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Geminate charge pair recombination in sensitized photoconducting polymer

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Recombination kinetics of the geminate charge pairs, generated by photoexcitation of charge transfer (CT) complexes in sensitized poly-N-epoxypropylcarbazole, have been investigated by transient absorption and time-resolved fluorescence techniques and modeled by Monte Carlo method. The quantitative agreement of simulations with experimental data is obtained by assuming the distance between the thermalized charge pairs to be several times longer than the typical distance between electron donor and acceptor in CT complexes. Faster recombination is observed in the films with higher sensitizer concentrations and explained by assuming that electron acceptor molecules act as scattering centers for hole motion during thermalization, thus reducing the thermalization distance. The dynamical blue shift of the fluorescence band and comparison of hole density with fluorescence kinetics suggest that heterogeneity of CT complexes results in different radiative probabilities and in distribution of the initial charge pair separation distances. © *1999 American Institute of Physics.* [S0021-9606(99)51236-1]

INTRODUCTION

According to the present understanding of charge carrier photogeneration in organic photoconductors at least two steps can be distinguished in this complex process. A bound electron–hole pair is generated immediately after the light quantum absorption. Subsequent step of the charge separation driven by an applied electric field and temperature yields the free charge carriers.[1,2] The second step is quite adequately described by the Onsager theory. To obtain the agreement between theoretical modeling of the charge generation and the corresponding experimental data, the initial electron–hole separation of several nanometers should be assumed. However, charge separation, which can be created directly by the light quantum via excitation of the charge transfer (CT) state, usually occurs on the scale of a few Å only. Several models are suggested to explain the subsequent separation of charges against the Coulomb field attraction. By exciting a molecule to high electronic states, a very fast charge separation is explained by the well-developed autoionization–thermalization model, as driven by the excessive electronic energy.[1,3] The Noolandi–Hong model considers the charge tunnelling at large distances through the Coulomb potential barrier modified by an applied electric field.[4] The Kalinowski macrotrap model supposes that charge separation is achieved due to favorable structural peculiarities.[5] Sebastian *et al.* proposed that the environment polarization energy might be used to assist the charge separation at the relatively large, up to several tens of Å, distance.[6]

The photoconductivity of the sensitized polymeric compounds is observed by excitation of low energy CT states of the polymer–sensitizer complex. Almost two decades ago Yokoyama *et al.* studied the field-induced fluorescence quenching in poly-N-vinylcarbazole (PVK) films doped with tetracyanobenzene (TCNB).[7–9] The experimental data has been explained by assuming that the loosely bound ion pairs

with a separation distance $r_{th} = 30$ Å are created via thermalization of the higher excited CT state. Similar estimations of r_{th} were also obtained from photocurrent data.[10] The main idea of this explanation, based on the assumption that the charge generation proceeds from the nonrelaxed excited state, is similar to the above-mentioned autoionization–thermalization process. The charge separation driven by thermalization of the excess nonrelaxed exciplex state energy was also assumed by Itaya *et al.* on the basis of studies of the decay kinetics of the exciplex fluorescence and the ion pair absorption.[11,12] However, recent transient dichroism studies of the PVK oligomer solutions[13] and films[14,15] doped with sensitizer molecules led authors to the conclusion that only rather slow (competing with charge recombination) hole drift between the carbazolyl moieties takes place during 0.5–2 ns. It implies a negligible impact of the excess thermalization energy on the charge separation.

The impact of the structural disorder on the charge separation and recombination processes was demonstrated by Ries and Bässler by modeling the geminate pair recombination (GPR) kinetics by Monte Carlo approach.[16] Their investigations were directed to the long-time limit, and the GPR kinetics on the short-time scale as well as the initial charge separation mechanism were not considered. Recently the GPR kinetics in the sensitized PVK were investigated experimentally and modeled by the Monte Carlo simulations by Watanabe *et al.*[17,18] They also analyzed GPR kinetics in PVK doped with some scavenger molecules in order to estimate the charge separation distance. The energy disorder was concluded to be an essential and sufficient condition for the charge separation process. It was suggested that only the nearest-neighbor charge pairs were produced during the first step, while charge separation on subsequent steps was caused by the energy disorder. However, in order to get a reasonable agreement with the experimental data, a very broad distribu-

tion of site energy values (0.3 eV) had to be assumed. Moreover, the calculated hole scavenging efficiency was lower than the experimentally observed one.

In our previous article we presented the picosecond and femtosecond absorption and dichroism data which are relevant to the charge pair separation and recombination processes in oligomeric poly-N-epoxypropylcarbazole (PEPCz) films and solutions sensitized with electron-accepting 2,4,7-trinitrofluorenone (TNF).[19] It was shown that a dominating charge pair separation took place in a subpicosecond time domain.

In this work the picosecond absorption and fluorescence spectroscopy is applied to study the GPR kinetics in PEPCz with different TNF concentrations. The experimental data are analyzed by comparing the results with the corresponding Monte Carlo simulations. Absorption and fluorescence kinetics are explained by assuming an ultrafast initial long-range charge separation and by taking into account the CT state properties of the Cz–TNF complex.

EXPERIMENT

Recombination kinetics in PEPCz films doped with a typical electron-accepting substance, 2,4,7-trinitro-9-fluorenone (TNF), is considered. PEPCz is an oligomer with an oxygen atom in the main backbone and the carbazolyl (Cz) chromophore being somewhat further (by methylene group) removed from the main chain in comparison with the structural organization of PVK. Sensitized films were prepared by casting the solution onto glass substrates and drying for 5–6 h at 60 °C–65 °C. The film thickness, determined by the Linnik microinterferometer, was about 5μm. Films with different TNF concentrations were prepared.

Transient absorption spectra and kinetics were measured with 3 ps time resolution using a conventional pump–probe spectrometer based on a passively mode-locked, feedback-controlled, and regeneratively amplified Nd^{3+}: glass laser with 1 Hz pulse repetition rate. Samples were excited directly into the CT band (at 527 nm) by the second harmonic of the basic laser radiation, and the difference absorption was monitored by continuum light pulse at 760 nm. Kinetics was obtained for films with various TNF concentrations ranging from 0.5 to 30 mol %.

The fluorescence decay kinetics was measured by means of the single photon timing. The samples were excited at 593 nm by 15 ps duration pulses of the cavity dumped dye laser with 800 kHz repetition rate. The instrumental response function was about 100 ps.

RESULTS AND DISCUSSION

Hole density dynamics

The maximum of the longest wavelength absorption band of carbazolyl moiety is at 345 nm, while the TNF molecules absorb at ca. 390 nm. Absorption bands at 460 and 550 nm appear in PEPCz with the TNF admixture and are attributed to the CT states of Cz–TNF complexes (Fig. 1). Electron transfer from Cz to the TNF molecule in these complexes is initiated by 527 nm excitation light. The absorption band with maximum at $\lambda \approx 800$ nm resulted from the Cz cat-
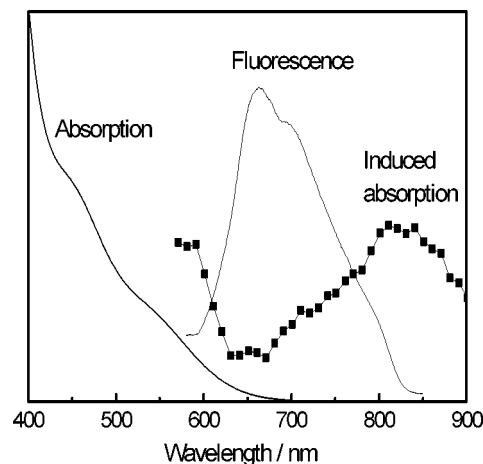

FIG. 1. Absorption, fluorescence (noncorrected for fluorimeter sensitivity), and zero delay time induced absorption spectra of PEPCz film with 2 mol % TNF concentration.

ion radical and the absorption at $\lambda \leq 600$ nm resulted from the TNF anion radical are induced by the excitation.[20] Spectroscopic properties of the charge pair in PEPCz films sensitized by TNF have been recently described in detail.[19] In particular, it was shown that the transient absorption kinetics measured in both these bands are identical and the transient absorption spectra do not change their shape in time. Thus, the kinetics of these induced absorption bands reflect the temporal evolution of Cz^+ and TNF^- concentrations, i.e., the generated electron–hole pairs regardless of pair separation distance. The light-induced absorption kinetics at 760 nm in PEPCz films with 0.5 mol % of TNF is shown in Fig. 2. The induced absorption, being proportional to the concentration of the Cz^+ cation radicals, is evidently nonexponential. A fast component approximately characterized by 150 ps decay time and a slow one in the nanosecond time domain are distinguished.
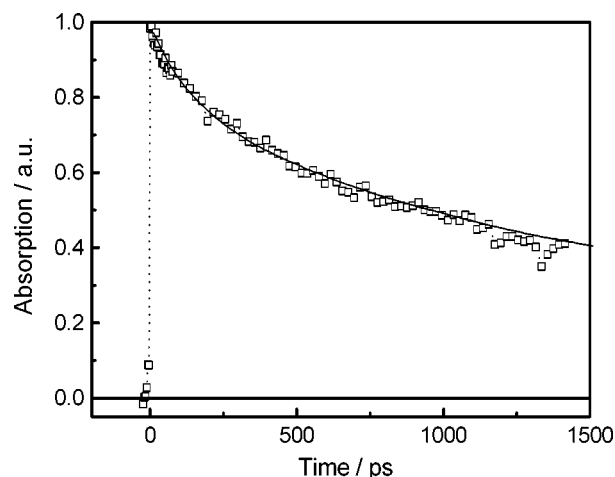

FIG. 2. Induced absorption kinetics measured at 760 nm in PEPCz film with 0.5 mol % TNF concentration (points). Solid line shows the Monte Carlo simulation results obtained with the following parameters: $\sigma_e = 0.09$ eV, $\sigma_{off} = 0.3$, $\eta = 0.7$, $r_{th} = 2.6$, $\tau = 50$ ps, $\tau_{CT} = 150$ ps.

Monte Carlo simulations

In order to describe the evolution of the hole density after the charge pair separation and the subsequent recombination with anion radicals, the Monte Carlo simulation of the hole diffusion and the recombination reaction was carried out. The starting approach is based on the cubic lattice (the lattice constant is $a = 6.8$ Å) containing two types of sites in the framework: the hole sites (for the hole motion) and the electron sites (for the electron motion). The diagonal (self-energy) and off-diagonal (positional) disorders of the lattice sites are taken into account. The basic principles of the modelling are similar to those developed by Ries and Bässler.[16] The main modification is inclusion of the Cz–TNF complexes into the model. Thus, the hole sites correspond to the bulk polymer chromophores–carbazolyls, while the electron sites are attributed to the sensitizer molecules. Electron transfer from Cz to TNF can occur only inside the complex by CT state excitation. The distance between TNF and Cz within the complex is assumed to be $r_{CT} = 3.5$ Å, which is a typical value for weak CT complexes. This formalism should be also valid in the case when only a part of TNF molecules create complexes, since the molecules not forming complexes cannot be excited by 527 nm light and, thus, give no contribution to the charge pair generation. After excitation into the CT state, the hole may be transferred away very rapidly before CT state equilibration, to other Cz creating the long-range charge pair, or to remain on the same Cz of the complex (CT pair). CT pairs recombine with the time constant τ_{CT}, which, according to experimental data, is equal to 150 ps.[19,21] For the sake of simplicity it is assumed that all the long-range charge pairs are separated by the same distance r_{th}. Thus, the initial distribution of the charge separation distances $n_0(r)$, i.e., the starting point for stochastic hole motion, is supposed to be a superposition of two δ-functions:

$$n_0(r) = (1 - \eta)\delta(r - r_{CT}) + \eta\delta(r - r_{th}), \qquad (1)$$

where η expresses the yield of the long-range charge pairs. The CT complex size r_{CT} is taken into account by assigning the special value of the hole energy to the electron site: $\varepsilon_{CT} = q/r_{CT}$ (where $q = e^2/4\pi\varepsilon\varepsilon_0$). It is also supposed that the hole is restricted to move only over the hole sites and it is not allowed to occupy the electron site unless the electron is currently present on this electron site. The other parameters used for modeling are selected to be close to the real PEPCz in the solid state, i.e., the cubic lattice constant $a = 0.68$ nm, which is equal to the mean distance between Cz chromophores in the solid PEPCz, and the dielectric constant of the system, $\varepsilon = 3$.[22]

The stochastic hole motion is described as a sequence of random jumps. The jump probability depends on the distance between two sites and the site energies. Thus the jump rate is

$$\nu_{if} = \nu_0 e^{-2\gamma|\vec{r}_i - \vec{r}_f|} \cdot k_{if}(\Delta U), \qquad (2)$$

where ν_0 is a frequency prefactor, γ is a wavefunction overlap factor,

$$k_{if}(\Delta U) = \begin{cases} e^{\Delta U/kT}, \Delta U < 0, \\ 1, \quad \Delta U > 0, \end{cases} \qquad \Delta U = U_i - U_f \qquad (3)$$

where U_i and U_j are hole energies at lattice sites i and j, respectively. The hole energies are determined by the Coulomb interaction as well as by the energy disorder.

$$U_i = -\frac{q}{|\vec{r}_i - \vec{r}_e|} + \varepsilon_i, \qquad (4)$$

where $\vec{r}_e$ is the electron coordinate on the lattice, ε_i is the diagonal disorder of this site. By assuming the Gaussian shape of the site self-energy distribution, the width of the energetic disorder σ_e according to the Bässler estimation, was assumed to be equal to 0.09 eV.[23] The probability of the $i \rightarrow j$ jump is then given by

$$P_{if} = \frac{\nu_{if}}{\Sigma_{l \neq t}\nu_{il}}. \qquad (5)$$

An ordinary hopping process is described by the mean jump time τ in the ordered framework in the absence of opposite charge. Thus

$$\tau = \nu_0^{-1}\left(\sum_j \exp(-2\gamma|\vec{r}_i - \vec{r}_j|)\right)^{-1}. \qquad (6)$$

In the regular lattice the sum is independent of the index i. Thus, because of the direct correspondence between τ and ν_0 [Eq. (6)], τ was used as the basic time scale parameter.

Due to the Coulomb interaction, the hole finally occupies the electron site where the electron is currently present, resulting in their recombination with the CT complex recombination time τ_{CT}, or the hole can escape again to the bulk.

The overlap parameter of the wave function is assumed to be $2\gamma a = 10$ also according to the assumption of Ries and Bässler.[16] The mean hole jump time τ and the initial long-range charge pair separation distance r_{th} were obtained from the best fit with the experimental data.

As the first step we performed the Monte Carlo calculations by assuming that the yield of the long-range charge pairs is zero ($\eta = 0$), i.e., all charge pairs are initially separated within the CT complexes by $r_{CT} = 3.5$ Å. These calculations are similar to those presented in Refs. 17 and 18. However, the latter model[17,18] was more simplified as the existence of the CT complexes was not taken into account, i.e., the initial charge separation distance was assumed to be equal to the lattice constant $a = 6$ Å. A good agreement between the experimentally determined hole density decay and the calculation data was demonstrated,[17] which was obtained, however, by assuming quite a broad (0.3 eV) diagonal disorder.

The difference between the initial charge separation (in our case it is almost two times shorter) appeared to have a decisive influence on the calculation results. Practically no hole transfer from the CT complex was obtained in our calculations and, in contrary to the experimental results, the major part of the hole density decayed with 150 ps time constant. The Coulomb barrier at 3.5 Å distance of the initial separation appeared to be too high to be overcome even for a large disorder up to 0.3 eV being assumed. However, it should be noted that the accuracy of simulations is uncertain in the closest vicinity of the counterion. The point charge approximation for the Coulomb energy calculation for the
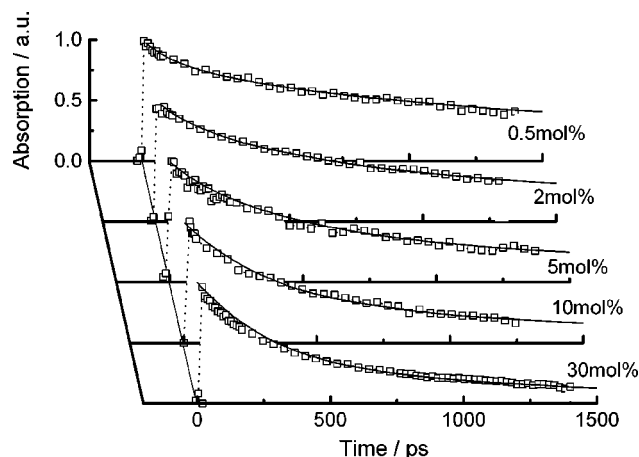
FIG. 3. Induced absorption kinetics in PEPCz films with different TNF concentrations measured at 760 nm (points). Solid lines show the Monte Carlo simulation results obtained with the following parameters: σ_e = 0.09 eV; σ_{off} = 0.3; η = 0.7; τ = 50 ps; τ_{CT} = 150 ps, and r_{th} equal to 2.6, 2.2, 1.9, 1.6, and 1.4 for TNF concentrations of 0.5, 2, 5, 10, and 30 mol %, respectively.

CT states is very rough since the distance between ions is close to the molecule dimensions. Moreover, the macroscopic dielectric permittivity ε probably cannot be directly applied to the microscopic distances.

A good agreement of the calculation results and the experimental hole decay kinetics measured in the film with a low concentration of the sensitizer (0.5 mol %) was obtained when the long-range charge pair yield was taken to be equal to 0.7, as estimated experimentally in our previous work[19] and by assuming the width of the diagonal disorder to be 0.09 eV in accordance with estimations of Bässler.[23] The relative width of intermolecular distance distribution σ_{off} (by assuming the Gaussian distribution function), corresponding to the off-diagonal disorder, was set to 0.3 a.[24] The fitting parameters, the initial long-range charge separation distance, and the mean hopping time, were obtained to be equal to r_{th} = 18 Å and τ = 50 ps.

Concentrational dependence

The induced absorption kinetics measured in the PEPCz films with various sensitizer concentrations is shown in Fig. 3. All the decays have a fast, approximately 150 ps, decay time component and a slow component being dependent on the sensitizer concentration. At low concentrations, 0.5 and 2 mol % of TNF, the kinetics is almost identical, but at higher concentrations the kinetics becomes faster. It indicates that sensitizer molecules starting from several mol % concentration exert influence on the charge pair recombination. No changes of the kinetics was observed at ten-fold changes of the excitation intensity. Since nongeminate pair recombination rate should be very sensitive to the concentration of the electron–hole pairs the nongeminate pair recombination can be ruled out. We examined two, to our opinion, most probable mechanisms of the concentration effect on the hole density decay kinetics: (i) the electron mobility over the sensitizer molecules, and (ii) the hole scattering by sensitizer molecules. Electrons can move in the sample by hopping via

the TNF molecules. When both charge carriers are mobile, they can approach each other and, therefore, speed up the recombination kinetics. Evidently, the electron mobility depends on distances between TNF molecules, therefore, this effect is feasible only at high sensitizer concentrations. However, the modeling results show that the electron mobility starts to play a substantial role only at very high sensitizer concentrations exceeding 30 mol %, when the direct contiguity of the electron sites becomes probable. Moreover, at very high sensitizer concentrations the hole mobility decreases due to lowering of the hole site density. Thus, the effect of the electron mobility on the recombination rate is too weak to explain the experimental dependence.

By analyzing the hole scattering by the sensitizer molecules we assumed that the sensitizer molecules create obstacles for the hole motion during the thermalization process, thus reducing the long-range charge pair separation distance. This assumption is based on higher electron affinity of sensitizer molecules, what prevents holes to be located on sensitizer sites. However, the scattering type as well as the scattering radius determining the hole scattering process and modification of the initial hole distribution remain unknown. Therefore, as the simplest approach we assumed that the separation distance is reduced preserving its δ-type distribution shape. The initial separation distance r_{th} is then the single fitting parameter, while other parameters remain the same as they are in the case of the low concentration. Figure 3 demonstrates the reasonable agreement of the simulation results with the experimental data. The separation distances obtained from the fitting are also presented there. However, these values should be assumed only as orientational ones, indicating the magnitude of the effect, since the δ-type distribution is evidently rough approximation even at low concentrations of the sensitizers. It should be noted that quite similar density decay kinetics were also obtained by means of the Monte Carlo simulation for different types of the initial distribution of the long-range charge pair separation distances. Thus, the density decay kinetics contains not enough information to make the decisive conclusion concerning the shape of the initial hole distribution.

Meanwhile, reduction of the separation distance caused by the hole scattering seems to be an obvious reason of an earlier observed saturation of the photosensitivity of the PEPCz-based electrophotographic films at high sensitizer concentrations.[25]

Fluorescence dynamics

The fluorescence kinetics of the PEPCz film with 2 mol % of TNF recorded at different emission wavelengths is shown in Fig. 4. Since both the Cz chromophores and the TNF molecules emit at shorter wavelengths, the observed fluorescence evidently originates from the radiative electron–hole recombination and its intensity (Φ) is related to the hole density dynamics by the following relations:
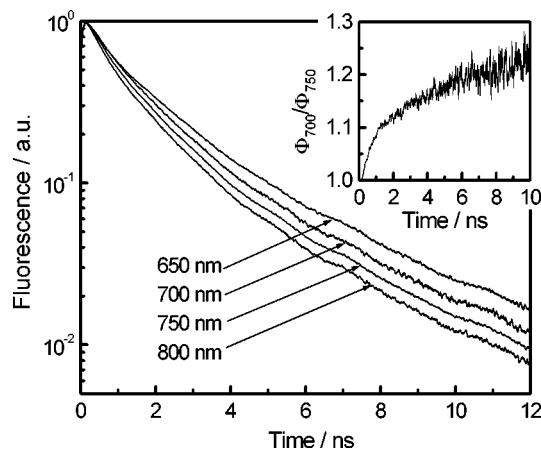
$$\Phi = \left(\frac{dn}{dt} \right)_r \qquad (7)$$

FIG. 4. Fluorescence intensity decays at different wavelengthes. Excitation wavelength was 593 mn. The insert shows the time dependence of the ratio of the fluorescence intensity measured at 700 and 750 nm.

$$\frac{dn}{dt} = \left(\frac{dn}{dt}\right)_r + \left(\frac{dn}{dt}\right)_w , \tag{8}$$

where n is the time dependent hole density. The first term on the right-hand side of Eq. (8) expresses the radiative, and the second one, the nonradiative recombination rates of the charge pairs. In the simplest case, when the ratio of the radiative and nonradiative recombination rates does not change in time, the fluorescence intensity Φ should be proportional to dn/dt. Such a relationship between the hole density and the fluorescence kinetics on a nanosecond to microsecond time scale was reported for PVK doped with 1,2,4,5-tetracyanobenzene.[26] The fluorescence kinetics at 700 nm and the first derivative of the simulated hole density dynamics are compared in Fig. 5 (the accuracy of the experimentally determined hole density kinetics is too low to obtain its derivative). The initial part of the fluorescence decay kinetics is significantly slower than that calculated from the simulated hole density kinetics, however, later it shows a good agreement with the simulation results, indicating that
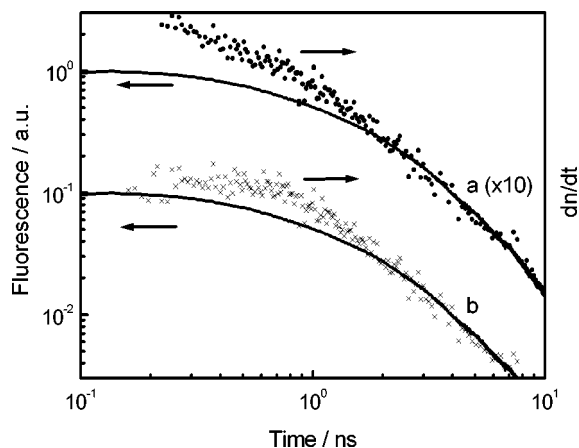

FIG. 5. Fluorescence intensity dynamics of PEPCz film with 2 mol % of TNF measured at 700 nm (solid lines) and the first derivative of the corresponding simulated hole density kinetics. The solid points correspond to the recombination of all the charge pairs (a), the crosses reflect the contribution of the long-range pair recombination (b).

the simulation results adequately describe the fluorescence kinetics on a time scale of tens of nanoseconds, which was out of range in the present pump–probe investigation. A significant disagreement in the initial time domain indicates that the ratio of the radiative and nonradiative decay rates changes in time. The nonradiative recombination prevails at short delay time, while later the contribution of the radiative decay increases. The constant ratio between the two recombination channels settles down approximately within 1–2 ns.

As evident from Fig. 4, the fluorescence intensity decays faster at longer wavelengths indicating the dynamic shift of the fluorescence band to the short wavelength side. The insert shows the time dependence of the ratio of the fluorescence intensity measured at short-wavelength (700 nm) and long-wavelength (750 nm) slopes of the fluorescence band (Fig. 1) approximately demonstrating the fluorescence shift dynamics. The spectrum shifts rapidly during the initial 1–2 ns, and the shift proceeds much slower during the subsequent 10 ns. The similar dynamical blue shift of fluorescence band was also reported by Itaya et al. in their study of the charge transfer fluorescence kinetics of the PVK doped with 1,2,4,5-tetracyanobenzene.[26] The fast fluorescence shift takes place approximately during the same time when the ratio of the radiative and nonradiative recombination rates changes. Thus, both these kinetic changes seem to be related to the same process. Itaya et al. explained the blue shift of the fluorescence as being caused by the heterogeneity of the system.[27] According to their explanation, CT complexes with slightly different parameters exist in the film and the charge pairs created from the different complexes show different recombination dynamics. The dynamical blue shift implies that the complexes characterized by the shorter wavelength fluorescence recombine slower, probably because the charge pairs with longer initial separation distance are created after their excitation. The observed dynamics of the radiative and nonradiative recombination implies that the complexes recombining later have higher probability to recombine radiatively. Itaya et al. determined that the exciplex fluorescence corresponds to the shorter wavelength, the higher fluorescence yield, and the longer decay time than the fluorescence from the CT complexes.[27] Thus, the short wavelength fluorescence of the Cz–TNF complexes show the features similar to those of the exciplex fluorescence. Therefore, it is reasonable to assign the short wavelength fluorescence to the Cz–TNF complexes with larger intermolecular separation and/or with a nonoptimal mutual molecular orientation. Such complexes may be considered as being an intermediate species between CT complexes and exciplexes. Excitation of these complexes create the CT states with larger distance of charge separation, that due to the lower Coloumb binding energy makes easier a long-range charge transfer. Consequently, long-range charge pairs with larger initial separation r_{th} are produced from complexes with larger r_{CT} and these pairs recombine later giving shorter wavelength fluorescence, while complexes with short r_{CT} produce mainly CT pairs which recombine mostly nonradiatively.

In order to verify the proposed mechanism by the Monte Carlo simulations, we used our simplified model with two types of complexes, yielding long-range pairs and CT pairs.

According to the proposed model, we assumed that the complexes producing CT pairs recombine only nonradiatively. The curve b in Fig. 5 shows the calculated fluorescence kinetics that corresponds to the recombination of initially produced long-range charge pairs. This kinetics much better resembles the experimental data, though complete agreement was not obtained probably due to the simplified model.

However, the higher fluorescence quantum yield of the large distance CT complexes and exciplexes is not obvious. It is known that only contact complexes possess a nonnegligible dipole moment for the optical CT transitions, while the nonradiative electron tunneling can take place over larger distances. However, the distance dependence of the radiative and nonradiative decay rates of CT complexes, which occurs in the inverted Marcus region, is still not clear. Therefore one cannot exclude the possibility that the nonradiative recombination rate increases faster than the radiative one when ions approach each other.

SUMMARY

The experimentally measured hole density kinetics in poly-N-epoxypropylcarbazole (PEPCz) sensitized with trinitrofluorenone (TNF) are considered on the basis of the Monte Carlo simulations. These simulations are performed by assuming that the charge separation by the light quantum appears within the Cz–TNF complex characterized by 3.5 Å intermolecular distance. Further hole transfer outside the CT complex over several carbazolyls may occur during its thermalization process. The two charge separation steps yield a complicated initial hole distribution, which is roughly approximated by two delta-functions. The subsequent hole motion is driven by temperature and the intrinsic disorder. A good agreement between the simulated recombination kinetics and corresponding experimental data was obtained with parameters determined in our previous work: the Cz–TNF complex relaxation time being equal to 150 ps and 70% yield of initial hole transfer.[19] The width of the diagonal disorder according to Bässler investigations[23] was assumed to be close to 0.1 eV. The long-range thermalization distance and the mean hole jump time were the fitting parameters and were obtained to be equal to 18 Å and 50 ps, respectively. Practically no hole escape from the CT complex can be achieved if the initial hole transfer is not assumed in the simulation; in this case the Coulomb barrier is found to be too high to be overcome even when a very broad distribution of diagonal disorder (0.3 eV) is assumed. Thus, our simulations confirm the assumption of initial hole separation over several carbazolyl moieties. However the exact shape of transferred hole distribution remains unclear.

Faster charge recombination is observed in films with higher sensitizer concentration. It is explained and successfully modeled by assuming that the sensitizer molecules reduce the initial pair separation distance by creating obstacles for the hole motion. This is probably one of the reasons of commonly observed saturation of photosensitivity in PEPCz films containing large amount of sensitizers. Electron mobility via the sensitizer molecules was found to be less important to the recombination dynamics even at high sensitizer concentration.

The unusual fluorescence properties of Cz–TNF complexes, the dynamical blue shift of the fluorescence band, and the increase of the radiative recombination probability in time, are explained within the considered approach as resulting from the heterogeneity of the system. Complexes with different fluorescence properties existing in the polymer film produce charge pairs with different initial separation distances resulting in distribution of holes coming back and in the recombination times.

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