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Mendeleev Commun., 1995, **5(1)**, 4–5

Mendeleev Communications

Magnetic Field Effects on Exciplex Fluorescence of the Pyrene–Azacrown Ether System in the Presence of Alkali and Alkaline Earth Salts

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Paramagnetic species are produced in solutions of the pyrene–azacrown ether exciplex system during light excitation in the presence of diamagnetic metallic ions Li$^+$ and Ca^{2+}.

It is well-known[1] that typical exciplex systems (*e.g.*, pyrene–dimethylaniline) provide the possibility of observing magnetic field effects (MFE) detected by exciplex fluorescence on cage recombination of photoinduced radical-ion pairs (RIP). Applied external magnetic fields ($B \approx 10$ mT) affect the spin-correlated RIP, removing the degeneracy of their triplet sublevels, T_0 and $T_{\pm1}$. When the energy separation between them exceeds the size of the hyperfine interaction of unpaired electrons, $T_{\pm1}$ cannot mix with the singlet state S. Thus, external magnetic fields diminish the probability of intersystem crossing and, therefore, change the relative concentration of both the singlet and triplet states of the RIP. Singlet RIP concentration can be monitored through the intensity of the exciplex fluorescence produced during RIP cage recombination.

A characteristic feature of the above MFE is that paramagnetic species added to the reaction system affect the spin evolution of radical pairs *via* Heinsenberg exchange, leading to the diminution of MFE relative values detected (see, *e.g.*, ref. 2). In particular, for the pyrene–dimethylaniline system Chowdhury[3] observed quenching of the exciplex-fluorescence MFE by paramagnetic lanthanoid ions. Within the framework of the above model the diamagnetic alkali and alkaline-earth ions should not affect the MFE at all. Nevertheless, we found that diamagnetic metal ions affect the MFE detected by exciplex fluorescence in the pyrene–phenyl-aza-15-crown-5 ether system. This azacrown ether can be regarded as an analogue of dimethylaniline, in which methyl groups are replaced by the macrocycle. This seems promising since the introduction of crown ethers into the exciplex system allows the use of MFE techniques in the study of complex supramolecular aggregates.

In this preliminary report we consider the above fact based on the hypothesis that in such an exciplex system, paramagnetic species are produced through interaction of RIP with azacrown ether molecule complexed by metal ions, using as an example alkali ion Li$^+$ and alkaline-earth ion Ca^{2+}, which are interesting from a biological viewpoint.

The relative change of exciplex fluorescence $R(\mathrm{B}) = [F(\mathrm{B})/F(0)]^{-1}$ was detected at $\lambda \simeq 500$ nm under a steady-state regime with an accuracy of *ca.* 0.2% during the course of pyrene photoexcitation (*ca.* 300–400 nm). Magnetic fields applied to the sample were produced by Helmholtz coils ($B \leqslant 30$ mT). Samples were saturated by inert gas before measurements, which were carried out at room temperature. As a solvent we used a 35 vol.% acetonitrile mixture with benzene. A typical concentration of pyrene was *ca.* 10^{-4} mol dm^{-3} and 1-phenyl-4,7,10,13-tetraoxa-1-azacyclopentadecane (aza-15-crown-5), 10^{-2} mol dm^{-3}. For more details see ref. 4.

We found that in interaction with electronically excited pyrene molecules, azacrown ether can play the role of donor species in a manner similar to dimethylaniline, producing fluorescent exciplexes. This exciplex system is also suitable for observing exciplex-fluorescence MFE. The plots of the R values at $B = 30$ mT *versus* the concentration of metal salts added to reaction solution are shown in Fig. 1. It is worth noting that there can be a trivial reason for this MFE diminution. Having formed complexes with ions, azacrown ether molecules obtain higher ionization potentials and cannot quench electronically-excited pyrene. As a result, the yield of

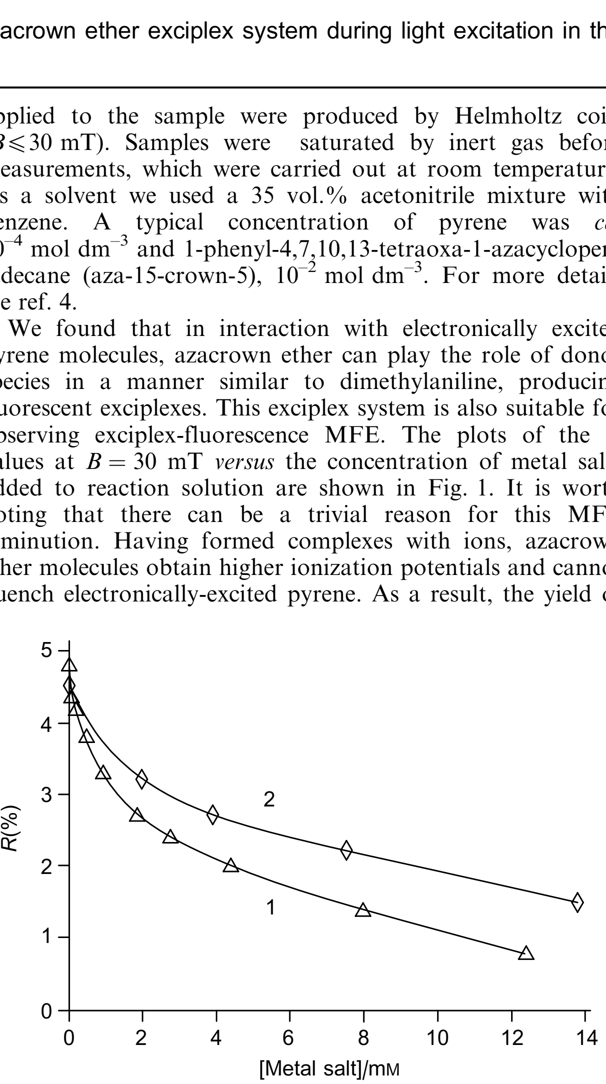

Fig. 1 The relative value of MFE, R, *versus* the concentration of metal salts added to the pyrene (phenyl aza-15-crown-5 ether) exciplex system in a 35 vol.% liquid mixture of acetonitrile with benzene: (1) Ca(ClO$_4$)$_2$; (2) Li(ClO$_4$).

exciplex fluorescence diminishes and observable MFE values become smaller. However, this is not the case. Using the definition of the stability constant K_s (for Li^+ and Ca^{2+} ions $\log K_s = 2.50$ and 3.72, respectively[5])

$$K_s = [Me^{n+}L]/[L][Me^{n+}],$$

and bearing in mind that

$$[L]_0 = [L] + [Me^{n+}L], \qquad (1)$$

where $[Me^{n+}L]$, $[Me^{n+}]$ and [L] are the molar concentrations of complexed cations, uncomplexed cation, and uncomplexed macrocyclic ligands, respectively; $[L]_0$ is the initial concentration of the latter, we can recalculate the relationships from Fig. 1 as a function of the concentration of complexed cations. As is seen in Fig. 2, the corresponding concentrations, at which *R* significantly diminishes, are *ca.* 3 mM. It follows from equation (1) that this value corresponds to *ca.* 7 mM of uncomplexed azacrown ether. On the other hand, the deficiency of the latter makes quenching of excited pyrene ineffective only at concentrations less than 3 mM. We confirmed this by direct experiment, decreasing the concentration of azacrown in the exciplex system without metal salt additives (see Fig. 3). Therefore, there should be another origin for the significant decrease in MFE caused by the addition of the salts.

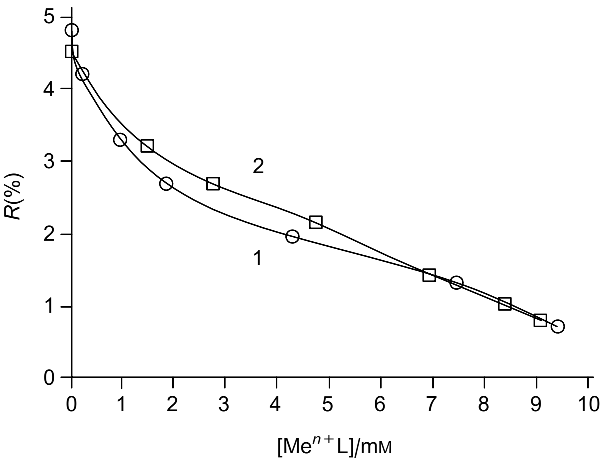

Fig. 2 The relative value of metal ions complexed by phenyl aza-15-crown-5 ether in a 35% liquid mixture of acetonitrile with benzene: (1) Ca^{2+}, (2) Li^+.

In ref. 6, stable organic radicals were used for quenching MFE in the pyrene–dimethylaniline system and it was found that the $B_{\frac{1}{2}}$ value (*i.e.*, the magnetic field at which half the MFE saturation value is observed) is approximately constant as a function of the stable radical concentration when MFE is significantly decreased. Here, we observe the same behaviour of $B_{\frac{1}{2}}$ for the pyrene–azacrown ether exciplex system. Thus, the magnetic field effect features observed indicate that paramagnetic species might be produced in the system employed.

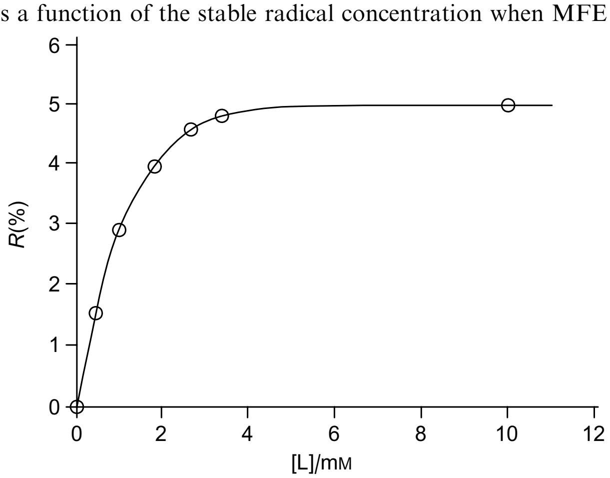

Fig. 3 The relative value of MFE, *R*, *versus* the concentration of phenyl aza-15-crown-5 ether without salt additives in a 35 vol.% liquid mixture of acetonitrile with benzene.

Grätzel and coworkers[7] observed the photoreduction of metal ions (silver, copper) complexed by azacrown ethers, which was ascribed to a direct interaction with photoexcited molecules present in the system (pyrene, cyanine dye). A similar process can be responsible for producing paramagnetic species in our case. However, in measuring fluorescence spectra of pyrene in the systems employed for various concentrations of metal salts added, we have found that electronically excited pyrene molecules are quenched by azacrown ether molecules rather than by $Me^{n+}L$ complexes.

Therefore, it is likely that paramagnetic species are produced through the interaction of azacrown ethers complexed by metal ions with RIP, which leads to the reduction of metal ions to paramagnetic species. By analogy with the process of sodium atom transfer in a dilute solution of sodium ketyl in the presence of benzophenone,[8] we suggest the following scheme:

$$L^{\bullet+} + (MeL)^{n+} \Longleftrightarrow L^{+} \ldots Me^{\bullet(n-1)+} \ldots L^{+} \Longleftrightarrow (LMe)^{n+} + L^{\bullet+}$$

The paramagnetic species produced are most likely to be metal atoms sandwiched by two crown ether cations. They need not be stable (their life time should be on the 10–100 ns scale, *i.e.*, comparable to the life of RIP), and can reduce the *R* value, through Heisenberg spin exchange with pyrene anion-radical, another partner of the pair (in the fashion outlined in ref. 1). After the above intermediate complexes decay, cation radicals $L^{\cdot+}$ can form RIP that are not yet spin-correlated, *i.e.*, insensitive to external magnetic fields. Thus, this hypothesis at least qualitatively describes the results obtained.

It is worth noting that use of binary solvents with components of different dielectric properties can facilitate the production of such paramagnetic molecular aggregates since in these solvents polar microdomains are generated in the vicinity of RIP during the course of light excitation,[9] diminishing coulombic interactions.

In conclusion, during the course of photoinduced electron transfer in the pyrene–azacrown ether system in the presence of diamagnetic metal ions, paramagnetic species are produced, which can affect MFE by exciplex fluorescence. The nature of these species needs further investigation.

We thank Dr. S. P. Gromov for placing aza-15-crown-5 ethers as well as lithium and calcium perchlorates at our disposal. This work has been supported by the Russian Foundation for Fundamental Research (project no. 93-03-4350).

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Received: Moscow, 13th July 1994
Cambridge, 31st October 1994; Com. 4/04477K