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Exciplex Formation of *rac*- and *meso*-2,4-Di(*N*-carbazolyl)pentane with *m*-Dicyanobenzene. Model Systems for Fluorescence Quenching in Poly(*N*-vinylcarbazole)

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ABSTRACT: *N*-Isopropylcarbazole, *trans*-1,2-di(*N*-carbazolyl)cyclobutane, and the two diastereomers of 2,4-di(*N*-carbazolyl)pentane, model compounds for poly(*N*-vinylcarbazole), were quenched with *m*-dicyanobenzene. The fluorescence spectra of *N*-isopropylcarbazole and *trans*-1,2-di(*N*-carbazolyl)cyclobutane in the presence of *m*-dicyanobenzene show a new emission band with a maximum at 410 nm. This band was assigned to the emission of a normal exciplex. The fluorescence spectra of *meso*- and *rac*-2,4-di(*N*-carbazolyl)pentane, model compounds respectively for iso- and syndiotactic sequences in poly(*N*-vinylcarbazole), in the presence of *m*-dicyanobenzene both show a new emission band, with a maximum at 510 and 460 nm, respectively. These bands, more bathochromic than that of the normal exciplex, are assigned to the emission of a triple excited complex formed between the respective excimers and a *m*-dicyanobenzene acceptor molecule. The excimer formed by the meso compound (total spatial overlap of carbazole chromophores) has better donor properties than the excimer formed by the racemic compound (partial spatial overlap of the carbazole chromophores).

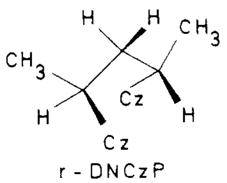
1. Introduction

Spectroscopic and kinetic studies of excited molecular aggregate systems in solution are among the most active fields of chemistry. Recently, there have been a number of reports concerning energy- and electron-transfer processes in micellar and polymer solutions, in biological cells, and in solid–liquid interfaces. For a detailed understanding, one should correlate the dynamics of these systems with the chromophore distribution and the configurational structure.

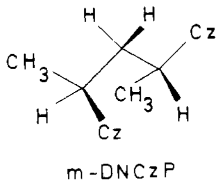
Studies on exciplexes with a structure (DDA)* composed of two donors and one acceptor and analogues $(D_nA_m)^*$ with higher aggregation number are necessary in addition to those of the normal exciplex (DA)*. Emission properties[1,2] and enhanced intersystem crossing[3] have been reported in a limited number of excited triple complexes (a complex, existing only in the excited state, consisting of three chromophores).

It has been pointed out that the fluorescence quenching of excited aromatic molecules and of their exciplexes obeys similar laws concerning a relation between quenching rate constant and free energy change due to electron transfer.[4] The polar electronic structure of the excited triple complex was directly confirmed by laser photolysis measurements. The absorption spectrum of the complex is reproduced by the superposition of bands of donor dimer cation and acceptor monomer anion.[5]

The occurrence of an excited triple complex was also suggested in quenching investigations of poly(*N*-vinylcarbazole) by dimethyl terephthalate.[6,7] In view of the structural inhomogeneity of poly(*N*-vinylcarbazole), adequate model systems for respective isotactic and syndiotactic sequences of this polymer were synthesized and their photophysical properties were reported.[8] *meso*-2,4-Di(*N*-carbazolyl)pentane (*meso*-DNCzP), the model for the isotactic sequence, gives the low-energy excimer, with total spatial overlap of the carbazole groups. *rac*-2,4-Di(*N*-carbazolyl)pentane (*rac*-DNCzP), the model for the syn-



r - DNCzP



m - DNCzP

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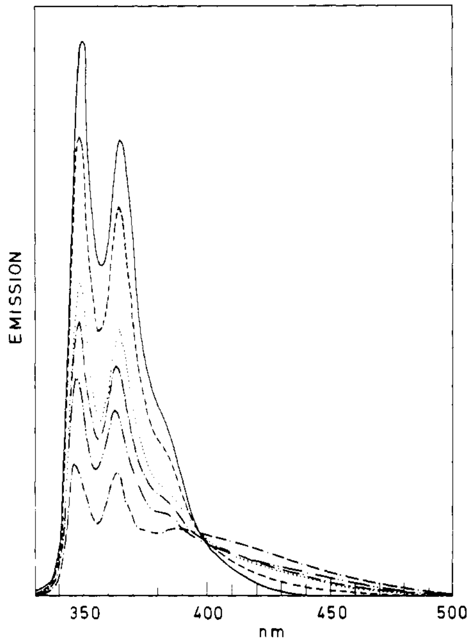
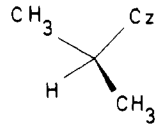


Figure 1. Fluorescence spectra of $\sim 10^{-4}$ M NIPCz–*m*-DCNB in di-*n*-butyl ether at room temperature: (—) 0, (---) 1.8×10^{-3}, (···) 4.7×10^{-3}, (-·-) 6.8×10^{-3}, (··-) 9.7×10^{-3}, and (--·) 1.8×10^{-2} M *m*-DCNB. $\lambda_{ex} = 320$ nm, $k_q = 1.1 \times 10^{10}$ M^{-1} s^{-1}.

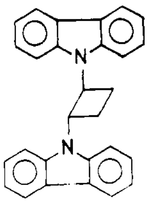
diotactic sequence, gives the so-called high-energy second excimer, which takes a geometrical structure with partial overlap between the two carbazole groups.[8] Here the spectroscopic aspects of the quenching reaction of these compounds are described.

2. Experimental Section

meso-DNCzP and *rac*-DNCzP are the same as used before.[8] *N*-Isopropylcarbazole (NIPCz) was purified by thin layer chromatography. *m*-Dicyanobenzene (*m*-DCNB) was purified by several recrystallizations and by sublimation in vacuo. *trans*-1,2-Di(*N*-carbazolyl)cyclobutane (*trans*-DNCzB) was kindly supplied by Professor S. Tazuke, Tokyo Institute of Technology, Japan. Di-*n*-butyl ether and ethyl acetate (Aldrich spectrophotometric grade) were used without further purification. Sample solutions were prepared to have a carbazole chromophore concentration between 10^{-4} and 10^{-5} M, eliminating intermolecular interaction in the ground and excited states. Fluorescence spectra were measured with a Fica-55 spectrophotofluorimeter and a Spex Fluorolog equipped with an emission corrector. Absorption spectra were measured with a Cary 17D. Time-resolved spectra were recorded with single-photon-counting apparatus.[9]



NIPCz



t-DNCzB

3. Results

A. Fluorescence Spectra. The quenching of NIPCz with *m*-DCNB in di-*n*-butyl ether leads to a new emission with a peak at 410 nm, as shown in Figure 1. Since its excitation spectrum is identical with the absorption spectrum of the carbazole chromophore and its energy is close to that of the charge-transfer fluorescence of the *N*-ethylcarbazole–*o*-dicyanobenzene system,[10] it is concluded that the present emission is due to an exciplex. The quenching rate constant at room temperature obtained by applying a simple Stern–Volmer plot equals $(1.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}.

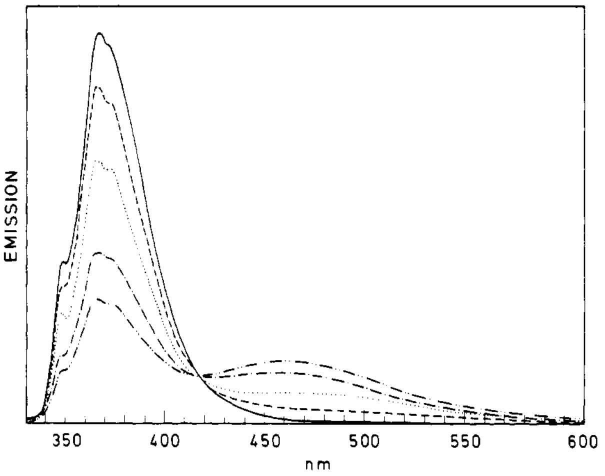


Figure 2. Fluorescence spectra of $\sim 10^{-4}$ M *rac*-DNCzP–*m*-DCNB in di-*n*-butyl ether at room temperature: (—) 0, (---) 7.8×10^{-4}, (···) 2.2×10^{-3}, (-·-) 6.5×10^{-3}, and (··-) 1.03×10^{-2} M *m*-DCNB. $\lambda_{ex} = 320$ nm, $k_q = 1.1 \times 10^{10}$ M^{-1} s^{-1}.

The *trans*-DNCzB–*m*-DCNB system in di-*n*-butyl ether behaves identically. There is a new emission with a maximum at 410 nm. The quenching rate constant at room temperature equals $(1.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}.

The emission spectrum of *rac*-DNCzP is composed of monomer fluorescence of carbazole (a shoulder at 347 nm) and the so-called second excimer (a peak at 370 nm) at room temperature. Their relative intensities correspond to a conformational distribution in the ground state.[8] This ratio is almost independent of the quencher concentration although the total fluorescence intensity is diminished (Figure 2). The apparent quenching rate constant for the second excimer is identical with that obtained for the NIPCz–*m*-DCNB system.

Since the fluorescence lifetime of the carbazole monomer and of the second excimer are almost the same (15–17 ns), these results suggest that both fluorescent states are quenched equally well. As shown in Figure 2, a new broad and structureless emission band was observed, with its maximum at about 460 nm. The excitation spectrum analyzed between 370 and 460 nm is the same as the absorption spectrum of *rac*-DNCzP, indicating the formation of a new complex between an excited-state configuration characteristic of *rac*-DNCzP complexed with *m*-DCNB. The band at 460 nm is due to an excimer–*m*-DCNB complex.

In order to obtain detailed information, the temperature dependence of this emission was investigated. As the temperature is changed from room temperature to 235 K, the fluorescence maximum shifts from 460 to 500 nm. This red shift can be related to the change of the dielectric constant of di-*n*-butyl ether since the latter value increases from 3 to 6 in this temperature range.[11] Ethyl acetate, whose dielectric constant is 6.08 at room temperature, was used as a solvent. The observation of the triple complex emission maximum at 520 nm in ethyl acetate substantiates this possibility. When the temperature is lowered from 293 to 253 K, the relative quantum yield increases 50% in this temperature range.

The emission spectrum of *meso*-DNCzP is composed of monomer fluorescence of carbazole and the so-called excimer emission (maximum 420 nm). Upon addition of *m*-DCNB in di-*n*-butyl ether, the excimer emission is quenched more efficiently than the monomer fluorescence

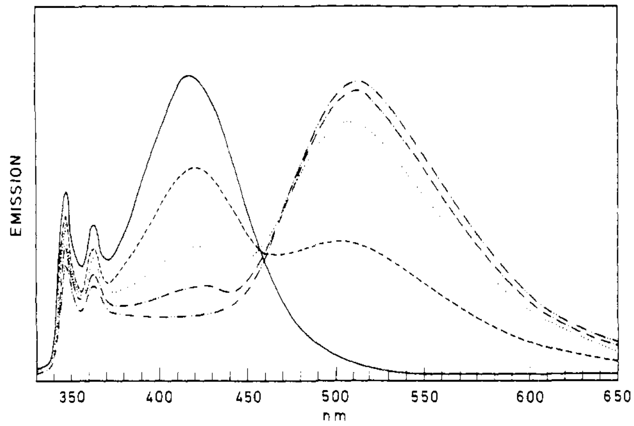


Figure 3. Fluorescence spectra of ~10^{-4} M *meso*-DNCzP-*m*-DCNB in di-*n*-butyl ether at room temperature: (—) 0, (- - -) 8×10^{-4}, (···) 2×10^{-3}, (-·-) 6×10^{-3}, and (··-) 1×10^{-2} M *m*-DCNB. $\lambda_{ex} = 320$ nm, $k_q = 1.2 \times 10^{10}$ M^{-1} s^{-1}.

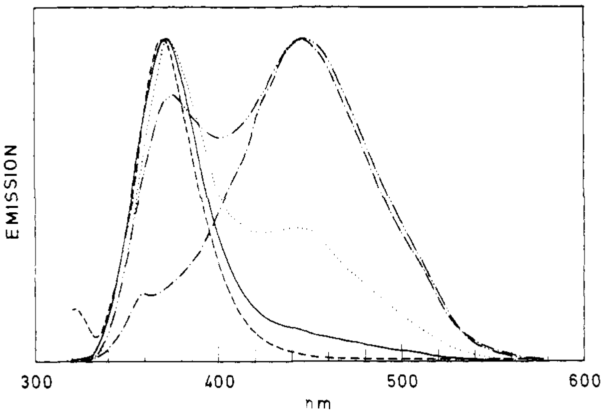


Figure 4. Time-resolved spectra of ~10^{-4} M *rac*-DNCzP–6×10^{-3} M *m*-DCNB in di-*n*-butyl ether at room temperature, normalized at maximum. Time window (0 = onset of lamp): (—) (A) 0–3.9, (- - -) (B) 34.5–44.5, (···) (C) 49.5–64.2, (-·-) (D) 69.6–84.8, and (··-) (E) 100–120 ns. $\lambda_{ex} = 320$ nm.

(Figure 3) and a new emission with a maximum intensity at 510 nm is discovered. The quenching rate constant at room temperature obtained by applying a simple Stern–Volmer plot is $(1.2 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}.

The excitation spectrum analyzed between 370 and 510 nm is identical with the absorption spectrum of *meso*-DNCzP, indicating the formation of a complex with a characteristic configuration of *meso*-DNCzP. The emission at 510 nm is due to a complex between the excimer and *m*-DCNB. When the temperature is changed from 293 to 235 K, the emission maximum of the new band shifts from 510 nm to approximately 530 nm. With ethyl acetate as solvent, the maximum of the new emission lies at approximately 560 nm.

B. Time-Resolved Spectra. The concentration of *m*-DCNB in di-*n*-butyl ether in the solutions used for time-resolved measurements is about 6×10^{-3} M. Figure 4 shows the time-resolved spectra of the *rac*-DNCzP-*m*-DCNB system in di-*n*-butyl ether. The second excimer is formed immediately after excitation (<1 ns, Figure 4A), although the shoulder at 347 nm disappears because of the low spectral resolution. After longer time settings the intensity of the excimer relative to the intensity of the excited triple complex decreases (Figure 4D,E). The diminishing contribution of the second excimer emission to the spectra suggests the absence of return to the second excimer from the excited triple complex.

The time-resolved spectra of the *meso*-DNCzP-*m*-DCNB system in di-*n*-butyl ether are shown in Figure 5.

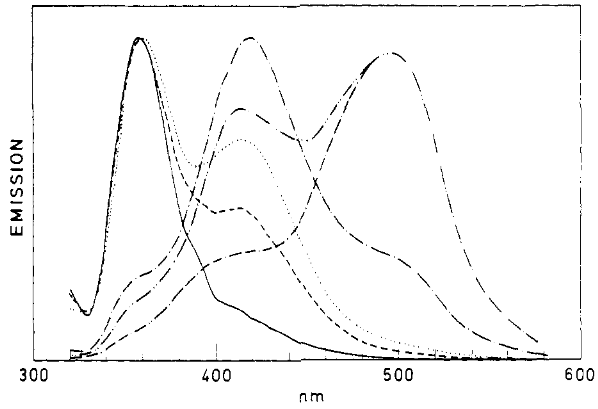


Figure 5. Time-resolved spectra of ~10^{-4} M *meso*-DNCzP–6×10^{-3} *m*-DCNB in di-*n*-butyl ether at room temperature, normalized at maximum. Time window (0 = onset of lamp): (—) (A) 0–4.9, (- - -) (B) 15.1–20.0, (···) (C) 31.1–41.7, (-·-) (D) 40.4–60.2, (··-) (E) 75.8–89.3, and (- - ·) (F) 110–140 ns. $\lambda_{ex} = 320$ nm.

First appears the emission of the locally excited carbazolyl group (Figure 5A). This is followed by the growing in of the excimer (Figure 5B,C). At this time the emission of the triple complex is already observed and this emission becomes the strongest one when the time window is chosen at longer times from the onset of the lamp (Figure 5D,E).

4. Discussion

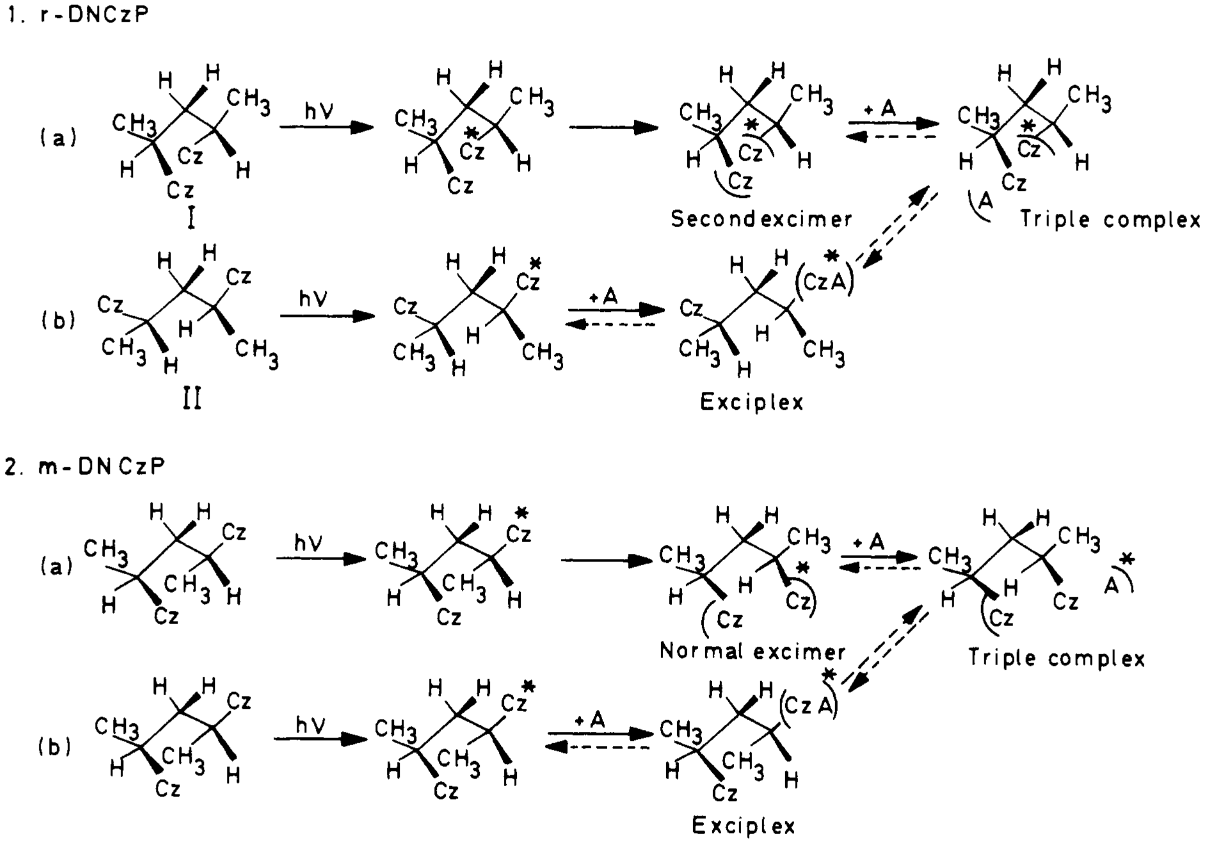
The two carbazole chromophores of *trans*-DNCzB have no mutual interaction in the ground and excited state because of its rather open form, and its absorption spectrum, fluorescence spectrum, and lifetime are identical with those of NIPCz.[12] Furthermore, the exciplex emission maximum of the *trans*-DNCzB-*m*-DCNB system is the same as that of the NIPCz-*m*-DCNB system. On the other hand, the results for the *rac*-DNCzP-*m*-DCNB and *meso*-DNCzP-*m*-DCNB systems are quite different, indicating that the peculiar geometrical structure of the two carbazole groups leads to a new fluorescent state, namely, an excited triple complex (DDA)*, which is different for the different excimer precursors. This polar electronic structure is directly demonstrated by the solvent effect on the emission maxima.

The idea of a polar structure is consistent with the results of other excited triple complexes, e.g., naphthalene-*p*-dicyanobenzene (*p*-DCNB),[1] β,β- and β,α-1,3-dinaphthylpropane-*p*-DCNB,[2] *p*-DCNB in α-methylnaphthalene,[5] and tetracyanobenzene in liquid donors.[5] Assuming for the different conformations of the excited triple complexes the same total spheric volume, a different dipole moment was found. μ^2/ρ^3 was obtained with eq 1,[13]

$$\nu = \nu_{\mathrm{vac}} - \frac{2\mu^2}{hc(4\pi)\epsilon_0\rho^3}\left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{4n^2 + 2}\right) \qquad (1)$$

where n is the refractive index of the solvent, ϵ_r is the dielectric constant of the solvent, μ is the dipole moment of the exciplex in the solvent, ρ is the radius of the solvent cavity, ϵ_0 is the permittivity of the vacuum, c is the velocity of light in a vacuum, h is Planck's constant, ν_{vac} is the maximum of the emission in a vacuum, and ν is the maximum of the emission in the solvent. The value of μ^2/ρ^3 of the *rac*-DNCzP-*m*-DCNB system is 2.7×10^{-29} C^2 m^{-1}. For the *meso*-DNCzP-*m*-DCNB system, 1.9×10^{-29} C^2 m^{-1} was found. This could indicate that the *rac*-DNCzP-*m*-DCNB excited triple complex is more polar than the

Scheme I



meso-DNCzP–*m*-DCNB excited triple complex.

Beens and Weller calculated the oxidation potential of the naphthalene dimer[1] using eq 2, where $E_{(D/D^+)}$ is the

$$E_{(D/D^+)} - E_{(DD/DD^+)} = \nu' - \nu'' \qquad (2)$$

oxidation potential of alkylcarbazole (1.12 V vs. SCE),[10] $E_{(DD/DD^+)}$ is the oxidation potential of the excimer, ν' is the exciplex maximum frequency, and ν'' is the triple complex maximum frequency. The oxidation potential obtained for the *rac*-DNCzP excimer was $E_{(DD/DD^+)}$ = 0.8 V (vs. SCE); for the *meso*-DNCzP excimer, $E_{(DD/DD^+)}$ = 0.6 V was found. These results could be explained by considering the conformation of the excimers. The "normal" excimer has a greater spatial overlap of the carbazole functions than the "second" excimer. Stabilization of a positive charge will be larger in the former system.

Concerning the formation process of the triple complex, Scheme I can be proposed. In Scheme I, I and II represent the conformation suitable and unsuitable for the second excimer formation, respectively. As described in the Results, experimental foundation for process 1a has been obtained. The monomer fluorescence of conformation II is also quenched by *m*-DCNB, leading to a normal exciplex state (DA)*. However, time-resolved spectral data do not show that this exciplex was obtained. This suggests that the formed (DA)* is quenched by the other D chromophore. It is difficult to obtain information about this process, since the contribution of this conformation is only 18% in CD_2Cl_2 at room temperature.[8]

Time-resolved data suggest pathway 2a being the most important one, although pathway 2b cannot be excluded since the quenching rate constant for monomer fluorescence and excimer emission quenched by *m*-DCNB is identical within experimental error.

From these data it is clear that quenching of respectively isotactic and syndiotactic sequences in poly(*N*-vinylcarbazole) can lead to different excited triple complexes.

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