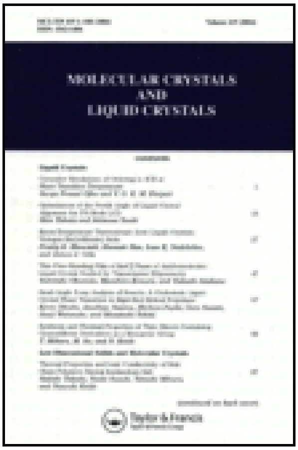

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Efficient Photochemical Switching of Metal-Ion Complexation by Malachite Green Leuconitrile Derivatives Carrying Bis(crown ether)

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Efficient Photochemical Switching of Metal-Ion Complexation by Malachite Green Leuconitrile Derivatives Carrying Bis(crown ether)

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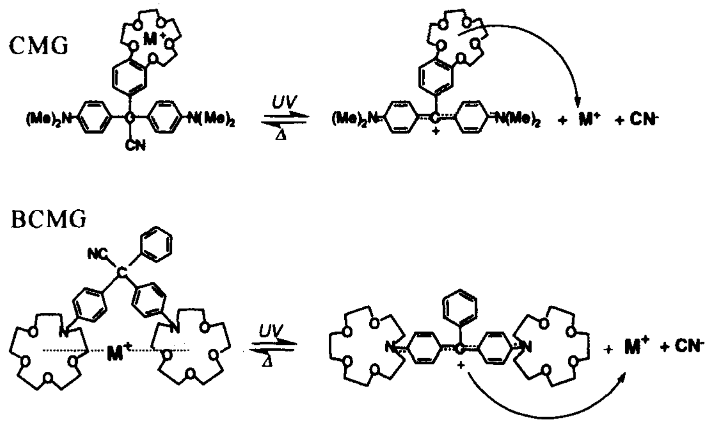
A Malachite Green derivative incorporating a bis(monoazacrown ether) structure enables efficient photocontrol of metal ion complexation. Its photochromism in the presence of alkali metal ions is examined by kinetics measurements and molecular-orbital (MO) calculation.

Keywords: crown ether; Malachite Green; metal-ion complexation; photoionization; kinetics; MO calculation

INTRODUCTION

Efficient photochemical switching of metal-ion complexation has been achieved in our previous work.[1] A Malachite Green derivative incorporating a bis(monoazacrown ether) structure (BCMG) showed drastic change, so-called all-or-none type switching in the cation binding upon photoionization (Scheme 1). On the contrary, a benzocrowned Malachite Green (CMG) cannot release a metal ion completely on photoirradiation. It is considered that this difference results from the modification of crown ether on Malachite Green moiety. A metal ion in CMG does not undergo electrostatic repulsion effectively on

Scheme1



photoionization. On the other hand, the repulsion is very effective in BCMG because its crown ethers rings include nitrogen atoms where a positive charge is delocalized in the photoionized Malachite Green. Also, BCMG binds a cation by the two crown rings and its photoisomerization accompanies a significant conformation change from its pyramidal form to plane one. We have already reported an electrospray-ionization mass-spectrometric evidence for the photocontrol of metal-ion complexation by BCMG[1,2]. Here, we discuss the photochromic behavior of BCMG by using the photoinduced coloration rate, activation energy on thermal decoloration reaction, and MO calculation.

EXPERIMENTAL

Coloration rate constant "K" was obtained by Equation (1),

$$K \cdot t = -\log(A_t - A_0)/(A_\infty - A_0) \qquad (1)$$

where "t" is time and "A" with a subscript is absorbance at 625nm at each time. The measurement system consisted of a Xe lamp, a sample cell, a monochrometer, and a photodiode. A light from a Xe lamp through a sample solution was collected by a monochrometer and the light at 625 nm was detected by a photodiode. Thermal decoloration rate constant "k" and its activation energy "Ea" were obtained by Equations (2) and (3), respectably,

$$k \cdot t = -\log(A_\infty - A_0)/(A_t - A_0) \qquad (2)$$

$$\ln k = -Ea / RT + \ln B \qquad (3)$$

where "R", "B", and "T" are gas constant, preexponential factor, and temperature, respectively. The sample solution was exposed for 5 min by UV light (240-400 nm), which was obtained by passing light from a Xe lamp through a Toshiba UV-D33S color filter. The sample was heated at 30, 40 and 50℃ after turning off the UV light. Decoloration rate constants were plotted against the temperature and the straight-line slope afforded Ea values.

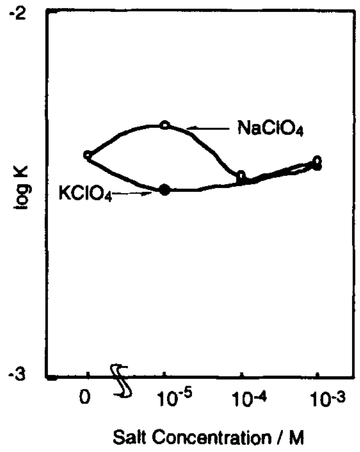


Figure 1. Coloration rate constants for acetonitrile solution of BCMG(1 X10^{-5} M) with $NaClO_4$(○) and $KClO_4$(●)

RESULTS AND DISCUSSION

Photoinduced Coloration

The quinoid form resulted from the photoionization of BCMG is generally stabilized in polar solvents, which increases the photoinduced coloration rate. The addition of 1 X 10^{-5} M $NaClO_4$ to a BCMG solution therefore promoted the photoinduced coloration to the quinoidform (Figure 1). However, the further addition of $NaClO_4$ lowered the coloration rates. This is because the metal-ion complexation by the crown ether rings of BCMG stabilizes its leuconitrile form, thus preventing its photoionization. For the potasium addition system, the lowest K value was observed in BCMG solution with 1 X10^{-5}M $KClO_4$ and the K value increased slightly with the salt concentration. This suggests strong 1:1 complexation of BCMG and potassium ion.

Activation Energy on Reverse Reaction

Heating under dark conditions induces the reverse reaction from the quinoid form to leuconitrile one, that is, thermal decoloration. The presence of a metal ion affected the reverse reaction and therefore the activation energy, Ea. Considering 55.76 kJmol^{-1} for BCMG (1 X 10^{-5} M in acetonitrile) without any salt, the presence of potassium ion contributes to the Ea decrease (Table 1). This is due to the stabilization of the leuconitrile form of BCMG by complex formation of its crown ether moiety with a potassium ion. The lowest Ea value was found in the solution containing 1 X 10^{-4} M $NaClO_4$. When the quinoid form undergoes

Table1. Activation energy for thermal decoloration in acetonitrile solutions of BCMG with $NaClO_4$ and $KClO_4$

Ion Species	Na^+	K^+
Concentration(M)	(kJ mol^{-1})	(kJ mol^{-1})
0	55.76	55.76
1 X 10^{-5}	66.59	39.23
1 X 10^{-4}	17.92	28.57
1 X 10^{-3}	43.17	24.32

the reverse reaction in the presence of enough amount of sodium ion (1 X 10^{-4} M), it holds two sodium ions with the two crown ether rings. The electrostatic repulsion between the two sodium ions and quinoid cation makes the resulting quinoid form unstable, causing the significantly small Ea value.

MO Calculation

The leuconitrile and quinoid forms of BCMG were compared in the conformation and net charge obtained by MO calculation (Figure 2 and Table 2). The leuconitirle form has smaller dihedral angle and shorter nitrogen-atom distance than quinoid form. The leuconitrile conformation has some advantage over the quinoid one on binding a metal ion by the

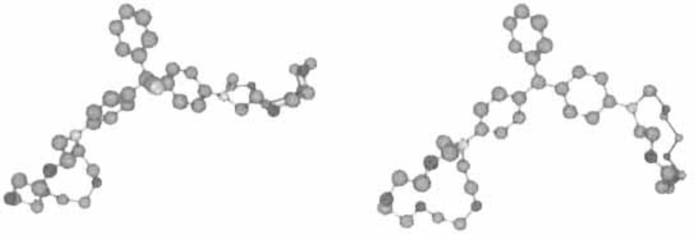


Figure 2. BCMG conformation of leuconitrile form (left) and quinoid form (right) obtained by MNDO-PM3 method

Table2. Dihedral angle of two phenylazacrown units, distance between two crown ether nitrogen atoms, and total electric charges on crown ether heteroatoms in BCMG isomers obtained by MINDO-PM3 method

	Leuconitrile From	Quinoid Form
Dihedral Angle	124.044°	179.909°
Distance between two nitrogens	9.522Å	9.974Å
Total ElectricCharges	-2.039	-1.807

cooperative action of the two crown ether rings. Moreover, the more negative electric charges on crown ether rings of the leuconitrile form is also preferable for the cation accommodation. These results support the dramatic photoinduced changes of metal-ion complexation by BCMG.

CONCLUSION

We investigated the photochromism of BCMG by photoirradiation and heating in acetonitrile solutions containing alkali metal ions. Its behavior was affected not only by metal-ion species but also by metal-ion concentrations. Since potassium ion forms strongest complexes with BCMG (1:1 complex), the complexation depressed BCMG photoionization. Potassium ion also contributed to the decrease in activation energy on thermal decoloration reaction. The complex formation of sodium ion and BCMG affected the activation energy in a different way. MO calculation supported the results of the efficient photochemical switching of metal-ion complexation by BCMG.

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