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Tuning of Photoinduced Energy Transfer in a Bichromophoric Coumarin Supermolecule by Cation Binding

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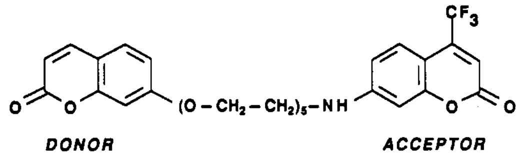
A bichromophoric molecule consisting of two coumarins linked by a pentakis(ethylene oxide) spacer can efficiently bind Pb^{2+} ions in acetonitrile and in propylene carbonate. The resulting changes in photophysical properties are reported with special attention to photoinduced electronic energy transfer. Steady-state data allow one to determine the transfer efficiency and stoichiometry of the complex, whereas subpicosecond time-resolved experiments by the excite-and-probe technique provide information on the transfer kinetics. The stoichiometry of the complex is 1:1 in acetonitrile and 1:3 (ligand:metal) in propylene carbonate. A significant increase in efficiency and rate of energy transfer for the complex is observed in acetonitrile, whereas there is almost no change in propylene carbonate. The results are discussed in terms of a possible structure of the complex which is different in the two solvents.

Introduction

Photoinduced energy transfer is a photoprocess of paramount importance involved in many fields: molecular and supramolecular photophysics, polymer physics, laser physics, biology, and molecular devices. Systems of particular interest are bichromophoric molecules containing a donor able to transfer its excitation energy to an acceptor linked to it by a spacer. Such supermolecules are well suited for the study of fundamental aspects of electronic energy transfer and for applications as laser dyes, frequency converters of light, and more generally, as molecular devices.[1] An interesting basic question arises as to whether it is possible to control and tune electronic energy transfer. Since this process is distance and orientation dependent, the rate of transfer can be modified by inducing changes in the mutual distance and orientation of the donor and acceptor moieties by means of an external perturbation acting on the spacer. Figure 1 illustrates two possibilities: (i) the spacer is a short chain able to form a complex with metal ions (e.g., polyether chains, or more generally chains containing O, N, or S atoms), and the external perturbation is the addition of a cation; (ii) the spacer is photoisomerizable, and the external perturbation is light. The supermolecule DXA described in this paper offers an example of the first case.



DXA

This supermolecule consists of two coumarins linked by a short flexible chain (pentakis(ethylene oxide)) capable of complexation with cations; the spacer is indeed an open-chain ligand of the crown type (podands).[2] The emission spectrum of the coumarin donor strongly overlaps the absorption spectrum of the coumarin acceptor so that efficient electronic energy transfer is possible after optical excitation. In previous papers, we reported studies of the distribution of interchromophoric distances by means of conformational calculations,[3] and steady-state[3] and time-resolved[4] energy-transfer experiments. Here we report the photophysical changes induced by cation binding with special attention to electronic energy transfer. A preliminary account was published recently.[5]

Materials and Methods

Materials. The synthesis of DXA was previously described.[3] As model compounds, 7-ethoxycoumarin and coumarin 500 were used for the donor and acceptor moieties, respectively.

Lead perchlorate ($Pb(ClO_4)_2{\cdot}3H_2O$) from Aldrich was kept in vacuum. Acetonitrile (spectroscopic grade) was purchased from Janssen. Propylene carbonate was from Aldrich and doubly distilled prior to use.

Preparation of Solutions. A stock solution of DXA ($1-2.5 \times 10^{-5}$ M) in acetonitrile or propylene carbonate containing a supporting electrolyte (tetraethylammonium perchlorate, 0.1 M) was prepared at the appropriate optical density (0.15–0.45). Part of this solution was taken, and lead perchlorate ($Pb(ClO_4)_2{\cdot}3H_2O$) was added to a concentration of 1.2×10^{-2} M in acetonitrile and 6.2×10^{-2} M in propylene carbonate. This solution of Pb^{2+} was gradually added by means of micropipets to 2 mL of the stock solution of DXA directly into the cuvette. In this way, the concentrations in DXA and supporting electrolyte were kept constant.

Instruments. The absorption spectra were recorded on a Kontron Uvikon 940 spectrophotometer. The corrected emission and excitation spectra were measured on a SLM 8000C spectrofluorometer.

Transient absorption spectra were recorded with a laser system combining an excimer laser with a colliding-pulse mode-locked (CPM) dye laser. It produces pump pulses at 308 nm with pulse durations of less than 250 fs (fwhm), and pulses at 616 nm with less than 100-fs duration. The red pulses are used for the generation of the spectral continuum, which probes the transient absorption of the DXA after donor excitation by the short UV

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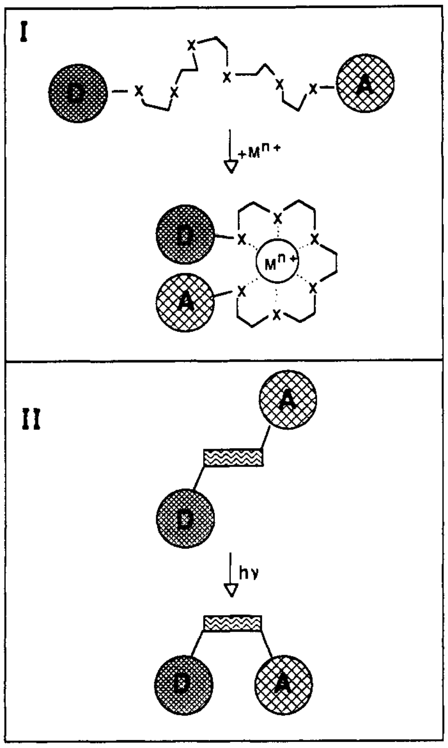

Figure 1. Illustration of possible mechanisms for the tuning excitation energy transfer.

pulse. The temporal evolution of the transient spectra, and thus of the acceptor excitation through intramolecular energy transfer, was followed by varying the delay between pump and probe pulses. For each setting of the relative delay, 100 separate spectra were recorded at 10 Hz and averaged numerically. Temporal resolution was better than 300 fs. Further details have been published in ref 6.

Determination of Transfer Efficiency. The transfer efficiency Φ_T can be determined by a comparison of the absorption and excitation spectra of the bichromophore.[7] In the case of total transfer ($\Phi_T = 1$), these two spectra are identical in shape. But for any value of Φ_T lower than 1, the excitation band corresponding to the donor is lower than the absorption band. The comparison of the absorption and excitation spectra can be made at two wavelengths, λ_D and λ_A, corresponding to the absorption maxima of the donor and the acceptor moieties, respectively. If there is no absorption of the donor at λ_A, combination of eqs 7 and 10 of ref 7 leads to

$$\Phi_T = \frac{A_A(\lambda_A)}{A_D(\lambda_D)}\left[\frac{F_A(\lambda_D)}{F_A(\lambda_A)} - \frac{A_A(\lambda_D)}{A_A(\lambda_A)}\right] \tag{1}$$

where A and F are the absorbance and fluorescence intensities, respectively; the wavelength of absorption or excitation is indicated in parentheses. By using 7-ethoxycoumarin, we confirmed that there is indeed no absorbance of the donor at the wavelength of maximum absorption of the acceptor. We used also the absorption spectrum of 7-ethoxycoumarin to resolve the absorption spectrum of the bichromophore into its donor and acceptor components in order to determine $A_D(\lambda_D)$ and $A_A(\lambda_D)$. Since there is no significant change in the absorption of the donor moiety upon cation binding, the same procedure was applied to the determination of $A_D(\lambda_D)$ and $A_A(\lambda_D)$ in the complex.

Determination of Stoichiometry and Stability Constant of the Complexes. The equilibrium

$$L + nM \rightleftharpoons M_nL$$

is characterized by the stability constant K_n of the complex defined as

$$K_n = \frac{[M_nL]}{[L][M]^n} \tag{2}$$

The absorbance of the initial solution of the free ligand is, at a given wavelength, λ:

$$A_0 = \epsilon_L(\lambda)\ lc_0 \tag{3}$$

where c_0 is the molar concentration in ligand, ϵ_L is its molar extinction coefficient and l is the optical path length (cm). After the addition of a given amount of salt, the absorbance becomes

$$A = \epsilon_L(\lambda)\ l[L] + \epsilon_{M_nL}(\lambda)\ l[M_nL] \tag{4}$$

At full complexation, we have

$$A_{lim} = \epsilon_{M_nL}(\lambda)\ lc_0 \tag{5}$$

These relations together with $c_0 = [L] + [M_nL]$ lead to

$$A = \frac{A_0 + A_{lim}K_n[M]^n}{1 + K_n[M]^n} \tag{6}$$

If the concentration in free cation [M] is much larger than that of the complexed cation, [M] can be replaced by the overall concentration in cation c_M:

$$A \cong \frac{A_0 + A_{lim}K_nc_M{}^n}{1 + K_nc_M{}^n} \tag{7}$$

The absorbance data were analyzed by using a nonlinear least-squares method for successive values of n. The correct value of n corresponds to the maximum of the correlation coefficient. The analysis also provides the stability constant K_n.

The efficiency of complexation in acetonitrile is quite high so that the assumption of a large excess of free metal ions with respect to bound ones is not strictly valid in the first part of the titration curve. We must then consider that the overall concentration in cation is

$$c_M = [M] + [ML] \tag{8}$$

For $n = 1$ (this is indeed the case for the complex in acetonitrile), it is easy to derive a more general relation by combining eqs 2–5 and 8:

$$A = A_0 + \frac{A_{lim} - A_0}{2c_0}[c_0 + c_M + 1/K_S - [(c_0 + c_M + 1/K_S)^2 - 4c_0c_M]^{1/2}] \tag{9}$$

The accuracy of the fit for the acetonitrile solution was improved by using this relation instead of eq 7 rewritten (with $n = 1$) in the form of the well-known relation

$$\frac{A_0 - A}{A - A_{lim}} = K_1c_M \tag{10}$$

Results and Discussion

Acetonitrile and propylene carbonate (PC) were chosen as solvents for this investigation because they are known to be favorable to the complexation of macrocycle ligands. We mainly report the results obtained with lead(II) cation. Comments on other cations will be given at the end of the paper.

Figure 2 shows the absorption and fluorescence spectra of the model compounds in acetonitrile. The absorption spectrum of DXA is virtually identical to the sum of the absorption spectra of the model compounds.

Cation-Induced Changes in Absorption, Excitation, and Emission Spectra. The changes in the absorption spectrum of DXA upon addition of Pb^{2+} observed in acetonitrile are shown in Figure 3. The acceptor band (maximum at 382 nm) undergoes a blue shift and a hypochromic effect. This can be explained by the fact that, in the complex, Pb^{2+} attracts the lone pair of the nitrogen atom and thus reduces its electron-donating character (anti-auxochromic effect). In contrast, there is no shift of the donor absorption band (maximum at 321 nm) but an increase in absorbance. This increase is only due to the shift of the underlying acceptor band because a compound consisting of the coumarin donor linked to the spacer, but without the acceptor moiety, exhibits no significant

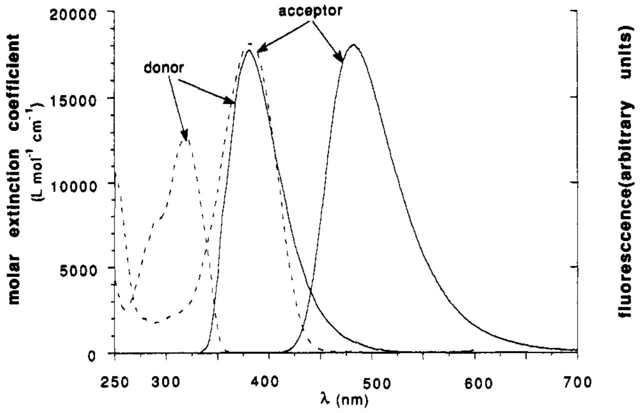

Figure 2. Absorption (- - -) and fluorescence spectra (—) of the model compounds for the donor (7-ethoxycoumarin) and for the acceptor (coumarin 500) in acetonitrile.

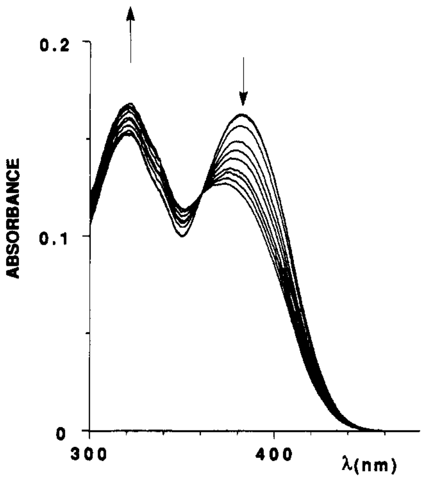

Figure 3. Changes in the absorption spectrum of DXA induced by the addition of lead perchlorate. The solvent is acetonitrile containing tetraethylammonium perchlorate (0.1 M) as a supporting electrolyte. The concentration in DXA is 1.0 × 10^{-5} M. The range of concentration of Pb^{2+} is 0–5 × 10^{-4} M. The temperature is 20 °C.

change in absorption upon addition of Pb^{2+}.

Regarding the emissive properties, a question arises as to whether the presence of Pb^{2+} in the supramolecular complex induces a heavy atom effect on the donor and acceptor moieties. Direct excitation of the acceptor at its maximum of absorption (where the donor does not absorb) permits a comparison of the quantum yield of the acceptor moiety in the free ligand and in the complex: the difference is less than 5%. Regarding the donor moiety, the compound consisting of the coumarin donor linked to the spacer, but without the acceptor moiety, undergoes a change in quantum yield of less than 5% upon addition of Pb^{2+}.

The emission and excitation spectra in acetonitrile are given in Figure 4 (the excitation spectra were recorded at an observation wavelength of 480 nm). The emission band of the donor moiety cannot be seen because the fluorescence quantum yield of 7-ethoxycoumarin (which is a good spectroscopic model for this moiety) is very low (8 × 10^{-3} in acetonitrile at 20 °C) and even lower in the presence of energy transfer. Upon excitation at 321 nm, i.e., in the donor absorption band, the addition of Pb^{2+} induces a blue shift and an enhancement of the acceptor emission band. The explanation of the blue shift of the acceptor absorption band also holds for the emission band. Regarding the enhancement, it is due to the increase in absorbance at 321 nm, and possibly to an increase in transfer efficiency as a result of the conformational changes of the bichromophoric molecule induced by complexation with Pb^{2+}.

The spectra in PC have already been reported[5] and show similar trends upon addition of Pb^{2+}. However, in the excitation spectrum, the changes in the donor band are less pronounced than in acetonitrile.

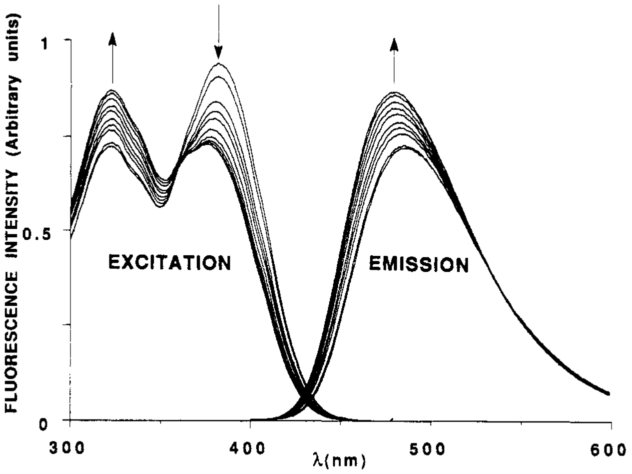

Figure 4. Emission and excitation spectra under the same conditions as those indicated in Figure 3. The excitation spectra are recorded at an observation wavelength of 480 nm. The concentration in DXA is 1.0 × 10^{-5} M.

TABLE I: Transfer Efficiencies Φ_T and Förster Radii R_0 of the Free Ligand and Complex

solvent		Φ_T[a]	R_0[b] (Å)
CH_3CN	free ligand	0.77	19.3
	complex (1:1)	0.89	18.3
PC	free ligand	0.86	21.6
	complex (1:3)	0.89	20.0

[a] Calculated according to eq 1 (accuracy 5–10%). [b] Calculated according to eq 11 with $\kappa^2 = {}^2/_3$. The donor quantum yield is 8 × 10^{-3} in acetonitrile and 1.5 × 10^{-2} in PC. The overlap integrals for the free ligand and complex are calculated according to eq 12. The standard error in R_0 is about 0.5 Å.

Cation-Induced Changes in Transfer Efficiency. In a previous paper,[4] we showed that time-resolved absorption measurements on DXA can be well described by a dipole–dipole interaction model (Förster's resonance transfer[8]) which takes into account a Gaussian distribution of intramolecular distances between the two chromophores. However, if complexation by Pb^{2+} results in a close approach of the chromophores, transfer according to the exchange mechanism may also occur in the complex.

The values of the transfer efficiency, defined as the fraction of excited donors that transfer their energy to the linked acceptor, are reported in Table I. The difference in behavior in acetonitrile and PC deserves further attention. It should first be noted that the transfer efficiency depends not only on the interchromophoric distance R, but also on the critical distance R_0, the distance at which transfer and spontaneous decay of the excited donor are equally probable. According to the Förster theory, R_0 is given by[8]

$$R_0^6 = \frac{9000(\ln 10)}{128\pi^5 N_A} n^{-4} \kappa^2 \Phi_{0,D} J \tag{11}$$

where n is the refractive index of the medium, N_A is Avogadro's number, $\Phi_{0,D}$ is the donor quantum yield in the absence of transfer, and J is the overlap integral:

$$J = \int_0^\infty F_D(\lambda)\, \epsilon_A(\lambda)\, \lambda^4\, d\lambda \tag{12}$$

in which the extinction coefficient, ϵ_A, of the acceptor is expressed in units of L·mol^{-1}·cm^{-1}, whereas the spectral distribution of the donor fluorescence $F_D(\lambda)$ is normalized so that

$$\int_0^\infty F_D(\lambda)\, d\lambda = 1 \tag{13}$$

κ^2 is an orientation factor arising from the relative orientation of donor and acceptor transition dipoles and can be given as a function of two angles:[9]

$$\kappa^2(\theta,\varphi) = (3 \cos^2 \varphi + 1) \cos^2 \theta \tag{14}$$

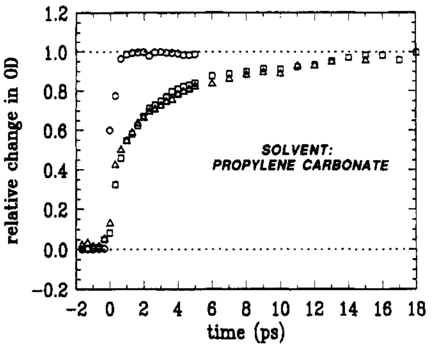

Figure 5. Experimental rise of acceptor gain at 500 nm for DXA (triangles) and its complex with Pb^{2+} (squares) in propylene carbonate. For comparison the "instantaneous" bleaching of DASBTI at 500 nm is indicated by the circles.

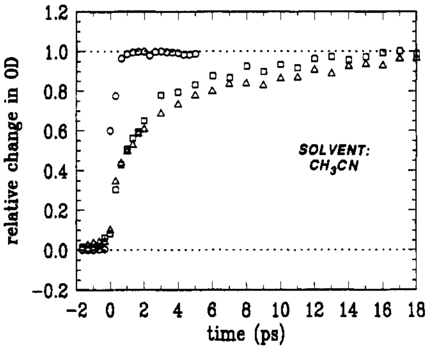

Figure 6. Experimental rise of acceptor gain at 500 nm for DXA (triangles) and its complex with Pb^{2+} (squares) in acetonitrile.

with $0 \leq \varphi$ and $\theta \leq \pi$. In the absence of Pb^{2+}, there is no preferred orientation of the acceptor with respect to the donor,[4] whereas randomicity of mutual orientation cannot be asserted in the complexes with Pb^{2+}, and calculation of κ^2 is not possible in the absence of information on the structure of the complexes. Nevertheless, it is of interest to calculate the value of R_0 with $\kappa^2 = {}^2/_3$ (usual dynamic average) only for looking at possible changes in R_0 as a function of the solvent nature and upon complexation. According to eqs 11 and 12, R_0 is solvent dependent through the overlap integral and the quantum yield of the donor (8×10^{-3} in acetonitrile and 1.5×10^{-2} in PC). The changes in the absorption spectrum of the acceptor moiety upon complexation affect R_0 through the overlap integral. The values of R_0 are reported in Table I. The fact that the transfer efficiency of the complexes in both solvents is the same within experimental error does not mean that the average interchromophoric distance is identical. This average distance is shorter in acetonitrile than in PC because R_0 is shorter in acetonitrile.

At first sight, the very slight change in transfer efficiency in PC is surprising because complexation is expected to reduce the distance between the donor and acceptor moieties and thus to increase the efficiency of transfer. This point will be discussed later.

Cation-Induced Changes in Dynamics of Energy Transfer. Figure 5 shows the rise of acceptor gain after excitation of the DXA bichromophoric molecule with a short UV pulse in PC for the free ligand and for the complex. As shown in a previous paper[4] the data were analyzed in terms of a distribution of interchromophoric distances. In the case of DXA the distribution could be well described by a Gaussian distribution. In PC the transfer kinetics is not significantly affected by complexation. This is consistent with the very slight change in transfer efficiency.

Figure 6 shows the rise of the acceptor gain of the DXA bichromophoric molecule in acetonitrile for the free ligand and for the complex. A faster transfer kinetics is observed for the complex which is consistent with the increase in transfer efficiency measured by stationary methods. It should be noted, however, that the transfer kinetics for the complex cannot be simulated by assuming a Gaussian distribution of interchromophoric distances. This suggests that the shape of this distribution is significantly altered in the complex.

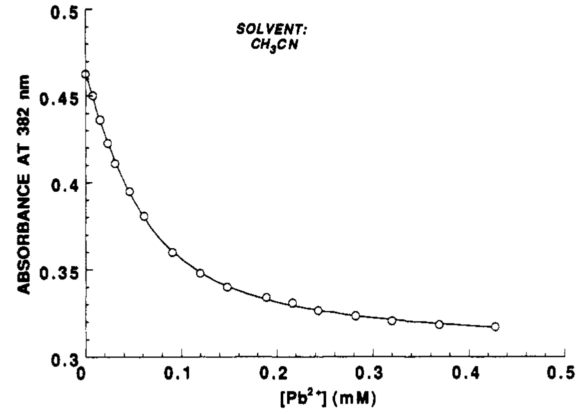

Figure 7. Variations in absorbance of a solution of DXA in acetonitrile at 382 nm as a function of the lead concentration (○). The concentration of DXA is 2.5×10^{-5} M. The solid line represents the best fit corresponding to a stoichiometry of the complex of 1:1 (eq 9). The correlation coefficient is 0.999 85.

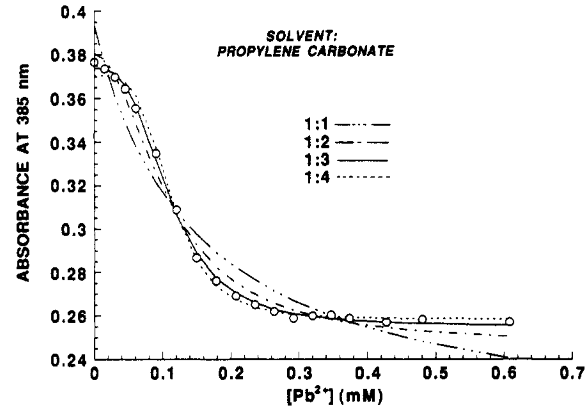

Figure 8. Variations in absorbance of a solution of DXA in PC at 385 nm as a function of the lead concentration (○). The concentration of DXA is 2.1×10^{-5} M. The solid line represents the best fit corresponding to stoichiometries of the complex of 1:1, 1:2, 1:3, and 1:4 (eq 7). The correlation coefficients are 0.972, 0.9946, 0.9993, and 0.9984, respectively.

Stoichiometry and Possible Structures of the Complexes. The stoichiometry of the complex can be determined from the changes in photophysical properties induced by cation binding. It turned out to be convenient to monitor the changes in absorbance at the wavelength corresponding to the absorption maximum of the acceptor band (382 nm in acetonitrile and 385 nm in PC). For the interpretation of the data, we consider the equilibrium describing the complexation with n metal ions per ligand:

$$L + nM \rightleftharpoons M_nL$$

The determination of n from the absorption data is described under Materials and Methods.

Figure 7 shows the variations of absorbance at 382 nm in acetonitrile. The stoichiometry of the complex is found to be 1:1, and the stability constant is 3.1×10^4 M^{-1}; it should be emphasized that this value is quite high and comparable to those observed with macrocyclic ligands. It is interesting to note that the stoichiometry of the complex is 1:1 but the transfer efficiency is not close to 1; therefore, the donor and acceptor moieties are not very close to each other, and helical wrapping of the ligand around one cation may explain the observations. Examples of such helical wrapping of acyclic ligands can be found in the literature.[2]

In contrast to acetonitrile, the sigmoidal shape of the titration curve observed in PC is remarkable and characteristic of cooperative binding (Figure 8). The best fit corresponds to a stoichiometry of 1:3 (ligand:metal ion), and the stability constant is 7.5×10^{11} M^{-3}.[10] The structure of the complex is likely to be helical, as often observed with oligoethylene glycol ethers.[2] Such

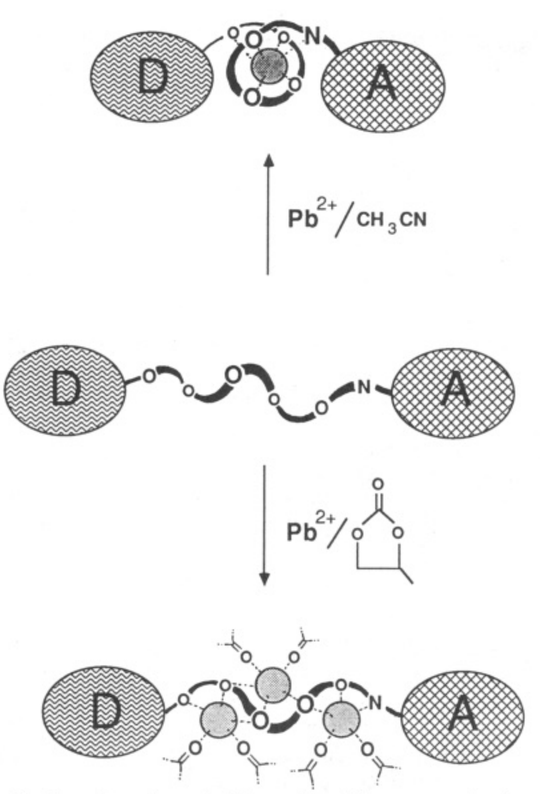

Figure 9. Tentative schematic illustration of the supramolecular complexes formed in acetonitrile and PC. D is the coumarin donor, and A the coumarin acceptor. The carbonyl groups of some PC molecules are also shown.

a structure is consistent with a slight change of transfer efficiency (Table I) and rate of transfer (Figure 5), because the spacer is very flexible[3] and the average center-to-center distance in the free ligand may not be very different from that in the complex which has an elongated form.

The difference in the structure and stoichiometry of the complexes in acetonitrile and PC may be explained by the possibility of PC molecules participating in the complexation through their carbonyl group. Water of crystallization of the salt and the perchlorate anion may also participate, whereas the carbonyl groups of the coumarins do not seem to be in a favorable position to be involved. Tentative schematic models of the complexes are shown in Figure 9; these models are consistent with the observations, but their uncertain nature should be stressed. Further studies are necessary to confirm these suggested structures. Comment should be made on the size of Pb^{2+}: its ionic radius is 1.18 Å, but it should be noted that Pb^{2+} probably has an active lone pair, and as such behaves as a very much smaller ion.[11]

Effects of Other Cations. The changes in photophysical properties upon addition of perchlorate salts of Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, and Ba^{2+} are very weak or insignificant owing to the very weak stability of the complexes. Silver perchlorate produces changes similar to lead perchlorate, but we observed a time evolution of the donor absorption band due to oxidation by silver ions, which precludes reliable studies. Addition of aluminum perchlorate leads to a drastic decrease in the acceptor absorption band without a significant shift. This effect is likely to be due to protonation of the nitrogen atom of the acceptor moiety resulting from induced acidity by Al^{3+} ions in residual water molecules of the solvent. Unfortunately, this masks possible effects due to complexation. Lanthanide ions were expected to be efficiently complexed by DXA, as previously reported with linear polyethers.[12] However, with Eu^{3+} we observed an effect similar to Al^{3+}.

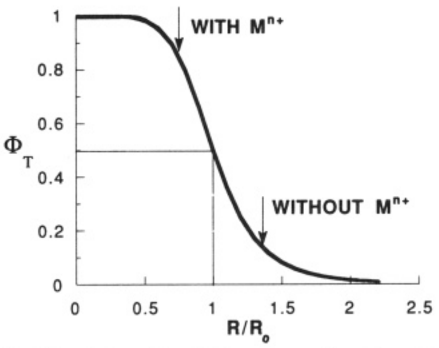

Figure 10. Variation in transfer efficiency as a function of the donor–acceptor distance. The arrows indicate favorable average distances before and after complexation for the tuning of transfer efficiency in a broad range.

Conclusion

Lead ions are efficiently complexed by the coumarin supermolecule DXA. This induces marked changes in the photophysical properties which can be used for recognition of lead ion. The structure of the supramolecular complex depends on the solvent. In particular, cooperative binding of three cations in PC is remarkable, and the resulting supramolecular complex is likely to be helical because there is only a slight change in transfer efficiency. In contrast, energy transfer efficiency in acetonitrile is significantly increased upon cation binding. It should be noted that a much broader tuning range could be obtained in systems where the average interchromophoric distance is larger than the Förster critical radius in the free ligand and lower in the complex. In fact, because of the sixth power of the ratio R/R_0 involved in the expression of transfer efficiency[8]

$$\Phi_T = \frac{1}{1 + [R/R_0]^6}$$

Φ_T varies drastically around R/R_0 (Figure 10). Therefore, a large change in transfer efficiency could in principle be observed with a relatively small variation in distance.

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