Templated Assembly of a Monolayer Consisting of a Coordination Nanobox at Air–Water Interface

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The monolayer formation consisting of an amphiphilic terpyridine ligand and a biphenyl template on aqueous solution of a palladium complex was examined with varying the mixing ratios. Templated self-assembly resulted into a stable monolayer of a box-shaped host–guest complex at air–water interface.

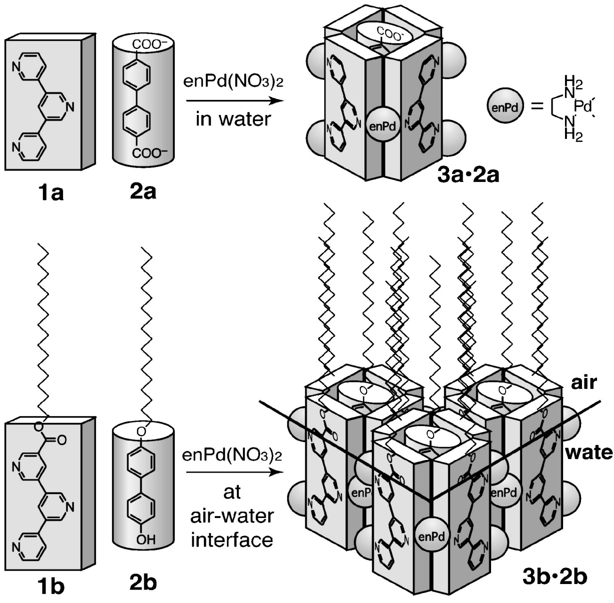
Lamgmuir–Blodgett (LB) films of macrocylic compounds have been intensively studied in terms of biomimetics and application to functional devices based on their guest inclusion abilities in the cavities.[1–5] Amphiphilic cyclodextrins in monolayer can encapsulate cholesterol depending on their ring size.[1] LB films of the amphiphilic cyclodextrins encapsulating azobenzene derivatives are also known to show photochromism.[2] Furthermore, calixarene derivatives can form stable monolayers at air–water interface and recognize the size of metal cations in subphase.[3] These inclusion phenomena are all based on the stability of the covalently linked cyclic structures of the hosts. On the other hand, templted formation of host–guest complexes has been accomplished in bulk solution.[6] These kinds of assemblies more resemble biosystems and prompt us to examine generation of different host structures from identical components upon complexation with guest molecules. Applying this concept to LB films will enable us to design the cavity in the film made to order for various guests.[7] In this paper, we describe the templated formation of a box-shaped host framework (nanobox),[8] where a template molecule fills the cylindrical cavity at air–water interface.

The nanobox **3a**·**2a** assembled from four terpyridine ligand **1a**, one biphenyl template **2a**, and six enPd$(NO_3)_2$ molecules had been reported.[8a] To apply the nanobox motif for Langmuir-Blodgett monolayers, we have designed a hyrdophobized terpyridine derivative **1b** and a guest **2b** by attaching a long alkyl chain[9,11] as shown in Scheme 1. Upon coordination with enPd, **1b** is expected to assemble around **2b** and form the monolayer of **3b**·**2b** at air–water interface.

We examined the complexation of enPd$(NO_3)_2$ with **1b** at air–water interface by measuring *π*–*A* isotherm of the monolayer of **1b** on pure water, or a 1.0 mmol dm^{-3} aqueous solution of enPd$(NO_3)_2$. The isotherm data showed that the molecular area of **1** on pure water was 0.26 nm^2 (curve a, Figure 1). When using the 1.0 mmol dm^{-3} aqueous solution of enPd$(NO_3)_2$, we found an enlarged area of 0.52 nm^2 (curve b). This finding indicates the formation of a coordination monolayer consisting of enPd with **1b** at air–water interface. The observed molecular area is not large enough to prove the formation of nanobox **3b**. Because the nanobox **3a**·**2a** in the crystal structure showed larger mean molecular area (0.55 nm^2, divide the outline area of **3a**·**2a** by number of the ligand; 2.19 nm^2/4)[8a] than the observed molecular area.

In order to determine the interaction between the palladium complex of **1b** and **2b**, we measured *π*–*A* isotherms of the monolayers of **1b** and **2b** by varying the mixing ratios (**1b**/**2b** = 89/11, 80/20, 67/33, 50/50, 33/67, and 20/80) on the 1.0 mmol dm^{-3} enPd$(NO_3)_2$ subphase. The isotherm data were normalized by the total number of amphiphile molecules (Figure 2a).

Relation between the molecular area of the monolayers and



Scheme 1.

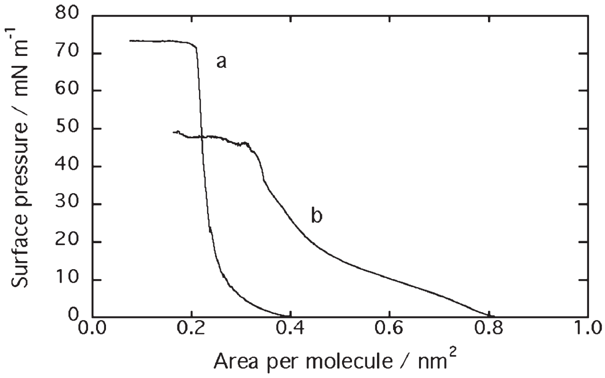


Figure 1. *π*–*A* isotherm of monolayers of **1b**. (a) On pure water. (b) On the 1.0 mmol dm^{-3} aqueous solution of enPd$(NO_3)_2$.

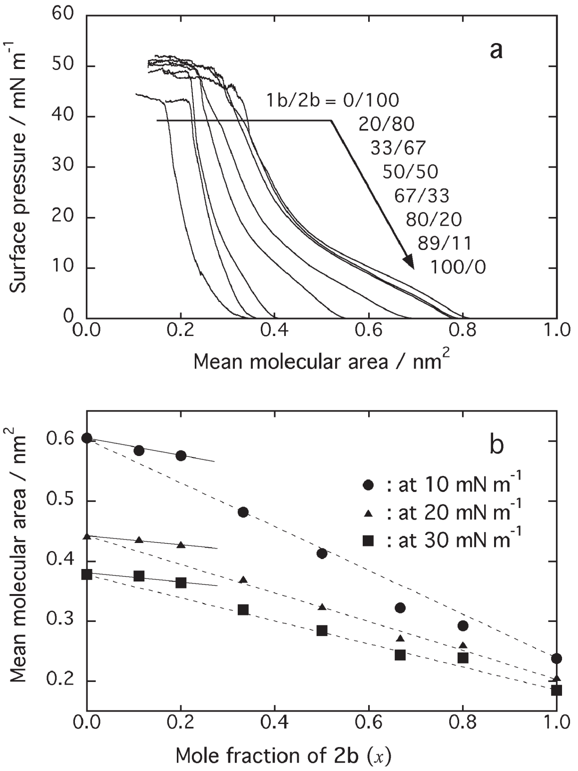


Figure 2. (a) π–A Isotherm of the mixed monolayers of **1b** and **2b** on the 1.0 mmol dm^{-3} aqueous solution of enPd(NO$_3$)$_2$, (b) Plots of the mean molecular area against the mole fraction of **2b** at 10, 20, and 30 mN m^{-1}.

the mole fraction of **2b** (x) is shown in Figure 2b. The dependence of the molecular area on x exhibits following three stages with an increase in x. (1) In a range of $x \leq 0.2$, the molecular area slightly decreases as x increases. (2) In $0.2 < x < 0.67$, decreases in the molecular area prove more clearly, showing linear relationships. (3), in $0.67 < x$, the slopes in this range are relatively smaller.

XPS measurement of the LB film of the **1b/2b** (4:1) mixed monolayer on a gold-coated glass plate showed signals corresponding to carbon, nitrogen, oxygen, and palladium. Particularly, the atomic ratio of nitrogen in the ligands (ethylenediamine and **1b**) and nitrate was estimated as 2:1 from the peak areas of nitrogen 1s at 401 eV (in ligands) and at 407 eV (in nitrate). Uncoordinated nitrogen in the ligands was not observed. This observed ratio corresponds to 3:2 stoichiometry of enPd(NO$_3$)$_2$ and **1b**, suggesting that all coordination sites on the palladium center and the ligands participate complexation and form a chain-like infinite polymer or cyclic oligomers in the monolayer.

Figure **2b** shows the presence of the bent point at the molecular fraction x of 0.2 (**1b/2b** = 4:1). This x value of the bent point kept constant for the 10, 20, and 30 mN m^{-1} surface pressures, meaning that a single species consisting of **1b**, **2b**, and enPd(NO$_3$)$_2$ with 4:1:6 stoichiometry assembles in the monolayer. This stoichiometry suggests the formation of the nanobox structure. ^{1}H NMR of the 4:1:6 mixture of **1b**, biphenyl guest, and enPd(NO$_3$)$_2$ in D$_2$O also indicates the formation of a nanobox **3b**·biphenyl.[8a] From these observations, we can conclude that the formation of the nanobox **3b·2b** also performed at air–water interface. The molecular area of the **1b/2b** (4:1) mixed monolayer (2.54 nm^2) is larger than that of the ideal mixture (2.34 nm^2). In present monolayer system, it is reasonable that the formation of the box-shaped structure should result latger mean molecular area of the monolayer.[12] The larger molecular area may be attributed to an internal void space between **3b** and **2b**, and an additional space between nanoboxes.

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