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. The purpose of our recent work was to investigate the electrochemistry of highly reducible double–decker lutetium(III) phthalocyanines in a cationic matrix of tetrachlorophosphonium bromide (4C\(_2\)PhBr\(_2\)) 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\(_2\)PhBr\(_2\) cast film on a quartz plate in H\(_2\)O containing a reducing agent (Na\(_2\)S\(_2\)O\(_3\)) were also investigated by UV–vis/near–IR absorption spectroscopy. A gel–like membrane of 4C\(_2\)PhBr\(_2\) lipid analogue is known to provide a suitable microenvironment for examining the electrochemistry of redox–active molecules, such as fullerences, at an electrode surface in aqueous media. The same methodology is used in the present study for examining the multiple reductions of alkylthio–substituted double–decker lutetium(III) phthalocyanines, [(RS)\(_2\)Pc\(_n\)]\(^+\) where \(n = 4 (R = C\(_2\)H\(_8\)) (1) or \(n = 8 (R = C\(_8\)H\(_{16}\)) (2) and Pc = the dianion of phthalocyanine. Both compounds undergo four of the five theoretically predicted reductions in organic media.

Experimental Section. Typical procedures for preparation of gel–like membranes of 1/4C\(_2\)PhBr or 2/4C\(_2\)PhBr (molar ratio, 1:1/9) on a basal plane pyrolytic graphite (BPG) electrode are as follows: A 28 microliter portion of 1 or 2/4C\(_2\)PhBr in chloroform (1 or 2) = 0.27 mM and [4C\(_2\)PhBr\(_2\)] = 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\(_2\)PhBr or 2/4C\(_2\)PhBr were prepared on a quartz plate in a similar manner for UV–vis/near–IR absorption spectroscopy. The modified substrates were immersed in H\(_2\)O under Ar atmosphere at 25°C, then Na\(_2\)S\(_2\)O\(_3\) was added as a reducing agent.

Results and Discussion. We have recently reported that [(C\(_2\)H\(_8\))\(_2\)S\(_2\)]Lu underwent 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\(_2\)H\(_8\))\(_2\)S\(_2\)]Lu/4C\(_2\)PhBr\(_2\) on a BPG electrode. The fifth reduction was observed for the first time at the 4C\(_2\)PhBr\(_2\) modified electrode and had not previously been detected for any other double–decker lutetium(III) phthalocyanine. Similar electrochemical properties are also observed for [(C\(_2\)H\(_8\))\(_2\)S\(_2\)]Lu/4C\(_2\)PhBr\(_2\) 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)\(_2\)Pc\(_n\)]Lu/4C\(_2\)PhBr\(_2\) 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)\(_2\)Pc\(_n\)]Lu on the electrode surface. Generation of the first reduced forms [(RS)\(_2\)Pc\(_n\)]Lu\(^+\) and the second reduced forms [(RS)\(_2\)Pc\(_n\)]Lu\(^0\) in a composite film with 4C\(_2\)PhBr\(_2\) was observed in H\(_2\)O containing Na\(_2\)S\(_2\)O\(_3\) 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)\(_2\)Pc\(_n\)]Lu or composite films with an anionic lipid didodecylphosphosphate (2C\(_12\)PO\(_4\))H. These results suggest that the ion–pairing between the reduced forms of [(RS)\(_2\)Pc\(_n\)]Lu and the matrix cations plays an important role for the generation of reduced species in aqueous media.

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