Electrochemical and Chemical Reduction Properties of Fullerenes C_{60} and C_{70} Embedded in Cast Films of Cationic Lipid

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The chemistry of fullerene anions is among the most fundamental in the field of fullerene science.[1] The monoanions of fullerenes have been generated by chemical reducing agents[2] as well as electrochemical methods.[3] Most of these studies were examined in organic homogeneous solutions, since the generation of fullerene anions in aqueous solvents is difficult due to their kinetic instability. No report has been published describing the chemical generation of fullerene anions in films on substrates in water. We have recently described stable electrochemistry at C_{60}/cationic amphiphile-modified electrodes in aqueous system.[4,5] Nanqiang Li *et al*. have published the electrochemistry of C_{70} embedded in the cationic di-*n*-dodecylmethylammonium bromide film in aqueous solution.[6] We describe here the generation of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ using $Na_2S_2O_4$ as a reducing agent acting upon C_{60} or C_{70} embedded in cationic amphiphilic matrix films on quartz plates in aqueous media by means of vis-near IR spectroscopy.

In this work, C_{60} and C_{70} were embedded in thin films of amphiphiles on quartz plates. The matrix lipids used were: tridodecylmethylammonium bromide ($3C_{12}N^+Br^-$),[4] tetraoctylammonium bromide ($4C_8N^+Br^-$),[5] tetraoctylphosphonium bromide ($4C_8P^+Br^-$),[5] didodecylglycerol ($2C_{12}Gly$) and didodecylphosphate ($2C_{12}PO_4H$), which are shown in Figure 1.

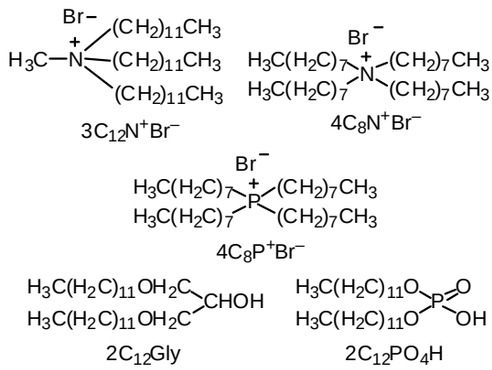

Figure 1. Chemical structures of matrix lipids.

Experimental Section. The procedure for preparing a cast film on a quartz plate is as follows. A 300 microliter portion of C_{60} or C_{70}/lipid (molar ratio, 1/19) in toluene ([C_{60} or C_{70}] = 0.5 mM) was placed on a quartz plate, and then air-dried. Vis–near IR absorption spectral measurements for the modified quartz plate were carried out in Milli-Q water for C_{60} and in D_2O for C_{70} in the absence or the presence of $Na_2S_2O_4$ as a reducing agent at 25 ˚C under an argon atmosphere.

Results and Discussion. The vis-near IR spectra revealed for the first time that $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ are chemically produced in cationic amphiphilic matrix films in aqueous media. These are indicated by a λ_{max} of 1077 nm for $C_{60}^{\bullet-}$ (Figure 2) and of 1376 nm for $C_{70}^{\bullet-}$ when embedded in a cast film of $3C_{12}N^+Br^-$. The chemical generation of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ were strongly dependent upon the charge of the matrix lipids. Vis–near IR absorption spectra of C_{60} and C_{70} solely cast films were essentially the same before and after the addition of $Na_2S_2O_4$. Also, the vis–near IR absorption spectra for cast films C_{60} (or C_{70})/$2C_{12}Gly$ and C_{60} (or C_{70})/$2C_{12}PO_4H$ did not change after the addition of $Na_2S_2O_4$.

We have already reported that the ion–pairing between the electrochemically generated fullerene anions and matrix lipid cations plays an important role in the generation of fullerene anions in aqueous media. The results obtained in this study strongly suggests that similar electrostatic binding is crucial for the generation of $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ using the chemical reducing agent.

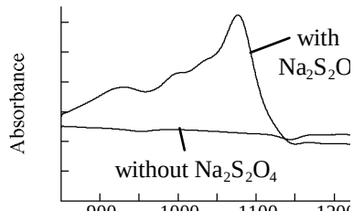

Figure 2. NIR absorption spectra for a cast film of $C_{60}/3C_{12}N^+Br^-$ (molar ratio, 1/19) on a quartz plate in water in the absence or the presence of $Na_2S_2O_4$ under Ar.

References:

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