Anomalous Photochromism and Photochemical Cation-binding Control of Crowned Malachite Green Leuconitrile Based on Intramolecular Electrostatic Repulsion

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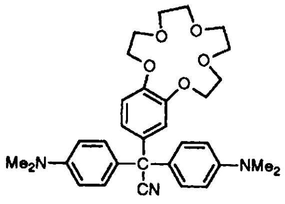
A Malachite Green leuconitrile incorporating a crown-ether moiety has been designed, exhibiting anomalous photochromism and photoinduced switching of cation binding on the basis of intramolecular repulsive interaction between its crown-complexed metal ion and photoionized cationic species.

Many triphenylmethane dyes like Malachite Green (MG) exhibit photochromism accompanying heterolytic bond cleavage, thus undergoing photoionization.[1] For instance, UV light causes isomerization of MG-leuconitrile to its corresponding triphenylmethyl cation (and quinoid cation showing a green colour) and cyanide anion, which are then reverted to the initial electrically-neutral molecule by heating in the dark. This photochromism of MG dyes is an attractive tool for photocontrol of ionic environments. Ionic conductivities can be regulated photochemically, using MG dyes both in solution and in polymer films.[2–4] Photochemical control of polymer rheology is also feasible by using a MG dye.[5] Polymeric membranes containing a MG moiety can modify membrane transport of anions by photoirradiation.[6] Recently, we have studied incorporation of a MG dye into a crown-ether moiety, to determine whether the photochromism of the resulting crowned MG is affected by cation complexation of its crown-ether moiety. It was also expected that the photoionization of crowned MG-leuconitrile would alter the cation-complexing ability of the crown-ether moiety. Reported herein are the anomalous photochromism and photoinduced switching of cation-binding ability for the crowned MG-leuconitrile **1**.

The crowned MG dye, **1**, was synthesized by the Grignard reaction of 4′-lithiated benzo-15-crown-5 with 4,4′-bis(*N*,*N*-dimethylamino)benzophenone, followed by cyanization of the resulting crowned MG-leucohydroxide.† Photochromism of MG-leuconitrile is a reversible change between its electrically-neutral and ionic species. Solvent polarity, therefore, stabilizes the UV light-induced photoionization product of MG dyes and depresses the thermal back (decolouration) reaction from the ion pair to the electrically-neutral molecule. Thus, in 'uncrowned' MG-leuconitrile, **2**, the first-order rate constant for the thermal decolouration reaction‡ decreased regularly with increasing concentration of $NaClO_4$ in MeOH.

Cation complexation of the crown moiety of crowned MG-leuconitrile **1** significantly affects its photoionization behaviour (Fig. 1). An anomaly was observed in the plots of rate constant *vs*. $NaClO_4$ concentration for the crowned MG-leuconitrile solution. Of course, for the crowned MG-leuconitrile, the increase in solvent polarity by the salt addition is likely to retard its thermal back reaction. However, Na^+ complexation by the crown-ether moiety of **1** destabilizes its photoinduced triphenylmethyl cation due to the intramolecular electrostatic repulsion toward the crown-complexed Na^+, thus accelerating the thermal back reaction. As a result, the acceleration exceeds the retardation effect on the thermal back reaction for the crowned MG-leuconitrile system in the salt concentration range of 10^{-3}–10^{-2} mol dm^{-3}. The employment of Li^+ instead of Na^+ sheds light on different cation complexation effects on the thermal back reaction, which resulted from the lower complexing ability of the crowned MG derivative towards Li^+ than Na^+.



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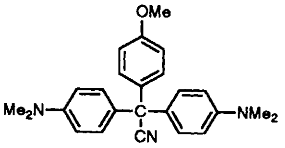

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In view of the reciprocal aspect of the cation-complexation effect on photochromism for the crowned MG-leuconitrile system, its photoisomerization between the electrically-neutral and ionic molecules must modulate cation-complexation equilibria of its crown-ether moiety. Potentiometry by using a Na^+-selective glass electrode§ was carried out to obtain information about the cation-complexation equilibrium changes of crowned MG-leuconitrile induced by its photochromism. In the dark, the crown-ether moiety of **1** can complex Na^+ even in MeOH–H_2O (95 : 5) solution. UV irradiation of the **1** solution raised the electrode potential (Fig. 2). This means that photoionization of crowned MG-leuconitrile **1** to its corresponding cation releases Na^+ from its crown-ether moiety due to the intramolecular electrostatic repulsion between the resulting two cations. Subsequent heating of the solution in the dark, which causes a thermal back reaction from the ionic to electrically-neutral molecules, promoted cation binding by the crown-ether moiety owing to the disappearance of the inter-cationic interaction. On the other hand, hardly any potential change was observed on photoirradiation in the system of the uncrowned MG **2**. We conclude that the cation complexation of crowned MG-leuconitrile **1** can be controlled photochemically on the basis of intramolecular electrostatic repulsion (Scheme 1).

In previously designed photochromic crown compounds,

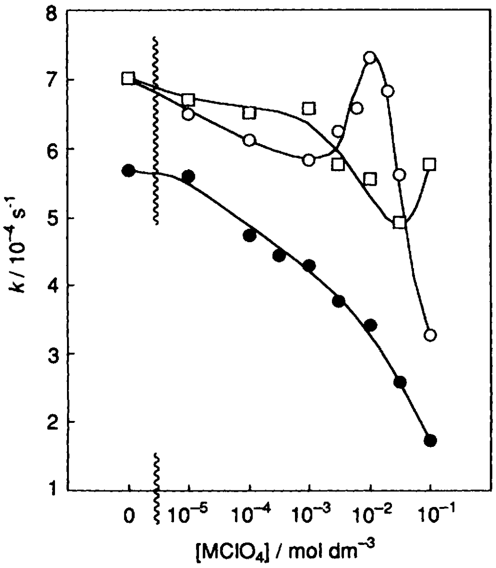


Fig. 1 Relation between alkali metal perchlorate concentration and first-order rate constants (*k*) for thermal back (decolouration) reaction of crowned and uncrowned MG-leuconitriles. (○) **1**-Na^+, (□) **1**-Li^+ and (●) **2**-Na^+.

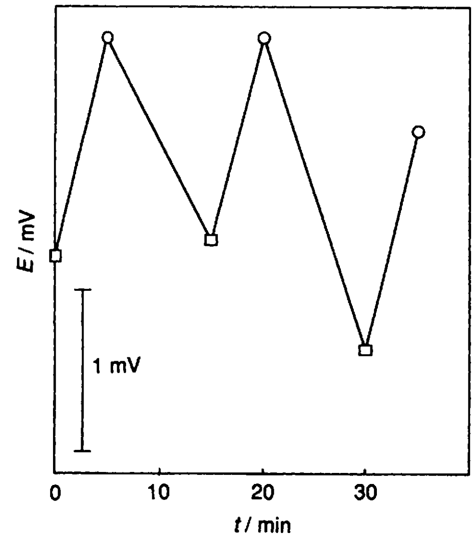
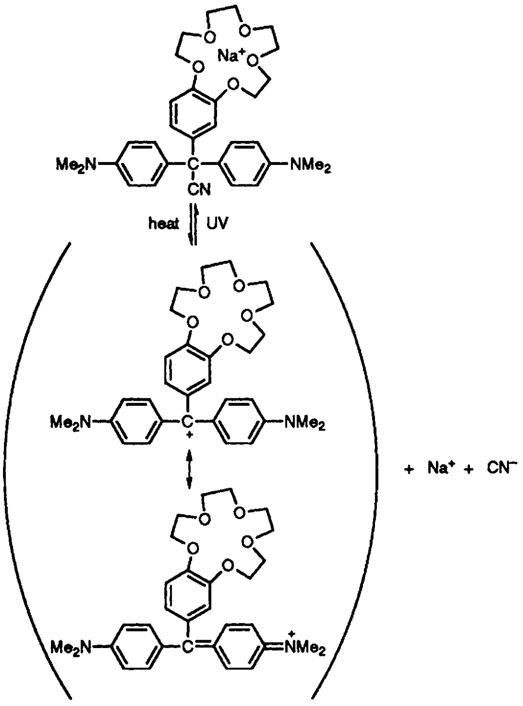


Fig. 2 Cation-binding switching of crowned MG-leuconitrile **1** by alternating UV-light irradiation and heating. Photoirradiation started at each point of □ and then finished at the point of ○, and *vice versa* for heating in the dark.



Scheme 1

such as crowned azobenzenes[7] and spirobenzopyrans,[8] their cation-complexing abilities were increased by their UV light-induced isomerization, due to the contribution of their additional binding sites. The crowned MG is quite different in that the photoisomerization and thereby cation formation effectively repels a crown-complexed cation by the intramolecular electrostatic repulsion. Also, the crowned MG-leuconitrile–metal ion system, in which occurrence of free ions is amplified by photoirradiation, may be useful for photoinduced drastic changes of polarity and ionic conductivity in various media.

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Footnotes

† Colourless crystal: mp 146–147 °C; ^{1}H NMR($CDCl_3$) δ 3.0 (12H, s,NCH_3), 3.8–4.3 (16H, m, OCH_2), 6.7–7.3 (11H, m, ar. H).

‡ After irradiation with UV light (passing light of a 500 W xenon lamp through a Toshiba UVD-33S colour filter) for 10 min, a MeOH solution (1×10^{-5} mol dm^{-3}) of **1** was heated to 40 °C. The first-order rate constant for the thermal back reaction was determined from initial slopes for plots of absorbance at 605 nm *vs.* time.

§ A MeOH–H_2O (95:5) solution (20 cm^{-3}) containing equimolar **1** and $NaClO_4$ (1×10^{-4} mol dm^{-3}) was placed in a measurement cell equipped with a quartz window for UV-light irradiation. E.m.f. measurements were made at 23 °C, using a Na^+ electrode (type 1100) and a double-junction-type reference electrode whose inner and outer barrels contained a saturated KCl solution and an 0.1 mol dm^{-3} NH_4NO_3 aqueous solution, respectively.

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