Construction of positively-charged layered assemblies assisted by cyclodextrin complexation

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A β-cyclodextrin dimer is found to be effective in preparing a layer-by-layer architecture of positively charged ferrocene-appended poly(allylamine) presumably on the basis of strong β-cyclodextrin–ferrocene host–guest interaction.

The layer-by-layer adsorption of charged polymers (polyelectrolytes) formed on a solid support has been established within the last decade,[1–3] to prepare organic thin films. The preparation of the multilayer assemblies by this method is quite simple as a solid material is alternately soaked in solutions containing positively or negatively charged polymer materials. The ease of preparation of multilayer assemblies as well as their potential applicability may allow us to obtain sophisticated biosensors and bioelectronics.[4] Since the driving force for building up polymer layers is electrostatic attraction between oppositely charged polymers, formation of multilayer assemblies of uncharged and uniformly charged polymers would be impossible. Other types of interaction have to be employed to overcome this. In this regard, biotin–avidin interaction,[5] Watson–Click type base pairing[6] and charge-transfer interaction[7] have been used for binding two polymers. In this context, we considered that cyclodextrin (CyD) complexation[8] would be effective as an attractive force to construct layer-by-layer polymer thin films, if the polymers had suitable moieties to be bound by CyD. Here, we present that β-CyD dimer (**1**)[9] is a good binder for the construction of thin films of positively charged poly(allylamine) modified with ferrocenyl moieties (FcPAA).[10]
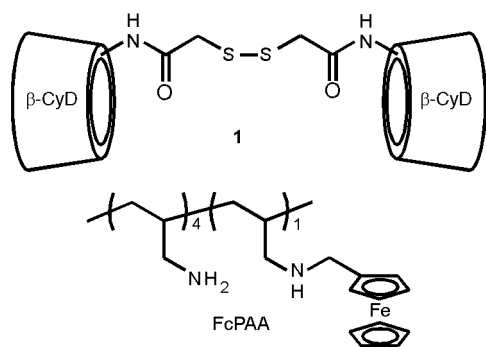

Fig. 1 shows a typical response curve for adsorption of FcPAA, which was recorded on a SEIKO EG&G QCA-917 quartz crystal microbalance (QCM) apparatus with a gold-covered 9 MHz AT-cut quartz oscillator. The oscillator was first soaked in a solution containing **1** (DMF–EtOH, 1 mmol dm^{-3}) to form β-CyD monolayer,[9] though this process was not essential for the adsorption of FcPAA. However, this pretreatment of **1** would minimize the spontaneous adsorption of **1** during the multilayer formation between FcPAA and **1**.† The surface-modified oscillator was then placed in a QCM cell filled with a buffer solution (acetate, pH = 5.0). After the oscillation frequency had reached a constant value, a concentrated solution of FcPAA was carefully added to give a final FcPAA concentration of 1.0 g dm^{-3}. An abrupt frequency change was observed and the frequency fell 118 Hz from the original value

within 20 min. This frequency change strongly indicates the spontaneous adsorption of FcPAA onto the oscillator. After washing with buffer solution, the oscillator was exposed to a buffer solution containing 1.0 g dm^{-3} of **1**. A small but apparent frequency change ($\Delta f = -10$ Hz) was observed, indicating that **1** is incorporated into the adsorbed FcPAA film. The oscillator was again exposed to FcPAA solution, then the frequency fell by 148 Hz. This frequency change strongly indicates that a second layer of FePAA was able to be deposited on the first FcPAA layer. Using the same technique of alternate soaking of the oscillator in **1** and FcPAA solutions, a third layer of FcPAA was also successfully deposited. These results suggest that **1** has an important role as a binder for overlayer formation of positively charged FcPAA, in overcoming the electrostatic repulsion between FcPAA molecules. Without treatment with **1**, FcPAA could never form overlayers on the first layer of FcPAA (Table 1, entry 2).

The large difference in the frequency changes between FcPAA and **1** treatments may be due to the difference in the deposition amounts. Since FcPAA is a macromolecule with a lot of counter anions, the deposition of **1** may result in larger frequency changes. On the other hand, **1** is a non-ionic, relatively small molecule. In addition, strong interaction of **1** to FcPAA should be limited at the ferrocenyl moieties of FcPAA. Thus, we consider that the smaller frequency changes during the treatment of **1** are reasonable.

To clarify the role of **1** in the FcPAA multilayer formation, we attempted the deposition of poly(allylamine) (PAA) without ferrocenyl moieties (Table 1, entry 3), because it is well known that ferrocene derivatives are excellent guests for β-CyD. In this experiment, although the first layer was able to adsorb, a smaller frequency change ($\Delta f = -7$ Hz) was observed for the second treatment of FcPAA after the treatment with **1**. Similarly, we
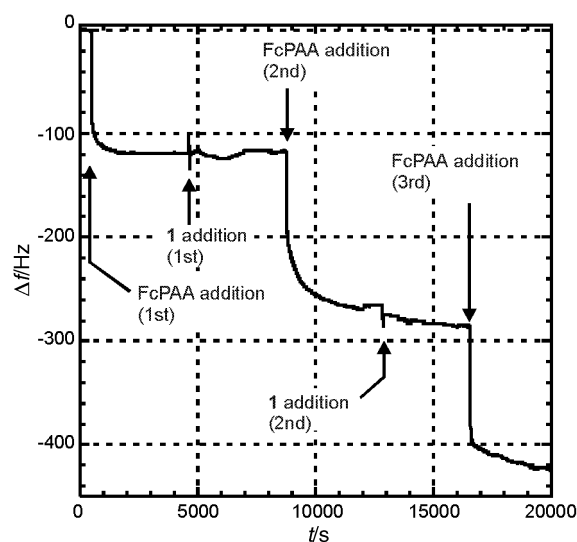

Fig. 1 Frequency changes of a gold-covered quartz crystal oscillator associated with the addition of FcPAA and **1** in a pH 5.0 aqueous buffer solution.

Table 1 Frequency changes (Δf) of the QCM oscillators upon the exposure of polymer and **1** solutions[a]

Entry	Condition	Δf/Hz		
		1st[b]	2nd[b]	3rd[b]
1	FcPAA + **1**	−118	−148	−138
2	FcPAA only	−132	−6	ND[c]
3	PAA + **1**	−74	−7	ND[c]
4	FcPAA + β-CyD	−136	−33	ND[c]
5	FcPAA + **1** + FcA	−140	−18	ND[c]
6	FcPAA + **1** + CyH	−137	−55	ND[c]

[a] Measurements were carried out at about 20 °C. A unit frequency change corresponds to a 1.10 ng mass change at the surface of the oscillator. [b] 1st, 2nd, and 3rd correspond to polymer layer formation. At least three runs were carried out and the values were averaged. The frequency changes corresponding to the deposition of **1** or β-CyD are not included. [c] Not determined.

attempted the deposition of FcPAA by the use of β-CyD instead of **1** (Table 1, entry 4). β-CyD was found to be ineffective as a binder, as revealed by the small frequency change for the second FcPAA layer formation.

If the ferrocene–β-CyD interaction actually promotes the multilayer formation of FcPAA, the overlayer formation should be suppressed by the presence of a guest compound to be bound by β-CyD cavity in the buffer solution containing FcPAA and **1**. In this regard, we attempted the overlayer formation of FcPAA in the presence of 10.0 mmol dm^{-3} of cyclohexanol (Table 1, entry 5) and 1.0 mmol dm^{-3} of ferrocenecarboxylic acid (Table 1, entry 6). Cyclohexanol and ferrocenecarboxylic acid are accommodated into β-CyD cavity with their binding constants being 500 and 2000 dm^3 mol^{-1}.[11,12] The first layer of FcPAA which was deposited onto the **1** monolayer was insensitive to the presence of cyclohexanol and ferrocenecarboxylic acid. This suggests that the first layer deposition would not be due to the ferrocene–β-CyD complexation, rather non-specific adsorption of FcPAA would be reasoned for the first layer deposition. On the other hand, both cyclohexanol and ferrocenecarboxylic acid suppressed the second layer formation of FcPAA. As predicted from the binding constants, the degree of the suppression was more apparent for ferrocenecarboxylic acid; in the presence of 1.0 mmol dm^{-3} of ferrocenecarboxylic acid, the frequency change of the oscillator was only −18 Hz, this change being about one third of that induced by the presence of 10.0 mmol dm^{-3} of cyclohexanol. These facts indicate that the suppression of the overlayer formation of FcPAA depends on the binding constants; a guest species that is bound well by the

β-CyD cavity of **1** can strongly prevent the overlayer formation of FcPAA. In other words, deposition of the FcPAA assisted by **1** can be controlled by the use of guest compounds for β-CyD. Recently, Kaifer *et al.* have demonstrated that a β-CyD monolayer deposited on a surface of novel metal nano-particles was effective in their self-organization in the presence of difunctionalized guest species.[13] Combining this with our results, CyD–guest interaction may be useful in preparing self-assembled organized materials.

In conclusion, we first demonstrated the interaction between the neutral β-CyD derivative **1** and guest moieties in the polymer chains can be used to fabricate the overlayer formation of FcPAA, overcoming the electrostatic repulsion. Our results may be applicable to fabricating sensing devices.

Notes and references

† ATR-FTIR spectroscopy is a powerful tool for elucidating the layered structure of thin films. In the case of the FcPAA–**1** film, however, the large difference in the deposition amounts between FcPAA and **1** may not allow further confirmation of its structure.

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