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Voltammetric study of insoluble 4-pyridyl-terminated surfactant binary-component films prepared by multiple horizontal touching method on a Au(1 1 1) electrode

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ABSTRACT

Potential dependent behaviors and structures of binary-component bilayers and multiple layers of two different water-insoluble 4-pyridyl-terminated surfactants (**C15-O-Py** and **C15-(C=O)-Py**, see Fig. 1) on a Au(1 1 1) electrode were investigated by voltammetric techniques. Film preparation was based on repetitive horizontal touching of the electrode to the spread film of the surfactants at a gas/water interface. When bilayer formation was made by sequential touching to the neat spread films of the two different surfactants, the resultant bilayer structure was always of Au(1 1 1)/**C15-O-Py**/**C15-(C=O)-Py**, being independent of whether the first touching was made with **C15-O-Py** or **C15-(C=O)-Py**. This reflects the stronger affinity of **C15-O-Py** for the electrode surface, which works dominantly over mixing. When multiple-touching was made to the spread film of two-component mixture at a given mixture ratio, the resultant first layer appeared a **C15-O-Py** monolayer as long as its monolayer amount was supplied. Further increase in the number of the multiple-touchings to the mixed spread film resulted in the formation of **C15-O-Py** bilayer in the bilayer thickness region of the film. Implications of these results were discussed in regards to the structures and properties of the films. When binary-component bilayers and multi-layers are prepared by horizontal touching methods such as a Langmuir-Schaefer technique, care must be taken to the fact that the resultant film structure does not always turn out as the procedural deposition order.

Keywords:

binary-component surfactant film

multiple horizontal touching

interlayer place-exchange

differential capacitance-potential curve

adsorption

1. Introduction

Much has been recently becoming known about the potential dependent behavior of surfactant adsorption films possessing weak interaction with an electrode surface. Such a surfactant monolayer can be prepared by simply touching a flat electrode surface horizontally to a gas/water interface covered with a water-insoluble surfactant spread film or to a gas/surfactant aqueous solution interface [1]. Multi-layer formation is readily available by multiple touching [2], or even spontaneously in some cases [3]. These films exhibit potential-driven reversible dynamics such as adsorption/desorption, reorientation and condensed film formation [1-10], attracting considerable interests of interfacial electrochemists. When forming bilayers or multiple layers, an enhanced contrast of interfacial capacitance and sharper phase transition accompanied by greater amplitude of optical property changes compared to their monolayers can often be brought about, holding promise to application to switching devices.

Typical surfactants exhibiting such potential dependent behavior include a family of 4-pyridyl terminated surfactants. Their behavior on the Au(111) electrode has been extensively described using the results of electrochemical and spectroscopic measurements [3,5,9,11-14]. Several factors determining the behavior have been elucidated in our previous studies [13,14]. Interaction between the 4-pyridyl head group as the adsorption site and the electrode surface plays a key role as well as the intermolecular interaction between surfactant molecules. The affinity of the pyridyl group for the electrode surface as one of the most important factors can be changed by molecular design of its electronic property.

Herein, we ask by ourselves a question how an insoluble film of binary-component surfactant responds to the potential change. Especially, what is the structure of the binary-component surfactant films prepared by repetitive horizontal touching procedures?

Penfold and coworkers prepared a binary-component surfactant film through spontaneous adsorption from the mixed solution onto a hydrophilic silica or silicon surface and evaluated the composition and structure of the bilayer using specular neutron reflection techniques [15-18]. They found that one of the components exhibiting stronger affinity for the substrate dominantly adsorbs in direct contact to the surface and that a bilayer possessing

an asymmetrical composition between the first and second layers is formed. The asymmetrical distribution induced by the difference of molecule-substrate interaction for two different molecules is also observed in biological lipid membranes [19-21]. The distribution was deduced by the use of quartz crystal microbalance with dissipation technique, fluorescence recovery after photo-bleaching, and neutron reflectance.

In most of these works, binary-component bilayers were prepared by spontaneous adsorption of micelles or vesicles to the surface from solution bulk, on one hand [15-21]. On the other hand, there are few examples of binary-component bilayer preparation using the Langmuir-Schaefer (LS) method. Recently, Crane and coworkers found, using fluorescence probe measurements, that a lipid bilayer formed by the Langmuir-Blodgett (LB)-LS method, in which the second layer was formed by the LS method, exhibits a flip-flop [22]. Their results suggest that actual composition distribution in mixed bilayers is not necessarily determined by the order of deposition of the two different surfactants and that the molecule-substrate interaction is of importance even in the use of LS method.

In the present study, we prepare binary-component bilayer and multilayer films on a Au(1 1 1) electrode surface using repetitive horizontal touching procedures. The horizontal touching method may be said in another way as a pseudo-LS method. The aim of this work is at the characterization of the structures of these binary-component films by the use of voltammetric techniques. The voltammetric measurements were made after each of the latest touching of the electrode to the spread film of the water-insoluble surfactant on an electrolyte solution subphase at a hanging-meniscus (H-M) configuration right there. The structures of binary-component films formed on the electrode surface may be determined by a difference of affinity of adsorption functional groups for the substrate surface, free energy of mixing, and susceptibility of the molecular displacement.

To highlight the effect of the affinity of the surfactants for the electrode surface upon the film structure, we use two water-insoluble 4-pyridyl terminated surfactants, 1-pyridin-4-yl-hexadecan-1-one (**C15-(C=O)-Py**) and pentadecyl 4-pyridyl ether (**C15-O-Py**). Their structures are depicted in Fig. 1-a. **C15-O-Py**, which has a higher excess electronic charge on pyridyl nitrogen, exhibits stronger attractive interaction of the 4-pyridyl head group with a Au(1 1 1) electrode surface compared to **C15-(C=O)-Py** [14].

Fig. 1

We use two types of successive touching procedures to prepare binary-component films. First, so as to prepare bilayers, monolayer formation of **C15-O-Py** or **C15-(C=O)-Py** on a bare Au(1 1 1) surface by horizontal touching is followed by the second layer formation of different molecule from the first one. Second, successive touching to a mixed spread film of **C15-O-Py** and **C15-(C=O)-Py** is made to form the films of up to six layers equivalent or more.

2. Experimental Section

2.1. Materials

Milli-Q water with 18 M Ω cm resistivity was used to wash the glassware and to prepare all the aqueous solutions. Potassium perchlorate (KClO₄) was prepared by neutralizing HClO₄ (Ultrapure Analytical grade, Tama Chemicals) with KOH (Suprapure grade, Merck), collected by filtration, recrystallized twice from water, and dried in vacuum at 100 °C. Potassium bicarbonate (KHCO₃, reagent grade, Kanto Chemicals) and chloroform (spectral grade, Nakalai Tesque) were used as received. Wetted Ar gas (99.9995%) was used to deaerate the electrolyte solution. Synthetic procedures of **C15-O-Py** and **C15-(C=O)-Py** have been described in our previous report [14].

A Au(1 1 1) of a single crystal disk (Techno Chemicals Inc., facet precision < 1 °) with a surface area of 0.264 cm² was used as a working electrode. Before each experiment, it was flame-annealed and quenched with Milli-Q water. The quality of the Au(1 1 1) electrode was checked by recording the cyclic voltammogram (CV) and differential capacitance-potential (*C-E*) curve in 50 mM KClO₄ before the experiments with surfactants. The reference electrode was a Ag/AgCl/sat-KCl in a separate compartment connected to the electrochemical cell through a salt bridge. All potentials reported here are referenced to this electrode. The counter electrode was a flame-annealed gold coil. Electrolyte solution used in the experiments with surfactants was 50 mM KClO₄ + 2 mM KHCO₃.

2.2. Film Preparation and electrochemical measurements

Experimental setup for electrochemical measurements was the same as described previously [14]. Formation of the first monolayer in direct contact with a Au(1 1 1) surface was made by the “single-touch” method [14]. Briefly, surfactant solution (1 mM) in chloroform was spread onto an Ar gas/50 mM KClO₄ + 2 mM KHCO₃ aqueous electrolyte solution interface (G/S interface) in a cell to form a Langmuir film of the surfactant at its equilibrium spreading pressure (*ESP*) after the solvent evaporation. A pretreated clean working electrode cooled to room temperature was horizontally touched to the Langmuir film at G/S interface at 0.0 V (Fig. 1-b(i)). In the pretreatment, the electrode was flame-annealed, quenched with Milli-Q water, and flame-annealed again. By setting the electrode in a H-M configuration, behavior of this single-touch film was accessed by the measurements of CV and *C-E* curve. The secondary touching of the first-monolayer-covered electrode onto a Langmuir film of a different surfactant was conducted in another cell as follows. The electrode was detached from the electrolyte solution (Fig. 1-b(ii)). The remaining solution droplets on the surface were removed using a capillary. The electrode was horizontally touched to the Langmuir film at its *ESP* in another cell at 0.0 V (Fig. 1-b(iii)). Electrochemical measurements were then carried out in a H-M configuration. When detaching in above-mentioned procedure, if the first layer was **C15-O-Py**, the **C15-O-Py** spread film at the G/S interface surrounding the electrode was completely removed by suction (see *1 in Fig. 1-b(ii)) before detaching. Note that the detaching procedure without suction resulted in additional incorporation of **C15-O-Py** surfactants in excess of the monolayer onto the electrode surface, as confirmed by electrochemical measurement after its transferral to a film-free Ar-gas/water interface. When the first layer was **C15-(C=O)-Py**, the suction was unnecessary, because its omission never affected the response after the transferral.

To represent the electrode modification after the secondary touching, we use a notation of “Au/A (1)/B (2)” where A and B are the surfactants, (1) stands for the component of the first monolayer, and (2) does for the component of the secondary touching. We examined herein both Au/**C15-(C=O)-Py** (1)/**C15-O-Py** (2) and Au/**C15-O-Py** (1)/**C15-(C=O)-Py** (2). (Note that these notations do not necessarily describe the actual bilayer structure but the order

of two step touching procedures.)

Repetitive touching of a Au(1 1 1) electrode to a Langmuir film of a binary-component (**C15-(C=O)-Py** + **C15-O-Py**) was also made. Detaching followed by next touching was conducted as described above without suction procedure. The spread chloroform solution contained **C15-(C=O)-Py** + **C15-O-Py** with a molar ratio of 1:1 or 3:1 with a total concentration of 0.5 mM. After each additional touching, electrochemical measurements were made. To represent the mixture solution composition and total number of touchings (n), we use a notation of $(3/1)^n$, for example.

A potentiostat (Toho Giken, Polarization Unit PS-06 with a 50 μ s response time) and a digital lock-in-amplifier (EG&G Instruments, DSP 7265) were employed to control and measure the electrical variables of the interface. The differential capacitance (C) was measured by superimposing an ac perturbation of 5 mV_{rms} and 14 Hz on a 5 mV s⁻¹ voltage ramp. In the calculation of C , a constant resistor-capacitor series equivalent circuit was assumed. All the electrochemical measurements were conducted at room temperature (25 ± 1 °C).

3. Results and discussion

3.1. Bilayer formed by two-successive touching to different single-component spread films at G/S interfaces

Fig. 2

Fig. 2 shows representative CVs and C - E curves for the electrodes of Au/**C15-(C=O)-Py** (1)/**C15-O-Py** (2) and Au/**C15-O-Py** (1)/**C15-(C=O)-Py** (2). The CVs were recorded after multiple cyclic potential scans. For the C - E curves, the first and second scans as well as the curve after multiple potential scans are displayed. One can immediately pointed out that:

(i) For both electrodes, the change of the C - E curve during multiple cyclic potential scans is minor.

(ii) Steady state responses reached after multiple potential scans are inconsiderably different from the response of the initial scan.

(iii) The responses of the two differently prepared electrodes are quite similar, being almost indistinguishable.

The C - E curves for two different electrodes exhibited common features of potential-driven film structure changes. The value of C around 0.20 V was as low as $4 \mu\text{F cm}^{-2}$, indicative of compact film formation. In the negative potential scan, a gradual increase of C reflecting the commencement of the transformation from compact to loose film was observed around -0.35 V. At further negative potentials, a steep increase of C reached the value of a bare Au(1 1 1) electrode around -0.80 V due to film desorption. In the positive scan from desorption state, re-adsorption of the surfactants onto the electrode surface gave rise to gradual decrease of C from ca. -0.73 V. At positive potentials, the initial value of $4 \mu\text{F cm}^{-2}$ was restored due to the re-formation of the compact film. The peaks of CV corresponded well to the differential capacitance changes.

The potential dependent behavior of 4-pyridyl terminated surfactant films depends on the substrate-surfactant interaction and intermolecular interaction [13,14]. The shapes of CV and C - E curve and capacitance level reflect the structure of adsorbed film. Applying this perspective, aforementioned result (i) indicates that repeated potential scans hardly change the film structure. Results of (ii) and (iii) indicate that, after the beginning of the secondary touching procedure but before the initial potential scan, the film structures of the two differently-prepared electrodes became almost identical. As a tentative conclusion, the obtained structure of the film does not depend on the order of the touching procedures of two different surfactants, at least in terms of the factors that affect CV and C - E curve.

To gain insight into the bilayer structure, C - E curves of single-component single- and double-touch films of **C15-(C=O)-Py** (Fig. 3-a) and **C15-O-Py** (Fig. 3-b) are used as references.

Fig. 3

The details of the behavior for these neat surfactant films were described previously [14]. Distinct features of the single-touch films of the two different molecules include a sharp

transition of **C15-(C=O)-Py** from compact to loose-packed states (in the potential region of -0.35 V to 0.0 V) and a narrower potential region of a compact film formation for **C15-(C=O)-Py** (around 0.1 V) than that for **C15-O-Py** (from -0.25 V to 0.0 V). The double-touch film of **C15-(C=O)-Py** exhibits similar curve shape to its single-touch film, while the value of C is lower except for at the potential of desorption. In sharp contrast, the double-touch film of **C15-O-Py** exhibits markedly different curve shape from its single-touch film as being highlighted by the wider potential region of the compact film formation (down to -0.6 V) and approximately 0.2 V more negative potentials of steeper capacitance rise for the double-touch film than single-touch one.

The common C - E curve shape for both Au/**C15-(C=O)-Py** (1)/**C15-O-Py** (2) and Au/**C15-O-Py** (1)/**C15-(C=O)-Py** (2) in Fig. 2 has the closest similarity to the single-touch film of **C15-O-Py** among others in Fig. 3. Essentials of the similarity include the subtle phase transition peak around -0.2 V, the onset potentials of desorption/re-adsorption and inflections of the C - E curve around -0.3 V. The level of C in the potential range from -0.3 to 0.0 V in the curves of Fig. 2 is near to the double-touch film of **C15-(C=O)-Py** but not as low as that of **C15-O-Py**. This indicates that these binary-component bilayers of interest are not as close-packed as the double-touch film of **C15-O-Py** but loose as that of **C15-(C=O)-Py**. In such a loose film, the surfactant in the first layer in direct contact with the electrode surface determines the C - E curve shape. This interpretation is based on the following general tendency of the potential responses of the family of 4-pyridyl surfactants.

The potential dependent behavior of a bilayer reflects the intrinsic behavior of the first layer under the influence of the second layer through interlayer interaction and ability to block the permeation of electrolyte solution to the electrode surface. These influences are enhanced in a closely packed bilayer. In the case of 4-pentadecylpyridine (**C15-Py**) [3], *N*-4-pyridinyl-hexadecanamide (**C15-CONH-Py**) [13], and **C15-O-Py** [14], the bilayers are close-packed. As a result, the bilayers appear rigid and their potential dependence is quite different from the single-touch films, exhibiting wider potential region of the compact film state than the single-touch film. This is exemplified by Fig. 3-b. In the contrast case of *N*-pentadecyl-4-pyridinecarboxamide (**C15-NHCO-Py**) [13] and **C15-(C=O)-Py** [14], the bilayers have looser molecular packing than above three counterparts. The interlayer interaction cannot effectively increase the rigidity of the bilayers, resulting in a similar

potential dependence to the single-touch films. This is exemplified by Fig. 3-a.

Taken together, the *C-E* curve shape and the level of *C* in Fig. 2 indicate that both Au/C15-(C=O)-Py (1)/C15-O-Py (2) and Au/C15-O-Py (1)/C15-(C=O)-Py (2) have almost the same loose bilayer structure, in which the first layer in contact with Au(1 1 1) surface predominantly consists of **C15-O-Py**, independent of the procedural order of touching. This structure is in line with stronger attractive interaction of **C15-O-Py** with the Au(1 1 1) surface than **C15-(C=O)-Py** [14]. The preferential adsorption of **C15-O-Py** is therefore energetically favorable than mixing of these two different 4-pyridyl surfactants. The bilayer prepared as Au/C15-(C=O)-Py (1)/C15-O-Py (2) transforms actually into the structure to be represented as Au/C15-O-Py/C15-(C=O)-Py. Capability of interlayer place-exchange may be a prerequisite to reach an equilibrium molecular distribution across the film, which may be different from procedural initial structure.

As the possible place-exchange process, trans-bilayer flip-flop movement in biological bilayer is invoked. Liu and Conboy measured the flip-flop exchange rate for a supported asymmetric lipid bilayer using sum-frequency generation vibrational spectroscopy [23]. They claimed that the rate is very slow below the phase-transition temperature (T_m) whereas extremely fast above T_m . This claim was later challenged by Crane and coworkers [22]: because heating of the supported bilayer in gel-phase induces the appearance of defects and budding of vesicles, the method used by Liu and Conboy cannot distinguish the flip-flop from the loss of lipids from the surface upon heating. Crane and coworkers investigated several supported lipid bilayers formed by LB/LS and combined LB/vesicle-fusion (LB/VF) methods, using fluorescence probe [22]. They found that, during the formation of the second layer through the LS method, transverse place-change of the lipid molecule takes place even in the condition that the LB/VF bilayer did not exhibit the flip-flop.

As described above, the results in Fig. 2 indicate that the transformation from Au/C15-(C=O)-Py/C15-O-Py into Au/C15-O-Py/C15-(C=O)-Py occurred before initial potential sweep. Presumably, as in the above case of LB/LS lipid film, the formation of Au/C15-O-Py/C15-(C=O)-Py structure takes place during the second horizontal touching procedure but not through flip-flop of initially formed Au/C15-(C=O)-Py/C15-O-Py precursor structure.

3.2. $(1/1)^n$ and $(3/1)^n$ C15-(C=O)-Py/C15-O-Py films

Fig. 4

Fig. 4 shows $C-E$ curves for the electrodes covered by the $(1/1)^n$ and $(3/1)^n$ **C15-(C=O)-Py/C15-O-Py** films. The single-touch films, $(1/1)^1$ and $(3/1)^1$, showed an obvious peak of C around -0.2 V due to the 4-pyridyl head group reorientation of **C15-(C=O)-Py** molecules. The peak height decreased as the detaching-touching cycles were repeated. The $C-E$ curve of $(1/1)^2$ -film resembled the curves in Fig. 2, suggesting that the film takes a Au/**C15-O-Py**/**C15-(C=O)-Py** structure. Most of **C15-(C=O)-Py** molecules previously in the first layer are likely expelled from the electrode surface into the second layer, because the free energy for adsorption of **C15-O-Py** onto the Au(1 1 1) surface is far more negative than that for mixing of these two molecules. The $C-E$ curve of $(3/1)^4$ -film also resembled the curves in Fig. 2, while when $n < 4$, the feature of reorientation around -0.2 V remained observable. The quadruple touching is the minimum requirement to attain enough content amount of **C15-O-Py** molecules to form its first monolayer in the $(3/1)^n$ -film. This reveals that the interlayer place-exchange of the surfactant molecules takes place not only within a bilayer but also in triple- and quadruple-touch films.

The capacitance levels of $C-E$ curves gradually lowered with increasing n to reach convergence of the curves on a unique one, which resembled the $C-E$ curve of the double-touch film of **C15-O-Py** (Fig. 3-b, solid line), in terms of $C-E$ curve shape and minimum value of C . The convergence occurred at $n \geq 5$ for $(1/1)^n$ -films and $n \geq 8$ for $(3/1)^n$ -films. This observation indicates that the bilayer thickness region from the electrode surface in these higher n -number multiple touching films takes nearly the same structure of **C15-O-Py** double-touch film even when **C15-O-Py** is the minor component, i.e., $(3/1)^n$. Not merely the preferential **C15-O-Py** first monolayer formation but bilayer formation underwent. On a speculative basis, high rigidity of **C15-O-Py** bilayer due to commensurate stabilization between the first and second layers effects this bilayer formation.

Assuming that these n -multiple-touching films have compact n -layers lamellar structures, the differential capacitance in the compact film potential region should continuously decrease

in proportion to the reciprocal of the total film thickness and thus to n^{-1} . Such a tendency was not seen experimentally for the higher n -numbers. Either of following two situations may explain the convergence not only of the capacitance but also the $C-E$ curve shape.

(i) When the electrode was detached from a G/S interface, a large part of the newly attached uppermost layer was left on the subphase because of weak adhesion. Therefore, the multiple touching procedure above a certain n (possibly $n = 3$) did not add further overlayers on the electrode surface.

(ii) The overlayers after the triple or quadruple touching does not have compact layers with lamellar structures but form a swelled gel-like film or diffuse micellar aggregates that largely contain electrolyte solution. This disordered overlayer is alike the desorbed double-touched film around -0.8 V so that such aggregates never contribute to the measurable interfacial capacitance. Because of the support by the flat electrode surface, the first few layers can assume a stratified structure. This has been confirmed for **C15-Py** films [9,12]. However, the overlayers in the present case do not take a stratified one.

Either interpretation is consistent with the **C15-O-Py** bilayer formation in the bilayer thickness region.

4. Conclusion

Potential dependent behavior and structure of the binary-component bilayers and multiple layers of **C15-O-Py** and **C15-(C=O)-Py** on a Au(1 1 1) electrode were investigated by voltammetric techniques. The films were prepared by the use of repetitive horizontal touching methods.

When bilayer formation was made by sequential touching to the neat spread films of the two different surfactants, the resultant bilayer structure was of Au/**C15-O-Py**/**C15-(C=O)-Py**, being independent of whether the first touching to the bare electrode surface was made with **C15-O-Py** or **C15-(C=O)-Py**. When initially the first layer was of **C15-(C=O)-Py**, the structure changes into Au/**C15-O-Py**/**C15-(C=O)-Py** through, most likely, transverse place-exchange during the formation of the second layer. This structure change originates from the stronger affinity of 4-terminal pyridyl group of **C15-O-Py** for the electrode surface

than **C15-(C=O)-Py**, which works dominantly over mixing.

When multiple-touching was made to the spread film of a two-component mixture at a given mixture ratio, the resultant first layer became **C15-O-Py** monolayer after the number of touchings reached the number needed to form a complete **C15-O-Py** monolayer in molecular amount. Moreover, when further increasing the number of touching procedures, formation of **C15-O-Py** bilayer in the bilayer thickness region was observed even when **C15-O-Py** surfactant is the minor component in the spread film. Predominant formation of **C15-O-Py** films on the electrode surface is due to its high rigidity of its films as well as stronger affinity of **C15-O-Py** for the substrate surface compared to **C15-(C=O)-Py**.

The present study points out that, when a mixed bilayer is formed on a substrate through a LS/LS method, one needs to take into account the relative strength of affinity of individual components for the substrate surface to control the heterogeneity of composition across the mixed bilayer.

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Figures

Fig. 1

Fig. 1. (a) Surfactants used in this work, **C15-O-Py** and **C15-(C=O)-Py**. The excess electronic charges on pyridyl nitrogens obtained by MOPAC2000 calculations are noted. (b) A scheme showing film formation procedure. [A = **C15-O-Py** and B = **C15-(C=O)-Py**] or vice versa. *1) When A = **C15-O-Py**, suction of the G/S interface to remove remaining surfactants at the interface was made prior to the detachment of the electrode.

Fig. 2

Fig. 2. C - E curves (a-c, e-g) and CVs (d, h) for Au/C15-(C=O)-Py (1)/C15-O-Py (2) (a-d) and Au/C15-O-Py (1)/C15-(C=O)-Py (2) (e-h) in 50 mM KClO₄ + 2 mM KHCO₃ solution at a H-M configuration. C - E curves were obtained from ac voltammetric data measured at a frequency of 14 Hz, an ac amplitude of 5 mV_{rms}, and a dc potential sweep rate of 5 mV s⁻¹ with the initial potential at the positive end of the curve (0.25 V). The dotted line represents the C - E curve for a bare Au(1 1 1) electrode. The first scan after secondary touching (a and e) and the second scan (b and f) are shown, together with the steady-state curves obtained after multiple scan (c and g). CVs were obtained after multiple scan with initial potential of 0.00 V and a sweep rate of 20 mV s⁻¹.

Fig. 3

Fig. 3. C – E curves of single-touch films (broken line) and double-touch films (solid line) for **C15-(C=O)-Py** (a) and **C15-O-Py** (b) in 50 mM KClO_4 + 2 mM KHCO_3 solution (frequency, 14 Hz; ac amplitude, 5 mV_{rms} ; dc potential sweep rate, 5 mV s^{-1} ; initial potential, 0.20 V). The dotted line represents the C – E curve for a bare Au(111) electrode.

Fig. 4

Fig. 4. Representative C - E curves for horizontal touching films to 1/1 **C15-(C=O)-Py/C15-O-Py** (a and b), and to 3/1 **C15-(C=O)-Py/C15-O-Py** (c and d) spread films. For the sake of comparison, curves for $(1/1)^3$ and $(3/1)^4$ are duplicated. The numbers of touching to the spread films (n) are shown in the figures. Measurement conditions were the same as those in Fig. 2.