

PE06

Electrochemistry of Amphiphilic Ferrocene Derivatives in the Monolayers 양친매성 페로센 유도체 단분자막의 전기화학적 특성

김재호, 임준완, 임정혁, 계광열*

아주대학교 화학생물공학부, *아주대학교 기초과학부

4-(ferrocenylvinyl)-4'-octadecycloxyazobenzene (FVOA) and 4-(ferrocenylcarbonyl amino)-4'-octadecycloxyazobenzene (FAOA) π -donor-acceptor conjugated, amphiphilic ferrocene derivatives have been synthesized and fabricated into the monolayer either at the air-water interface or on various solid substrates including metal electrodes for electrochemical and surface-enhanced Raman scattering (SERS) measurements. Results obtained from surface pressure-area isotherms and Brewster angle microscopy at the air-water interface indicated that both FAOA and FVOA formed well organized monolayers only on the subphase containing a mixture of NaClO_4 , NaHCO_3 and CdCl_2 at 15 °C. Highly ordered molecular arrangement was also confirmed by atomic force microscopy of both ferrocene derivatives LB monolayers transferred at 20 mN/m. FAOA and FVOA formed organized molecular films at the air-water interface, and structural regularity and molecular packing were improved by formation of AA mixed monolayer on mixed salts subphase. FT-IR reflection absorption and transmittance spectra of LB films indicated that the chromophore of FAOA was tilted ca. 25° to the surface normal while alkyl tails maintained the highly ordered trans zig-zag packing structure. SERS spectra on electrochemically roughened Ag electrodes revealed that azo moiety in LB monolayers has nearly perpendicular orientation to the electrode surface while it tilted at lower angle in the self-assembled films. In-situ SERS electrochemical measurements of both FAOA and FVOA LB monolayers showed that redox reaction of azo and ferrocene moieties were not proceeded due to impermeability of the counter ions through the densely packed molecular layer. However, defect site contained structures such as self-assembled films in aqueous media or LB films exposed to an organic solvent showed irreversible reduction of azo to hydrazone form. The effect of structural integrity of LB films on the electron transfer kinetics of ferrocene and azo groups in FAOA and FVOA will be discussed.