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Dynamic dendrimer at electrified interface: potential dependent adsorption–desorption and reorientation of a 4-pyridyl-modified PAMAM dendrimer

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Potential-dependent dynamic adsorption–desorption and reorientation of a 4-pyridyl modified PAMAM G2 dendrimer at a Au(111) electrode has been demonstrated.

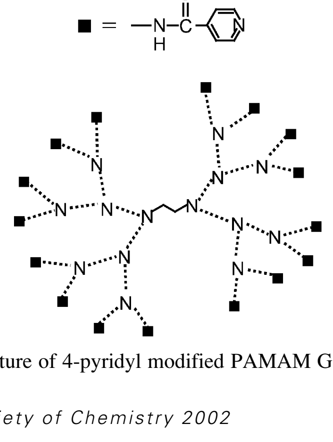
Among the uses of dendrimers as a novel class of functional units, of our interest is the use of dendrimers as a modifier of an electrode surface. Emergence of novel functions of dendrimers has been examined at electrified interfaces.[1] To mention just one example, Crooks and coworkers reported a molecular filter approach in which dendrimer thin films on Au electrodes are used for enhancing the chemical sensor selectivity.[2] A dendrimer can also be regarded as a model of biological polymers for the understanding of protein electrochemistry, because both dendrimers and proteins possess a number of functionalities interactive with the electrode surfaces. The conformations of proteins on electrode surfaces are known to be potential dependent.[3] Dendrimers also may exhibit potential dependent changes of adsorption structures. Abruna *et al.* have noticed potential dependent reshape and reorientation of dendrimers on an electrode surface.[4] However, the dynamic aspect of the potential dependent adsorption state change of dendrimers has so far, to our best knowledge, never been considered.

It has recently been known that an adsorption layer of a molecule bearing a long alkyl chain with a 4-pyridyl end group changes the molecular assembling structure reversibly as a function of potential.[5,6] The change ranges from a compact film to desorbed micellar structures. The 4-pyridyl group is the key to introduce such a dynamic behaviour, because the potential dependent adsorption–desorption and reorientation of such a molecule is in line with that of pyridine.[7]

In the present work, we modified the periphery of a dendrimer with 4-pyridyl groups and examined its behaviour on a Au(111) single crystal electrode. We observed for the first time a potential dependent dynamic adsorption state change including a partial desorption and reorientation.

A poly(amidoamine) (PAMAM) dendrimer of generation 2 (Starburst® dendrimer, Aldrich) was reacted with an excess of isonicotinic acid in dimethylacetoamide in the presence of DCC and HOBt for over 100 h at room temperature according to the reported procedure.[8] The PAMAM dendrimer modified with sixteen peripheral 4-pyridyl groups (**1** in Scheme 1) was isolated and identified by MALDI-TOF MS (*m*/*z* 4937.65 for MH^+ [calc. 4937.68]), ^1H NMR and HPLC gel chromatography. Compound **1** is insoluble in alkaline aqueous solution and almost insoluble in a neutral solution. Compound **1** can be spread at a gas/aqueous solution interface. It was confirmed that **1** forms a water-insoluble Langmuir film at an air/water interface by π–*A* curve measurements. The equilibrium spreading pressure of **1** was found by surface tension measurements to be 8.5 and 11.4 mN m^{-1}, respectively, on 0.05 M $KClO_4$ (pH ≈ 5.3) and 0.05 M $KClO_4$ + 2 mM $KHCO_3$ (pH = 9.6). On a deaerated electrolyte solution, either 0.05 M $KClO_4$ or 0.05 M $KClO_4$ + 2 mM $KHCO_3$, in an electrochemical cell, a solution of **1** (in chloroform + methanol: 19/1 (v/v)) was spread and solvent allowed to evaporate. An Au(111) single crystal electrode (area: 0.502 cm^2) was flame annealed and cooled to room temperature in Ar gas. The electrode was then horizontally contacted to the Ar gas/solution interface at 0.0 V and then settled in a hanging-meniscus configuration. As a reference electrode, Ag/AgCl sat-KCl was used. All the potentials in this paper are referenced to this electrode. These procedures followed those in the previous report.[5] This electrified interface was characterized by cyclic voltammetry (CV), differential interfacial capacity† (*C*)–potential (*E*) curve obtained from ac voltammetry (ac frequency, 14 Hz; amplitude, 5 mV_{rms}; potential sweep rate, 5 mV s^{-1}), and potential step transient of *C*.

Fig. 1 shows *C*–*E* curves at various spread amounts of **1** on 0.05 M $KClO_4$ + 2 mM $KHCO_3$. In the presence of **1**, the value of *C* was smaller than that in the absence, indicating that **1** is adsorbed on the electrode surface. At spread amounts of 0.19 and 0.25 nmol cm^{-2}, a capacity peak was observed at −0.1 V. Both anodic and cathodic peaks were observed at the same potential in CVs. This peak potential corresponds to the potential at which reorientation of the pyridyl group takes place from a nearly flat-lying orientation at more negative potentials to a nearly right-up one at less negative potential.[5–7] At greater spread amounts, this peak became unclear, indicating that the movement of peripheral groups is more strongly restricted by denser packing of **1**. It has been established that pyridine is desorbed at more negative potentials than −0.7 V.[7] However, no rise of *C* value as a sign of desorption was seen at this potential in Fig. 1. We confirmed in a separate experiment that *N*-pentadecyl-4-pyridinecarboxamide (**2**), which possesses the same amide linkage with 4-pyridyl group as **1**, is desorbed from a Au(111) electrode at −0.75 V[9] as is 4-pentadecylpyridine.[5] Although dendrimer **1** can be regarded as a bundle of a number of molecules **2**, desorption does not take place. This fact may be understood in the context of the multiple equivalent adsorption site effect as seen previously for linear polymers.[10] That is, as



Scheme 1 Structure of 4-pyridyl modified PAMAM G2 dendrimer (**1**).

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long as the adsorption Gibbs energy of one site is more negative than $-kT$ (k is the Boltzmann constant and T is the temperature), the majority of polymer species are adsorbed with all of the available sites. We confirmed that this is also true for a dendrimer by a model calculation.[11] In the model, assuming a dendrimer possessing N equivalent adsorption sites, fractions of all possible $N + 1$ species ranging from desorbed one to one adsorbed with all N sites were calculated. When there is no interaction between the sites, the species adsorbed with N sites is the majority.

To enable **1** be desorbed at negative potentials, one possible method is, therefore, to weaken the adsorptivity of the pyridyl groups. The calculated pK_a value of an isolated, protonated peripheral pyridyl group is estimated to be *ca.* 4.‡ By omitting the addition of $KHCO_3$ into the electrolyte solution, partial protonation of the pyridyl group may be attained. Therefore, we measured *C*–*E* curve on 0.05 M $KClO_4$ (Fig. 2). The curve shape was greatly different from that on 0.05 M $KClO_4$ + 2 mM $KHCO_3$. Rather, it resembled the *C*–*E* curve for a bilayer of 4-pentadecylpyridine.[12] The apparent differences from Fig. 1 were the positive shift of capacity peak of pyridyl reorientation to 0.1 V and the appearance of a steep increase of *C* with hysteresis at negative potentials. The latter represents at least partial desorption of dendrimer from the electrode surface. Because **1** is almost insoluble and the *C* value at −0.8 V is still lower than that at a bare Au(111) electrode, it is likely that the desorption of peripheral pyridyl groups is accompanied by the reshaping of **1**, resulting in the decrease in the electrode surface area contacting with the dendrimer molecules.

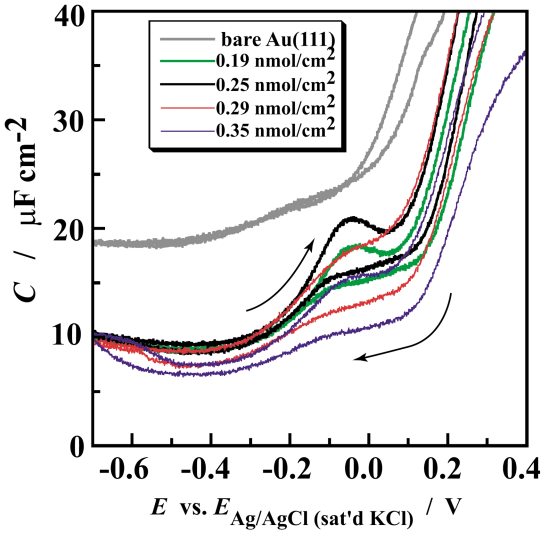

Fig. 1 Capacity–potential curves of aa Au(111) electrode horizontally contacted to an Ar gas/solution (0.05 M $KClO_4$ + 2 mM $KHCO_3$) interface where dendrimer **1** was spread in various amounts prior to contacting.

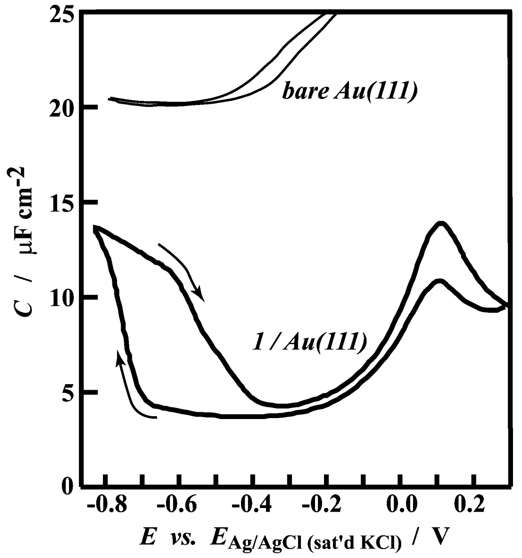

Fig. 2 Capacity–potential (*C*–*E*) curves of a Au(111) electrode horizontally contacted to an Ar gas/solution (0.05 M $KClO_4$) interface. For the lower curve, dendrimer **1** was pre-spread at an amount of 0.23 nmol cm^{-2}.

When potential was stepped from −0.4 V to −0.8 V or to 0.2 V, a steep change of *C* within 3 s was followed by a slow decay longer than 150 s for the remaining *ca.* 15% change of *C* with respect to its total change. On the other hand, when stepped from −0.8 V or 0.2 V to −0.4 V, such a slow decay component was not observed. The processes of adsorption and reorientation from upright to flat-lying states to reach steady states are much faster than the reverse processes.

It is important to note that such a dynamic behaviour as described above has never been observed in identical experiments for a linear polymer, poly(4-vinylpyridine).[11]

Addition of Zn^{2+} ion in 0.05 M $KClO_4$ solution resulted in further change of the *C*–*E* curve. The reorientation capacity peak at 0.1 V became much higher than the peak height in the absence of Zn^{2+}. It is known that 4-pyridyl groups act as ligands to Zn^{2+}. Therefore, Zn^{2+} may function as a glue weakly tethering the neighbouring adsorbed dendrimers. The enhancement of the peak may be due to a cooperative effect, change of dendrimer conformation in the presence of Zn^{2+} or sudden reversion of adsorption energy at the peak potential relative to the coordination energy.

In summary, we demonstrate for the first time potential dependent dynamic behaviour of a dendrimer and regulation of the behaviour by pH and addition of a metal ion. The dynamic behaviour is chemically reversible. Spectroelectrochemical measurements to see the dynamics at a molecular level, for example the correlation between the motions of periphery, interior and core, are currently in progress in our laboratory.

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Notes and references

† The value of *C* was obtained by assuming an equivalent circuit in which a capactitor of *C* and a resister are connected in series.

‡ ACD software Solaris V. 4.67 on SciFinder.

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