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Multilayered supermolecular structures self-assembled from polyelectrolytes and cyclodextrin host–guest complexes

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Supermolecular multilayers with high levels of compositional and structural complexities have been fabricated with an example that involves formation of stable host–guest complexes from bolaamphiphiles and cyclodextrins, followed by sequential build-up of multilayered films by these complexes in combination with anionic polystyrene sulfonate polymer chains.

Self-assembly is the spontaneous organization of molecules or objects into stable, well-defined structures by non-covalent forces.[1] The concept of self-assembly mainly originates from biological processes such as the folding of polypeptide chains into functional proteins, the formation of the DNA double helix, and the organization of phospholipids into cell membranes. This concept has now been extensively explored in chemistry and materials science as an effective strategy for fabricating a wide variety of complex structures that are difficult or impossible to generate using traditional approaches. Examples of these self-assembled structures include: self-assembled monolayers (SAMs),[2] multilayered thin films,[3] metal nanoparticles,[4] aggregates (micelles, liposomes) derived from surfactant molecules,[5] host–guest inclusion complexes,[6] phase-separated block copolymers,[7] crystalline arrays of proteins or colloidal particles,[8] and aggregated structures of mesoscale objects.[9] Functional materials (usually in the form of ultrathin films) produced using this approach are potentially useful in a number of areas such as sensing,[10] photonics,[11] and electrochemistry.[12] Most of these systems, however, only deal with one type of driving force for self-assembly, with a few exceptions such as those systems demonstrated by Sagiv,[13] Stupp,[14] Mirkin,[15] and Alivisatos.[16] Here we wish to report an approach that employs two types of self-assembly: formation of stable host–guest complexes *via* hydrophobic interactions[6] and stepwise deposition of multilayered structures *via* electrostatic interactions.[17] The incorporation of more than one type of self-assembly into a single procedure provides a potentially useful route to supermolecular architectures that have higher levels of structural complexity, more compositional combinations, and/or more functionalities.

Fig. 1 shows the schematic procedure. Since the bolaamphiphiles are rigid molecules with highly polar end groups, they are supposed to adsorb end-on at charged surfaces, while looping is suppressed. The stilbenoid compound SBr_2 was synthesized using published procedures.[18] Treatment of SBr_2 with β-CD in water for 3 h (under continuous sonication) gave a stable host–guest complex CBr_2. The formation of this inclusion complex is mainly driven by hydrophobic interactions. Although doubly charged, salt SBr_2 is only sparingly soluble in water. Upon addition of 1.0 equiv. of β-CD, this salt becomes freely water soluble. Such a significant increase in solubility has been recognized as a manifestation of the formation of a host–guest inclusion complex. The inclusion complex CBr_2 could be isolated as a pure solid. The UV–Vis absorption spectra of salt SBr_2 and complex CBr_2 in water exhibit an absorption peak at 319 nm, which is mainly caused by the stilbene unit. The inclusion complex CBr_2 was characterized by ^1H-NMR (500 MHz, in D_2O). As reported in the literature, the formation of a host–guest complex induces upfield chemical shifts for the protons of β-CD, especially for H-3 and H-5 which are directed towards the interior of the cavity. These changes in chemical shifts can be interpreted in terms of the magnetic anisotropic effect arising from the aromatic rings of the guest molecule. The topology of the inclusion complex can also be more precisely determined by using the 1-D NOE difference spectrum or 2D ^1H–^1H NOESY, since the magnitude of these effects is a direct measure of the distance between the protons of the host and guest. Our 1-D NOE study on a similar inclusion complex has shown that the compound SBr_2 is preferentially inserted into the cavity of β-CD as shown in Fig. 1. The electrospray mass spectrum of complex CBr_2 shows that, in addition to fragments of salt SBr_2 and β-CD, the signal for the complex itself was recorded at relatively high abundance.

The multilayered thin films were built layer-by-layer on freshly cleaned substrates (quartz, glass, or silicon) that had been derivatized with 3-aminopropyltrimethoxysilane, by alternately dipping the substrate into aqueous solutions of polystyrene sulfonate (PSS) (0.01 M of the repeating unit in 0.01 M HCl) and the bolaamphiphile (0.0002 M) for 30 min, followed by rinsing with Milli-Q water for 5 min. In the case of

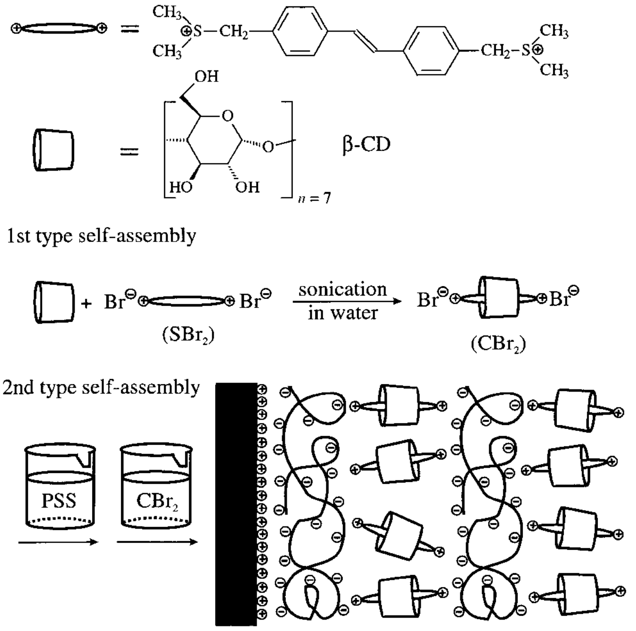

Fig. 1 Chemical structure of the bolaamphiphile SBr_2, formation of the host–guest inclusion complex CBr_2, and schematic illustration of the multilayered structure self-assembled from CBr_2 and PSS.

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the CBr_2 complex, a β-CD-saturated aqueous solution was used in order to prevent the dissociation of the inclusion complex. Precoating with three double layers (PSS–polydiallyldimethylammonium chloride) provided a homogeneous charge distribution on the substrate. Following the alternate dipping procedure, up to 21 Bola–PSS double layers were built up on each side of the substrate. The stepwise deposition of PSS and complex CBr_2 was followed using UV–Vis, ATR-FTIR, and ellipsometry. Fig. 2 shows the UV–Vis spectra of multilayered thin films after different adsorption cycles for complex CBr_2. The increase in intensity of the absorption band at 327 nm is directly related to the number of adsorbed layers. This is supported by the inset plot in Fig. 2, showing a linear relationship between the absorption intensity at the absorption maximum and the number of layers of complex CBr_2. ATR-FTIR measurements show several broad absorption bands in the region of 1150, 944, and 770 cm^{-1}, which also indicate the presence of the bolaamphiphile in the multilayered films. Since the absorption bands of β-CD molecules lie within these regions, we were unable to assign these absorption peaks to either salt S^{2+} or β-CD. Ellipsometry measurements on the multilayered assemblies at different numbers of double layers also indicate a linear increase in layer thickness. From these measurements, an increase in the thickness was calculated to be 1.8 nm per bilayer.[19]

UV–Vis spectra similar to Fig. 2 were also obtained when salt SBr_2 rather than complex CBr_2 was used as one of the building blocks for the multilayered films. We found that the absorption maximum of the stilbene unit was red-shifted (relative to that of the solution) by ~10 nm for the multilayers deposited from salt SBr_2 and ~8 nm for those formed from complex CBr_2. These results suggest that the stilbenoid compounds were aligned partially parallel to each other in each layer of the multilayered films. A comparison of the increment in absorption intensity for the salt SBr_2 (3.04×10^{-3} per layer) and the host–guest complex CBr_2 (2.71×10^{-3} per layer) leads to the conclusion that the amount of bolaamphiphiles deposited in each dipping cycle is mostly controlled by the surface charge of the preceding layer of PSS and to a minor extent by the lateral dimensions of the bolaamphiphile.[20] These two values also indicate that the packing density for the bolaamphiphiles within each layer seems to be relatively low.

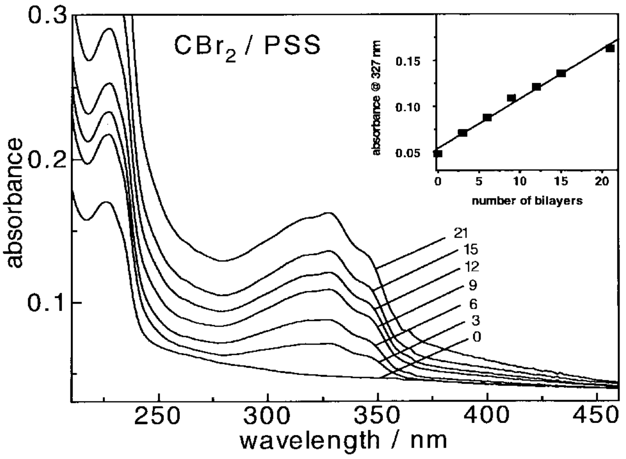

Fig. 2 UV–Vis absorption spectra of self-assembled multilayers of CBr_2 and PSS. In the inset, the maximum absorbance of the bolaamphiphile compound is plotted *versus* the number of double layers of CBr_2 and PSS.

The surface topology of the self-assembled multilayers was studied using tapping mode atomic force microscopy (AFM). Fig. 3A and B show the AFM images of multilayered assemblies terminated in complex CBr_2 and salt SBr_2, respectively. It is obvious from these images that multilayered films of complex CBr_2 and PSS possess a more homogeneous structure than those from salt SBr_2 and PSS. The surface roughness for the multilayered films including CDs was determined to be 5 nm. In comparison, the surface roughness for multilayers formed from salt SBr_2 and PSS is 15 nm, showing largely aggregated structures. This difference in surface roughness might be due to the fact that threading of bolaamphiphiles into bulky CDs prevents the bolaamphiphiles from forming large aggregates at the interface. Thus, a combination of bolaamphiphiles with CDs offers a potentially useful method for generating homogeneous distribution of charges at the interface of a multilayered film.

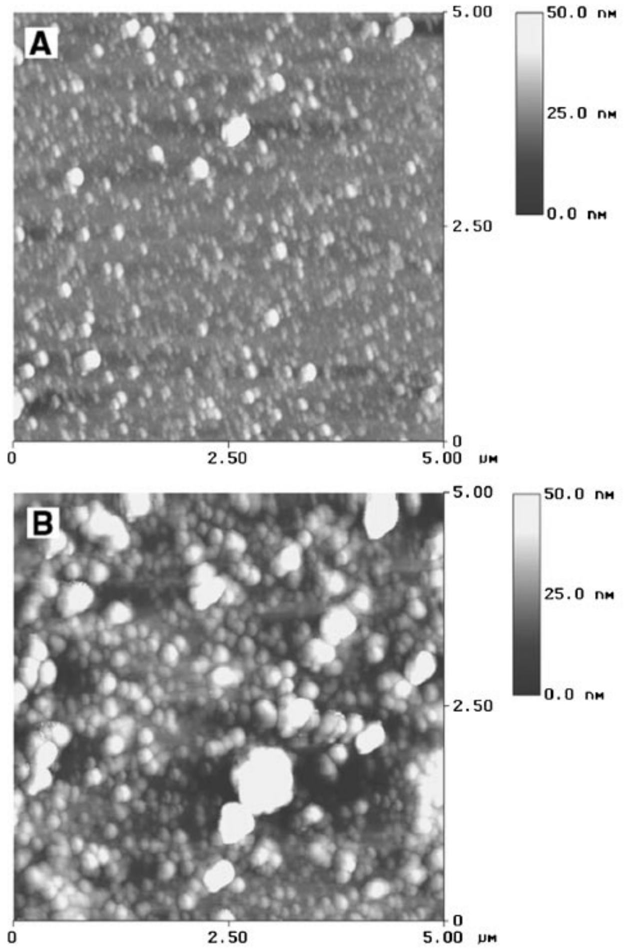

Fig. 3 AFM images (tapping mode) of the surface topology of self-assembled films consisting of (A) 12 double layers of CBr_2–PSS, and (B) 12 double layers of SBr_2–PSS.

In summary, we have demonstrated a procedure that uses two types of self-assembly to build multilayered films having complex, hierarchical structures. The key idea of this approach is that supermolecular structures formed *via* one type of self-assembly can be subsequently used as the building blocks in another type of self-assembly. A combination of different types of self-assembly should greatly extend the flexibility and capability of self-assembly in generating supermolecular structures with more types of functionalities. For example, by forming stable complexes with charged species, non-charged functional units such as cyclodextrin cavities can be incorporated into multilayered structures through electrostatic interactions. The multilayered structures described in this study are potentially useful as active components in fabricating sensors,[21] light-emitting diodes (LEDs),[22] and optoelectronic devices.[23] Besides cyclodextrins, other functional molecules or objects such as proteins, colloid particles, and surfactants can also be self-assembled into supermolecular structures and then be incorporated into another level of self-assembly.

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19 The ellipsometry measurements were carried out on an automatic instrument (Rudolph AutoEL). For each run, the refractive index of the multilayered film was self-determined by the machine and varied slightly around 1.560.

20 The cross-sectional area of a cyclodextrin inclusion complex molecule (β-CD: 176 Å^2) is rather large in comparison to that of the stilbenoid compound (S: ~20 Å^2).

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