Chinese Chemical Letters Vol. 11, No. 11, pp. 1027–1030, 2000

A New Strategy for Architecture of Robust Monolayer Based on Binuclear Palladium (II) Complex of Calix[4]arene Derivative

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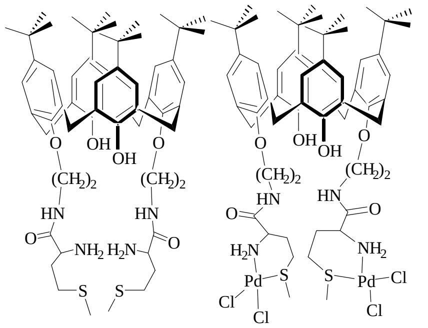
Abstract: A monolayer which is formed by a binuclear palladium complex of low rim methionine-disubstituted calix[4]arene exhibits extraordinary cohesiveness. Cohesiveness measurement and Brewster Angle Microscopy observation show that the monolayer is uniform and robust. This film is probably formed by self-assembly of precursor complex through strong chloride ion bridge between palladium centers.

Keywords: Monolayer, calix[4]arene, Brewster Angle Microscopy, robust membrane, viscosity.

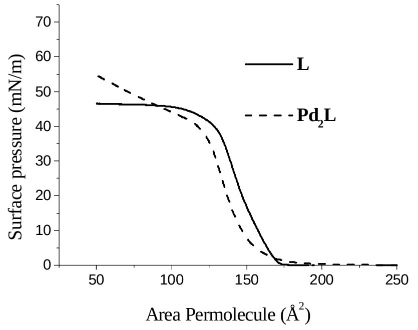
Since calixarenes and their derivatives have unique coordination abilities to metal ions and inclusion abilities toward neutral organic molecules, they have been widely studied in the field of molecular recognition, transportation and separation[1]. In order to explore these functions, membranes such as monolayers and Langmuir-Blodgett (LB) films formed by calixarenes, are often used for these purposes[2-6]. However, a crucial factor that hinders their application is the weak mechanical strength of these membranes. To enhance the strength of the monolayer, Regen *et al.* has prepared a composite membrane by depositing perforated disulfide calixarene monolayer whose mechanical strength was enhanced through self cross-linking under ultraviolet onto macroporous polymeric supports to obtain the permselectivity to He, N_2 and SF_6[7, 8]. In this report, we propose a new strategy for architecture of robust film from metal complex of calixarene derivative. Calixarene derivative (**L**)[9] was reacted with $PdCl_2$ to form a binuclear Pd (II) complex[9] (designated as **Pd$_2$L**). For comparison, **L** was also used as a surfactant to be studied together with **Pd$_2$L**. Monolayers were formed by spreading 90 μl of 5.0×10^{-4} M chloroform solution of surfactant dropwise onto the surface of deionized water (Purified by Milli-Q system, 18MΩ). The evaporation time is 15 min. The surface pressure–area isotherms shown in **Figure 1** were recorded by KSV5000 (Finland). The results indicate that both surfactants form monolayer at air-water interface. The limiting areas estimated by drawing a tangent from the condensed portion of π-A isotherms to 0 mN/m were 152 ± 3 Å^2 (For **Pd$_2$L**) and 162 ± 3 Å^2 (For **L**), which are in excellent agreement with 150 Å^2 and 163 Å^2 calculated from their optimized conformation using MM+ molecular mechanics modelling. A long plateau for **L** in **Figure 1** exhibits a coexistence region where the multilayers continue to grow from the monolayers[10]. For **Pd_2L**, a second compression region was observed, indicating that the multilayer formation was relatively difficult.

Compound **L** and compound **Pd_2L**



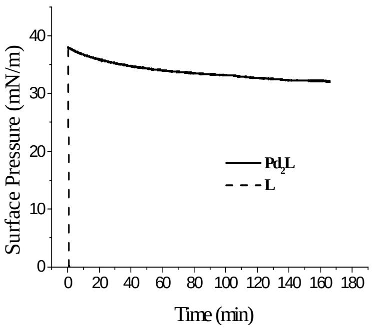
L **Pd_2L**

Figure 1. π-A isotherms of **Pd_2L** and **L** at 15 ± 0.2°C. Barrier speed is 10 mm/min.



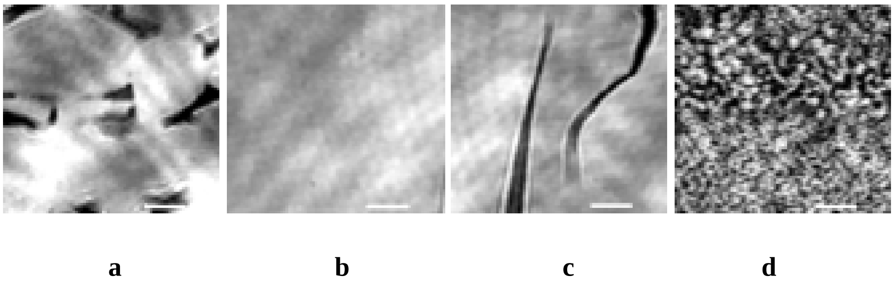
In the area relaxation experiments[10], the surface pressure was held at 43 mN/m for 120 min, and the change of film area was recorded at barrier speed of 2 mm/min. It was found that the area loss caused mainly by the formation of multilayer was much more for **L** ($A/A_0 = 0.70$) than for **Pd_2L** ($A/A_0 = 0.94$), implying that monolayer of **Pd_2L** is more robust and stable than that of **L** at high surface pressure.

Figure 2. The viscosity of **Pd_2L** and **L** at 15 ± 0.2°C



The mechanical properties of the monolayer were further studied by viscosity measurement based on a similar procedure used by Regen[7, 8]. After keeping equilibrium at 38mN/m, the slit (2 mm) in one barrier was cautiously opened to let the molecules of the monolayer disperse from measuring region to the dispersing region, and the surface pressure in the measuring region was recorded. **Figure 2** shows that the surface pressure of **Pd_2L** was reduced only 6 mN/m (from 38 mN/m to 32 mN/m) when exposing to the slit for 3 hours, even at high surface pressure of 38 mN/m. In contrast with **Pd_2L**, the surface pressure of **L** quickly descend to zero within 30 s. It is evident that **Pd_2L** forms a monolayer with extraordinary cohesiveness.

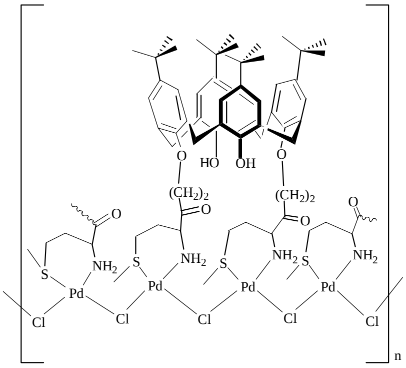
Figure 3. Brewster Angle Microscopy images of momolayers (**a**, **b**, **c** for **Pd_2L**, **d** for **L**, the bars represent 60 μm.)



Brewster Angle Microscopy (BAM) was used to observe the monolayers. After the surfactant of **Pd_2L** was spread on the water surface, blocks of bright region appeared floating on the water surface. When compressed, the blocks became close to each other and began to coalesce to form a uniform bright film (**Figure 3a**). When compressed further, a uniform and bright image was found, and the surface pressure began to rise abruptly. **Figure 3b** shows the BAM image at 5 mN/m which is uniform and appears as a whole bright surface without any domain. Further compression gave no significant changes, even the surface pressure had passed the inflection point. When expanded, no evident influence on it was observed until the surface pressure reduced to near 0 mN/m. As further expansion was made, rifts were gradually found on the bright surface. Although several rifts were produced (**Figure 3c**), the bigger block still remained. It seems that once the evaporation of solvent $CHCl_3$ is finished, the molecules of **Pd_2L** tend to aggregate to form blocks of brightness and exterior compression accelerates the coalescence of these blocks. Once the uniform bright block is formed, it is quite stable and difficult to break. As far as **L** is concerned, when **L** was compressed tightly, the closely packed bright dots were found as the domains of its monolayer (**Figure 3d**, 38mN/m). If expanded, the monolayer readily turned into 2-dimension networks again which were observed before the monolayer was formed with some residual multilayer patches as weak bright regions.

Based on the good ability of **Pd_2L** to self-assembly and the extraordinary cohesiveness of its monolayer, a possible polymer form is proposed (**Figure 4**). It is well known that the chloro-bridged palladium(II) complexes are readily formed and stable[11]. Therefore, the amphiphilic polymer film may be formed by intermolecular metal complexing *via* chloro-bridging at the air-water interface. This study provides a novel strategy for the design of robust film for potential practical application.

Figure 4. Possible form of self cross-linkage



Acknowledgment

This work was supported by the National Natural Science Foundation of China (Nos. 29771019, 29871017 and 29823001). The authors also thank Prof. Ming Hua LIU for his kind help in this study.

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9. 5,11,17,23-tetra-4-tert-butyl-25,27-di{[(2'-amino-4'-methylthio)-L-butyryl]aminoethoxy}-26, 28-dihydroxycalix[4]arene (**L**). mp: 200-202°C. R_f = 0.75 (8:1, $CHCl_3/CH_3OH$); ^1H NMR ($CDCl_3$, 500MHz) δ: 8.37 (br, 2H, CONH), 7.78 (s, 2H, OH), 6.97, 6.80 (2s, 8H, Ar-H), 4.14 (d, 4H, endo-ArCHAr, J=13.0Hz), 4.02(m, 4H, OCH_2), 3.86, 3.81 (m, 4H, NCH_2), 3.54 (m, 2H, COCH), 3.28 (d, 4H, exo-ArCHAr, J=13.0Hz), 2.52 (m, 4H, SCH_2), 2.07 (m, 2H, $CHCH_2S$), 1.80(m, 2H, $CHCH_2S$), 1.77 (br, NH_2), 1.92 (s, 6H, SCH_3), 1.19 (s, 18H, $C(CH_3)_3$), 0.94 (s, 18H, $C(CH_3)_3$). Calcd for $C_{58}H_{84}N_4O_6S_2$: C 69.84, H 8.49, N 5.62. found: C 69.58, H 8.62, N 5.93. ESMS (*m/z*): 997.5 [**L**+H]$^+$, 499.3 [**L**+2H]$^{2+}$. Binuclear Palladium(II) complex of **L** (**Pd$_2$L**). R_f=0.6 (8:1, $CHCl_3/CH_3OH$), mp: decomposition at 230-235°C. Calcd for $C_{58}H_{84}N_4$ S_2O_6 Cl_4Pd_2: C 51.52, H 6.26, N 4.14. Found: C 51.34, H 6.03, N 4.42. ESMS (*m/z*): 1279.1 [**Pd$_2$L**-2Cl-H]$^+$, 1317.2 [**Pd$_2$L** -Cl]$^+$, 1387.5 [**Pd$_2$L** +Cl]$^-$.
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Received 8 May 2000