

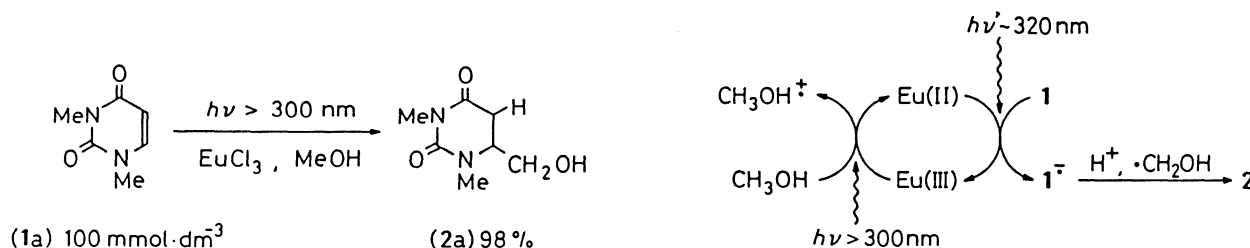
FLUORESCENCE QUENCHING STUDY OF Eu^{II} -CROWN ETHER COMPLEXES
BY 5-SUBSTITUTED-1,3-DIMETHYLURACILS

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Fluorescence of Eu^{II} -crown ether complexes was quenched by 5-substituted-1,3-dimethyluracils. The quenching rate constant increased with increasing the electron-withdrawing properties of the substituents which supports the electron-transfer mechanism proposed for the $\text{Eu}^{\text{III}}/\text{Eu}^{\text{II}}$ photoredox system. A cavity size of the crown ether also influenced the quenching process.

We have investigated a photoredox reaction of $\text{Eu}^{\text{III}}/\text{Eu}^{\text{II}}$ system in alcohols in the presence of an organic substrate.¹⁻³⁾ In this system, the reaction mechanism was found to be dependent on the substrate used. For alicyclic olefin and α -methylstyrene, a radical mechanism has been proposed where hydrogen atom and hydroxymethyl radical are initially formed by the photoredox reaction of methanol and react with olefin leading to the formation of the dihydrodimer and hydroxymethylated products competitively.^{1,2)} In the case of 1,3-dimethyluracil (**1a**), on the other hand, a regioselective hydroxymethylation of **1a** was observed in an almost quantitative yield upon irradiation ($\lambda > 300$ nm) of a methanol solution of **1a** and a catalytic amount of EuCl_3 .^{3,5)} This reaction was reasonably explained by one-electron reduction of **1a** and successive protonation of the radical anion of **1a**,⁴⁾ finally providing the hydroxymethylated product (**2a**) as shown in Scheme 1.



Scheme 1.

However, there has been no direct evidence for the electron transfer mechanism and it is not clear what controls the reaction mechanism. In the present paper, we report the fluorescence quenching of Eu^{II} which supports the above mechanism. The fluorescence intensity of Eu^{II} , which is a key intermediate for the hydroxymethylation, is very weak and the quenching behavior cannot be investigated. However, it has been known that the intensity is increased extremely by the addition of crown ethers.⁶⁾ The present hydroxymethylation of **1a** was confirmed to take place efficiently even in the presence of 18-crown-6 ether. Therefore, the quenching studies are useful to elucidate the reaction mechanism. In the course of the investigation, we found a novel aspect of the quenching process influenced by a mode of complexation of Eu^{II} -crown ether depending on the cavity size.

The laser irradiation (308 nm, 15 ns, 100 mJ) of a methanol solution of EuCl_3 (10 mmol dm^{-3}) and 18-crown-6 ether (100 mmol dm^{-3}) resulted in the oxidation of methanol and the corresponding formation of Eu^{II} which reached a photostationary state after about 60 pulses irradiation. The formation of Eu^{II} was confirmed by its absorption spectrum, $\lambda_{\text{max}} 324 \text{ nm}$ ^{6,7)} and also by the fluorescence spectrum, $\lambda_{\text{max}} 446 \text{ nm}$ ⁶⁾ as shown in Figs. 1 and 2.

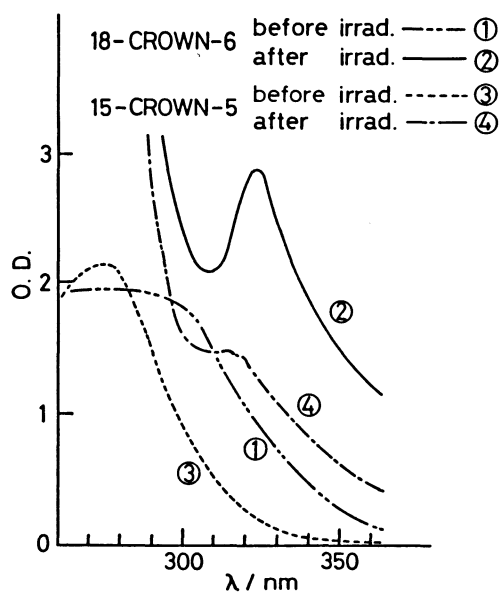


Fig. 1. Absorption spectra of methanol solutions of EuCl_3 containing crown ethers before and after 60 pulses laser irradiation.

$[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}] = 10 \text{ mmol dm}^{-3}$, $[\text{crown ether}] = 100 \text{ mmol dm}^{-3}$, Ar saturated, at room temperature.

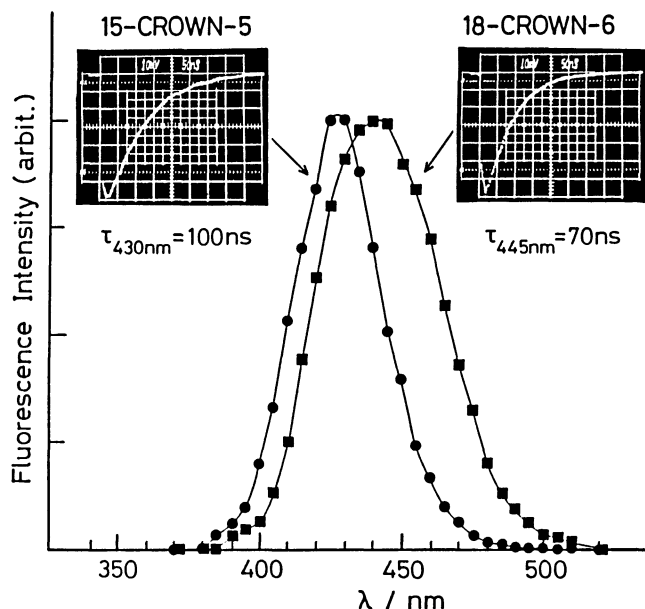


Fig. 2. Transient emission spectra of methanol solutions of EuCl_3 containing crown ethers.

The sample solutions are the same to those of used in Fig. 1. Inserts show the decay profiles of both emissions.

The fluorescence quenching of Eu^{II} -crown complexes by **1** was also carried out by laser flash photolysis of a methanol solution of EuCl_3 and the crown ether which was pre-irradiated to the photostationary state in the presence of changing amounts of **1**. A plot of the reciprocal of the fluorescence lifetime against the concentration of **1** provides the quenching rate constant (k_q). The quenching rate constants obtained with **1** are plotted against the Hammett σ_p as shown in Fig. 3.

The rate constant increases with increasing the electron-withdrawing properties of the substituents, suggesting the electron transfer character of the quenching process. The introduction of an electron-withdrawing substituent makes the pyrimidine ring electron deficient and lowers the reduction potential,⁸⁾ thus leading to an acceleration of the electron transfer quenching. The rate constants for α -methylstyrene for which a radical mechanism has been proposed,^{1,2)} is very low; $4.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (18-crown-6 complex) and $\leq 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (15-crown-5 complex). In the cases of alicyclic olefins, no quenching was observed. These observations are consistent with the reaction mechanism which has been presumed from the product analysis.^{1,2)}

Another interesting finding is the effect of the cavity size of the crown ether on the quenching behavior. The quenching rate constants for Eu^{II} -18-crown-6, which is proposed to be a 1:1 complex,⁶⁾ are very large and near diffusion-controlled, while Eu^{II} -15-crown-5 provides rather small rate constants but a high ρ value of the Hammett plot is obtained. In the latter complex which is proposed to be a 1:3 complex,⁶⁾ the collisional quenching of the excited state of Eu^{II} by **1** may be

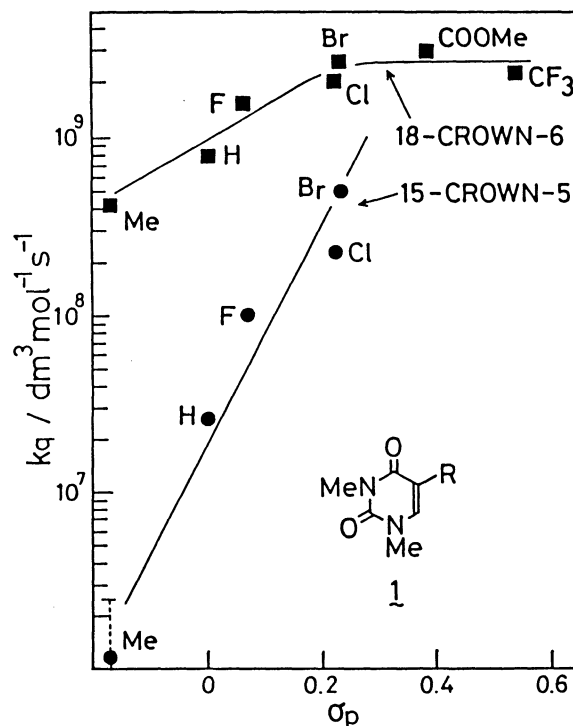


Fig. 3. Hammett plot of the quenching rate constants (k_q) of Eu^{II} -crown complexes by 5-substituted-1,3-dimethyluracils (see the text).

sterically more hindered and the reactivity is influenced by the complexation. This novel behavior of the quenching process may correlate with the significant effect on the fluorescence intensity by the complexation,⁹⁾ and further investigation is in progress.

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