

Supporting Information

Supramolecular Polymerization at Interface: Layer-by-layer Assembly Driven by Host-enhanced π - π Interaction

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1. Experimental section

1.1 Materials.

BNTI was synthesized according to previous publications.^[1] 3-Chloropropyltrimethoxysilane and *N,N,N',N'*-tetramethylethylenediamine were purchased from Alfa Aesar. 2-(Bromomethyl)naphthalene was purchased from J&K Scientific. Quartz slides were purchased from Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences.

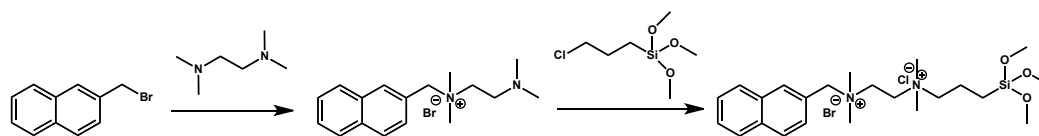
1.2 Synthesis of 2-(dimethylamino)-*N,N*-dimethyl-*N*-(naphthalen-2-ylmethyl)-ethanaminium bromide.

N,N,N',N'-Tetramethylethane-1,2-diamine (125 mg, 1.08 mmol) and 2-(bromomethyl)naphthalene (1 g, 4.52 mmol) were dissolved in 40 mL acetonitrile. The solution was stirred at 60 °C for 12 h. Then, the solution was added dropwise into 400 mL diethyl ether with ultrasonic agitation for twice to give to the solid precipitate 2-(dimethylamino)-*N,N*-dimethyl-*N*-(naphthalen-2-ylmethyl)ethanaminium bromide (yielding 90%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ H 8.14 (1H, s), 8.02 (3H, m), 7.63 (3H, m), 4.75 (2H, s), 3.49 (2H, t), 3.07 (6H, s), 2.78 (2H, t), 2.24 (6H, s).

1.3 Synthesis of NATMS.

2-(Dimethylamino)-*N,N*-dimethyl-*N*-(naphthalen-2-ylmethyl)ethanaminium bromide (315 mg, 0.93 mmol) and 3-chloropropyltrimethoxysilane (560 mg, 2.82 mmol) were dissolved in 20 mL super dry DMF. The solution was stirred at 85°C for 12 h and then added dropwise into 400 mL diethyl ether. After 2d's standing, the product gradually separated out from the solution, yielding 63%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ H 8.14 (1H, s), 8.05 (3H, m), 7.63 (3H, m), 4.75 (2H, s), 3.51 (4H, m), 3.30

(9H, s) 3.19 (6H, s), 3.07 (6H, s), 2.78 (2H, t), 1.82(2H, t), 0.61(2H, t).



Scheme S1. The synthetic route of NATMS.

1.4 Substrate preparation.

Quartz slides were treated in hot piranha solution (98% H₂SO₄:30% H₂O₂ = 7:3, v/v. *CAUTION: piranha solution is extremely corrosive, and appropriate safety precautions should be utilized*) for 2 h and then rinsed carefully with distilled water and dried in an oven overnight. Then the substrates were immersed into a mix toluene solution of 5 μM a trimethoxy silane containing naphthalene groups (NATMS) and 30 μM γ-chloropropyl trimethoxy silane (CITMS) overnight to form a self-assembled silane monolayer terminated with naphthalene functional groups at the surface. The substrates were subjected to ultrasonic agitation in THF and acetone for a short time to remove the physically adsorption and dried with nitrogen. The absorption peak at about 230 nm referred to the naphthalene group. Moreover, UV-Vis spectrum of the substrate confirmed the modification of the quartz slide as shown in Fig. S1.

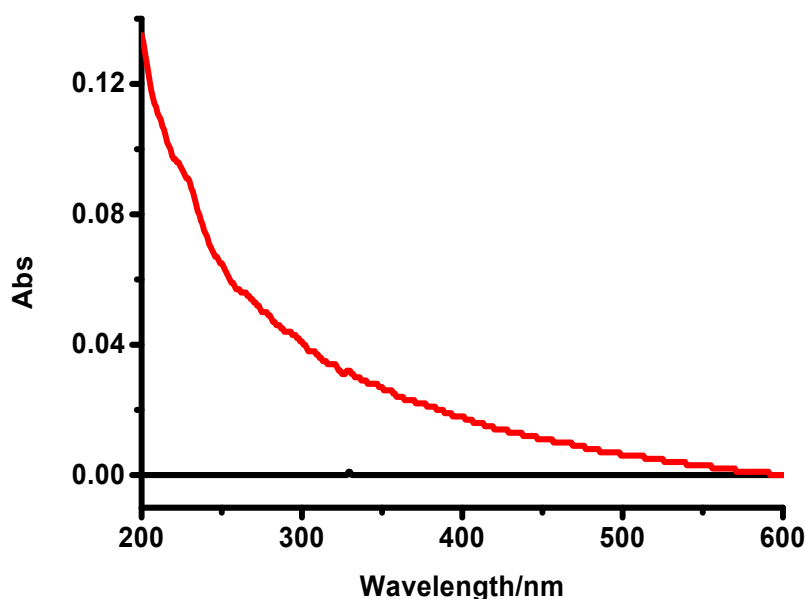


Fig. S1 UV-Vis spectra monitoring the substrate modification.

1.5 Measurement of adsorption kinetics of BNTI.

An naphthalene-modified quartz slide was first immersed into a CB[8] aqueous solution (0.1 mmol/L) for 10 min, followed by rinsing with distilled water and dried with nitrogen. Then the quartz slide was immersed into the solution of BNTI (1 mmol/L) for 15 min, UV-Vis spectroscopy and contact angel (CA) were recorded after the same rinsing and drying procedure.

2 Characterizations

¹H NMR spectra were recorded on a JOEL JNM—ECA300 apparatus. UV-vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Steady-state fluorescence spectra were obtained using a HITACHI F-7000 apparatus equipped with a Xe-900 lamp with an excitation wavelength of 464 nm. Atomic force microscopy (AFM) images were recorded on a Multimode Nanoscope IV (Veeco). Imaging was performed in tapping mode in air using silicon cantilevers (200-300 kHz).

3 The adsorption kinetics of CB[8] and BNTI

In order to optimize the adsorption time of CB[8] and BNTI for each layer by LbL assembly, the adsorption kinetics of CB[8] and BNTI are studied by contact angle and UV-Vis spectroscopy. The substrate is immersed into the solution of CB[8] (0.1 mM) for different times because CB[8] can adsorb onto the substrate by encapsulating naphthalene units of BNTI to form host-guest complexes. After 10 min adsorption of the substrate, UV intensity at 225 nm reaches the maximum value, indicating the saturate adsorption of CB[8] on the substrate (Fig. S2). Therefore, the absorbance time of the substrate in the solution of CB[8] is optimized to be 10 min. After that, according to the method of LbL assembly, the substrate is immersed into the BNTI solution (1 mM) for different time. The contact angle gradually increases with increasing the immersing time, then shows no significant changes upon being immersed for 50 min (Figure S3). Accordingly, UV-Vis absorbance of BNTI increases at 225 nm with increasing the immersing time (Fig. S3). These data indicate that in the first 10 min, monolayer absorption of BNTI on the substrate can be obtained. Upon increasing immersing time, then multilayer adsorption of BNTI can

occur. Therefore, the 10 min adsorption time for BNTI or CB[8] are optimized for fabricating LbL multilayer films.

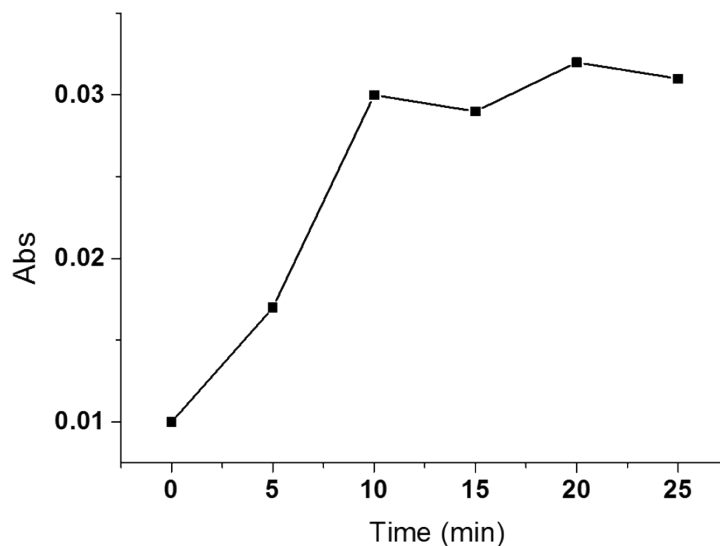


Fig. S2 UV-Vis absorbance of the substrate at 225 nm after immersing it into the solution of CB[8] for different time.

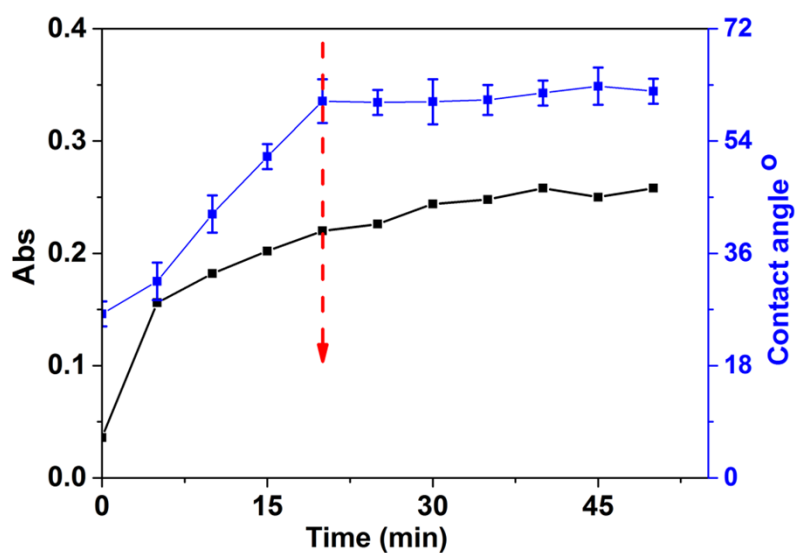


Fig. S3 UV-Vis absorbance at 225 nm and contact angle of the substrate after immersing it into the solution of BNTI for different.

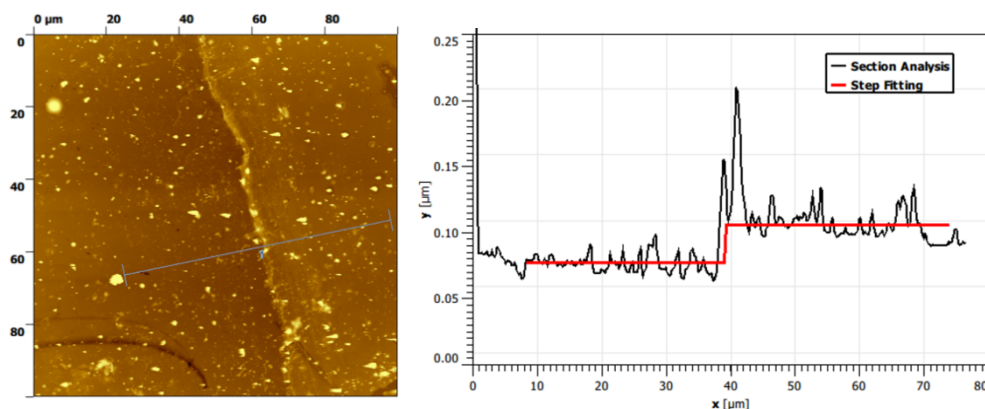


Fig. S4 AFM image and the thickness of LbL film. The film dipping 20 times in CB[8] and BNTI is around 25nm.

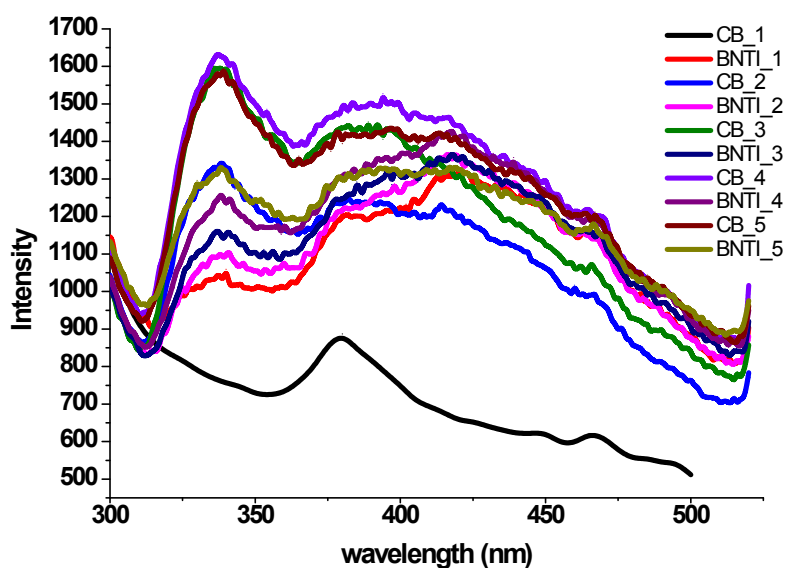


Fig. S5 Fluorescence spectra of the substrate after immersing it into the solution of CB[8] and BNTI alternately.

Reference

- [1] R. C. Fang, Y. L. Liu, Z. Q. Wang and X Zhang, *Polym. Chem.*, 2013, **4**, 900.