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Correlation of Exciplex Formation with Ground State Conformations in β-(1-Pyrenyl)ethyl Benzoates

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β-(1-Pyrenyl)ethyl p-cyanobenzoate (**P2CN**) which forms an emissive intramolecular exciplex has a "folded" conformation as detected by ^{1}H-NMR NOE. Precise decay lifetime analysis also confirms that the exciplex emission is mainly from that conformer. Exciplex emission was not observed for the p-chlorobenzoate (**P2Cl**) which did not show NOE.

Intramolecular exciplex emission of flexible molecules has been studied for a variety of combinations of donors **D**, spacers, and acceptors **A** such as amine-$(CH_2)_n$-pyrene, amine-$(CH_2)_nO(CH_2)_n$-pyrene, etc.[1] For these compounds, electron transfer from the donor to the acceptor in the excited state is followed by the approach of $\mathbf{D}^+$ and $\mathbf{A}^-$ to give exciplex emission, so that the certain length of lifetime of the excited state is required for exciplex formation.[2] Recently, Zacharisse reported that conformational analysis of 1,ω-dipyrenylalkanes by means of ^{1}H-NMR chemical shift reveals the presence of the "folded" conformation which is responsible for one of the three components of the emissive exciplex.[3] However, there are few studies of the relation between ground and excited state conformations of flexible bichromophoric compounds. We wish to report here preliminary results of our study on ground state conformation and photophysical behavior of β-(1-pyrenyl)ethyl p-substituted benzoates (**P2CN** and **P2Cl**).

The absorption and excitation spectra of both **P2CN** and **P2Cl** are essentially identical with equimolar mixtures of methyl 1-pyrenylmethyl ether and the corresponding methyl p-substituted benzoates. The ground state intramolecular interaction was excluded by the absence of new band at longer wavelength for the two.[4] On the contrary, their emission spectra showed striking difference. While **P2Cl** showed only emissions from the

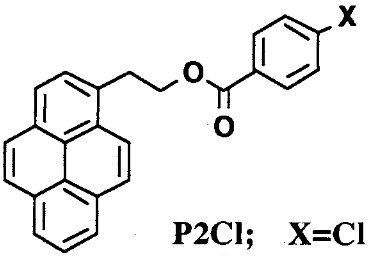

P2Cl; X=Cl
P2CN; X=CN

Table 1. Fluorescence Quantum Yields[a)]

Solvent	P2Cl	P2CN
Isooctane	0.26	0.078
Acetonitrile	0.19	0.006

a) Quantum yields for total emission.

pyrene chromophore in solvents of various polarity, structureless broad emissions from the intramolecular exciplex was observed in the longer wavelength region for **P2CN** in solvents of low and medium polarity as shown in Fig. 1. The solvent effects on the fluorescence quantum yields (Φ_f) reveal that electron transfer from the pyrene part to the benzoate part takes place more efficiently in **P2CN** than in **P2Cl** (Table 1).[5] The solvent-dependent emission maxima (ν/cm^{-1}) of **P2CN** showed linear correlation with solvent polarity parameter f(ε,n) as in Eq. 1. From the slope of the linear correlation, the excited state dipole moment (μ_{ex}) was calculated to be 14.6 D, by assuming ρ = 6Å. Since this value is within the range usually found for pyrene-amine intramolecular exciplexes, similar degree of charge separation presumably takes place in the excited state of the emitting species.

$$\nu = \nu_O - (2\mu_{ex}^2/hc\rho^3).\ f(\varepsilon,n) \qquad (1)^{6)}$$
$$f(\varepsilon,n) = (\varepsilon - 1)/(2\varepsilon - 1) - (n^2 - 1)/(4n^2 + 2)$$

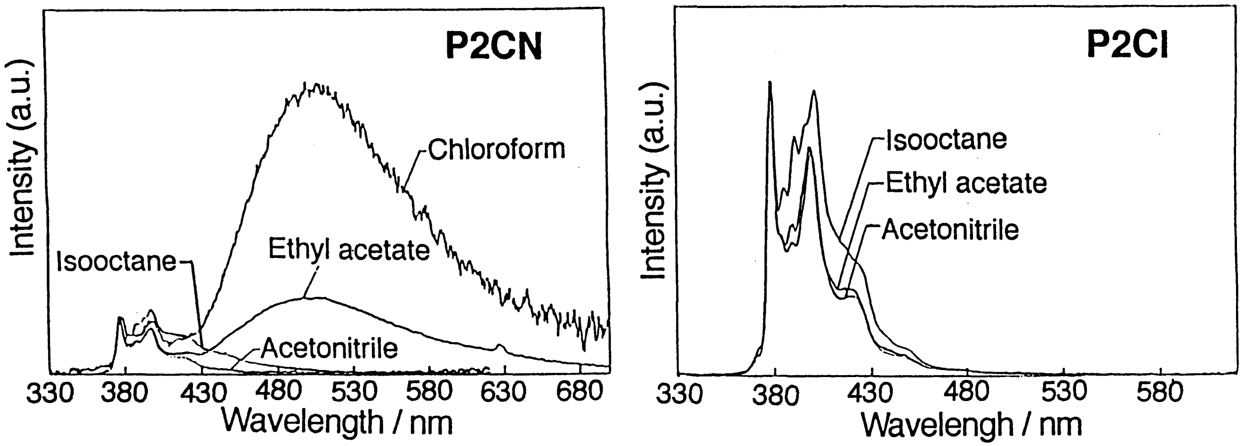


Fig. 1. Emission spectra of **P2CN** and **P2Cl** excited at 313 nm in different solvents at room temperature. The spectra were normalized at 377 nm.

Single photon counting (SPC) analysis of decay lifetimes (<1 ns) of **P2CN** in ethyl acetate, monitored at 370 nm, showed that there are two "locally excited" species whose lifetimes are 560 ps and 400 - 500 ps, respectively.[7] Another "locally excited" species with the lifetime of 80 ns was found by a SPC measurement of >1 ns time range. It was assigned to solvated ion pair (Scheme 1) since this species showed the lifetime of 150 ns in a strongly polar solvent, acetonitrile. On the other hand, an SPC measurement of the longer wavelength region (500 nm) was fitted with a single exponential giving the lifetime of 11.5 ns for the exciplex whose growing-in time (560 ps) was exactly the same as that of the one of the "locally excited" species.

^{1}H NMR NOE difference measurements were carried out to determine the ground state conformations. NOE was observed between the pyrene and benzene protons of **P2CN** as shown in Fig.2,[5] indicating the presence of "folded" conformation (in which p-orbitals of pyrene and benzene rings are more or less overlapped) as well as an "extended" conformation for the ground state **P2CN**. The results of both SPC and NMR NOE measurements prove that this "folded" conformer is exactly the one that is responsible for the exciplex emission of **P2CN** (Scheme 1). The loosely folded **D** and **A** of this comformer approach each other more closely to form the exciplex after excitation and internal electron transfer. The weak exciplex emission, observed in isooctane as a shoulder of the longest wavelength emission peak of the pyrene part,indicates the presence of the "folded" conformer even in solvents of low polarity. The excited state of the "extended" conformer is too short-lived to form exciplex by folding during its lifetime. On the other hand, **P2Cl**, for which exciplex emission was not observed,did not show NOE in any kind of solvents, suggesting that the "extended"conformations are more favorable for this compounds.

These NOE results indicate that the amount of donor-acceptor character also plays an importantrole for the ground state conformations. **P4CN** and **P4Cl** (four methylene chains between pyrene and benzoate) gave similar preliminary results and further studies are in progress.

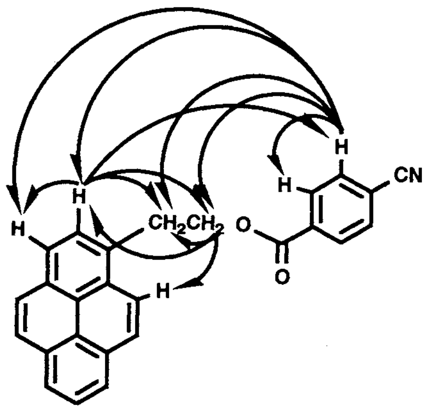
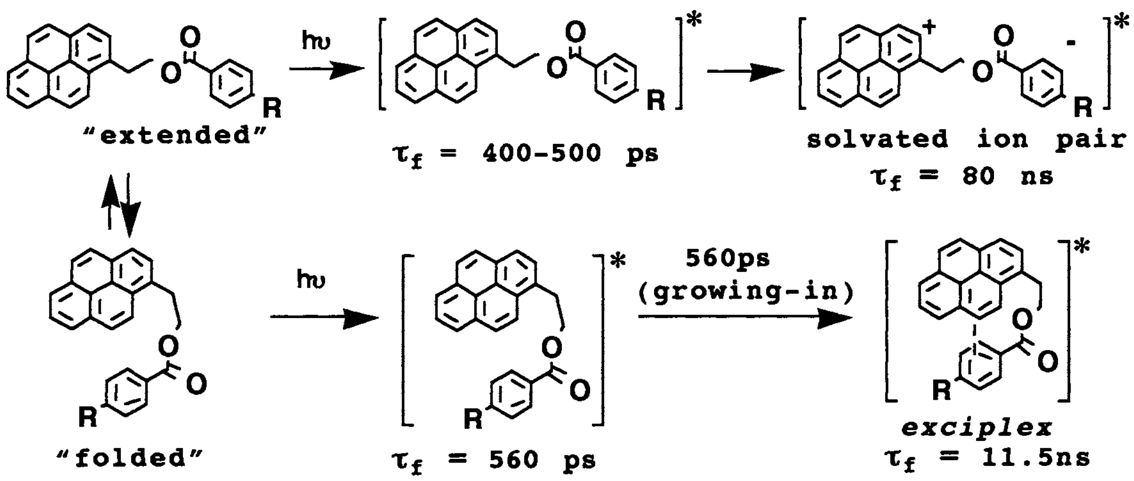


Fig. 2.



Scheme 1.

References

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2) J. W. Verhoeven,Pure Appl. Chem., **62**, 1585 (1990)

3) P. Reynders, W. Kühnle, and K. A. Zachariasse, J. Am. Chem. Soc., **112**, 3929 (1990).

4) A careful examination of the excitation spectra, which was suggested by the referee, showed that the shape and the relative intensity of bands remained unchanged irrespective of excitation wavelength.

5) $\Delta H°$,enthalpy for exciplex formation, is given by $\Delta H° = I_p - E_a - C - E_{0\text{-}0}(M^*) + \Delta H_{solv}$, where the parameters

have usual meaning. ΔH° for methyl 1-pyrenylmethyl ether either with methyl p-cyanobenzoate or with methyl p-chlorobenzoate was obtained to be -0.38 eV and 0.01 eV, respectively, from electrochemical measurements. Positive ΔH° value of the p-chlorobenzoate suggests that exciplex formation is difficult for **P2Cl**.

6) The parameters in Eq. 1 are as follows; ν_0, the emission maxima in vacuum; h, Planck's constant; c, the velocity of light; ρ, effective radius of solvent cavity; ε, dielectric constant of solvent; n, refractive index of solvent. The value of μ_{ex} was calculated from the slope in Eq. 1 by assuming ρ=6 Å.

7) Although the dacay curve obviously consisted of two components, thier lifetimes were too close to be analysed as consisting of two components under the present experimental conditions.

8) Positive NOE was observed in $CDCl_3$, CD_2Cl_2, and CCl_4. In CD_3CN, negative NOE was observed between pyrene 10-H, 9-H and benzene 4'-H. **P2CN** is assumed to have a similar "folded" conformation in ethyl acetate (ε=6.02), in which the SPC measurement was carried out, since the polarity of ethyl acetate is between $CDCl_3$ (ε = 4.80) and CD_2Cl_2 (ε = 8.93).

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