Photochemical Control of Ionic Conduction and Sensing for Lithium Ion by Cation-Complexing Photochromic Compounds

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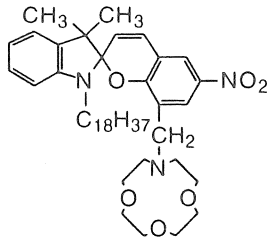
Photochromic compounds are useful tools for photochemical control of physical properties. We have incorporated crown ether moieties to photochromic compounds, aiming at photochemical control of cation-complexing ability of the crown ether moiety. Photochromic crown ethers we designed, such crowned spirobenzopyrans **1** and crowned Malachite Green **2**, were found to modify their cation-complexing efficiently by their photoisomerization on the basis of the molecular control. The photochromic crown ethers were successfully applied to lithium-ion extraction spectrophotometry, a photoresponsive membrane potential system, and a photoresponsive ion-conducting system.

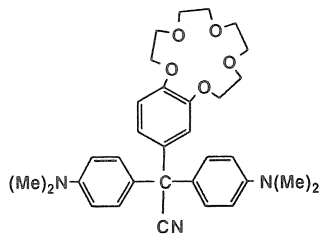
1) Crowned spirobenzopyran **1**(R=CH_3) are a promising reagent for lithium ion extraction spectrophotometry. The photochromic crown ether can undergo isomerization to its merocyanine form by the cation complexation of its crown ether moiety even under dark condition. Extraction of lithium ion from an aqueous solution with a dichloromethane solution of **1**(R=CH_3) caused remarkable absorption-spectral changes based on the cation-complexation-induced isomerization to its merocyanine form. The absorbance for the merocyanine isomer depended considerably on the lithium ion concentration of the aqueous phase. Photoisomerization of **1**(R=CH_3) enhanced the sensitivity for the extraction spectrophotomery.

2) Membranes containing lipophilic crowned spirobenzopyran **1**(R=$C_{18}H_{37}$) exhibited an intriguing potential photoresponse which resembles the active potentials in biological cell membranes. The phenomenon was explained by the fast proton response and subsequent cation response.

3) Crowned Malachite Green Leuconitrile **2** can undergo photochemical control of cation-complexing ability, based on intramolecular electrostatic repulsion between a metal cation complexed by its crown ether moiety and a triphenylmethyl(or quinoid) cation formed by its photoionization. The mechanism was verified by potentiometry under dark and photoirradiated conditions. The phenomenon was applied successfully to photoresponsive ion-conducting systems.



1 (R=CH_3,$C_{18}H_{37}$)



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