Electrochemical and Chemical Reduction Properties of Thin Films Containing Double–Decker Lutetium(III) Phthalocyanines in Aqueous Media

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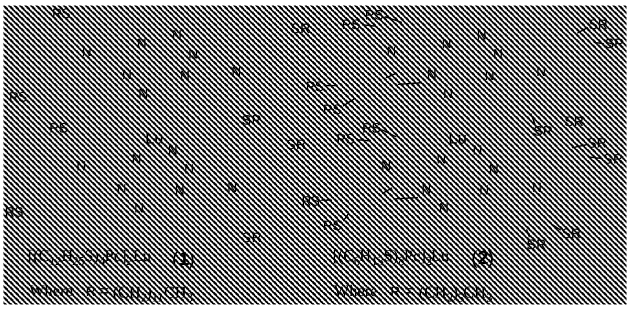
The solution and film electrochemical behaviour of double–decker lutetium(III) phthalocyanines has been extensively investigated under different conditions because of their electrochromic properties.[1] The purpose of our recent work was to investigate the electrochemistry of highly reducible double–decker lutetium(III) phthalocyanines in a cationic matrix of tetraoctylphosphonium bromide ($4C_8P^+Br^-$) which was deposited as a cast film on an electrode and immersed in an aqueous KCl solution. The chemical reduction properties of the double–decker lutetium(III) phthalocyanines/$4C_8P^+Br^-$ cast film on a quartz plate in H_2O containing a reducing agent ($Na_2S_2O_4$) were also investigated by UV–vis/near–IR absorption spectroscopy. A gel–like membrane of $4C_8P^+Br^-$ lipid analogue is known to provide a suitable microenvironment for examining the electrochemistry of redox active molecules, such as fullerenes, at an electrode surface in aqueous media.[2] The same methodology is used in the present study for examining the multiple reductions of alkylthio–substituted double–decker lutetium(III) phthalocyanines, $[(RS)_nPc]_2Lu$ where n = 4 (R = $C_{12}H_{25}$) (**1**) or n = 8 (R = C_6H_{13}) (**2**) and Pc = the dianion of phthalocyanine. Both compounds undergo four of the five theoretically predicted reductions in organic media.[3]



$[(C_{12}H_{25}S)_4Pc]_2Lu$ (**1**)
Where R = $(CH_2)_{11}CH_3$

$[(C_6H_{13}S)_8Pc]_2Lu$ (**2**)
Where R = $(CH_2)_5CH_3$

Experimental Section. Typical procedures for preparation of gel–like membranes of **1**/$4C_8P^+Br^-$ or **2**/$4C_8P^+Br^-$ (molar ratio, 1/19) on a basal plane pyrolytic graphite (BPG) electrode are as follows: A 28 microliter portion of **1** or **2**/$4C_8P^+Br^-$ in chloroform ([**1** or **2**] = 0.27 mM and [$4C_8P^+Br^-$] = 5.15 mM) was placed on a BPG electrode surface (geometric area, 0.36 cm^2) and then air-dried. The modified electrodes were then immersed in a 0.5 M KCl aqueous solution, and followed by electrochemical measurements made under N_2 atmosphere at 25 ˚C.

The gel–like membranes of **1**/$4C_8P^+Br^-$ or **2**/$4C_8P^+Br^-$ were prepared on a quartz plate in a similar manner for UV–vis/near–IR absorption spectroscopy. The modified substrates were immersed in H_2O under Ar atmosphere at 25 ˚C, then $Na_2S_2O_4$ was added as a reducing agent.

Results and Discussion. We have recently reported that $[(C_{12}H_{25}S)_4Pc]_2Lu$ undergoes a single oxidation and up to four reductions when dissolved in dichloromethane, while five reductions and one oxidation are observed in aqueous 0.5 M KCl solutions of a cast film of $[(C_{12}H_{25}S)_4Pc]_2Lu/4C_8P^+Br^-$ on a BPG electrode.[4] The fifth reduction was observed for the first time at the $4C_8P^+Br^-$ modified electrode and had not previously been detected for any other double–decker lutetium(III) phthalocyanine. Similar electrochemical properties are also observed for $[(C_6H_{13}S)_8Pc]_2Lu/4C_8P^+Br^-$ modified electrodes.

The cationic sites in the matrix stabilize the electroreduced forms of the double–decker lutetium(III) phthalocyanine compounds. Thus, half–wave potentials of $[(RS)_nPc]_2Lu/4C_8P^+Br^-$ at the modified electrode are all more positive by up to 0.51 V than the measured values in dichloromethane. A thermodynamic treatment of the electrochemical data was carried out at different concentrations of supporting electrolyte in order to explain the ion-pairing effects which exist between the cation of the matrix and the reduced forms of $[(RS)_nPc]_2Lu$ on the electrode surface.

Generation of the first reduced forms $\{[(RS)_nPc]_2Lu\}^-$ and the second reduced forms $\{[(RS)_nPc]_2Lu\}^{2-}$ in a composite film with $4C_8P^+Br^-$ was observed in H_2O containing $Na_2S_2O_4$ as a reducing agent by UV–vis/near–IR absorption spectroscopy. In contrast, no generation of any reduced forms were observed at either solely cast films of $[(RS)_nPc]_2Lu$ or composite films with an anionic lipid didodecylphosphate ($2C_{12}PO_4H$). These results suggest that the ion–pairing between the reduced forms of $[(RS)_nPc]_2Lu$ and the matrix cations plays an important role for the generation of reduced species in aqueous media.

References:

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