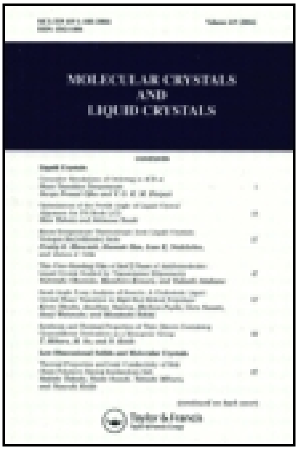

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Time Resolved Photoinduced Charge Separation in Pyridinium Substituted Anthryl-Methylenes and Anthryl-Polyenes

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TIME RESOLVED PHOTOINDUCED CHARGE SEPARATION IN PYRIDINIUM SUBSTITUTED ANTHRYL-METHYLENES AND ANTHRYL-POLYENES

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ABSTRACT

Intramolecular charge separation in the donor- bridge- acceptor molecule 4-(9-Anthrylmethyl)-N-methyl-pyridinium-tetrafluoroborate has been verified evolving in consecutive steps of excited states on sub-picosecond time scale. In the first step an excited anthracene intermediate and in the second an ionic anthracene state is formed, identified by its transient absorption. Instead, in systems with polyene as a bridge the formation of the anthracene radical state is modified by increased coupling strength of the molecular subunits.

1. INTRODUCTION

Photoinduced charge separation in molecules of the type donor-bridge-acceptor is a field of high current interest. The mechanism of charge separation, the nature of the charge-separated excited state and the contribution of the bridge to the process are of interest. As a first step, charge separation in molecules in solution are studied. The final goal of our work is to study these effects in rigid environment or in the solid phase.

We have studied previously the somewhat related problem of intramolecular transfer of energy in molecules with anthryl as donor and polyenes as bridge [1]. Charge separation using an anthryl group as acceptor, saturated hydrocarbons as bridge and dimethylaniline as donor has been reported already in [2], and with aromatic or non-saturated bridges in [3] and [4].

This work concerns molecules with anthryl as electron donor with two types of bridges, polyenes with π-bonds and methylene with σ-bonds, and two types of acceptors - pyridine and N-methyl-pyridinium, see fig 1. A time-resolved spectroscopic study is made of the influence of the bridge, its length and of the acceptor on the formation of the charge-separated state. By transient absorption spectroscopy with a time resolution of $\geq$100fs the excited and the charge separated state after pulse excitation of the donor are probed.

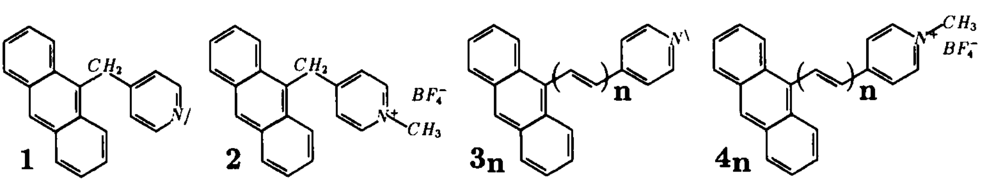

FIGURE 1 The molecules investigated: 4-N-pyridine and 4-N-methyl-pyridinium substituted 9-anthrylmethylene **1**, **2** and 9-anthryl-polyenes $\mathbf{3_n}$, $\mathbf{4_n}$ with n=1,3,5,7,9.

2. EXPERIMENTAL

We have studied the transient absorption spectra of the molecules shown in fig. 1 after exciting the donor part of the molecules, i.e. the anthryl-group, with a light pulse at 400nm. In addition, time-resolved fluorescence measurements were performed. All measurements were done at room temperature in solution, either n-hexane (molecules **1** and $\mathbf{3_n}$) or acetonitrile (molecules **2**, $\mathbf{4_n}$). For more details see [12].

3. RESULTS AND DISCUSSION

3.1 CH_2 as σ-bridge

In the transient absorption spectrum of the non-conjugated molecule **2** 9A-CH_2-4PyC, two consecutive excited states can be identified by their spectral and temporal behavior (fig. 2). Directly after the pulse excitation at 400nm the first transient absorption with maximum at 17500 cm^{-1} builds-up. This absorption can be attributed

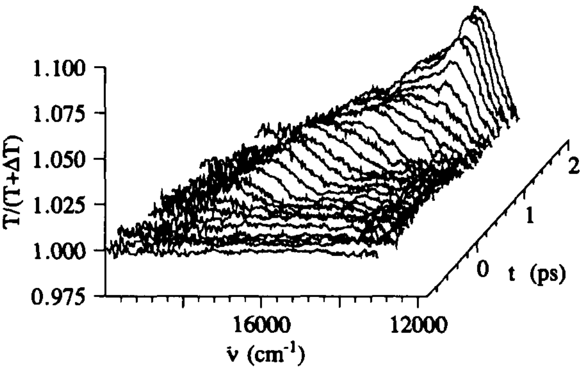

FIGURE **2** Transient absorption spectra measured as relative transmission T/(T+ΔT) of **2** 9A-CH_2-4PyC after excitation at 400*nm* (recorded in time intervals of 100*fs* and averaging 2000 pulses/spectrum).

to a higher singlet-singlet absorption S_1-S_n of anthracene [5], in other words a local excitation (LE). Its relaxation is superimposed by the build-up of a second transient absorption band which dominates the spectrum at longer times. The spectral characteristic of this absorption is attributed to a charge separated state (CS) due to its similarity with the absorption spectrum of an anthracene or 9-methyl-anthracene radical cation (fig. 3a), exhibiting, however, considerably broadened band-shape. The

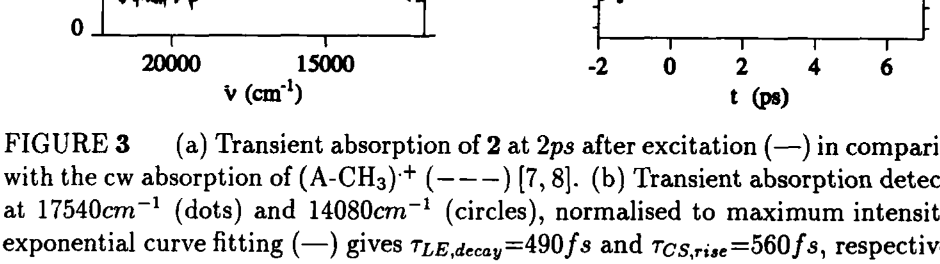

FIGURE **3** (a) Transient absorption of **2** at 2*ps* after excitation (—) in comparison with the cw absorption of $(A\text{-}CH_3)^{\cdot+}$ (– – –) [7, 8]. (b) Transient absorption detected at 17540cm^{-1} (dots) and 14080cm^{-1} (circles), normalised to maximum intensities; exponential curve fitting (—) gives $\tau_{LE,decay}$=490*fs* and $\tau_{CS,rise}$=560*fs*, respectively.

temporal behavior of the two transient absorption bands (fig. 3b) proves the dynamical coupling between the decay of the locally excited state $\tau_{LE_{decay}} \simeq \mathbf{490 \pm 40fs}$ and the charge separated state rise $\tau_{CS_{rise}} \simeq \mathbf{560 \pm 40fs}$. The charge separated state relaxes radiatively with a decay time of $\tau_{f,CS}$ = **1.1ns**, measured by time-correlated single photon counting.

On the other hand, the molecule **1**, this means with pyridine instead of pyridinium as substituent, was studied as a reference compound for which no charge separation is expected to occur on the basis of thermodynamic data ($E_{ox,anthracene} = +1.09eV$, $E_{red,pyridin} = +2.12eV$ [6]). In accord with this expectation no transient absorption other than that of the neutral anthryl group and a fluorescence lifetime of τ_f = **6.9ns** was measured. This shows that the locally excited state decays directly. With respect to this reference molecule and the rates given above the amount of charge separation on **2** 9A-CH$_2$-4PyC can be estimated to be **$\Phi \geq$ 98%**.

3.2 Polyenes P_n as π-bridge

All compounds **4_n** 9A-P$_n$-4PyC (n=1,3,5,7,9) exhibit only one transient absorption spectrum which builds-up with the system response and decays with $\tau_{n=1} = 65ps$ to $\tau_{n=9} = 1.8ps$ depending on n. A sequence of spectra for **4_9** 9A-P$_9$-4PyC in the time intervall 0...5ps is given in figure 4 as an example. The spectrum does not correspond to that of the anthracene radical ion. Upon increasing the polyene chain length between n=1 and n=9 the transient absorption shifts in energy. The measured spectral shifts, however, vary non-monotonically with n. In figure 5a, both, the maximum and the 1st. momentum of the transient absorption bands show a red-shift between n=1 and n=5 and a blue-shift between n=5 and n=9 (**from 17000 cm^{-1} to 13400 cm^{-1} and to 14600 cm^{-1}**, respectively). This pronounced dependence on the

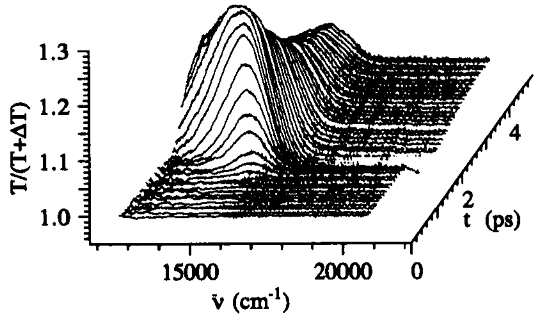

FIGURE 4 Transient absorption spectra measured as relative transmission T/(T+ Δ T) of 9A-P$_9$-4PyC (acetonitrile, T=295K). Recorded in successive time intervals of 100fs.

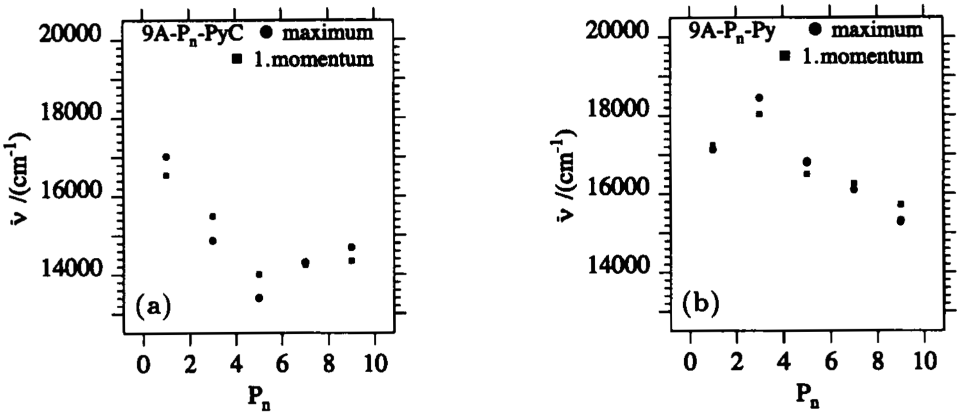

FIGURE 5 Chain length dependent energetic position of maximum and 1.momentum) of the transient absorption spectra (a) $\mathbf{4_n}$ 9A-P$_n$-4PyC (acetonitrile); (b) $\mathbf{3_n}$ 9A-P$_n$-4Py (n-hexane), T=295K.

polyene chain length indicates a distinct coupling between the polyene and anthryl electronic states in $\mathbf{4_n}$ 9A-P$_n$-4PyC. There is no clear evidence yet, for the formation of transient polyene radical cation states in $\mathbf{4_n}$ 9A-P$_n$-4PyC. The observed transient absorption spectra do not correspond to the ground state absorption of P_n^+ reported in the literature [10].

Moreover, when taking a similar series of transient absorption spectra for $\mathbf{3_n}$ as reference, again a different chain length dependence is obtained (fig. 5b), a blue-shift between n=1 and n=3, is followed by a monotonic red-shift up to n=9. The overall energetic energy shift is comparable to that shown in figure 5a.

At present, with regard to energetic position and band-shape of the transient absorption spectrum, only in the case of $\mathbf{3_1}$ 9A-P$_1$-4Py there is an evidence for a localised excited state on the anthracene subunit. For the molecules $\mathbf{3_3}$ ... $\mathbf{3_9}$, excitation is more delocalized on the polyene [11].

4. CONCLUSION

It has been shown that photoinduced charge separation in σ-bridged 9A-CH$_2$-4PyC can be identified by formation of the positively charged anthryl group. With a polyene-bridge of variable chain length, the positive charge is apparently not completely localised on the anthryl group but a mixed anthryl/polyene state is created. – So far, the transient absorption of the acceptor counterpart has not been identified spectroscopically.

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