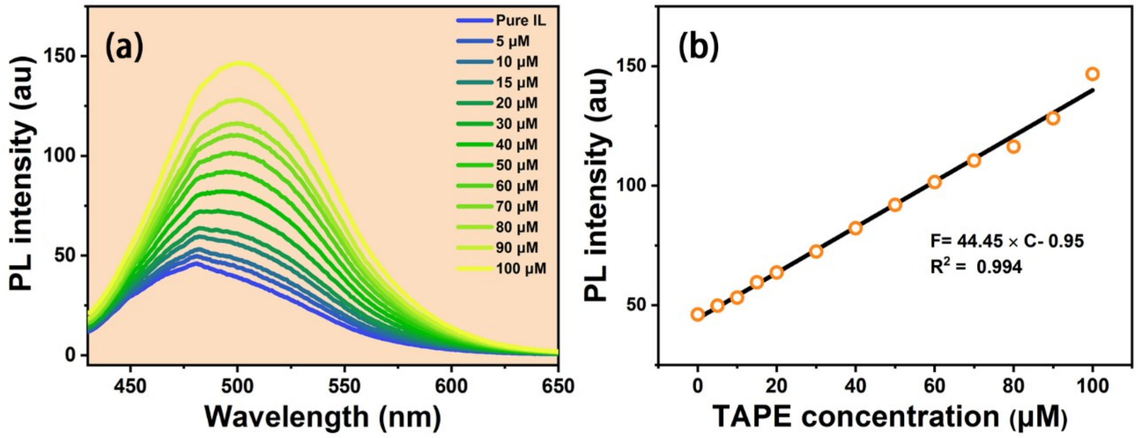


**Fig. S3** (a) PL spectra of TAPE in [Bmim][$BF_4$] of incremental concentration. (b) Linear fitting curve between PL intensity and TAPE concentration. The linear relationship is maintained within the concentration below $1\times10^{-4}$ M. The excitation wavelength $\lambda_{ex}$ is 420 nm.

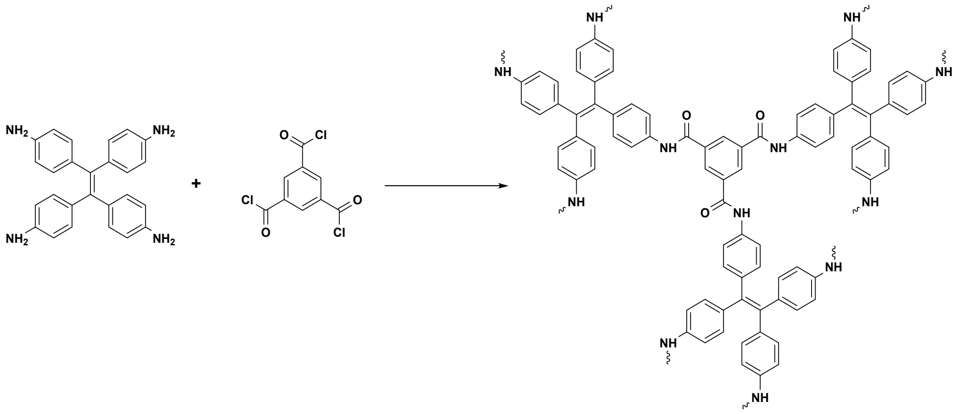


**Fig. S4** Polycondensation reaction between TAPE and TMC for synthesizing cross-linked polyamide films.

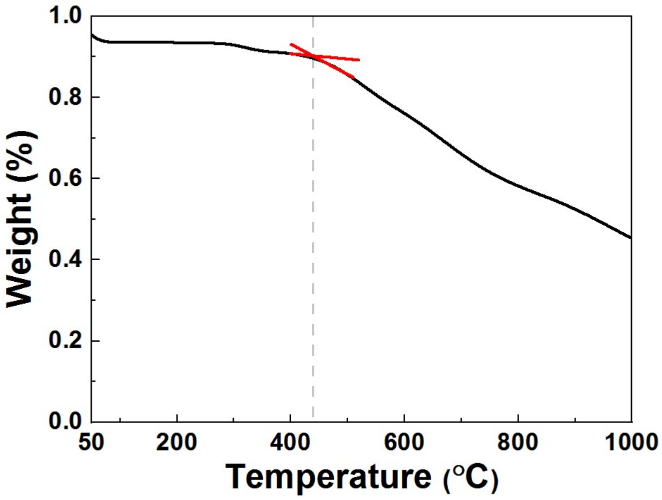


**Fig. S5** Typical TGA curve of the TAPE-TMC polyamide films.

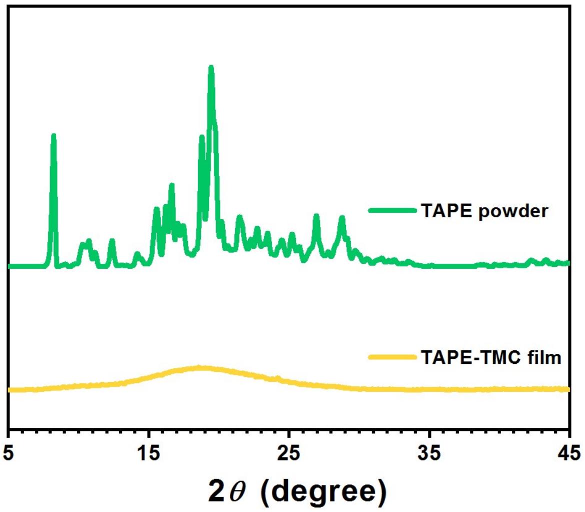


**Fig. S6** Powder X-ray diffraction patterns of TAPE powder and TAPE-TMC film. There is not obvious crystalline peak in the XRD spectrum of the TAPE-TMC polyamide film compared with the TAPE powder.

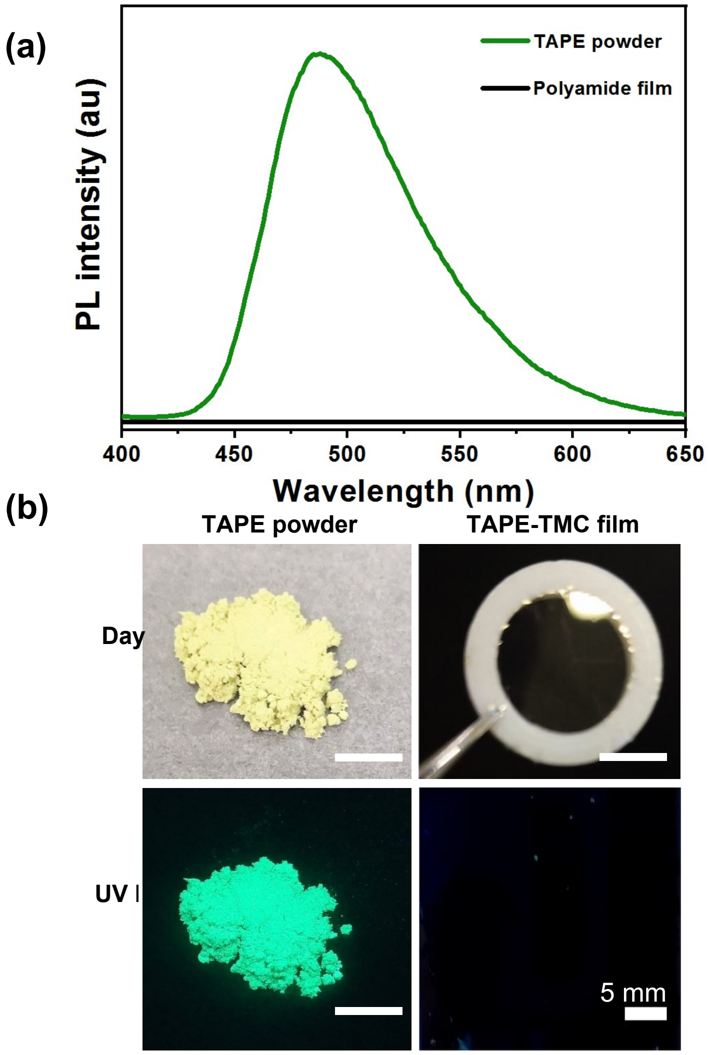


**Fig. S7** (a) PL spectra and (b) digital photographs of the TAPE powder and the TAPE-TMC polyamide film excited with 365 nm light.

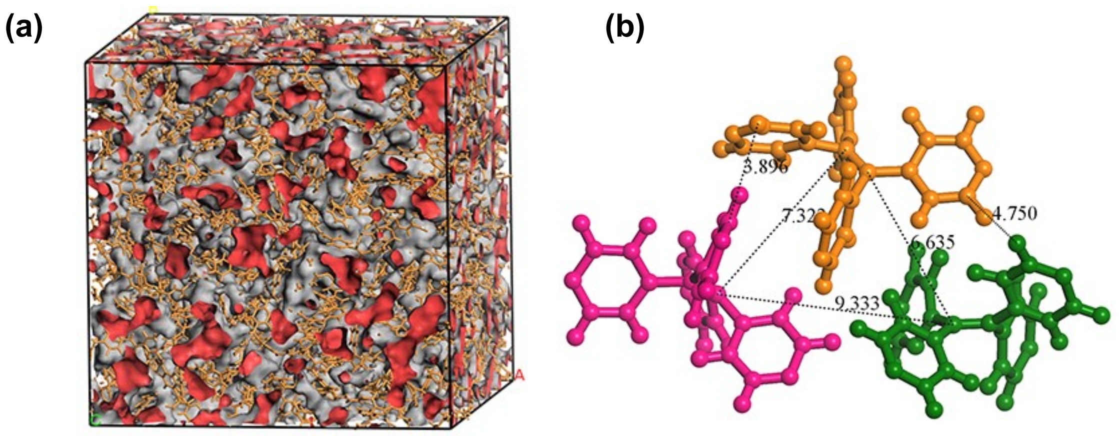


**Fig. S8** Three dimensional view of amorphous cell containing the cross-linked TAPE-TMC polyamide network. Red color: accessible surface of the probe with radius of 0.85 Å. The amorphous cell size: 58.2 Å× 58.2 Å × 58.2 Å. Calculated free volume is 48067.27 Å$^3$.

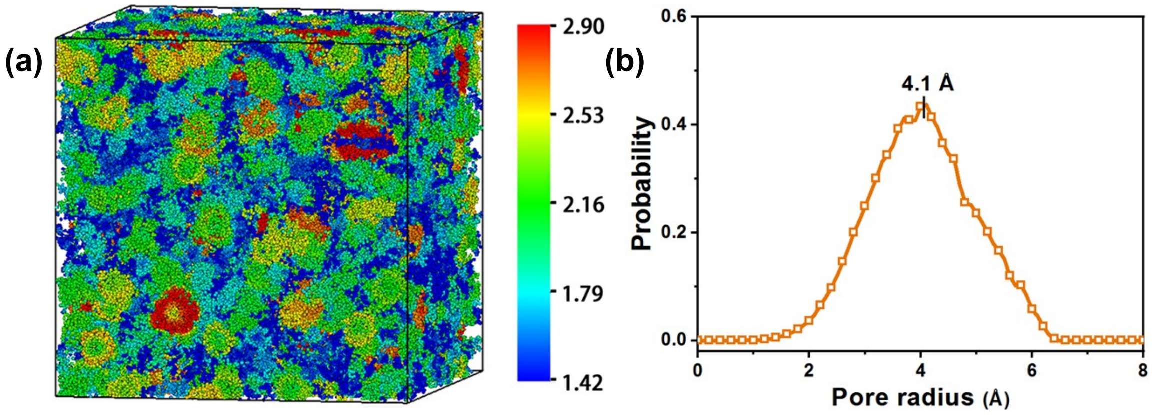


**Fig. S9** (a) Simulated pore size distribution in the energy-minimized amorphous cell of the cross-linked TAPE-TMC network. (b) The statistical probability density of different pore structures. Amorphous cell size: 58.2 Å× 58.2 Å × 58.2 Å.

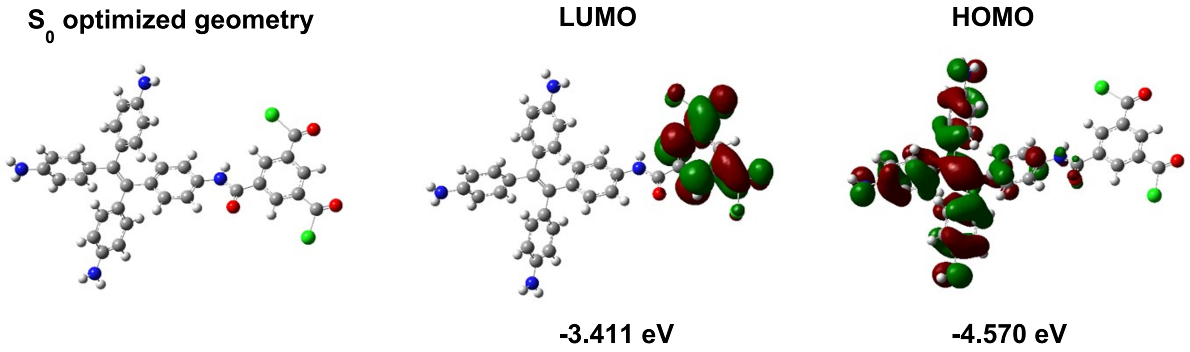


**Fig. S10** The optimized ground state ($S_0$) of molecule containing a TAPE unit and a TMC unit as well as the calculated LUMO and HOMO energy. The frontier orbital energy difference is smaller than TAPE molecule.[3]

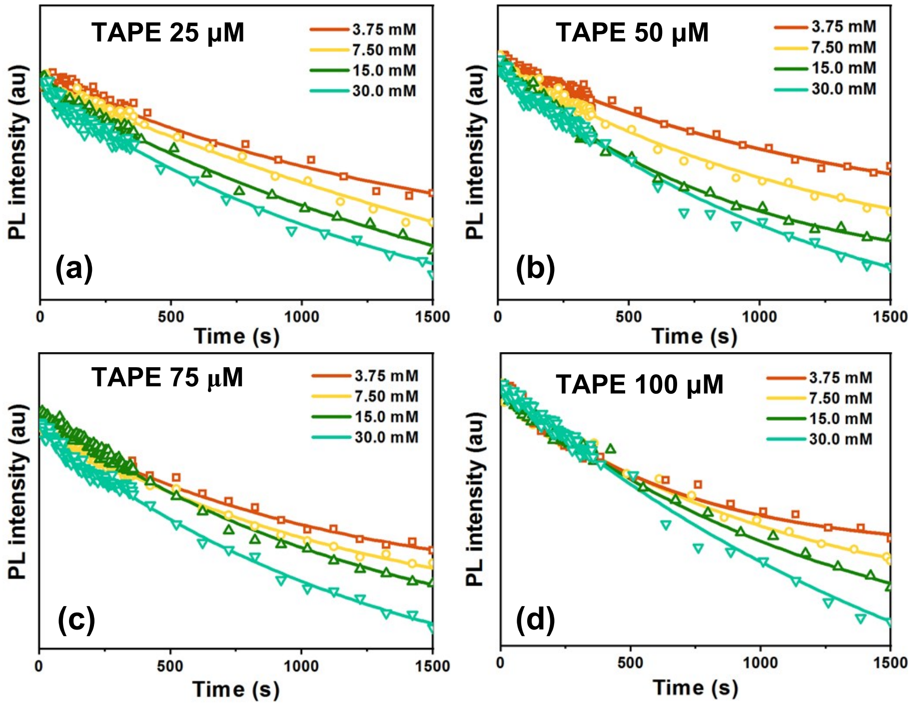


**Fig. S11** PL intensity of TAPE solution with reaction time during the interfacial polymerization between TAPE and TMC. Different TMC concentrations were used when TAPE concentration was fixed at (a) 25 μM, (b) 50 μM, (c) 75 μM, (d) 100 μM, respectively.

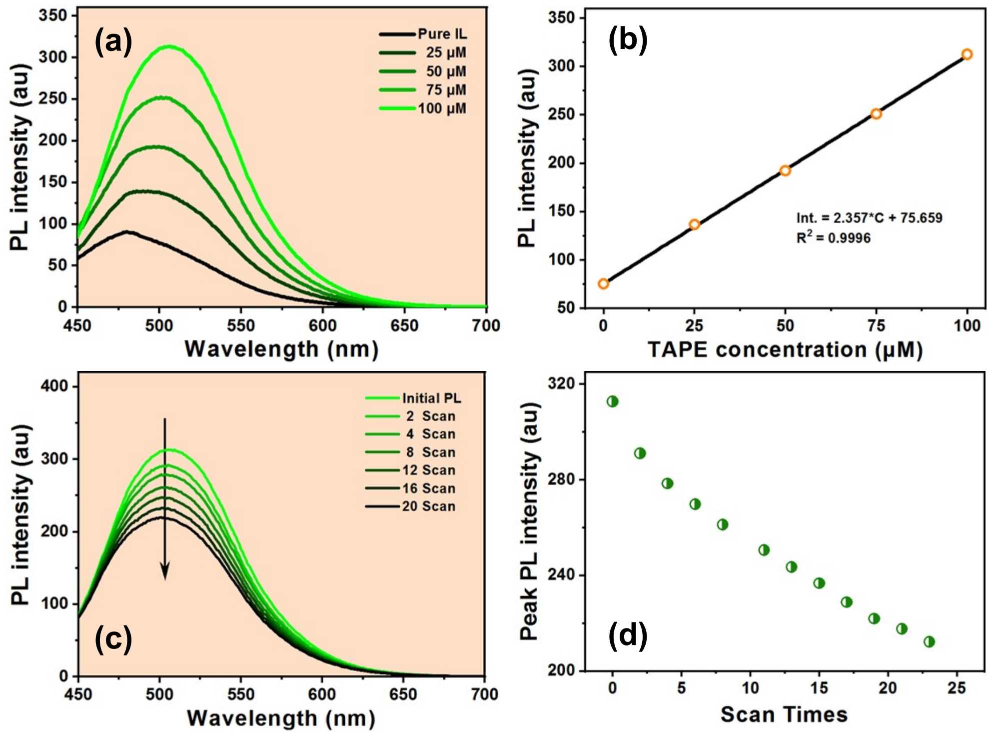
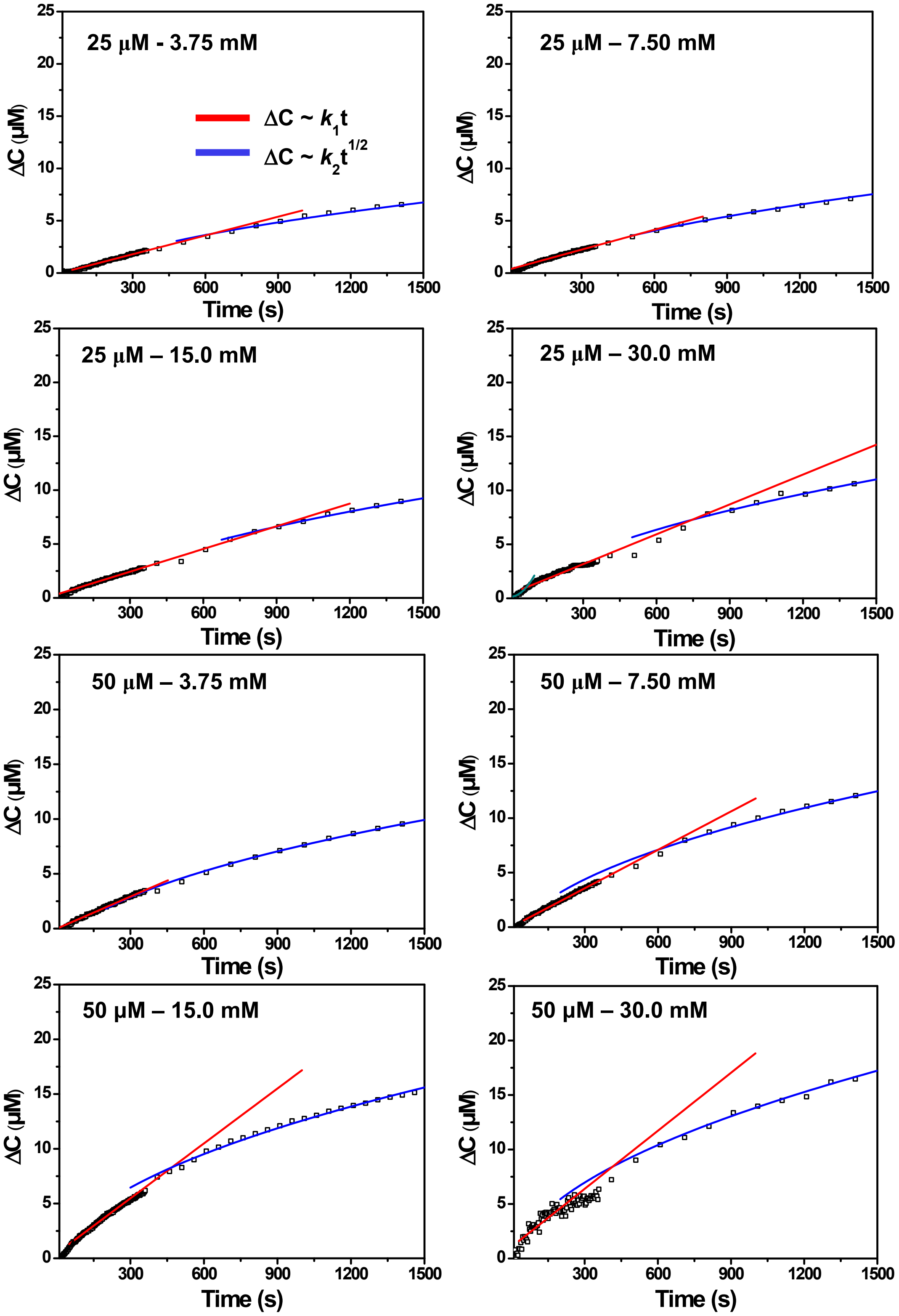


**Fig. S12** PL spectra of TAPE in [Bmim][BF$_4$] when a lab-made cuvette holder was used. (a) PL spectra of TAPE solution and (b) the calibration line between PL intensity (at 503 nm) and the TAPE concentration. $\lambda_{ex}$ 420 nm. (c) PL spectra change and (d) the peak PL intensity versus scan cycles during the interfacial polymerization between TAPE (100 μM) and TMC (30 mM).


25 μM - 3.75 mM
25 μM – 7.50 mM
25 μM – 15.0 mM
25 μM – 30.0 mM
50 μM – 3.75 mM
50 μM – 7.50 mM
50 μM – 15.0 mM
50 μM – 30.0 mM
$\Delta C \sim k_1 t$
$\Delta C \sim k_2 t^{1/2}$
ΔC (μM)
Time (s)
0
5
10
15
20
25
300
600
900
1200
1500

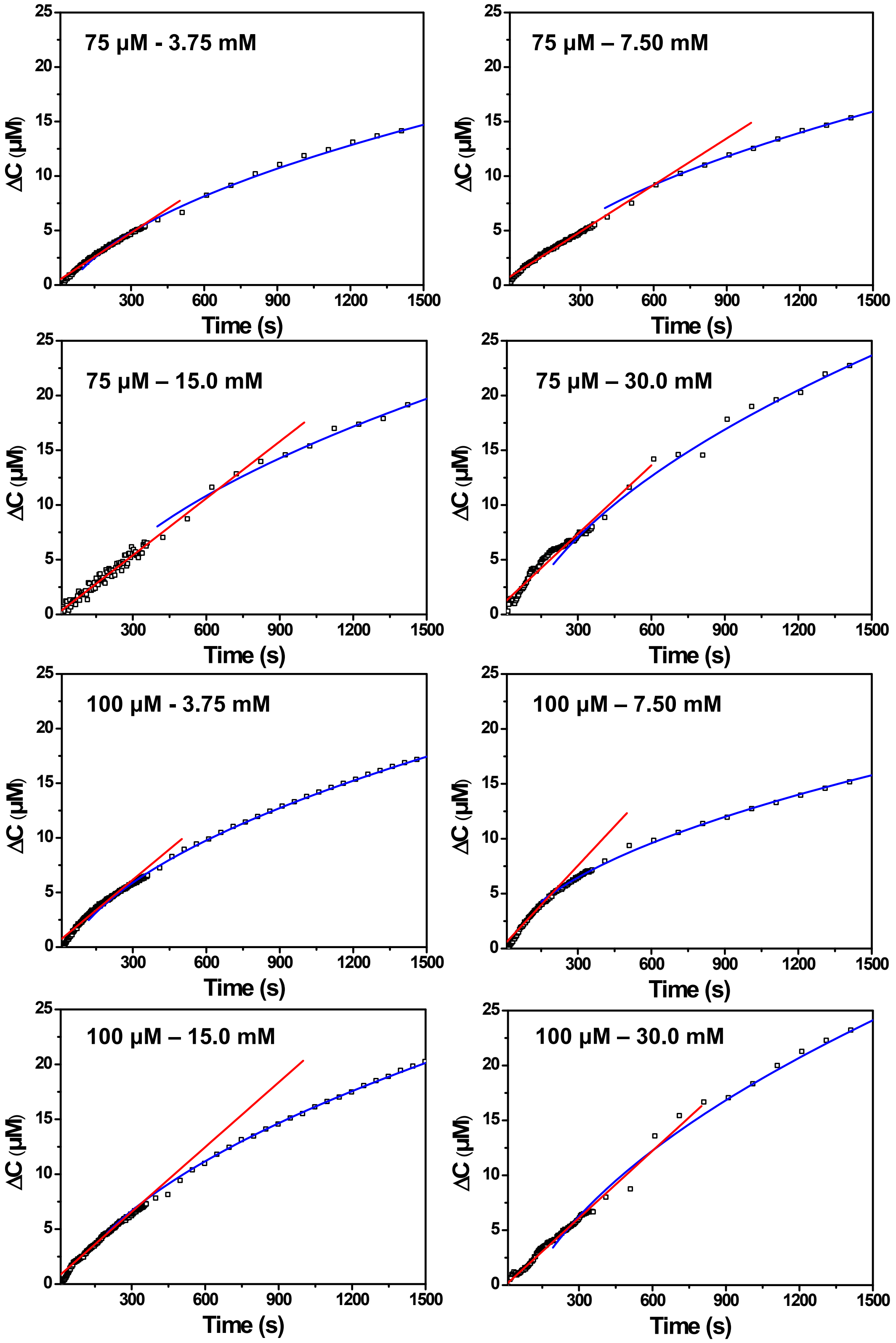


**Fig. S13** Segmental fitting plot of cumulative TAPE concentration change with polymerization time. Two equations, ΔC~$k_1 t$ (red line) and ΔC~$k_2 t^{1/2}$ (blue line) were applied to fit the overall process. The insert annotations "x-y" refers to the concentration of TAPE (x) and TMC (y).

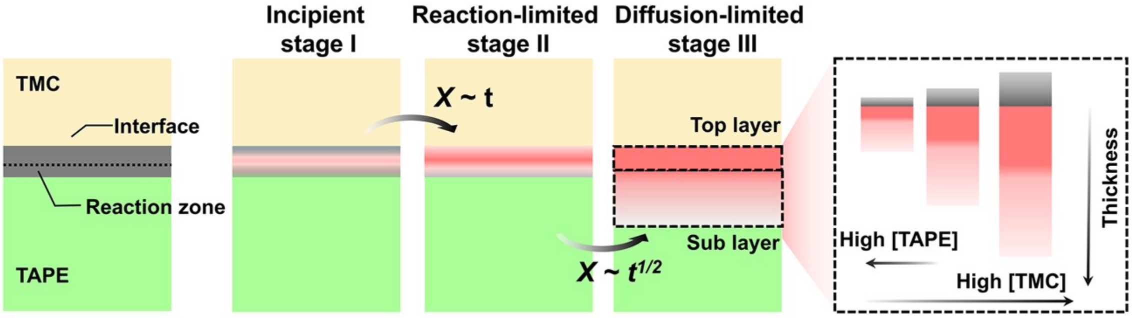


**Fig. S14** Hypothesis of polyamide film growth process at the interface between [Bmim][$BF_4$] and hexane during interfacial polymerization.

In this hypothesis, the interfacial reaction zone is located at the [Bmim][$BF_4$] phase. [Bmim][$BF_4$] would greatly restrict the diffusion of TAPE from ionic liquid phase to hexane phase due to the high viscosity.

Assume the same diffusion coefficients of TAPE and TMC in [Bmim][$BF_4$] or hexane. According Stokes-Einstein equation:

$$D_{A@b} = \frac{kT}{3\eta_b \pi d_A}$$

Where $D_{A@b} \propto 1/\eta_b$, meaning the diffusion rate of molecules A is inversely related to the viscosity of solvent *b*. We estimated that the diffusion coefficient would be about $5\times10^{-12}$ $m^2/s$ in [Bmim][$BF_4$] and $10^{-9}$ $m^2/s$ in hexane.

And we have calculated that the distribution coefficient, K(IL/HEX), was $10^{18}$ for TAPE and $10^{-1}$ for TMC, respectively. TAPE monomer mainly exists in the [Bmim][$BF_4$] and is hardly distributed in hexane.

$$K(IL/HEX) = \frac{C_{IL}}{C_{Hex}}$$

Then the initial position of interfacial polymerization is determined according to the equation below:[5]

$$X_{TAPE} = L_{TAPE}\frac{Kf_{TMC}C_{TMC}}{Kf_{TMC}C_{TMC} + f_{TAPE}C_{TAPE}}$$

$$X_{TMC} = L_{TMC}\frac{Kf_{TAPE}C_{TAPE}}{Kf_{TAPE}C_{TAPE} + f_{TMC}C_{TMC}}$$

Where $L_{TAPE}$ is the thickness of TAPE solution in which TAPE exists and polymerizes with the other monomer TMC, and $X_{TAPE}$ means the distance of polymerization reaction zone from the ionic liquid-alkane interface; *K* is the monomer distribution coefficient between ionic liquid and alkane. $f_{TAPE}$ and $f_{TMC}$ are functionality degree of monomers. Finally, $X_{TAPE}/X_{TMC}$ theoretically reaches up to ~$10^{16}$ under the same concentration of TAPE and TMC.

Therefore, the IP@AILI occurs in the ionic liquid phase as convinced by thermodynamic calculation. The initially generated TAPE-TMC polyamide would accumulate in the [Bmim][$BF_4$] phase. In the reaction-limited stage II, further polycondensation reaction would lead to relatively dense polyamide barrier. Then the reaction would transit to diffusion-limited stage III, where the TMC s diffuses across the barrier layer and result loose polyamide sublayer because of low local concentration. Increasing the TAPE concentration (or reducing TMC concentration) would effectively restrict the TMC diffusion and accelerate the formation of barrier layer, leading to thin and dense polymer structure.

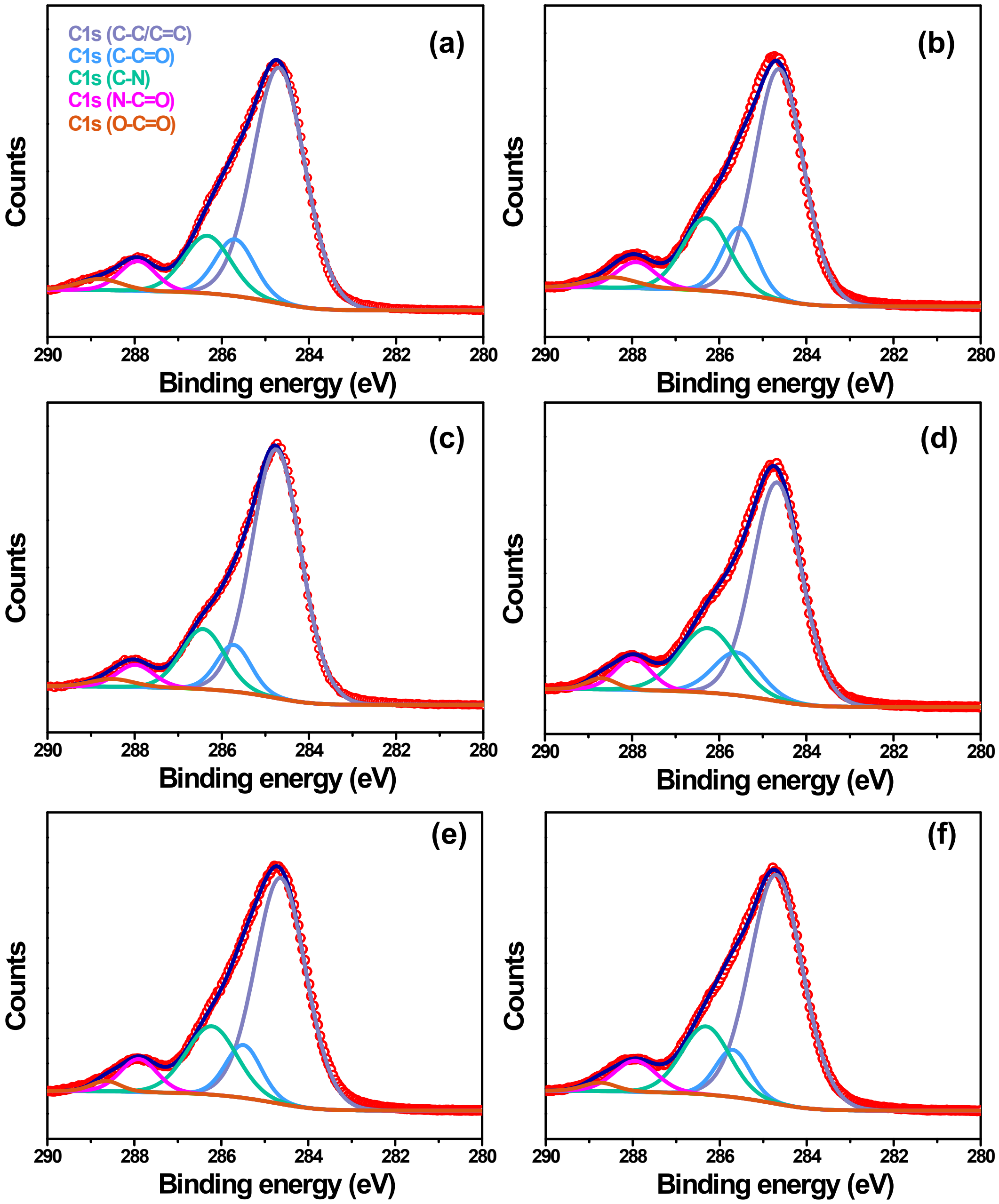


**Fig. S15** The narrow C1s photoelectron spectra of TAPE-TMC polyamide ultrathin films. (a-c) Films were synthesized with TAPE of 96 mM and TMC of (a) 6.00 mM, (b) 0.750 mM, (c) 0.188 mM, respectively. (d-f) Films were synthesized with TMC of 1.50 mM and TAPE of (d) 48 mM, (e) 96 mM, (f) 192 mM, respectively.

The surface chemical compositions of TAPE-TMC polyamide films were analyzed as shown in their XPS spectra (Fig. S15). The high-resolution narrow C1s peak was deconvoluted into five peaks at 284.8 eV (C-C/C=C/C-H), 285.7 eV (C*-C=O), 286.3 eV

(C*-N), 288.0 eV (N-C*=O) and 289.2 eV (O-C*=O).[4] The last two species show the existence of polyamide network. Further comparison of quantitative ratio of oxygen and nitrogen elements (Table S2) show different crosslinking degree of TAPE-TMC polyamide films. Hydrolysis of unreacted acyl chloride group brings up more oxygen element, thus increase the value of O/N ratio.

High O/N ratio meaning less crosslinking point and loose network. Comparing the surface elemental composition, the oxygen content decreases with low TMC concentration, and the nitrogen content increases with high TAPE concentration. The decreased O/N ratio values show that dense TAPE-TMC polyamide is generated with low TMC concentration and high TAPE concentration.

**Table S2.** Elemental compositions of TAPE-TMC polyamide films prepared with different TAPE and TMC concentration.

| Sample | Monomer concentration (mM) | | Element composition (%) | | | O/N ratio |
|---|---|---|---|---|---|---|
| | TAPE | TMC | C | N | O | |
| S15(a) | 96 | 6.00 | 78.04 | 7.14 | 14.82 | 2.08 |
| S15(b) | 96 | 0.75 | 79.05 | 7.27 | 13.68 | 1.88 |
| S15(c) | 96 | 0.19 | 80.00 | 7.16 | 12.84 | 1.79 |
| S15(d) | 48 | 1.50 | 79.16 | 6.89 | 13.95 | 2.02 |
| S15(e) | 96 | 1.50 | 78.96 | 7.39 | 13.65 | 1.85 |
| S15(f) | 192 | 1.50 | 79.23 | 7.43 | 13.35 | 1.80 |

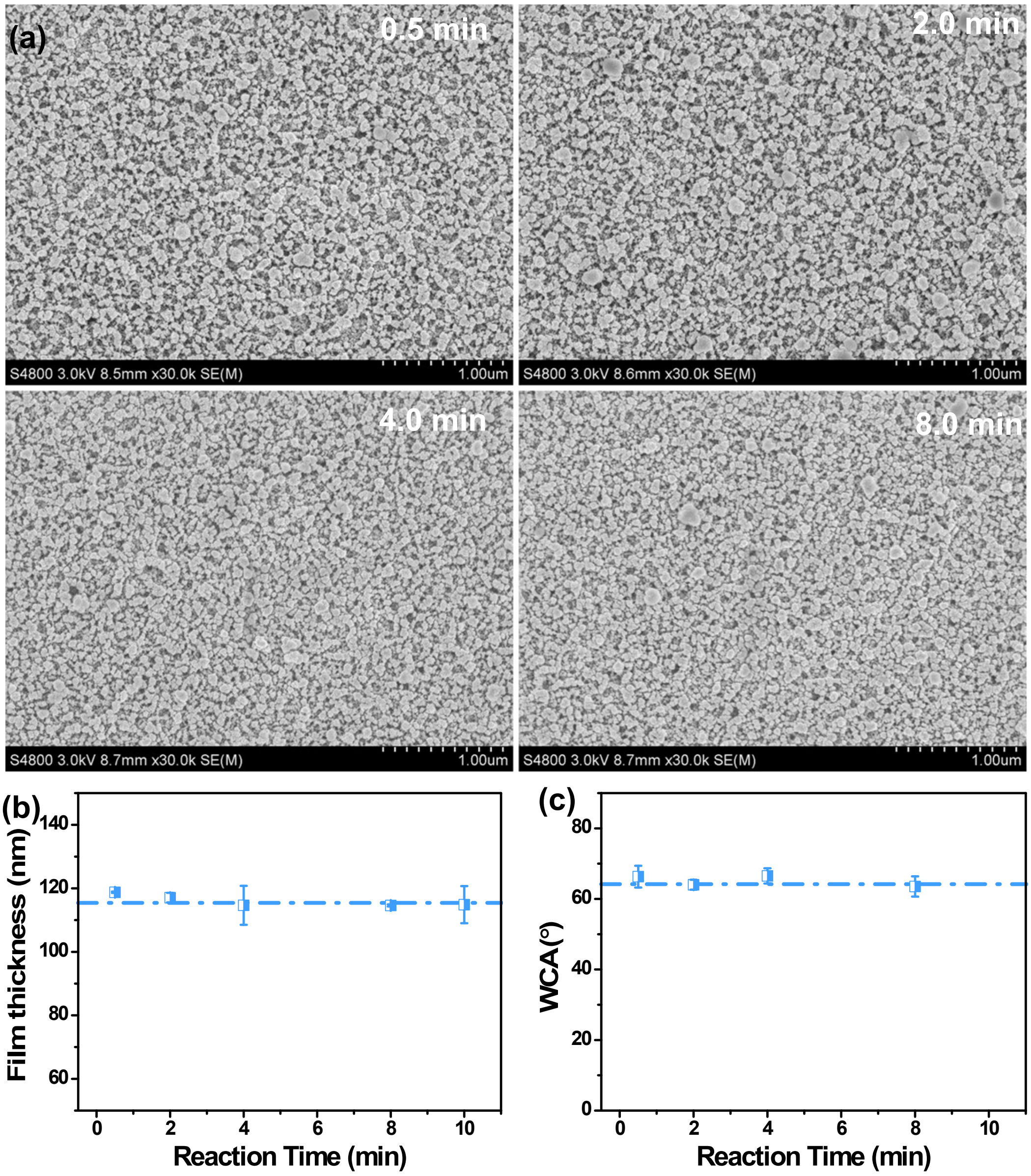


**Fig. S16** TAPE-TMC polyamide films synthesized with different reaction times. (a) The flip surface morphologies, (b) film thickness, and (c) surface wettability basically remain constant. The concentration of TAPE and TMC were 96 mM and 1.5 mM, respectively. The film growth was finished within 30 s.

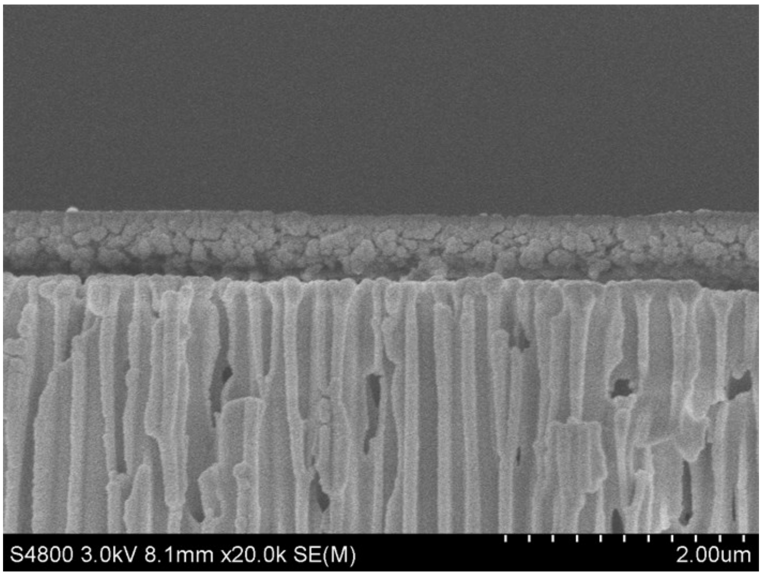


**Fig. S17** Cross-sectional image of TAPE-TMC polyamide film obtained with TAPE of 96 mM and TMC of 6.00 mM. It is clear that the polyamide film is comprised of flat top surface and granular bottom.

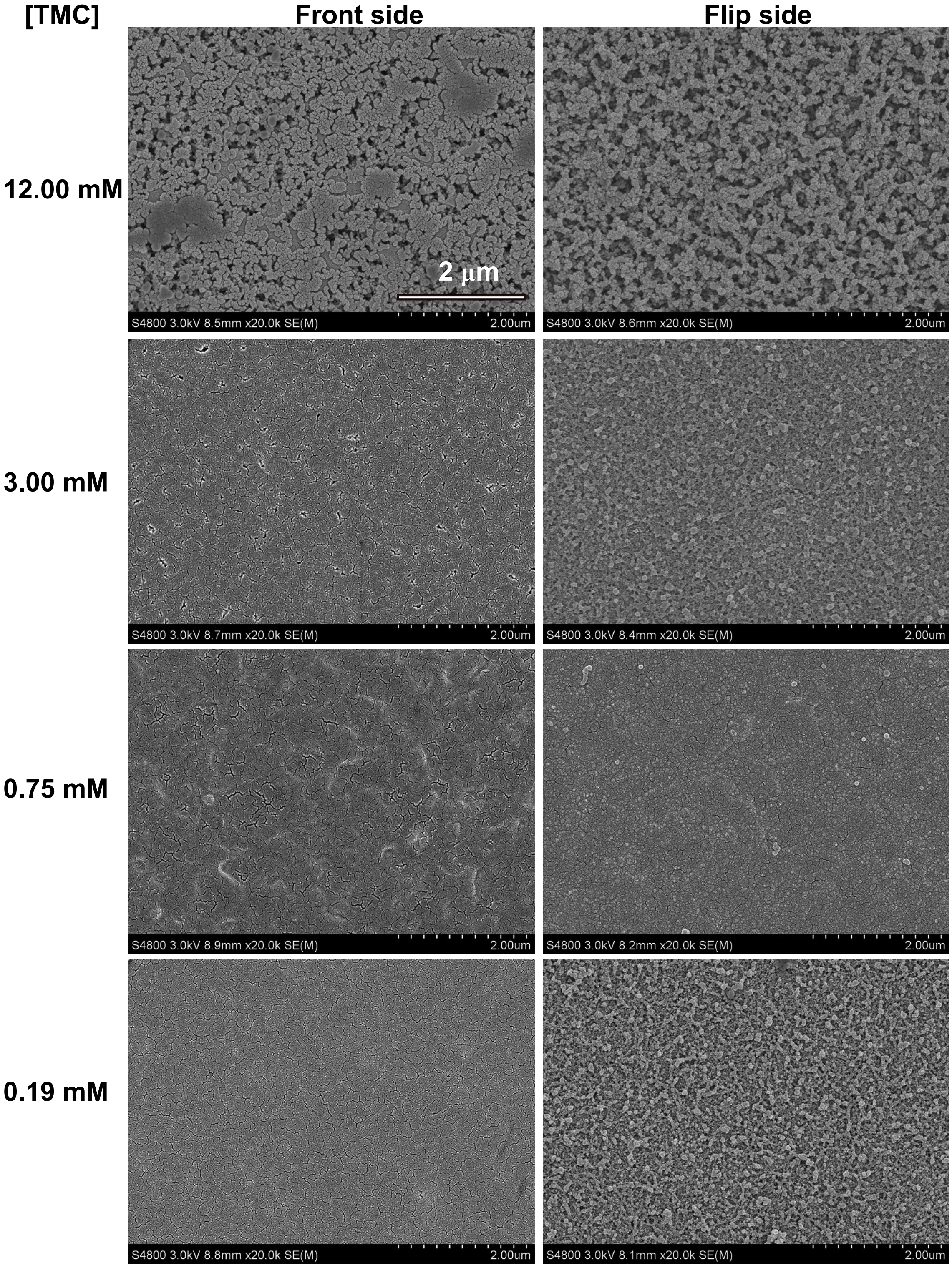
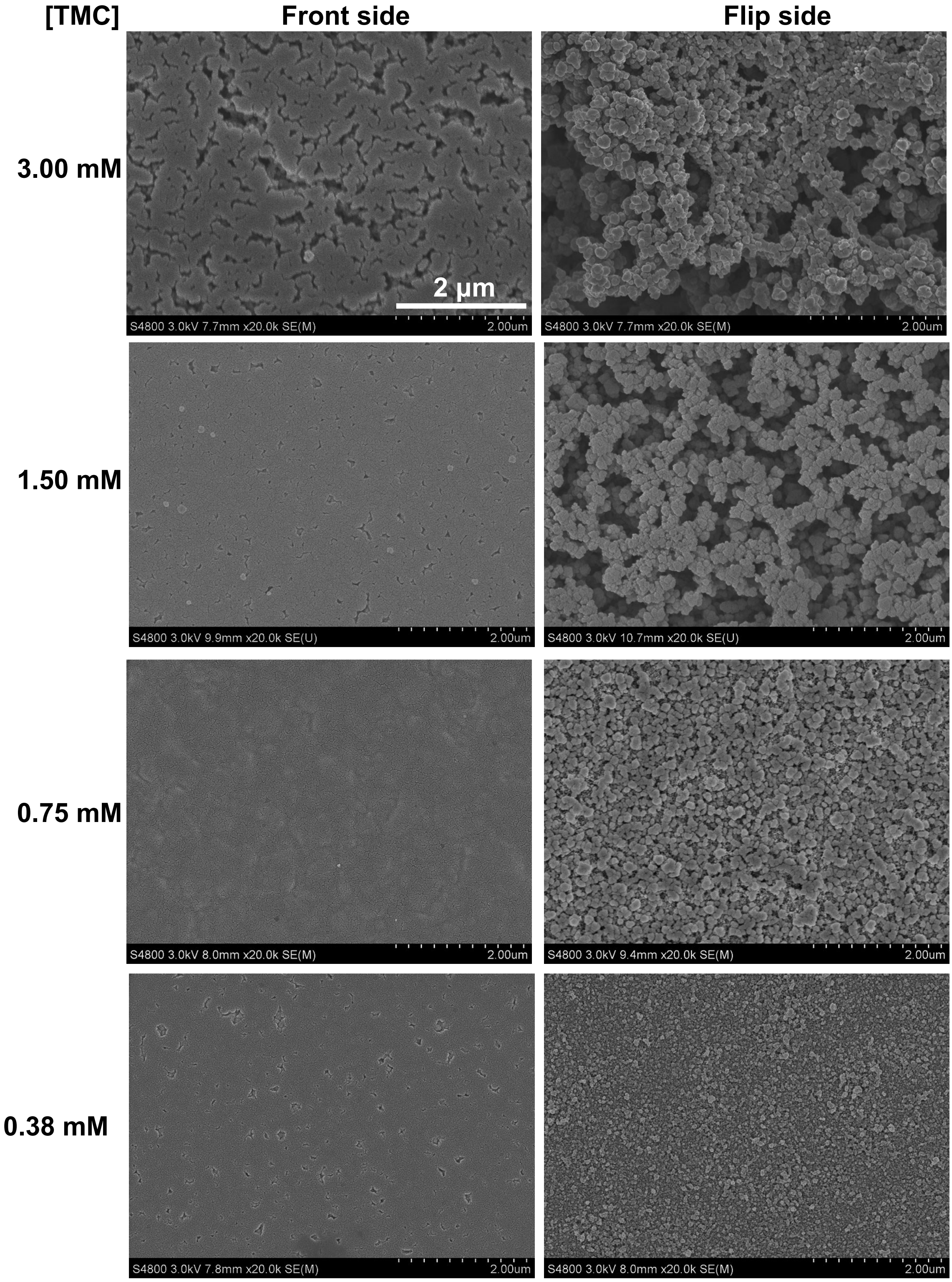


**Fig. S18** SEM images of the front and flip surfaces of TAPE-TMC polyamide films synthesized with different TMC concentrations when TAPE concentration was fixed at 96 mM. The interfacial polymerization was carried out for 10 min.


[TMC]
Front side
Flip side
3.00 mM
1.50 mM
0.75 mM
0.38 mM
2 µm
S4800 3.0kV 7.7mm x20.0k SE(M) 2.00um
S4800 3.0kV 7.7mm x20.0k SE(M) 2.00um
S4800 3.0kV 9.9mm x20.0k SE(U) 2.00um
S4800 3.0kV 10.7mm x20.0k SE(U) 2.00um
S4800 3.0kV 8.0mm x20.0k SE(M) 2.00um
S4800 3.0kV 9.4mm x20.0k SE(M) 2.00um
S4800 3.0kV 7.8mm x20.0k SE(M) 2.00um
S4800 3.0kV 8.0mm x20.0k SE(M) 2.00um

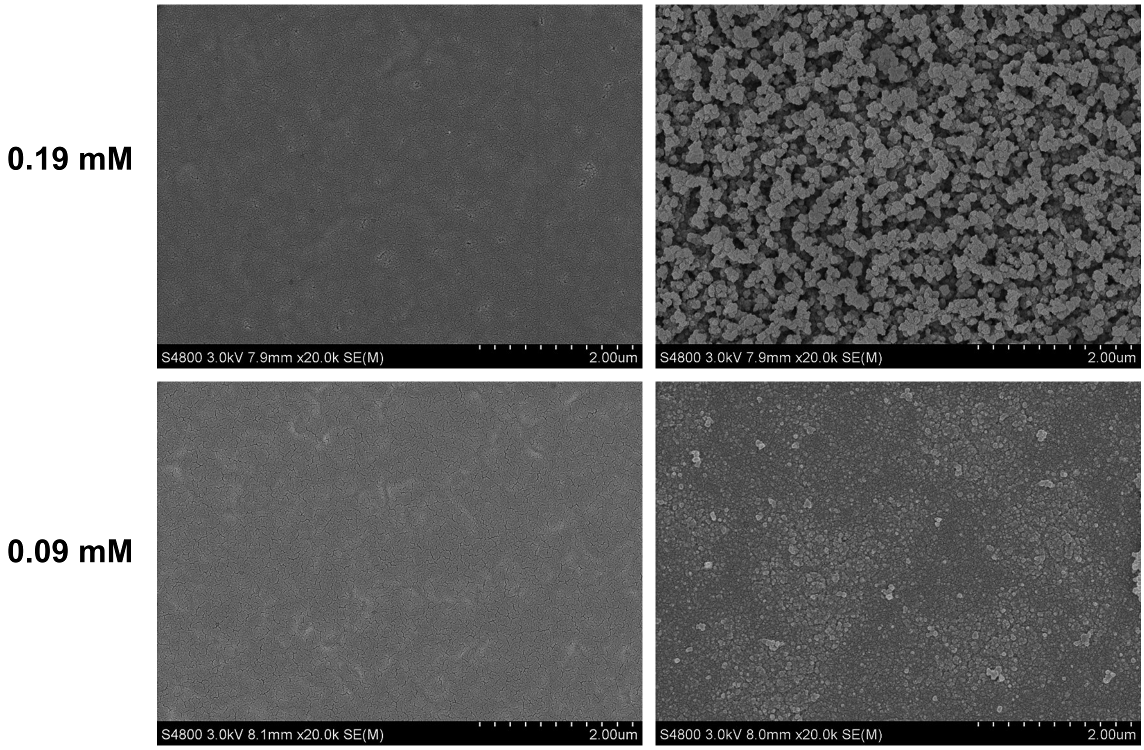
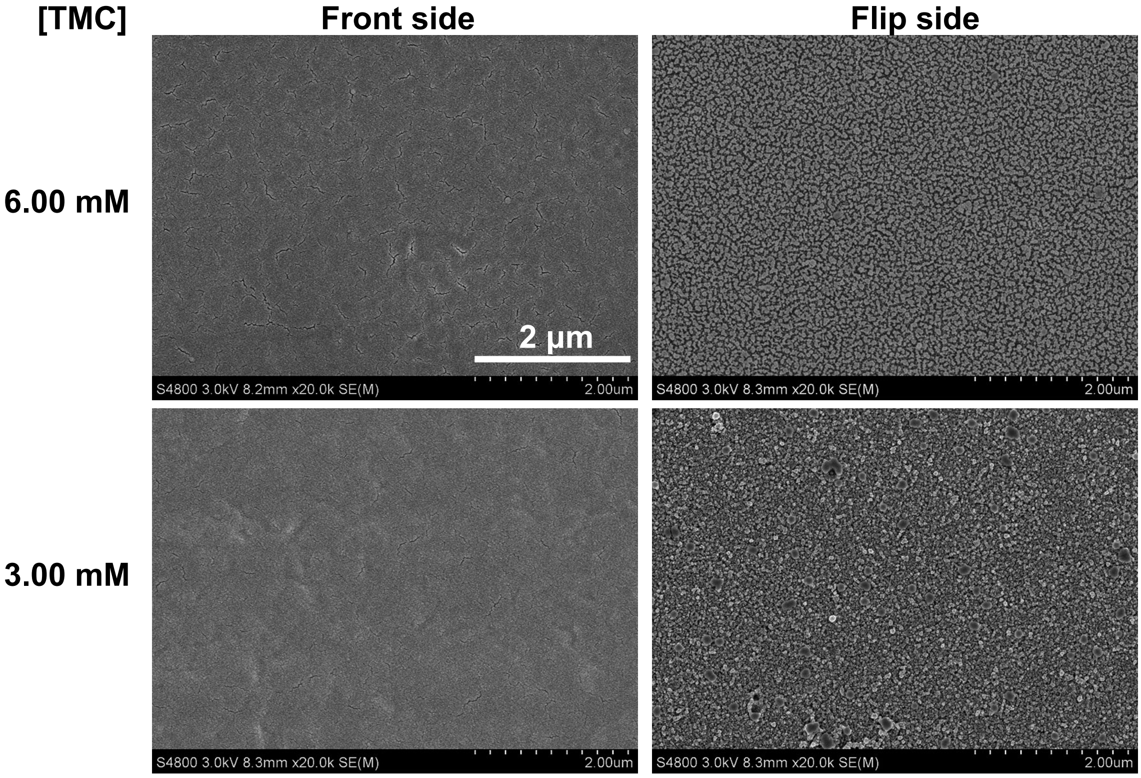


**Fig. S19** SEM images of the front and flip surfaces of polyamide films synthesized with varied TMC concentrations and fixed TAPE concentration of 48 mM. Reaction time was 10 min.



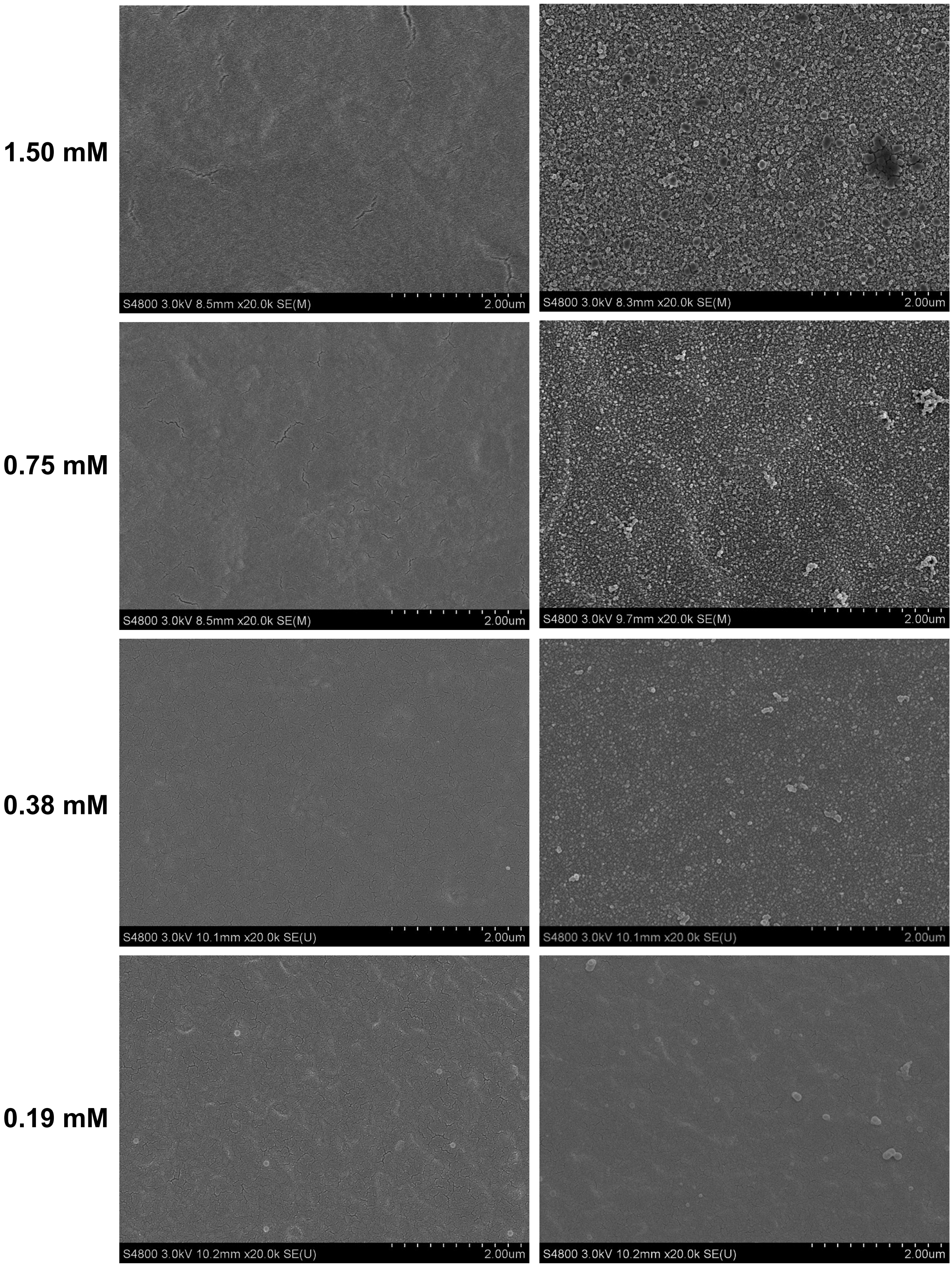


**Fig. S20** SEM images of the front and flip surfaces of TAPE-TMC polyamide films synthesized with varied TMC concentrations and fixed TAPE concentration of 192 mM. Reaction time was 10 min.

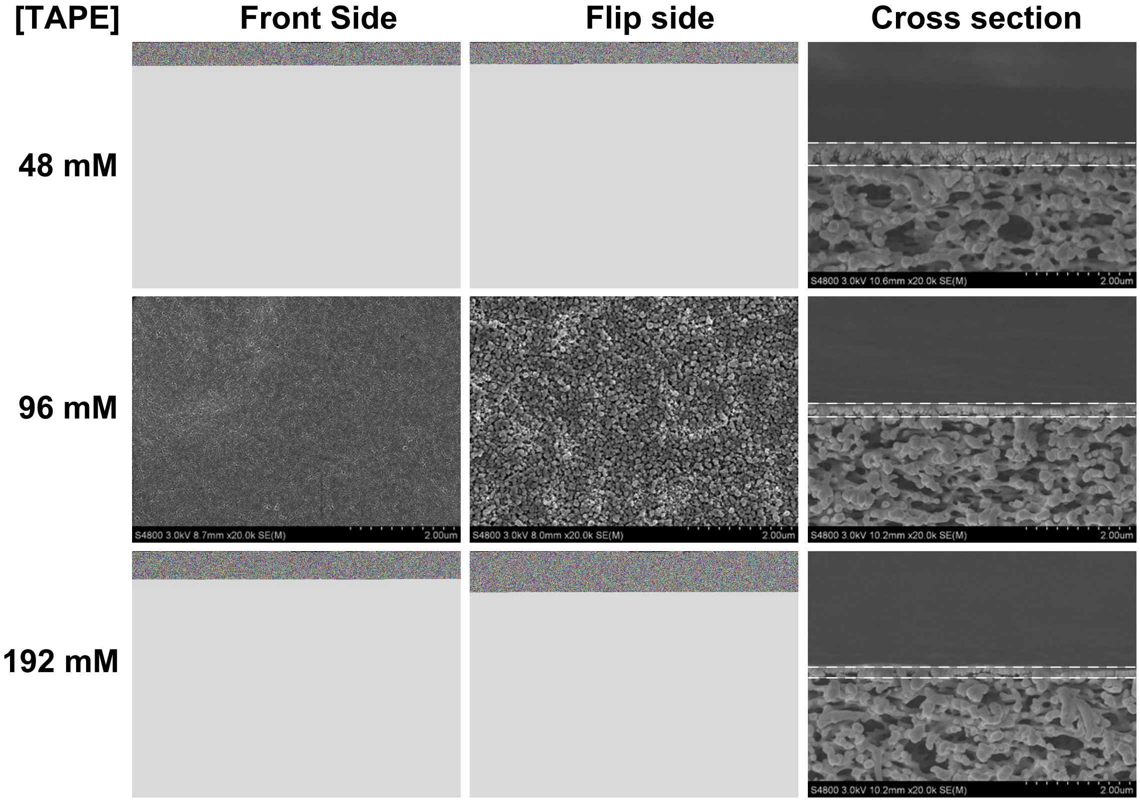


**Fig. S21** Surface and cross-sectional images of TAPE-TMC polyamide films synthesized with different TAPE concentrations. TMC concentration was fixed at 1.50 mM.

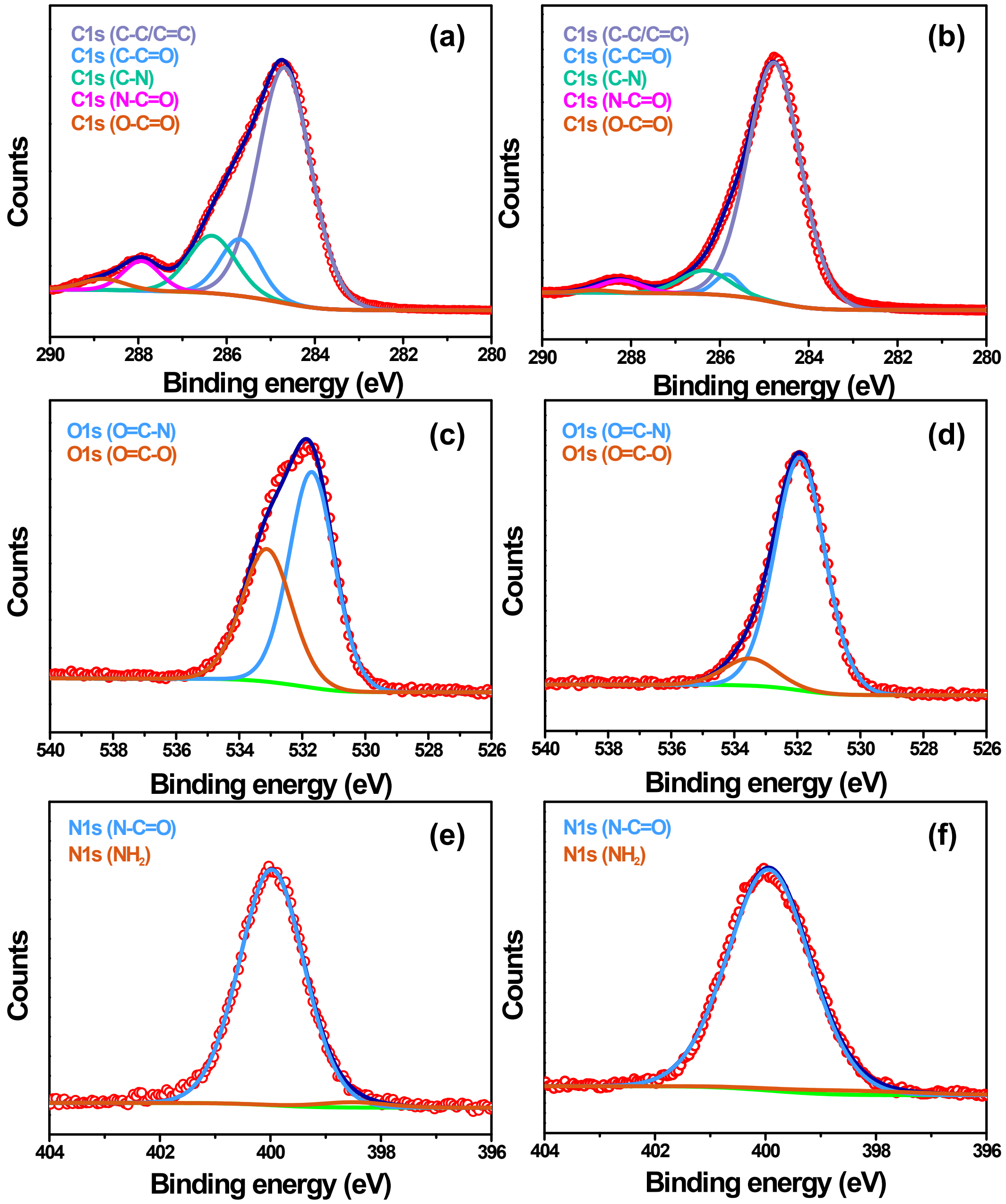


**Fig. S22** Narrow scan results of C1s (top), O1s (middle) and N1s (bottom) photoelectron spectra of the front surface (left) and the rear surface (right) of TAPE-TMC polyamide films. Polymerization condition: TAPE of 96 mM, TMC of 6.00 mM and the reaction time was 10 min.

In Fig. S22, the O1s spectra was deconvoluted into two peaks at 532.0 eV (O=C-N) and 533.5 eV (O-C=O). Due to incomplete reaction, remained acyl chloride would hydrolyze to carboxyl group leading to chemical shift. As for N1s spectra, it is often at 400.0 eV (N-C=O) referring to the strong amide bond, and a small peak at 398.5 eV ($NH_2$). From the deconvolution of elemental photoelectron spectra, asymmetrical chemical composition is obvious that more polyamide component is generated in front surface. The insufficient reaction of TMC leads to high carboxyl group contents. On the flip surface, TMC completely reacts with TAPE and so that the oxygen element content drops. It is consistent with the quantification of elemental composition (Table S3).[4]

**Table S3.** The elemental compositions of the front and rear surfaces of typical TAPE-TMC polyamide film.

| TAPE 96 mM<br>TMC 6.00 mM | Elemental composition (%) | | | O/N ratio |
|---|---|---|---|---|
| | C | N | O | |
| Front side | 78.04 | 7.14 | 14.82 | 2.08 |
| Flip side | 81.09 | 8.05 | 10.86 | 1.35 |

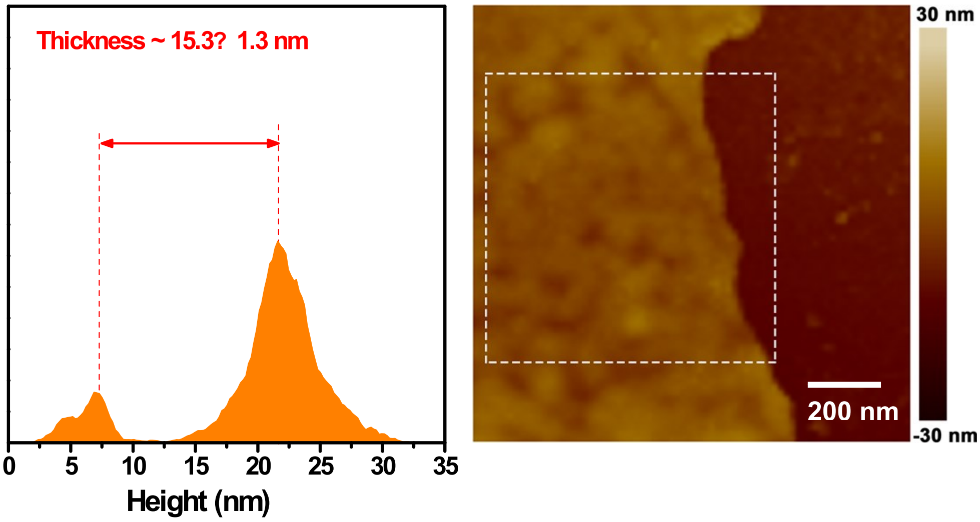


**Fig. S23** AFM image of the ultrathin polyamide film supported by silicon wafer. It was synthesized with TAPE of 96 mM and TMC of 0.047 mM within a reaction time of 10 min.

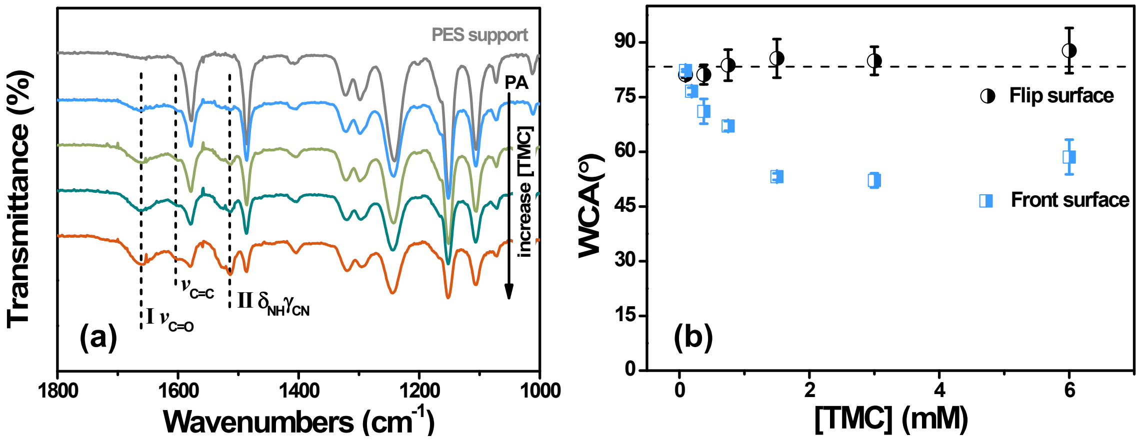


**Fig. S24** (a) FT-IR spectra and (b) water contact angle (WCA) of PES supported TAPE-TMC polyamide films, which were synthesized with different TMC concentrations when TAPE was fixed at 96 mM. With increasing TMC concentration, the polyamide films would grow thicker showing higher absorbance and more hydrophilic front surface. The flip surface of polyamide film keeps relatively hydrophobic with a WCA of 80°~90°.

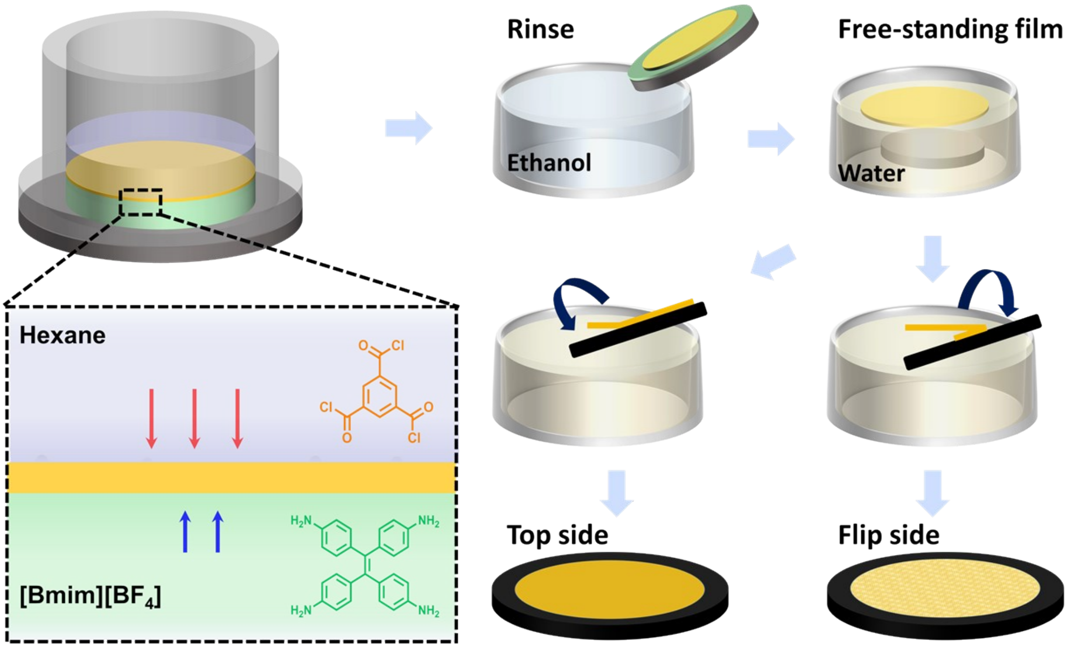


**Fig. S25** Preparation and transfer procedures of the freestanding TAPE-TMC polyamide film. After the interfacial polymerization, multiple rinses are required to remove the excess ionic liquid in order to obtain a clean freestanding ultrathin film. Various substrates can be used in this procedure for later characterizations and applications.

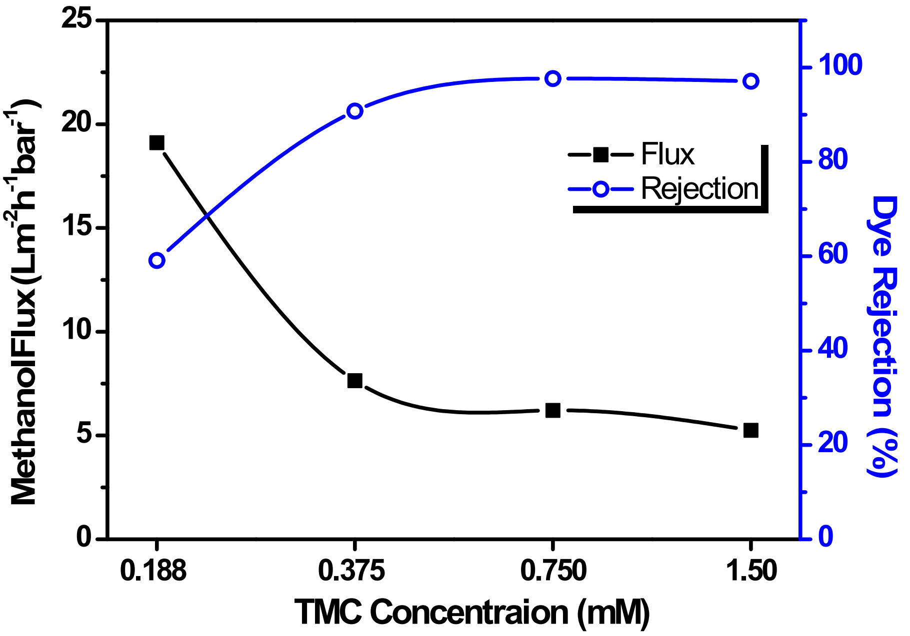


**Fig. S26** Organic nanofiltration performance of the composite TAPE-TMC polyamide membranes prepared with a fixed TAPE concentration of 96 mM. Feed solution: Evens Blue dye of 1000 ppm in methanol. It can be seen that the composite membranes show high methanol flux and high dye rejection.

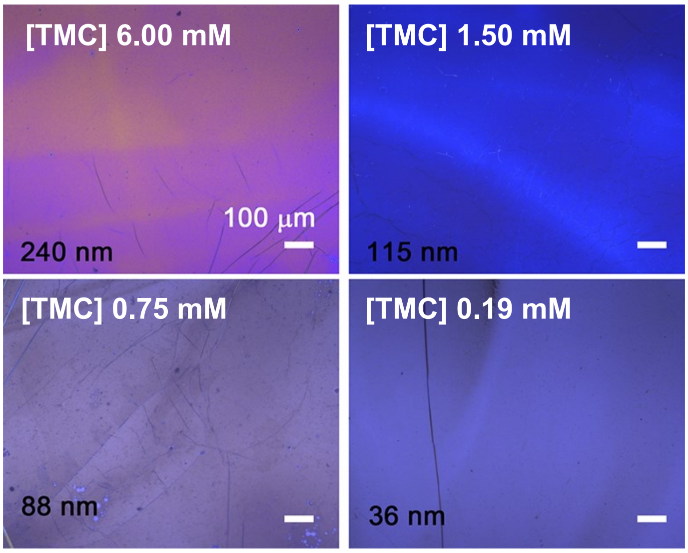


**Fig. S27** Thin-film interference of TAPE-TMC polyamide films with different thicknesses supported on silicon wafers. Controllable film thickness results in homogeneous and colorful coating by simply adjusting the concentration of TMC for the interfacial polymerization. Other reaction condition: TAPE concentration is 96 mM and reaction time was 10 min.

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