Metal-Ion Detection by the Magnetic-Field-Sensitive Fluorescence of Intramolecular Exciplexes Containing Aza-Crown-Ether Moieties as Electron Donor

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Magnetic field effects (MFE) detected by intramolecular exciplex fluorescence have been studied in acetonitrile solutions for new donor−acceptor compounds in which pyrene is linked to aza-15-crown ether by a polymethylene chain with 3, 9, and 16 CH_2 units. It was found that addition of alkali and alkaline-earth ions to the solutions decreases the observable MFE. The longer the chain and the greater the stability constants of the aza-crown complexes with metal ions, the more pronounced is the influence of the added metal ions. The data obtained are rationalized on the basis of a kinetic scheme that specifically includes photoejection of metal ions from the crown-ether complexes, accompanied by Coulombic interaction of the ions released with the solvent-separated radical ion pairs, the so-called special salt effect.

Introduction

Over the last few decades a significant interest has been directed at the field of crown-ether chemistry because of crown-ether ability to produce complexes with metal ions in solution. Although extensive literature has evolved on the subject (see for example ref 1) these publications deal mainly with the thermodynamics of complex production rather than with the kinetics of producing and decaying complexes of crown-ethers with metal ions despite importance of these kinetic processes.

Recently we have found that the *m*agnetooptically *de*tected *s*pin *c*onversion spectroscopy (MODESC), which is often useful in studying molecular and spin dynamics of systems involving radical-pair reactions, can give new insights into the dynamics of producing complexes of aza-crown ethers with metal ions.[2] The point is that crown ethers containing nitrogen atoms in their macrocycle can act also as electron donors in the photoinduced charge transfer with an appropriate electron acceptor.[3] This results in forming radical ion pairs (RIP) whose cage recombination may be affected by low external magnetic fields ($B \approx 100$ G), provided the exchange interaction between the radical ions is small. An external magnetic field removes the degeneracy of RIP triplet-state sublevels T_0 and $T_\pm$, by virtue of the Zeeman effect. When the energy separation between them exceeds the size of the hyperfine interaction (HFI) of the unpaired electrons with their nuclei, $T_\pm$ cannot mix with the RIP singlet state, i.e., external magnetic fields diminish the probability of intersystem crossing in the radical ion pair and, therefore, change the relative concentration of both the singlet and triplet states of the RIP. Relative singlet-RIP concentration can be monitored conveniently through the intensity of the exciplex fluorescence produced in the course of the geminate RIP recombination. A characteristic feature of the above magnetic field effects is that a change in the lifetime of spin-correlated RIP for one reason or other results in a change in the magnitude of MFE monitored. If aza-crown ethers (ACE) are introduced as electron donors in exciplex systems, reactions of them and their radical cations can be traced by MODESC spectroscopy. This has been confirmed by experiment.[2]

Previously we used freely diffusing pyrene/phenylaza-15-crown-5 ether exciplex systems in which metal ions were added.[2] Because of the general principle of the MODESC technique, the concentration of aza-crown ether has to be significantly higher than that of pyrene in order to quench the electronically excited acceptor (pyrene) significantly. In doing so, concentrations of ions added are normally also less than that of crown ether. Linked donor−acceptor compounds, $A{-}(CH_2)_n{-}D$, have favorable electron-transfer kinetic conditions.[4] They therefore allow the application of MODESC spectroscopy[4] to be extended to the case where metal ion concentrations exceed that of crown-ether moieties, i.e., the opposite kinetic limit with respect to metal ions can be easily reached.

The purpose of this article is to report studies about the influence of alkali and alkaline-earth ions on the MFE monitored by intramolecular exciplex fluorescence in new supramolecular compounds in which pyrene (Py) is linked to aza-15-crown-5 ether (ACE) by a polymethylene chain; in what follows, these compounds are denoted Py(n)ACE (or in short A(n)D) where $n = 3$, 9, and 16 are the number of CH_2 units in the flexible bridge.

Experimental Section

Fluorescence spectra were measured with a Perkin-Elmer LS50 spectrometer. Fluorescence lifetimes were determined with a single-photon-counting fluorimeter (Edinburgh Instruments). The relative change of the exciplex fluorescence intensity caused by external magnetic fields, $\Delta\varphi/\varphi = [\varphi(B) - \varphi(0)]/\varphi(0)$, was detected under steady-state conditions through an OG315 Schott filter during photoexcitation of pyrene (cutoff Schott filters BG18+UG2) by a xenon lamp. Magnetic fields, provided by a Bruker electromagnet and applied to the sample, were measured with a Hall-type Gaussmeter. For more details see refs 4 and 5. A typical concentration of 13-[4-(n-pyren-1-ylalkyl)phenyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane, i.e., Py(n)ACE, was of the order of 10^{-5} M. Acetonitrile, used as a solvent, was of spectroscopic grade (Merck, Uvasol). Following procedures given in the literature,[6] lithium, sodium, and calcium perchlorates were vacuum-dried for 24 h at elevated temperatures ($LiClO_4$ at 65 °C, $NaClO_4$ at 140 °C, $Ca(ClO_4)_2$ at 180 °C) and kept anhydrious over P_4O_{10} in a desiccator prior to use. Before each experiment, dry nitrogen was bubbled

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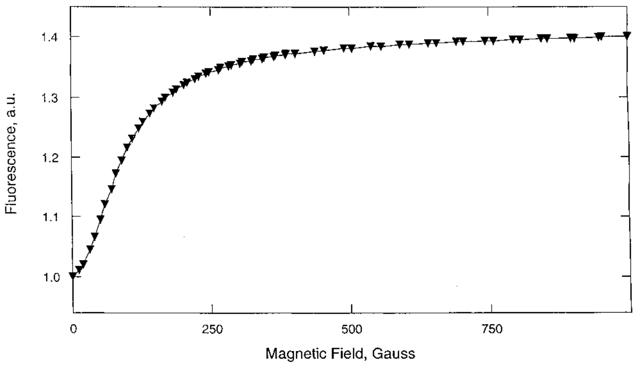


Figure 1. Relative change in exciplex fluorescence of acetonitrile solution of Py(16)ACE versus the external magnetic field strength.

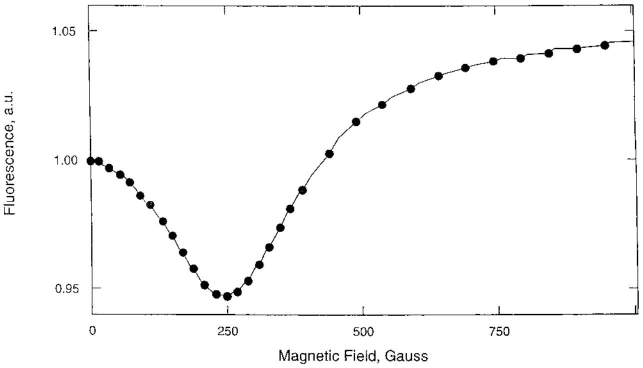
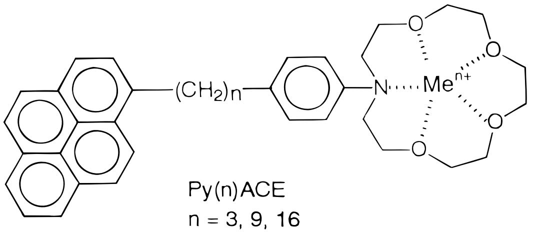


Figure 2. Relative change in exciplex fluorescence of acetonitrile solution of Py(9)ACE versus the external magnetic field strength.

SCHEME 1



through the samples for 15 min. All experiments were carried out at room temperature.

Results and Discussion

As seen from Figures 1 and 2, acetonitrile solutions of Py(*n*)ACE exhibit MFEs similar to well-known intramolecular systems, pyrene linked to dimethylaniline (DMA);[4] the saturation value of MFE is 40% for $n = 16$ and 5% for $n = 9$. The latter system shows a pronounced *J*-resonance behavior at a field strength of ca. 245 G. As expected, no MFE is detected for $n = 3$ because of the large exchange interaction in the short-linked radical ion pair.

When alkali and alkaline-earth perchlorates are added to the solution, the MFE decreases. Figure 3 gives the relative change in exciplex fluorescence intensity of Py(16)ACE at $B = 1$kG versus the concentration of lithium and sodium perchlorates. It is worth noting that in the case of Py(16)DMA no decrease in MFE is detected. Thus the decrease in MFE with the probe Py(16)ACE upon addition of the above perchlorate is evidently associated with the macrocycle in the donor moiety. Figure 4 provides the dependence of $\Delta\varphi/\varphi$ values at $B = 1$ kG and at $B = 245$ G (where the system shows resonance behavior[11]) on concentration of metal ions added to the solution of Py(9)ACE. Unlike with the Py(16)ACE system, this MFE is less pronounced, and both types of ions have almost the same effect. A typical value of concentration of alkali ions at which the MFE reduces significantly is about 1 mM. As seen from Figures 5 and 6, the influence of calcium ions has a more pronounced effect at a significantly small typical concentration of ca. 0.02 mM. Note that all relationships between MFE and ion concentration have pronounced minimum saturation values which are approached as the concentration increases. The value of $B_{1/2}$ (the magnetic field at which $\Delta\varphi/\varphi$ reaches half the maximum value), which is 90 G for Py(16)ACE, does not depend on the concentration of ions. This probably means that the molecular dynamics of spin-correlated pairs are not significantly disturbed by metal ions.

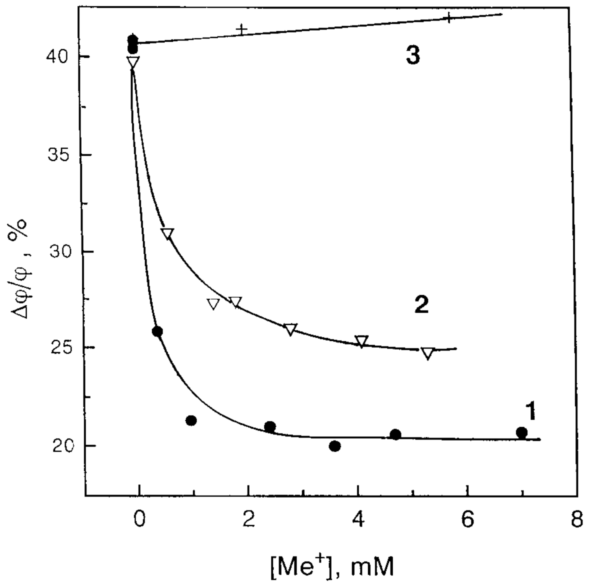


Figure 3. Relative change in exciplex fluorescence at B = 1kG versus the concentration of salt added: (1) Li^+ to Py(16)ACE; (2) Na^+ to Py(16)ACE; (3) Li^+ to Py(16)DMA.

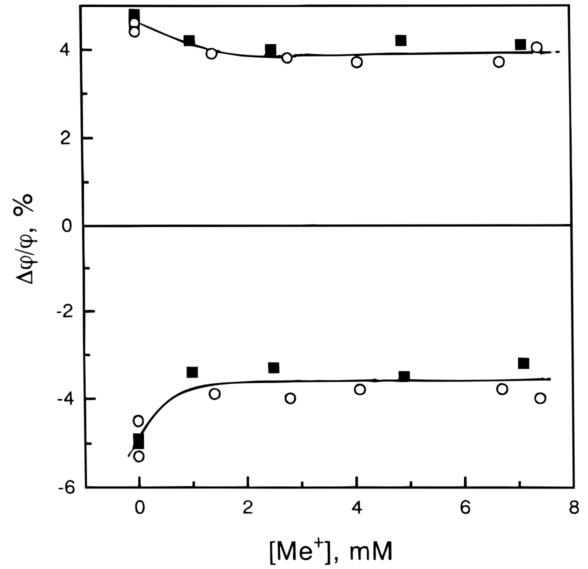


Figure 4. Relative change in the Py(9)ACE exciplex fluorescence at $B = 1$ kG (above) and $B = 245$ G (below) versus the concentration of salt added: Li^+ (square); Na^+ (circle).

In addition, the fluorescence intensity from the pyrene moiety, measured at about 380 nm, increases with increasing ion concentration, leading to its saturation values at large ion concentrations. A typical concentration corresponding to the increase in monomer fluorescence is approximately equal to that of the relationship between MFE and ion concentration. In other

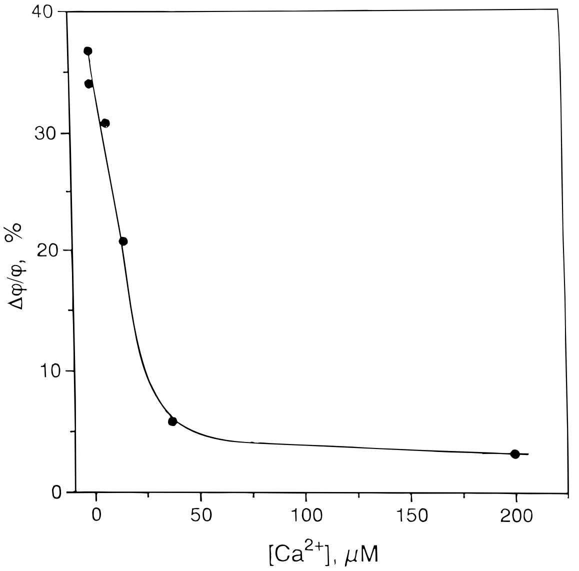


Figure 5. Relative change in the Py(16)ACE exciplex fluorescence at $B = 1$ kG versus the concentration of Ca^{2+}.

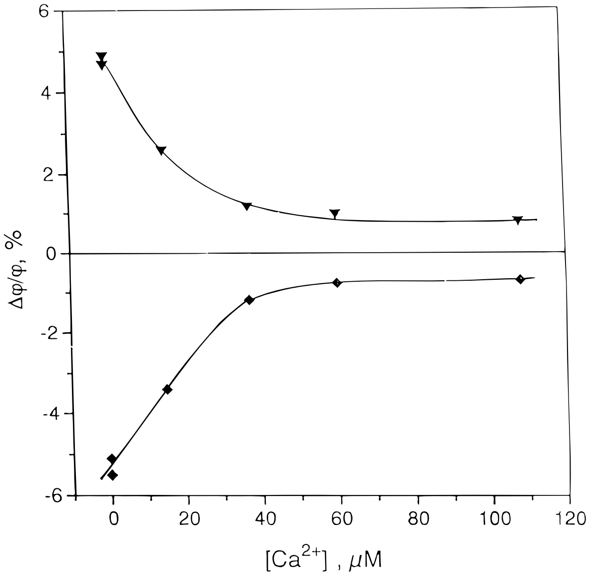


Figure 6. Relative change in the Py(9)ACE exciplex fluorescence at $B = 1$ kG (above) and $B = 245$ G (below) versus the concentration of Ca^{2+}.

words, increase in pyrene monomer fluorescence intensity and decrease in MFE show roughly the same dependence on alkali and alkaline-earth perchlorate concentration. It is worth noting that for calcium perchlorate monomer fluorescence intensity increases very strongly by an order of magnitude; for sodium and lithium perchlorates this does not exceed a factor of 2−3. The increase of steady-state fluorescence is concomitant with increase in the lifetime of monomer excited states (see Table 1).

The lifetime of exciplex fluorescence also increases when lithium and sodium metal ions are added in solution; the longer the $(CH_2)_n$ chain, the more significant this increase becomes. The influence of lithium is most pronounced. Typically, the lifetime of Py(16)ACE exciplexes is increased by sodium ions from 20.6 ns (without ions) to 26.5 ns at 5 mM ion concentration. It is worth noting that the risetime of exciplex fluorescence also increases when these metal ions are added to the solution. In the case of calcium ions, no significant changes have been detected in the lifetime and risetime of exciplex fluorescence. Moreover, because of a huge increase in monomer fluorescence, its long-wave tail can have a significant intensity in the wavelength region of the exciplex band, superimposing on the exciplex fluorescence. However, these two different intensities, comparable to each other for higher concentrations of calcium ions, can be easily distinguished by time-resolved measurement.

TABLE 1: Fluorescence Lifetimes of Acetonitrile Solutions of Py(*n*)ACE in the Presence of Metal Ions

system	metal ion concentration, mM	lifetime, ns	
		monomer	exciplex[a]
Py(16)ACE	0	3.0	16.7
Li^+	0.75	7.7	26.0
Na^+	5	13.1	26.5
Ca^{2+}	0.02	98.4	17.1
Py(9)ACE	0	2.1	22.9
Li^+	2	4.9	30.0
Na^+	5	12.2	25.0
Ca^{2+}	0.02	78.2	19.9
Py-CH3	0	180	

[a] 1/*e* time of an approximately exponential decay time.

To rationalize the data obtained, we propose the following kinetic scheme that includes three distinguishable groups of processes. *First*, these are reactions involving electronically excited metal-ion-free species, which are almost similar to those occurring generally in typical exciplex systems in polar solvents. Here, the singlet state of the RIP, $^1\{A^{\bullet-}(n)D^{\bullet+}\}$, is generated via photoinduced intramolecular electron transfer between acceptor (A) and donor (D) moieties:

$$^1A^*(n)D \rightarrow {}^1\{A^{\bullet-}(n)D^{\bullet+}\} \qquad (1)$$

Owing to hyperfine interaction in the RIP, intersystem crossing is possible. As mentioned above, the rate of this spin-conversion process depends on external magnetic field strength:[4,7]

$$^1\{A^{\bullet-}(n)D^{\bullet+}\} \Leftrightarrow {}^3\{A^{\bullet-}(n)D^{\bullet+}\} \rightarrow {}^3A^*(n)D \qquad (2)$$

Recombination of singlet RIP according to process (3) results in intramolecular exciplex formation whose fluorescence can be readily monitored in the green spectral region:

$$^1\{A^{\bullet-}(n)D^{\bullet+}\} \rightarrow {}^1(A^-(n)D^+)^* \xrightarrow{h\nu} A(n)D \qquad (3)$$

This recombination competes with the direct recombination to the ground state and with intersystem crossing according to eq 2; the latter can lead to the locally excited triplet state of pyrene. Since the rate constant of intersystem crossing in the RIP can be modulated by weak external magnetic fields, it affects the concentration of the singlet RIPs inversely to triplet RIP concentration.[4] Therefore, the concentration of singlet exciplexes are kinetically related to the singlet RIPs. Primary photophysical and photochemical processes in systems containing aza-crown ether as electron donor are almost the same as in their analogues (pyrene linked with *N*,*N*-dimethylaniline), which is confirmed by the fact that the MFEs detected in both systems are similar.

Second, the main reaction involving aza-crown ethers in their ground state in the presence of metal ions is the production of metal-ion complexes:

$$A(n)D + Me^{n+} \Leftrightarrow A(n)DMe^{n+} \qquad (4)$$

The donor ability of tertiary nitrogen in the ACE macrocycle is decreased significantly when the macroligand is loaded with an ion. Thus, the higher the concentration of metal ions, the smaller the fraction of ion-free ACE. Because the nitrogen potential of ionization is increased,[3] the nitrogen atom interacting with a metal ion cannot quench electronically excited pyrene as effectively as it does without metal ions. This manifests itself in an increase of the fluorescence of the pyrene moiety (monomer fluorescence). Obviously, the larger the stability constant of ion-complex production, the more pronounced is this feature. From the data on varying monomer fluorescence (i.e., pyrene moiety fluorescence) when metal ions are added in solutions, we roughly estimated the stability constant of reaction 4. This increases in the order $Na^+ \leq Li^+ < Ca^{2+}$ and for each ion is larger in the case of a longer polymethylene chain by a factor of ca. 2. In fact, the influence of calcium ions on MFE can be explained on the basis of reaction 4. The complexation diminishes the relative yield of exciplex fluorescence sensitive to external magnetic fields, and as a result, observable MFE values become smaller. This mechanism was mentioned earlier[2] as being unimportant for freely diffusing systems. However, this might play an important role in the linked systems.

Third, at least for sodium and lithium ions photoinduced electron transfer to the acceptor moiety, nevertheless, cannot be ruled out even when the macrocycle contains a metal cation (cf. stability constants above). This means that after a bond between crown nitrogen and a cation is broken, the latter can leave the macrocycle:

$$A^*(n)DMe^{n+} \rightarrow A^{\bullet -}(n)D^{\bullet +}...Me^{n+} \qquad (5)$$

Process 5 can account for the observed saturation feature in the relationship between MFE and ion concentration. Such a photoejection of cations was first proposed by Valeur and coworkers on their studying the absorption of a crown-ether-linked merocyanine compound by means of picosecond spectroscopy.[8] They found that for lithium and calcium complexes with aza-15-crown-5 moieties, the coordination bond with the nitrogen is broken very rapidly; in less than 5 and 20 ps, respectively. These times are too short for metal ions to diffuse a distance far apart from the macrocycle. Therefore, the cation is expected to be located in the proximity of the intramolecular RIP; obviously a process reverse to photoejection is plausible according to the so-called special salt effect, i.e., the cation can intervene electrostatically, interacting with the A^- moiety of the RIP. Simon and Peters studied this mechanism in particular by means of picosecond spectroscopy:[9]

$$A^-(n)D^{\bullet +}...Me^{n+} \Leftrightarrow Me^{n+}A^{\bullet -}(n)D^{\bullet +} \qquad (6)$$

Thus, the production of fluorescent exciplexes (i.e., contact RIP) from solvent-separated RIPs may be retarded significantly. It is worth noting that the spatial separation is a necessary stage of RIP spin dynamics in order to observe the MFE experimentally, i.e., during their lifetime radical ions should be sufficiently far from each other to make unpaired electron exchange interaction smaller than HFI. On the other hand, an increase in the RIP lifetime might result in a decrease of detectable MFE because, for example, spin−lattice relaxation could play a more important role under these conditions. In other words, that fraction of exciplexes which is produced from spin-correlated RIPs sensitive to external magnetic fields is reduced. Taking into account that the RIP lifetime relates to that of the exciplex fluorescence,[10] one may expect that a decrease in MFE with increasing metal-ion concentration should occur. It is worth while to note that according to Simon and Peters[9] processes similar to eq 6 are more effective if a type of ion pairs, $A^-(n)D^+$ (tight or loose), is the same as that of alkali perchlorates. Since the latter are known to be solvent separated in acetonitrile, the influence of the salts on Py(16)ACE should be stronger than on Py(9)ACE, which actually is in agreement with our experimental results.

Conclusion

The MODESC technique[4] is a useful tool in studying the dynamics of supramolecular exciplex systems in the presence of metal ions in polar solvents, i.e., systems that show metal complex kinetics. The data obtained can be rationalized at least qualitatively on the basis of the proposed kinetic scheme which particularly includes photoejection of metal ions from crown ether complexes, accompanied by Coulombic interaction of released ions with solvent separated RIP, the special salt effect.

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(11) J resonance: So-called J resonance prevails when the Zeeman splitting energy, $g\mu B$, equals 2 times the exchange interaction energy J: $g\mu B = 2J$ = singlet−triplet energy splitting. In this case, singlet−triplet mixing (intersystem crossing, spin conversion) is most effective (see for example ref 4b).