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Intramolecular charge transfer in bipolar molecules for electron and hole transporting materials

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The excited state relaxation of 6-(9H-carbazole)hexyl-9,10,10-trioxo-9H-3-thioxanthenecarboxyl (CHTT) molecules containing electron donating and electron accepting groups was investigated in solutions by means of picosecond pump–probe absorption spectroscopy. The excitation energy and charge transfer between electrondonating and electronaccepting molecule fragments takes place under molecular excitation and determine the excited state relaxation dynamics.

Introduction

Charge transport materials are used in a number of organic optoelectric devices,[1,2] such as electrophotographic receptors,[1] light-emitting diodes,[3,4] organic field-effect transistors[5,6] and solar cells.[7,8] The hole transporting materials are relatively easily produced and are commonly used. The production of electron transporting materials[9–12] is more difficult. For many applications bipolar hole- and electron-, *i.e.* both charge, transporting materials are desirable.[13–15] The bipolar conductivity may be realized by incorporating molecular fractions with electron-donating and electron-accepting properties into the material molecules. In the ideal case, both fractions could be incorporated into a single molecule. Conductive layers having such molecules would always lead to the uniform distribution of electron-donating and electron-accepting fragments. However, synthesis of such molecules is more problematic. Furthermore their spectroscopic properties are more complex because of the interaction between the two fragments. This is particularly important for application of such materials in optoelectrical devices, where they function in light. Optical charge transfer states may be formed if the two molecular fragments are strongly coupled. The charge transfer may also take place under local excitation of one of the molecule fragments. Relaxation may be furthermore complicated in a solid state due to intermolecular exciton and charge transfer interactions.

Here we present steady-state and transient absorption study of solutions of bipolar molecules, synthesized for electron and hole transport materials. Here we focus on intramolecular processes as a first step of investigation of electronic properties of the bipolar charge transfer material. We show that intramolecular excitation and electron transfer, and the back electron transfer determine the excited state relaxation dynamics.

Experimental

N-Ethylcarbazole (*N*-EtCz) and 9-oxo-9H-tioxanthene-3-carboxylic acid 10,10-dioxide (OTC) were purchased from "Aldrich". *N*-EtCz was purified by recrystallization from benzene (mp 69–70 °C), OTC was recrystallized from tetrahydrofuran (mp 282–283 °C).

6-(9H-Carbazole)hexyl-9,10,10-trioxo-9H-thioxanthene–3-oate (CHTT) was prepared by the two step synthetic route including alkylation of 9H-carbazole with 1,6-dibromohexane and the following esterification of OTC with 6-bromohexyl-9H-carbazole obtained in the first step.

The chemical structures of the materials are presented in Fig. 1. Acetone, benzene and chloroform solvents were used for the preparation of solutions. All solvents were reagent grade and used without additional purification. The concentration of solutions was about 10^{-4} mol l^{-1} for time-resolved experiments.

The main experimental technique used was transient differential absorption spectroscopy with ps-time resolution. The measurements were carried out in the visible spectral range. The transient absorption study was performed using absorption pump–probe spectrometer equipped with a home-made low repetition rate (2 Hz) Nd^+:glass laser generating pulses of about 2-ps duration. The samples were excited by the third harmonic of the fundamental laser radiation (351 nm) and probed by the white-light continuum generated in a water cell. Transient absorption kinetics at a selected wavelength was measured by optically changing the delay time between the excitation and the probe pulses. Transient differential absorption spectra at fixed delay times were recorded by scanning the probe wavelength and simultaneously moving the delay line in order to compensate for the group velocity dispersion effect.

A Beckman UV 5270 spectrophotometer was employed for studies of the steady-state absorption spectra. The fluorescence

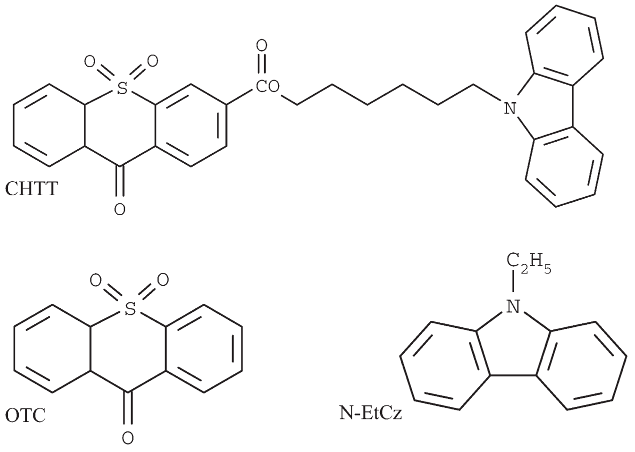

Fig. 1 Chemical structures of studied materials.

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(λ_{exc} = 350 nm) spectra were recorded on LS50B employing a Perkin Elmer luminescence spectrometer. The spectra were corrected for the instrument sensitivity. In order to avoid spectra distortion by reabsorption, the solutions used for luminescence investigations had an absorbance at absorption maxima of about 0.2 in a 1 cm cuvette. In this case the concentration of solution was about 10^{-5} mol l^{-1}. Solutions of CHTT in three different solvents were investigated. The CHTT molecules may be dissolved only in a limited number of solvents.

Results

The absorption and fluorescence spectra of CHTT, *N*-EtCz and OTC in acetone are presented in Fig. 2. Absorption and fluorescence spectra of CHTT and *N*-EtCz in benzene and chloroform are similar, whereas OTC molecules cannot be dissolved in these solvents. Absorption spectrum of CHTT molecules closely resembles the sum of the OTC and *N*-EtCz spectra indicating that the interaction between the two chromophores is relatively weak, so that it only slightly changes energetic positions of the ground and excited states of individual chromophores. No new absorption bands emerge in this case. One could expect the appearance of new bands due to the formation of optically allowed intramolecular or intermolecular charge transfer states. Such states are formed between chromophores having electronaccepting and electrondonating properties as is the case in photosensitive carbazolylcontaining polymers poly-*N*-vinylcarbazole or poly-*N*-epoxypropylcarbazole mixed with electronaccepting 2,4,7-trinitrofluorenone.[16–20]

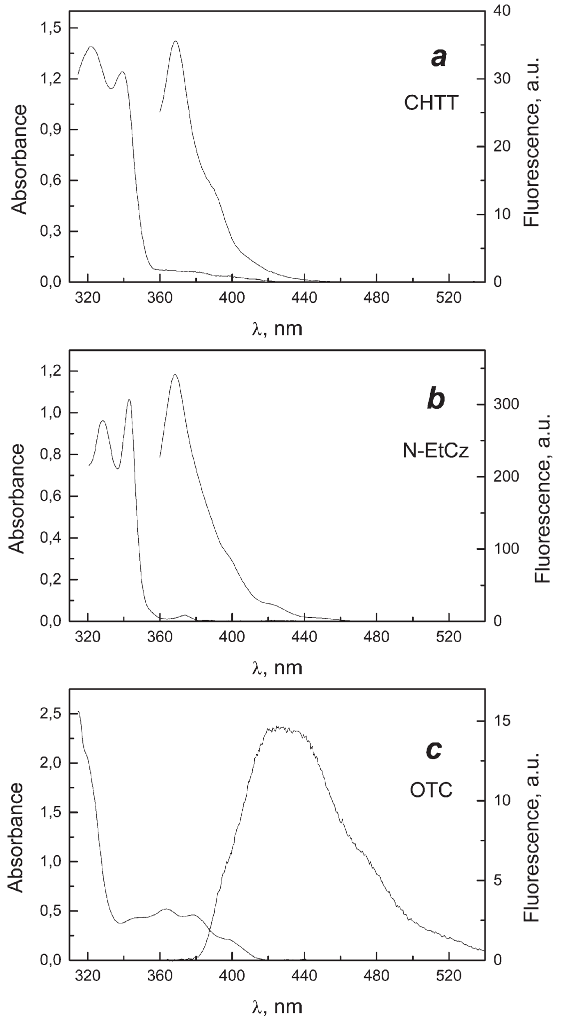

Fig. 2 The absorption and fluorescence spectra of CHTT (a), *N*-EtCz (b) and OTC (c) in acetone. Fluorescence was excited by 350 nm light.

It should be also noted that the absorption band at around 370–390 nm, observed in *N*-EtCz solutions, should be attributed to the residual antracene.[21] The anthracene molecules are an inevitable impurity in the *N*-EtCz synthesis.

Fluorescence spectra of CHTT molecules are independent of the excitation wavelength and are almost identical to the fluorescence spectra of *N*-EtCz. Fluorescence excitation spectra under detection at any fluorescence wavelength closely resemble absorption spectra of *N*-EtCz, however, the fluorescence yield of CHTT molecules is more than by order of magnitude lower. Fluorescence of the OTC fragment is completely quenched in CHTT molecules.

Fig. 3 shows the differential absorption spectra of CHTT and *N*-EtCz in the chloroform solution obtained at 0 and 200 ps delays after excitation at 351 nm. Since absorption and fluorescence spectra of both solutions are at shorter wavelengths than our investigation region, only excited state absorption was observed. At the 0 ps delay time, spectra of both solutions are quite similar. At the 200-ps delay time, the transient absorption spectrum of *N*-EtCz remains unchanged, while that of CHTT changes; the induced absorption at 650–820 nm increases. Later on the spectrum relaxes without changing its shape. The transient absorption spectrum of OTC was too weak for reliable measurements. It showed only a weak induced absorption below 700 nm. No transient absorption at longer wavelengths was observed. The transient absorption spectra of all compounds in benzene and chloroform are similar (not presented).

Transient absorption kinetics of *N*-EtCz and OTC in all solutions showed only weak decay during 1,5 ns indicating that excited state lifetime of these compounds is much longer than our investigation time domain. Transient absorption kinetics of CHTT in chloroform at different wavelengths is presented in Fig. 4. The kinetics shows two processes taking place on a picosecond time scale. The spectrum modification that is clearly evident in Fig. 3 occurs during the initial 100–200 ps. Later on, the differential absorption at all probe wavelengths decays exponentially with the same time constant. Thus, evidently the first process should be attributed to the formation of some intermediate species from the initially created excited state. The second process reflects the decay process of the produced intermediate state to the ground state.

Dynamics of the CHTT transient absorption depends significantly on the solvent. Fig. 5 shows the transient absorption kinetics of CHTT molecules at two probe wavelengths in three different solvents. Table 1 summarizes the time constants of the two processes and shows that the decay rate increases in more

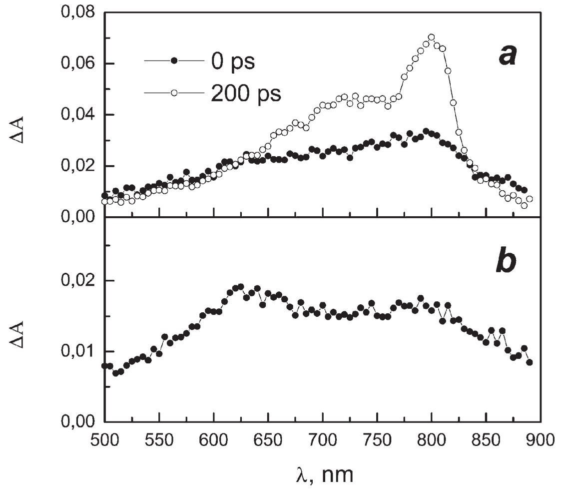

Fig. 3 The differential absorption spectra of CHTT (a) and *N*-EtCz (b) in chloroform obtained at 0 and 200-ps delay after excitation at 351 nm.

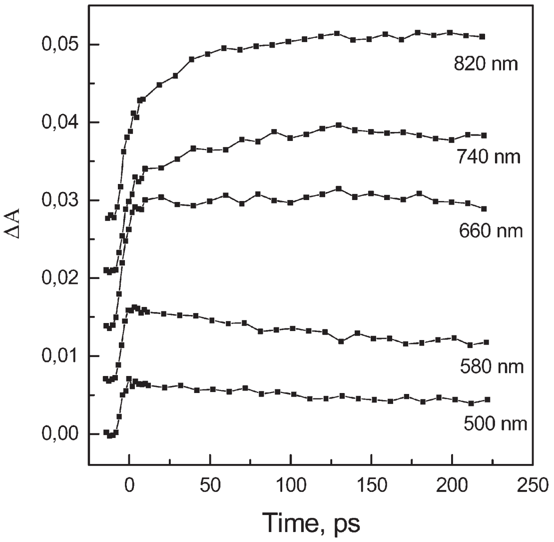

Fig. 4 The transient absorption kinetics of CHTT in chloroform at different wavelengths.

polar solvents, whereas the intermediate state formation rate within the experimental accuracy remains the same.

Kinetics at 800 nm in acetone is qualitatively different. The long-lived transient absorption component with the lifetime much longer than our investigation time domain is evident. Although determination of the lifetime of this component was not possible, it should be noted, that this component decayed completely during the 0.5 s time between laser pulses and no changes in the sample spectrum before and after experiment were observed. The insert to Fig. 5 shows a spectrum of the long-lived species. Similarly to the absorption of the transient photoproduct, the long-lived species exhibit an absorption maximum at about 800 nm, however, they do not absorb below 650 nm.

Discussion

According to the spectral position of the excitation pulse, and judging from the transient absorption spectrum at zero delay time, which is similar to that of excited *N*-EtCz, namely the *N*-EtCz fragment is predominantly excited by the 351 nm light, and the lifetime of this excited state in all solvents is about 60 ps. Similarity of the CHTT and *N*-EtCz fluorescence spectra confirm this assignment. Much lower fluorescence efficiency of the CHTT molecules as compared to *N*-EtCz is in agreement with much shorter lifetime of the initially created excited state than the lifetime of excited state of *N*-EtCz.

Judging from the absorption and fluorescence spectra positions, the lowest excited state of CHTT molecule corresponds to excitation of the OTC fragment, and one would expect a rapid excitation energy transfer from *N*-EtCz to the OTC fragment. However, a long spacer and a low transition dipole moment of the OTC fragment evidently slows down the energy transfer rate to at least 60 ps (the energy transfer rate is approximately proportional the product of transition dipole moments of energy-donor and acceptor).

Let us discuss the nature of the transient that forms with about 60 ps time constant. The absence of any fluorescence features of OTC fragment in CHTT spectrum provides no arguments to assign it to the excitation of the OTC fragment. The transient absorption spectra also show no indication of the population of the OTC excited state; excited OTC molecules show only very weak induced absorption and no induced absorption above 700 nm, whereas absorption of the observed transient is very strong in this spectral region. From the close similarity of the induced absorption spectrum, which appears with the 60-ps time constant with the absorption spectrum of *N*-EtCz cations reported in literature,[22,23] the transient species may be safely assigned to the charge transfer state. Owning to the electron donating and accepting properties of *N*-EtCz and OTC fragments respectively, excited state electron transfer from the *N*-EtCz to the OTC fragment is a very likely process. Then the relaxation process with a longer time constant should be assigned to the back electron transfer leading to the molecule relaxation to the electronic ground state The strong dependence of this relaxation rate on the solvent polarity is in line with this assignment. According to the Marcus theory, the electron transfer rate should depend on the difference between free energies of the initial and final states, which due to solvation processes is different in solvents of different polarity. Due to nonpolar nature of the initial state, the forward electron transfer rate may be less sensitive to the solvent

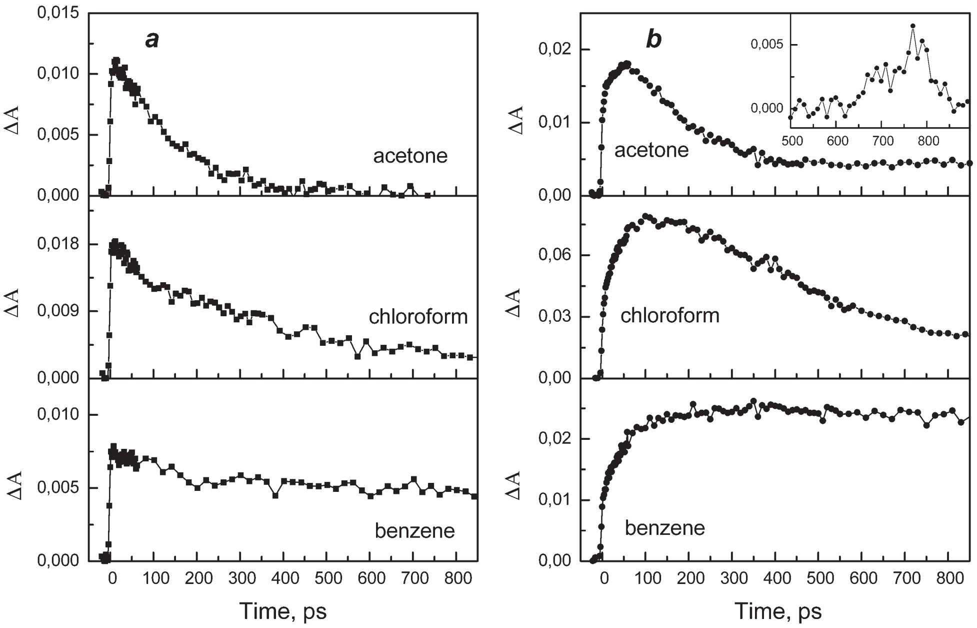

Fig. 5 The transient absorption kinetics of CHTT in various solvents at 600 nm (a) and 800 nm (b) wavelengths. The insert shows the differential absorption spectrum of CHTT in acetone at 800-ps delay.

Table 1 Time constants of relaxation processes in solvents

Solvent	ε	τ_1/ps	τ_2/ps
benzene	2.28	66 ± 3	7000 ± 1000
chloroform	4.81	64 ± 3	475 ± 10
acetone	20.7	56 ± 10	110 ± 10

polarity. However, almost equal relaxation rates in nonpolar solvent, benzene, and highly polar acetone, show that the 60 ps relaxation process cannot be identified with the electron transfer. It is more natural to relate it to the excitation energy transfer from *N*-EtCz to OTC fragment. As was shown in[24] the charge transfer in intermolecular charge transfer complexes may take place under excitation of electron-acceptor molecule. Such process is also typical for sensibilization of Cz containing polymers.[25] Thus, energy transfer from *N*-EtCz to OTC fragment may take place prior to electron transfer. If the energy transfer rate is slower than the subsequent electron transfer, then namely the energy transfer determines the charge transfer state formation kinetics. Since the energy transfer process is independent, or only weakly depends on the solvent polarity, the charge transfer state formation rate only weakly depends on the polarity as well. Population of the OTC fragment excited state in this case always remains negligible, what explains the absence of the OTC fragment fluorescence features in CHTT fluorescence spectrum.

The last relaxation process, the electron back-transfer, may be treated in terms of the Marcus electron transfer theory.[26] The energy of the charge transfer state should decrease in polar solvents due to the increase in the solvation energy. Thus, the difference between the charge transfer state and the ground state energies should diminish. In the "normal" electron transfer region, the transfer rate increases with increasing the energy difference between the reactant and product state. However, the back electron transfer in CHTT molecules evidently appears in the inverted Marcus region, and therefore shows opposite transfer rate dependence on the reaction free energy. Such dependence is typical of the electron transfer reactions with large reaction free energy and may be treated in terms of the energy gap law. Similar dependence of relaxation rates on the solvent polarity was typically observed in charge transfer complexes.[27]

Fig. 6 shows a schematic diagram of the excited state relaxation in the CHTT compound. After excitation of the molecule to the second singlet state S_2 corresponding to the excitation of the *N*-EtCz fragment, the energy transfer to the OTC fragment forms the S_1 excited state with the time constant k_1. Later on an electron is transferred from the *N*-EtCz fragment to the OTC fragment. The forward transfer appears in the "normal" region and is very fast, therefore, occupation of the S_1 state remains negligible and the population rate of the CT state is determined by the energy transfer rate k_1. The electron back transfer completes the relaxation process. Due to the large energy difference of the back transfer reaction, it appears in the inverted region. Therefore, the activation barrier decreases in polar solvents when the reaction energy decreases.

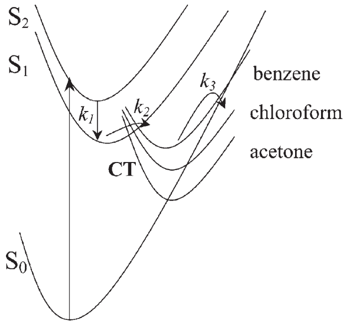

Fig. 6 Schematic diagram of the excited state relaxation of the CHTT compound.

The relaxation process in acetone solution is slightly more complex. Evidently only a fraction of molecules relax to the ground state on a picosecond time scale, whereas another fraction forms longer-lived transients, which disappear faster than over 0.5 s. The absorption spectrum of these transients in the 700–850-nm region is similar to the biradical state absorption, however, there is a difference at short wavelengths where the long-lived transients do not absorb. Judging from the absorption spectrum features of the long-lived transient, it should be also attributed to the *N*-EtCz cation radical. Probably some chemical reaction, like electron transfer between OTC chromophore anion radical and acetone or dissolved oxygen molecule competes with the intramolecular back electron transfer creating long-lived transients. Another possible mechanism may be related to the folding of molecules. If the molecules are folded so that the two fragments are close to each other, then under creation of the charge transfer state, solvation forces in highly polar solvent may unfold the molecule and stabilize the charge transfer state. This reaction needs additional investigation.

Conclusions

We have examined the photoinduced intramolecular charge transfer between electrondonating and electronaccepting fragments of the CHTT molecule in various solutions. The interaction between the OTC and *N*-EtCz chromophores is relatively week so that the chromophores retain their individual absorption properties, and the excitation energy transfer from the EtCz to OTC fragment is relatively slow, taking place on tens of picoseconds time scale. The charge transfer from the *N*-EtCz fragment to the OTC fragment occurs very rapidly after transfer of excitation energy to OTC fragment. The back transfer rate is much slower and strongly depends on the solvent polarity.

The photogenerated charge transfer states in the bipolar electron-hole transporting material produced from bipolar molecules may act as efficient charge carrier recombination centers. This should be accounted for in attempts to use such materials in electrooptical devices.

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