

# A New Concept of Photogeneration of Cations: Evidence for Photoejection of $\text{Ca}^{2+}$ and $\text{Li}^+$ from Complexes with a Crown-Ether-Linked Merocyanine by Picosecond Spectroscopy

M. M. Martin,<sup>1</sup> P. Plaza,<sup>1</sup> Y. H. Meyer,<sup>1</sup> L. Bégin,<sup>1</sup> J. Bourson,<sup>2</sup> and B. Valeur<sup>2</sup>

Received October 18, 1993

Time-resolved transient absorption and gain spectra of DCM-crown and its complexes with  $\text{Li}^+$  and  $\text{Ca}^{2+}$  in acetonitrile are measured in the wavelength range 370–670 nm after subpicosecond excitation at 425 nm. The results give evidence for the fast formation of free DCM-crown from both excited complexes, with a faster rate for the  $\text{Li}^+$  complex. A two-step mechanism is found for the initial decay (within 30 ps) of the free DCM-crown.

**KEY WORDS:** DCM-crown;  $\text{Ca}^{2+}$ ;  $\text{Li}^+$ ; merocyanine; picosecond spectroscopy.

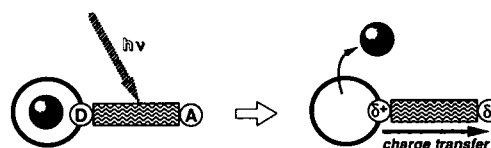
## INTRODUCTION

According to chemical relaxation methodology, the kinetics of the responses of chemical or biological systems to cation concentration jumps can provide valuable insights into these systems. Photochemical processes can induce very fast and spatially controllable concentration changes. Photorelease of cations from a "cage" is indeed possible by means of photocleavable chelators [1] or cryptands [2] or by photoinduced changes in the chemical structure of chelators [3].

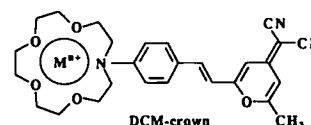
These processes are irreversible, and it is of interest to design reversible systems to improve the signal-to-noise ratio by accumulation. This can be achieved with systems in which the interaction between a cation and a coordinating atom (e.g., nitrogen) is broken as a result of photoinduced intramolecular charge transfer from this

donor atom toward an electron-withdrawing group farther in the molecule, as illustrated in Scheme I.

DCM-crown (Scheme II), consisting of the well-known merocyanine laser dye in which the dimethyl amino group has been replaced by a macrocycle (monooxa-15-crown-5), is a possible candidate for such a process. It is indeed admitted that fluorescence emission of DCM and its derivatives results almost solely from an



Scheme I



Scheme II

<sup>1</sup> Laboratoire de Photophysique Moléculaire du CNRS (UPR 3361), Bât 213, Université Paris-Sud, 91405 Orsay Cedex, France.

<sup>2</sup> Laboratoire de Chimie Générale (CNRS ER77), Conservatoire National des Arts et Métiers, 292 rue Saint Martin, 75003 Paris, France.

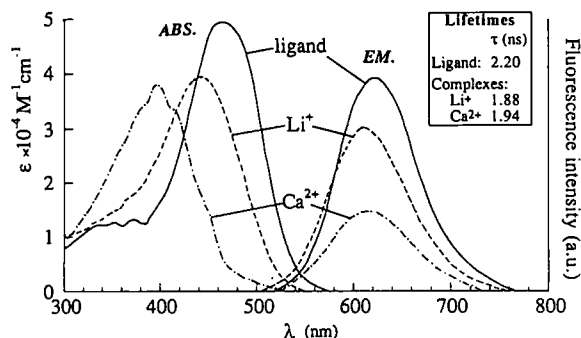


Fig. 1. Absorption spectra, corrected emission spectra, and excited-state lifetimes of DCM-crown and its complexes with Li<sup>+</sup> and Ca<sup>2+</sup>.

intramolecular charge transfer from the donor moiety (amino group) to the acceptor moiety (dicyanomethylene group) [4].

The absorption spectrum of DCM-crown is drastically blue shifted upon binding of Li<sup>+</sup> and Ca<sup>2+</sup> as expected from the reduction of the electron-donating character of the nitrogen atom, but the fluorescence spectrum undergoes no shift (Fig. 1), and the excited-state lifetime is almost unaffected by complexation, whereas the fluorescence quantum yield is reduced [5].

These observations seem to show that excitation of the ground-state complexes leads to an emissive species which is the free ligand as a consequence of photoinduced ejection of the cation. Similar conclusions have been drawn from the observation of "crowned" donor-acceptor stilbene derivatives [6]. A preliminary investigation of DCM-crown and its complexes by picosecond pump-probe spectroscopy has provided evidence for a disruption of the interaction between the cation and the nitrogen atom of the crown [7]. Further study of the excited-state phenomena by this technique is reported here.

## 2. EXPERIMENTAL

Time-resolved transient absorption and gain spectra are measured by the pump-probe technique using a 0.7-ps, 15- to 30- $\mu\text{J}$  pump pulse at 425 nm and a continuum probe produced by focusing a 0.3-ps, 100- to 200- $\mu\text{J}$ , 710-nm pulse in a 1-cm water cell. The 425- and 710-nm synchronized pulses are generated by the same dye laser system using a nano- to subpicosecond pulse shortening method [8]. The whole system is driven by a single, seeded, 10-Hz, Q-switched Nd:YAG laser (Quantel). Pump-probe experiments are carried out with a two-beam probe arrangement as in Ref. 7. The transient

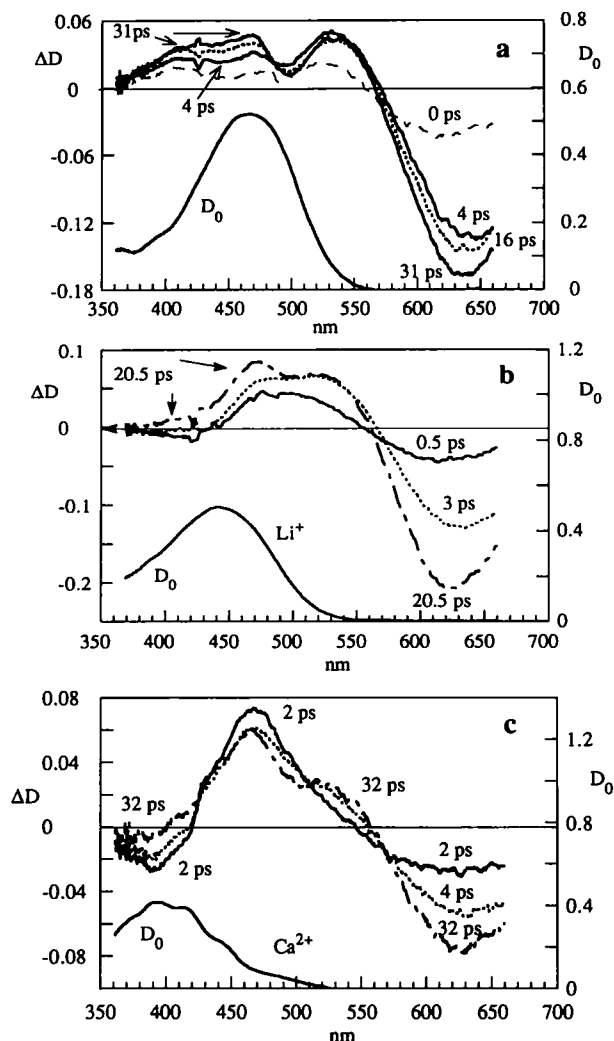


Fig. 2. Transient absorption and gain spectra ( $\Delta D$ ; left scale) of DCM-crown (a) and its complexes with Li<sup>+</sup> (b) and Ca<sup>2+</sup> (c) in acetonitrile after excitation with a 0.7-ps pulse at 425 nm. Time zero has been chosen at half of the initial rise of  $\Delta D$  at 470 nm of the complex solutions. The ground-state absorption spectrum is also given (optical density) for comparison,  $D_0$  (right scale).

spectra are accumulated over 500 laser shots. The solutions are recirculated to avoid permanent bleaching effects.

## 3. RESULTS AND DISCUSSION

The differential optical densities ( $\Delta D$ ) measured for solutions of DCM-crown and its complexes with Li<sup>+</sup> and Ca<sup>2+</sup> in CH<sub>3</sub>CN, within 30 ps after subpicosecond excitation at 425 nm, in the wavelength range 370–670 nm, are given in Fig. 2. A broad transient absorption band

( $\Delta D > 0$ ) showing three maxima, around 410, 470, and 530 nm, is observed for the free DCM-crown (Fig. 2a) within and immediately after excitation. This band is found to evolve within a few tens of picoseconds after excitation. The 410- and 470-nm maxima grow further, whereas the 530-nm maximum does not change much and a dip occurs around 500 nm, with a region of constant  $\Delta D$  (isosbestic point) around 482 nm, indicating a two-step or two-state photoinduced process. A striking observation is that the net gain band in the range 570–670 nm ( $\Delta D < 0$ ,  $D_0 = 0$ ) shifts to the red during the first step, then slightly shifts back to the blue during the second step and keeps increasing during the whole process. Similar changes are observed for the laser dye DCM in acetonitrile [9]. For further time delays, nanosecond decay of  $\Delta D$  without a noticeable change in shape of the transient spectrum is observed.

The transient spectra measured for the DCM-crown-Li<sup>+</sup> complex (Fig. 2b) show an initial broad transient absorption band in the wavelength range 440–550 nm. A slight bleaching ( $\Delta D < 0$ ) can be seen around 420 nm. Within 3 ps a strong increase in the transient absorption around 530 nm is observed, confirming our previous observations [7], which lead us to suggest rapid formation of the free DCM-crown by cation photoejection from the complex excited state. In the present experiment,  $\Delta D$  is also found to increase in the range 380–440 nm, where free DCM-crown transient absorption is also expected. Bleaching is no longer observed at 3 ps. At 20 ps, absorption bands can be seen around 410 and 470 nm, whereas the 530-nm band has not changed much and the gain band is blue-shifted, as observed when exciting free DCM-crown (Fig. 2a). Similar results are found for the complex with Ca<sup>2+</sup>, at a lower rate (Fig. 2c). The delayed increase in  $\Delta D$  around both 400 and 530 nm within a few tens of picoseconds after excitation shows formation of the free DCM-crown. The second step in its decay mechanism can be guessed by the dip

formed around 500 nm at long delays and the slight blue shift of the gain band. The two-step mechanism after ejection of Ca<sup>2+</sup> is not well resolved, indicating that it may occur on the same time scale as the photoejection process. Furthermore, a smaller photoejection yield is foreseen for Ca<sup>2+</sup> than for Li<sup>+</sup> [7].

#### 4. CONCLUSION

Our observations demonstrate that DCM-crown is less complexing in the excited state than in the ground state, giving direct evidence for the reduction of nitrogen electron-donating character upon electronic excitation. Furthermore, our experiments provide evidence for rapid evolution (within 30 ps) of the free DCM-crown excited state formed by cation ejection from the excited complex as well as from laser excitation, with a two-step or two-state mechanism. There is no indication of such a two-state decay mechanism in competition with the photoinduced cation ejection process from the complex excited state.

#### REFERENCES

1. J. H. Kaplan and G. C. R. Ellis-Davies (1988) *Proc. Natl. Acad. Sci. USA* **85**, 6571.
2. R. Warmuth, E. Grell, J. M. Lehn, J. W. Bats, and G. Quinkert (1991) *Helv. Chim. Acta* **74**, 671.
3. S. R. Adams, J. P. Y. Kao, G. Gryniewicz, A. Minta, and R. Y. Tsien (1988) *J. Am. Chem. Soc.* **110**, 3212.
4. M. Meyer, J. C. Mialocq, and B. Perly (1990) *J. Phys. Chem.* **94**, 98 (and references therein).
5. J. Bourson and B. Valeur (1989) *J. Phys. Chem.* **93**, 3871.
6. J. F. Létard, R. Lapouyade, and W. Rettig (1993) *Pure Appl. Chem.* **65**, 1705.
7. M. M. Martin, P. Plaza, N. Dai Hung, Y. H. Meyer, J. Bourson, and B. Valeur (1993) *Chem. Phys. Lett.* **202**, 425.
8. N. Dai Hung, P. Plaza, M. M. Martin, and Y. H. Meyer (1992) *Appl. Opt.* **31**, 7046.
9. P. Plaza, M. M. Martin, and Y. H. Meyer, unpublished results.