

SHORT COMMUNICATION

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The electrochemical behavior of $(C_{70})_2$ -*p*-*tert*-butylcalix[8]arene complex film

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Abstract Electrochemical behavior of $(C_{70})_2$ -*p*-*tert*-butylcalix [8] arene film on a glassy carbon electrode has been studied by cyclic voltammetry. Two pairs of reduction/reoxidation waves were detected in a mixed solvent of acetonitrile and water containing tetra-*n*-butylammonium perchlorate as the supporting electrolyte.

Key words $(C_{70})_2$ -*p*-*tert*-butylcalix[8]arene complex · Film · Cyclic voltammetry

Introduction

The electrochemistry of fullerene C_{70} has been studied both in solution and in film states [1–8]. Calixarenes [9] are cavity-shaped cyclic molecules made up of phenol units linked via alkylidene groups. Linking fullerene chemistry with the wide field of chemistry of calixarenes has become one of the aims of many researchers. Several interactions between fullerenes and calixarenes were reported [10–12] which might be used to purify C_{60} and C_{70} efficiently. A preliminary study of the voltammetric behavior of C_{60} -*p*-*tert*-butylcalix[8]arene inclusion complex film in acetonitrile was reported recently [13], but the complex was found to decompose after the first cathodic potential scan. Since C_{70} could react with *p*-*tert*-butylcalix[8]arene (**L**) to form a 2 : 1 complex in benzene [12], the electrochemical behavior of $(C_{70})_2$ -*p*-*tert*-butylcalix[8]arene [$(C_{70})_2$ -**L**] film on a glassy carbon electrode was studied in this work, many differences from C_{60} -**L** film were found.

Experimental

Cyclic voltammetric (CV) measurements were performed with a PAR (Princeton Applied Research) Model 273 potentiostat/galvanostat and a PAR Model 270 electrochemical system in a three-electrode cell designed by ourselves. A glassy carbon (GC) working electrode (4 mm in diameter), a platinum counter electrode, and a silver wire coated with AgCl reference electrode (saturated KCl in 1 : 1 MeCN and water) were employed in all measurements. Tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) and tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) were purchased from Sigma; benzene, toluene and acetonitrile (MeCN) were distilled from P_2O_5 prior to use. All other reagents were of analytical grade. Water was triply distilled from an all-quartz still. High-purity nitrogen was used for deaeration. All CV experiments were performed under nitrogen atmosphere and at room temperature (15 °C).

Elemental analysis was performed using a Perkin-Elmer –240 °C elemental analyzer.

The synthesis of C_{70} was performed as described elsewhere [14]; its purity was 99%, which was confirmed by mass spectrometry and HPLC; *p*-*tert*-butylcalix[8]arene (99%) was prepared in our laboratory according to the method described in [15].

Preparation of $(C_{70})_2$ -**L** complex

C_{70} and **L** were dissolved in benzene to give 1×10^{-3} M solutions respectively, and a mixed solution of C_{70} and **L** (1 : 1) was then heated under reflux for 12 h, yielding a brown precipitate [16]. After centrifugal separation and washing with benzene, the precipitate was dried under a dynamic vacuum. Elemental analysis: found C 92.46, H 4.51; calculated for $C_{228}H_{112}O_8$, C 91.91, H 3.79.

$(C_{70})_2$ -**L** complex was dissolved in toluene to give a 1×10^{-4} M solution.

C_{70} was also dissolved in toluene to give a 2×10^{-4} M solution.

Preparation of $(C_{70})_2$ -**L** and C_{70} film

The GC electrode surface was polished on alumina to produce a mirror-like surface, then washed with water and ethanol in an ultrasound bath and dried.

A solution of $(C_{70})_2$ -**L** (5 μ L, 1×10^{-4} M) or C_{70} (5 μ L, 2×10^{-4} M) in toluene was dropped onto the surface of the GC electrode using a 10 μ L syringe and dried under an infra-red lamp.

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Results and discussion

The CV behavior of $(C_{70})_2$ -L film in MeCN

In our previous work [13], a C_{60} -L inclusion complex film was formed by dropping a mixed solution of C_{60} and L on a GC surface and letting it dry quickly under an infra-red lamp. The film had a two-electron reduction wave in MeCN containing Bu_4NPF_6 as the supporting electrolyte. But the complex dissociated into its components after the first cathodic scan, and the anodic wave corresponded to the reoxidation of pure C_{60} in film; the CV behavior of the subsequent cycles was similar to that of C_{60} film.

The CV experiment on the $(C_{70})_2$ -L film shows two pairs of reduction/reoxidation peaks in MeCN containing Bu_4NClO_4 as the supporting electrolyte (Fig. 1A). It can be seen that the CV behavior of $(C_{70})_2$ -L film was different from that of C_{70} film (Fig. 1B), and was unstable. The electrochemical activity of the film decreased gradually from cycle to cycle, possibly because the reduced form of $(C_{70})_2$ -L was soluble in MeCN and only a small part of the complex decomposed after the first cathodic scan, since the anodic waves of $(C_{70})_2$ -L film were much smaller than those of C_{70} film.

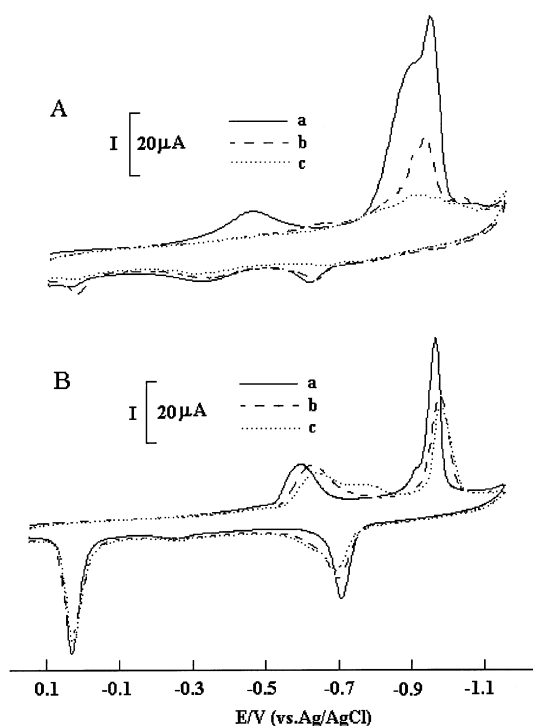


Fig. 1 A Cyclic voltammograms of $(C_{70})_2$ -L film in MeCN containing supporting electrolyte 0.04 M Bu_4NClO_4 ; 0.1 $V s^{-1}$ scan rate between 0.1 and $-1.15 V$; a first cycle, b second cycle, and c fifth cycle. B Cyclic voltammograms of C_{70} film in MeCN containing 0.04 M Bu_4NClO_4 ; 0.1 $V s^{-1}$ scan rate between 0.25 and $-1.15 V$; a first cycle, b second cycle, and c third cycle

The CV behavior of $(C_{70})_2$ -L film in mixed MeCN and water

As a certain amount of water was added to the MeCN, the CV behavior of $(C_{70})_2$ -L film became stable. This may be because the reduced form of $(C_{70})_2$ -L was less soluble in mixed MeCN and water than in pure MeCN. Two pairs of reduction/reoxidation peaks, Pc_1/Pa_1 and Pc_2/Pa_2 were observed. Figure 2A shows the CV behavior of $(C_{70})_2$ -L film in a 1 : 1 mixed solvent of MeCN and water containing 0.04 M Bu_4NClO_4 as the supporting electrolyte. A potential shift between the first cycle and subsequent cycles was observed, implied that there was a structural rearrangement accompanying the release of the solvent which was entrapped during the evaporation process and injection of Bu_4N^+ and a small amount of anions into film [17]. Upon continuous scanning for 1 h, the peak currents changed little after the second cycle. Because of the wave difference between the first cycle and subsequent cycles, the CV of the third cycle is used in the following work.

Figure 3 shows the effect of water in the solution on the CV behavior of $(C_{70})_2$ -L film. Less water ($\leq 25\%$) led to a higher reduction current, while the currents of all peaks decreased rapidly in successive cycles. When the amount of water was between 30% and 60% the

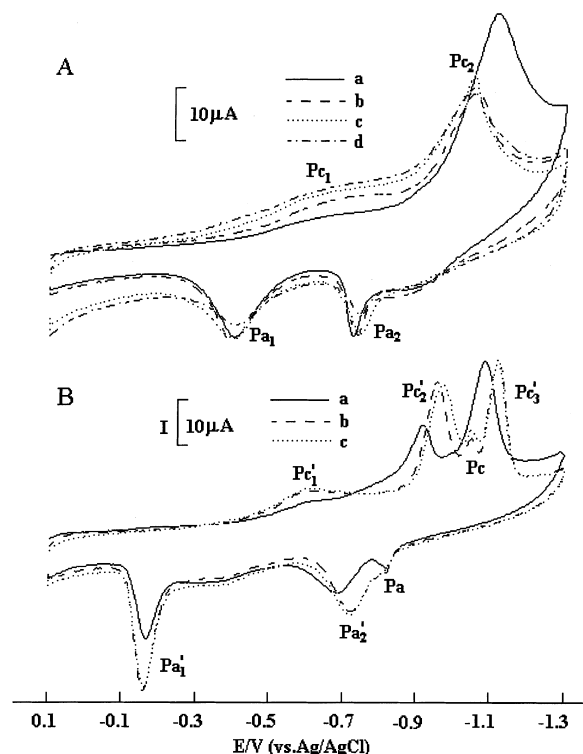


Fig. 2 A Cyclic voltammograms of $(C_{70})_2$ -L film in 1:1 mixture of MeCN and H_2O containing 0.04 M Bu_4NClO_4 ; 0.1 $V s^{-1}$ scan rate between 0.1 and $-1.3 V$; a first cycle, b second cycle, c after 30 min, and d after 1 h. B Cyclic voltammograms of C_{70} film in 1:1 mixture of MeCN and H_2O containing 0.04 M Bu_4NClO_4 ; 0.1 $V s^{-1}$ scan rate between 0.1 and $-1.3 V$; a first, b second, and c fifth cycle



Fig. 3 Cyclic voltammograms of $(C_{70})_2-L$ film for different amounts of water in the mixed solvent with 0.04 M Bu_4NClO_4 showing the third cycle; 0.1 V s^{-1} scan rate between 0.1 and -1.3 V . Amounts of water (v/v%): a 15%, b 25%, c 50%, and d 80%

reduction and oxidation waves were stable, and when it was $\geq 80\%$ the supporting electrolyte could not dissolve properly and the peak currents were very low. It was preferable to use 1 : 1 (v/v) mixed MeCN and water as the solvent.

It was reported [7] that C_{70} films had steady-state voltammograms in MeCN in the presence of electrolytes containing large cations such as Bu_4N^+ . This could also be achieved for $(C_{70})_2-L$ film, both in Bu_4NClO_4 and in Bu_4NPF_6 in the mixed solvent of MeCN and water. The effect of increasing the concentration of Bu_4NClO_4 from 0.01 to 0.06 M on the CV behavior of $(C_{70})_2-L$ film in 1 : 1 mixture of MeCN and water was tested. The peak currents of $(C_{70})_2-L$ film increased as the concentration of Bu_4NClO_4 increased, but when the concentration of Bu_4NClO_4 increased from 0.03 to 0.06 M the peak currents changed little. Lower concentrations of Bu_4NClO_4 caused higher solution resistance and also affected the injection of Bu_4N^+ into film, which resulted in lower peak currents. 0.04 M Bu_4NClO_4 was used as the supporting electrolyte in this work.

The potential scan rate also had an influence on the CV behavior of $(C_{70})_2-L$ film. A higher scan rate resulted in higher current flow, and the cathodic peak potential shifted in the negative direction while the anodic peak potential shifted in the positive direction, possibly because the reduction/reoxidation of $(C_{70})_2-L$ was irreversible, and higher scan rate would cause higher IR drop, which also resulted in large peak splittings. A scan rate as high as 0.5 V s^{-1} distorted the wave severely. Table 1 shows the peak potential and current values at

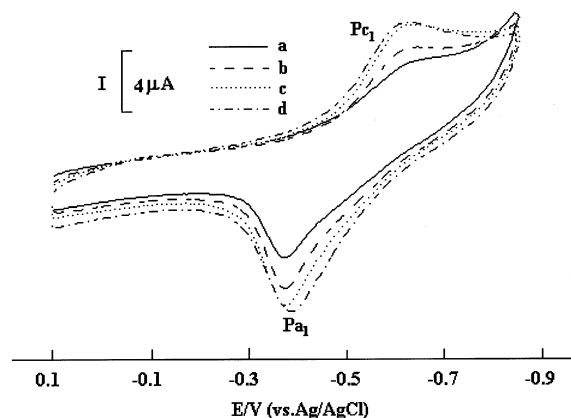


Fig. 4 Cyclic voltammograms of $(C_{70})_2-L$ film for the potential scan range 0.1–0.85 V. 1:1 mixture of MeCN and H_2O with 0.04 M Bu_4NClO_4 ; 0.1 V s^{-1} scan rate; a first, b second, c fifth, and d tenth cycle

different scan rates. As expected for a surface wave [18], the peak current depended linearly on the scan rate when this was less than 0.2 V s^{-1} .

The effect of varying the surface coverage from 4.0×10^{-10} to $1.6 \times 10^{-8} \text{ mol cm}^{-2}$ ($C_{70})_2-L$ on the GC electrode were investigated. The peak current increased as the amount of $(C_{70})_2-L$ increased, and when it was greater than $4.0 \times 10^{-9} \text{ mol cm}^{-2}$ the peak current increased less. A coverage of $4.0 \times 10^{-9} \text{ mol cm}^{-2}$ ($C_{70})_2-L$ was therefore used in most of this work, that is, dropping 5 μl of $1 \times 10^{-4} \text{ M}$ ($C_{70})_2-L$ solution onto the GC electrode surface.

If the reversal potential was limited to -0.85 V , only the first reduction wave occurred (Fig. 4). The peak currents increased over the initial few cycles, and after about 5 cycles the peak currents became stable. Also, the reoxidation peak (Pa_1) current was much smaller than that when the negative potential scan was reversed at -1.3 V . This might be because the first reduction step is a slow process. If the potential stayed at -0.85 V for some time, e.g. 1 min, to let the reduction process become more complete, and the anodic scan was then started, the peak current of Pa_1 would reach the same value as the reversal potential (-1.3 V) (Fig. 5A).

For comparison, the CV behavior of C_{70} film in 1 : 1 mixture of MeCN and water containing 0.04 M Bu_4NClO_4 was studied (Fig. 2B). Three reduction waves and two reoxidation waves were observed. A pair of pre-waves, Pc/Pa , could also be seen, since the cathodic prewave did not appear, but the anodic prewave appeared on the first cycle of potential scan. This might be

Table 1 Peak potentials and currents of $(C_{70})_2-L$ film at different scan rates

Scan rate (V s^{-1})	E_{Pc2} (V)	i_{Pc2} (μA)	E_{Pa1} (V)	i_{Pa1} (μA)	E_{Pa2} (V)	i_{Pa2} (μA)
0.02	-1.04	6.25	-0.42	3.27	-0.75	4.42
0.05	-1.05	12.56	-0.40	7.71	-0.74	7.31
0.1	-1.08	22.41	-0.39	15.90	-0.73	12.09
0.2	-1.11	41.24	-0.36	26.07	-0.72	16.35
0.5	-1.20	69.85	-0.31	44.03	-0.69	25.60

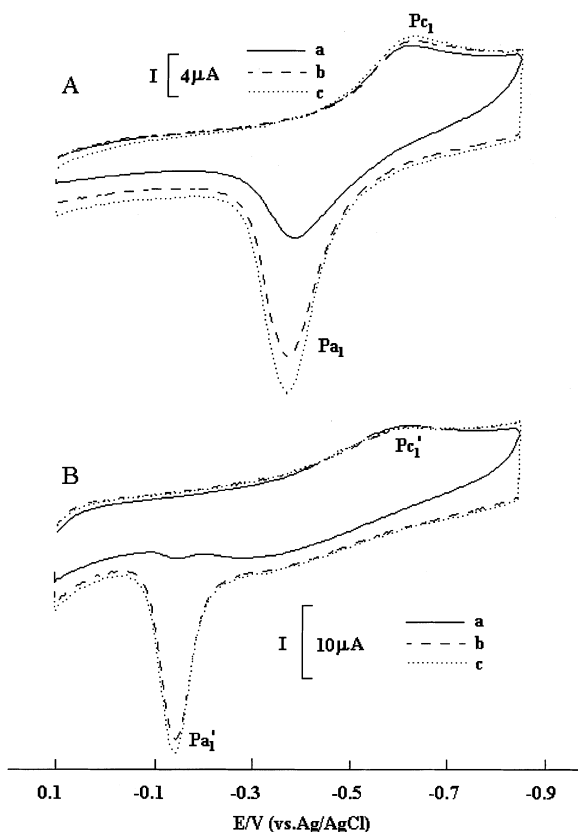


Fig. 5 Cyclic voltammograms of $(C_{70})_2-L$ film (A) and C_{70} film (B) in 1:1 mixture of MeCN and H_2O containing 0.04 M Bu_4NClO_4 . 0.1 $V s^{-1}$ scan rate between 0.1 and $-0.85 V$. Stayed at $-0.85 V$ for a 0 s, b 60 s, c 120 s, then started the reversal scan

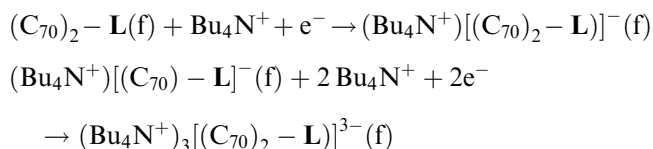
due to reduction of C_{70} domains restructured by the entrapped anion and/or electrolytes and/or solvent, releasing some species into solution [17]. The first reduction process was as slow as that of $(C_{70})_2-L$ film. If the potential stayed at $-0.85 V$ for some time, and when the reversal scan began, the reoxidation peak current increased greatly (Fig. 5B). When the reversal potential changed to $-1.05 V$, where the second reduction peak Pc_2' appeared, only one reoxidation peak Pa_1' could be observed, indicating that the second reoxidation peak Pa_2' corresponded to Pc_2' and Pc_3' .

As the peak potential of Pc_2 of $(C_{70})_2-L$ film is close to that of Pc_2' and Pc_3' of C_{70} film, it might be concluded that Pc_2 corresponds to Pc_2' and Pc_3' . Therefore, the first reduction process (Pc_1) of $(C_{70})_2-L$ film may be a one-electron transfer reaction, and the second (Pc_2) a two-electron transfer reaction.

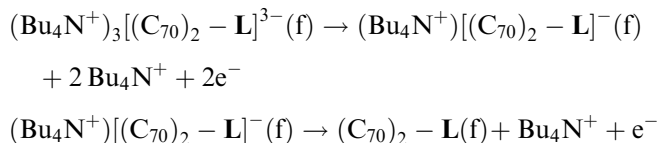
Upon reduction, $(C_{70})_2-L$ was reduced to $[(C_{70})_2-L]^-$, then to $[(C_{70})_2-L]^{3-}$, Bu_4N^+ ions diffused into the film to balance the negative charges. After reoxidation, Bu_4N^+ left the film. Thus, upon reduction and reoxidation, the film would expand and contract, allowing the structure to become more ordered. This might also be the reason that the reduction wave of the first scan is different from those of the following scans.

The results mentioned above suggest a possible mechanism for the reduction and reoxidation of $(C_{70})_2-L$ film as follows.

The reduction process:



The reoxidation process:



where "f" represents the film on the GC electrode.

Conclusions

$(C_{70})_2-p$ -tert-butylcalix[8]arene complex film has stable electrochemical behavior in a mixed solvent of MeCN and H_2O (1 : 1, v/v) containing 0.04 M Bu_4NClO_4 as the supporting electrolyte. Two pairs of reduction/reoxidation peaks were obtained. The first reduction and reoxidation process of $(C_{70})_2-L$ film is thought to be a one-electron transfer reaction, and the second a two-electron transfer reaction.

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