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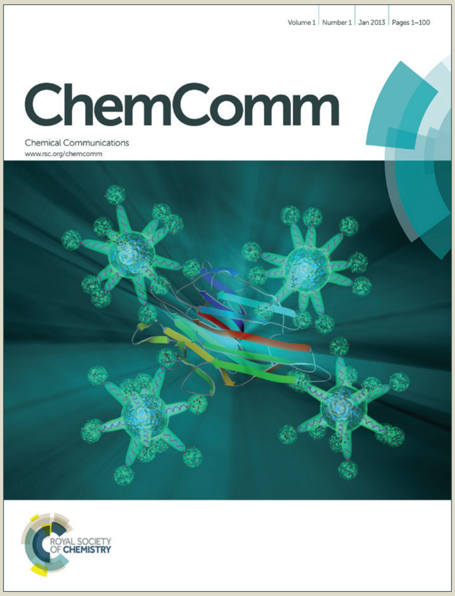

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ARTICLE TYPE

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

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Host-enhanced π-π interaction as a new driving force was used for fabricating layer-by-layer (LbL) films. This kind of LbL assembly can be regarded as a sort of supramolecular polymerization at interface and its degree of supramolecular polymerization can be controlled efficiently by adjusting layer pairs similar to living polymerization in solution.

Layer-by-layer (LbL) assembly is widely used for fabricating multilayer films with controlled compositions and functions, since it was rediscovered by Decher and co-workers.[1] Different functional building blocks, including some polyelectrolytes, proteins and enzymes, DNA, colloidal particles, and oligo-charged molecules such as porphyrin and phthalocyanine have been applied to fabricate multilayer films with various functions.[2] In principle, the building blocks should have multiple interactive sites, which allow for LbL assembly on the basis of different intermolecular interactions including electrostatic interaction, hydrogen bonding, host-guest interaction, Van der Waals force and charge transfer interaction.[3]

Supramolecular polymers refer to polymers that are formed on the basis of various intermolecular non-covalent interactions. To form supramolecular polymers with high molecular weight, these non-covalent interactions should be strong enough, such as quadruple hydrogen bonding, host-enhanced charge-transfer interaction or π-π interaction.[4] Although supramolecular polymerization has been well established in solution, many problems arise when it is transferred from solution onto interface.[5] For example, supramolecular polymers with low molecular weight could be only fabricated from solution to liquid-solid interface, because the living interactive sites are buried into the assemblies and effective concentration of the building blocks is low.[6]

We wondered if host-enhanced π-π interaction could be employed as a novel driving force for fabricating multilayer films by LbL assembly. For this purpose, we synthesized a three-arm monomer, 1,1’,1’’-(benzene-1,3,5-triyltris(methylene))-tris(3-naphthalene-2-methyl)-1H-imidazol) bromide (in short, BNTI, Fig. 1). Such triple functional monomers could bind with cucurbit[8]uril (CB[8]) to form supramolecular hyperbranched polymers in aqueous solution through host-enhanced π-π interaction.[7] To transfer this supramolecular polymerization from solution to interface, we could construct multilayer films by alternating deposition of CB[8] and BNTI at the liquid-solid interface. It can be regarded as supramolecular polymerization at interface, and moreover, the degree of supramolecular polymerization can be monitored by controlling the number of layer pairs of CB[8] and BNTI.

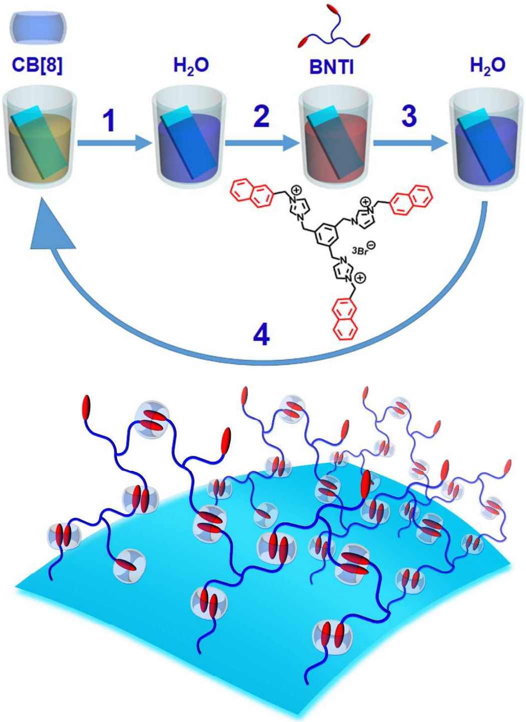

Fig.1 Supramolecular polymerization of CB[8] and BNTI at interface for fabricating LbL films by host-enhanced π-π interaction as the driving force.

The LbL assembling process of multilayer films was monitored by UV-Vis spectroscopy. Before LbL assembly, quartz slides were treated by a mixed self-assembled monolayer of trimethoxy silane containing naphthalene groups and γ-chloropropyl trimethoxy silane in a molar ratio 1:6. This surface modification allowed for naphthalene to effectively interact with CB[8] by host-guest interaction (seeing Supporting Information). Additionally, the adsorption time of the substrate into the solution of CB[8] or BNTI was optimized to be 10 min for fabricating LbL multilayer films in terms of kinetics study (supporting information, Fig. S2 and S3). As shown in Fig. 2a, the absorption band peaked at 225 nm is ascribed to the absorption of naphthalene units of BNTI. This absorption increases with increasing the number of layer pairs of CB[8] and BNTI. There is a good linear relationship between the absorbance at 225 nm and the number of layer pairs (Fig. 2b), indicating that the LbL deposition is progressive and uniform. In addition, the average thickness of the multilayer films with 20 layer pairs is around 25 nm measured by atomic force microscopy (AFM, Fig. S4). Considering the height of CB[8] (0.91 nm) and the size of three arm monomer of BNTI, the degree of supramolecular polymerization at interface is estimated to be 20. Therefore, we have successfully transferred supramolecular polymerization of CB[8] and BNTI from solution to surface through LbL assembly and the degree of supramolecular polymerization can be easily controlled by adjusting the number of layer pairs of CB[8] and BNTI.

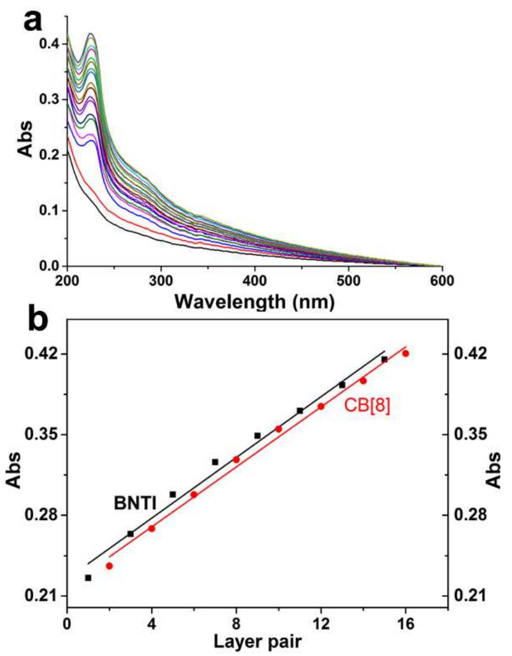

Fig. 2 (a) UV-Vis spectra of the substrate for monitoring LbL assembly; (b) UV-Vis absorbance at 225 nm of the substrate after alternately immersing it into the solution of CB[8] and BNTI.

To confirm that host-enhanced π-π interaction was the driving force for LbL films, fluorescence spectroscopy was further employed to study the host-guest interaction of CB[8] and BNTI at interface. After immersing the substrate into the aqueous solution of CB[8] (0.1 mM), fluorescence intensity of the substrate at 335 nm, ascribable to fluorescence emission of naphthalene units (NP), increases (Fig. S5) due to the shielding effect of CB[8]. It means that naphthalene units located on the substrate can bind with excess CB[8] to form 1:1 host-guest complex CB[8]/NP. After the immersion of the above substrate into the aqueous solution of BNTI (1 mM), fluorescence intensity at 335 nm decreases (Fig. 3) on account of the quenching effect induced by π-π stacking of naphthalene moieties inside CB[8]'s cavity. As expected, 1:1 host-guest complex CB[8]/NP can bind with BNTI to form 1:2 host-guest complex CB[8]/$(NP)_2$. Moreover, the alternating decrease and increase of fluorescence intensity at 335 nm were observed, which indicates not only a alternating deposition process of LbL assembly but also the host-enhanced π-π interaction between CB[8] and naphthalene units of BNTI as the driving force for LbL assembly.

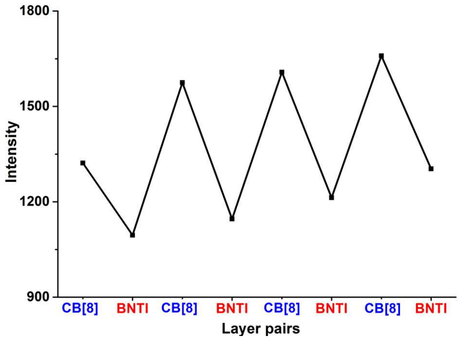

Fig. 3 The curve of fluorescence intensity of the substrate at 335 nm after immersing it into the aqueous solution of CB[8] and BNTI alternatively.

We wonder whether LbL assembly used for supramolecular polymerization at interface has significant advantages in contrast to the interfacial adsorption of supramolecular polymers from aqueous solution.[9] First, CB[8] were added into the aqueous solution of BNTI to form supramolecular hyperbranched polymers (CB[8]-BNTI) by host-enhanced π-π interaction. Upon extending the immersion time of the substrate into the CB[8]-BNTI solution to 60 min, UV-Vis absorbance of naphthalene units of BNTI at 225 nm increases from 0.032 to 0.056 (Fig. 4). The little increase of the absorbance indicates that few of supramolecular hyperbranched polymers could adsorb at interface by host-guest interaction due to the low effective concentration of the living interactive sites in the solution of CB[8]-BNTI. In contrast, upon increasing the number of layer pairs of CB[8] and BNTI, UV-Vis absorbance of naphthalene units at 225 nm increases from 0.129 to 0.418 (Fig. 2b). The absorbance of the substrate formed by LbL assembly has so much higher increase than that formed by the interfacial adsorption of supramolecular polymers in the solution. This indicates that a large number of supramolecular polymers can be fabricated at interface by LbL assembly. Therefore, LbL assembly is a novel strategy for constructing supramolecular polymers with high molecular weight at interface and controlling easily the degree of supramolecular polymerization.

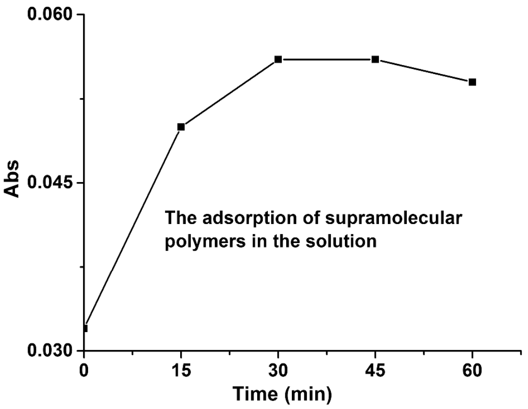

Fig. 4 UV-Vis absorbance at 225 nm of the substrate obtained by the interfacial adsorption of the solution of supramolecular polymers.

The dynamic nature of host-enhanced π-π interaction endows the LbL films to be dissembled by competitive binding of other guests, which exhibit much higher binding constants with CB[8] than BNTI.[8] This dissembling process of LbL films were studied by UV-Vis spectroscopy. After immersing LbL films into the aqueous solution of 1-amantadine (ADA, 1 mmol/L), UV-Vis absorbance of naphthalene units at 225 nm decreases (Fig. 5a). It indicates that LbL films can be dissembled by ADA on account of the higher binding constant between ADA and CB[8].[9] Moreover, we also immersed the substrate into the solutions of different competitive guests such as spermine, tyramine, dopamine and ADA. It was found that the release ratio of LbL films is about 50% after immersing it into ADA solution, which is the highest in all four kinds of competitive guests (Fig. 5b). It implies that LbL films through host-enhanced π-π interaction have a good stimuli responsiveness for ADA.

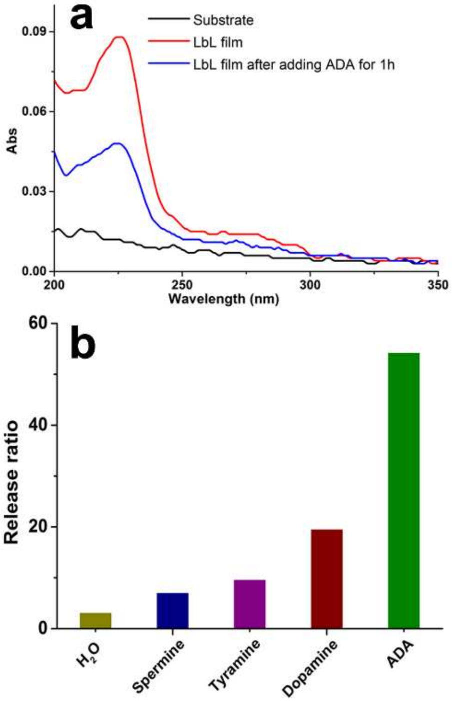

Fig. 5 (a) UV-Vis absorbance at 225 nm of the substrate after being immersed into ADA solution for 1 h, (b) the release ratio of the substrate after immersing it into the solution of different guests. The release ratio of LbL films was calculated by the equation Release ratio = (F-R)/(F-S), where F is the absorption of LbL films; R is the absorption of LbL films after immersing it into the aqueous solution of competitive guest molecule; S: the absorption of substrate.

In conclusion, we have successfully transferred supramolecular polymerization of CB[8] and BNTI from solution to surface by LbL assembly. In this process, host-enhanced π-π interaction was employed as a novel driving force to fabricate LbL assembly. Moreover, the degree of supramolecular polymerization at interface can be controlled efficiently through adjusting the number of layer pairs of CB[8] and BNTI. Furthermore, the dynamic multilayer films display a good selectivity for ADA due to the competitive effect of guest. It is anticipated that these multilayer materials formed by LbL assembly have potential applications in the field of stimuli responsive devices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and compound characterization; the thickness of of LbL film by AFM; fluorescence spectra of the substrate.

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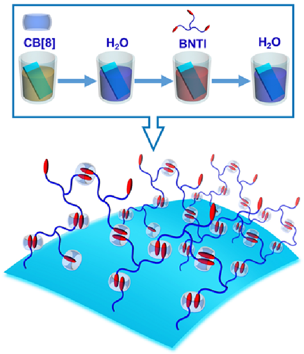

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