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## Energy transfers in weakly interacting oligothiophenes

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### Abstract

The optical properties of oligothiophene inclusion compounds in perhydrotriphenylene are reported. Excitonic effects are suppressed due to the large inter-molecular distances imposed by the host crystal. In a mixture of quinquethiophene and terthiophene inclusion compounds we observe very efficient long range energy transfers from the short to the long oligomer. Foerster theory indicates that quite large critical distances are involved in this system, thanks to the parallel relative orientation of the molecules within the channels of the host crystal. The fast rise times (shorter than 40 ps) of quinquethiophene excited state population, observed with time-resolved photoluminescence studies, suggest the presence of sizeable contributions from energy transfers among terthiophene molecules. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Oligothiophenes; Optical absorption and emission spectroscopy; Time-resolved fast spectroscopy; Energy transfer

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### 1. Introduction

Oligothiophenes (Tn) are widely studied both for their interest in the applications [1] and because they represent good model compounds for the study of the photoexcitations of thiophene based systems. Recently, many groups have devoted strong efforts in the preparation of ordered thin films and nanostructures based on these conjugated molecules, in order to increase and control their properties in view of a specific application. The strong excited state interactions, which are responsible for collective excitations in the solid state, strongly reduce the photoluminescence (PL) yield of this class of materials [2,3].

The reduction of inter-molecular interactions in the solid state can be obtained by increasing the inter-molecular distances both chemically, by side chain substitution [4], or by diluting the molecules in inert matrices. The latter strategy is of particular interest when the matrix is a crystal able to insert the molecules within its structure. The incorporation of polyconjugated molecules possessing a “long” molecular axis in host compounds as perhydrotriphenylene, urea, thiourea, tris-*o*-thymotide, deoxycholic acids, cyclo-dextrins and zeolites, yields channel type inclusion compounds [5,6].

The advantages of these systems, with respect to the dilution in amorphous matrices (polyethylene, polymethyl-metacrylate, etc.) is the fact that a much higher concentration of molecules can be obtained without microaggregation effects, and that a homogenous, controlled spatial organization of molecules within the matrix is obtained. The incorporation of conjugated molecules into such crystalline host structures provides an unique opportunity of exploring the photophysics of isolated, often oriented molecules.

In particular, in the studies of energy transfer (ET) processes, it becomes possible to single out the contributions related to intra-molecular processes propagation, without the complications arising from the inter-chain hopping of the excitation. It is then possible, in principle, to study long range ET processes by knowing the relative distance and orientation of the guest molecules [6]. Even though the isolated molecule properties can be investigated in dilute solutions, unwanted aggregation effects, changes of conformation of the conjugated backbone and the presence of a variety of conformers often prevent a clear understanding of solution optical and spectroscopic data. These problems are overcome in the channel inclusion compounds, where host–guest interactions allow for the presence of a very limited number of conformers (corresponding to different inter-ring twist angles), whose structural details can be worked out by molecular mechanics and dynamics calculations.

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Among the channel type class of host–guest systems, we have prepared and studied inclusion compounds of linear conjugated molecules in perhydrotriphenylene (PHTP). In particular, we have reported the photoexcitations of oligothiophene inclusion compounds (Tn-IC) in PHTP host matrix [7–10]. In this material the interactions among thiophene oligomers are strongly reduced due to the large (14 Å) inter-molecular distances. Moreover, inside the PHTP matrix, the torsional mobility and the overall rotation of the molecules appear to be hindered, although not as much as in the solid state, due to the helicoidal symmetry of the channels where the molecules are confined. For these reasons the spectroscopic data provided by the study of oligothiophene inclusion compounds yield information that are different and complementary to those obtained from crystals, where strong inter-molecular interactions between adjacent chains significantly affect the optical spectra, and from diluted frozen solutions, in which the conformations of the molecules are blocked.

Energy transfer processes and their dynamics have been widely studied in recent years in conjugated polymeric and molecular systems [11,12], due to the increased interest in materials, suited for optoelectronic applications, where losses in the active medium are reduced by a red-shift of the emission [13–15].

In this work we present a study of the energy transfer processes in oligothiophene inclusion compounds. To this purpose we have analyzed samples where mixtures of oligothiophenes with two different lengths, quinquethiophene (T5) and terthiophene (T3), are accommodated in the channels of the PHTP guest crystal. The study of samples possessing different ratios of long/short oligomers, performed with cw and time-resolved photoluminescence measurements, allows us to determine the presence of Foerster type energy transfer in PHTP inclusion compounds.

## 2. Experimental

Oligothiophenes inclusion compounds (Tn-IC) are obtained by melting and successively cooling the molecules with perhydrotriphenylene in excess respect to the stoichiometric value as described elsewhere [8]. Coinclusion of T3:T5 mixtures were obtained by the same procedure with different molar ratios ranging from 6:1 to 450:1.

Cw measurements on the coinclusion compounds are obtained on powders diluted in KBr pellets while time-resolved experiments are performed directly on the powders. Films are obtained by vacuum evaporation on quartz substrates, as reported elsewhere [8] and Tn powders are dispersed in KBr.

Due to the inhomogeneity of the crystalline powders, the relative concentration of T3:T5 can vary within the same preparation. For this reason we have determined the concentration of the samples for the cw study through absorption and PL measurements performed directly on the KBr

pellets or on dissolved samples in solution. For sample (1) and (2) a molar ratio of about 6:1 and 250:1 is obtained, respectively.

The optical absorption measurements are performed with a Cary 2400 spectrometer. Cw PL measurements are performed with a SPEX 270 M monochromator equipped with a N<sub>2</sub> cooled CCD detector by exciting with a monochromated Xe-lamp. Highly spectral resolved measurements, excited by the UV lines of an Argon laser, were performed by means a SPEX double monochromator equipped with a GaAs photomultiplier.

The time-resolved PL was studied both by using femto-second photoluminescence up-conversion spectroscopy technique with a resolution of 200 fs, and a Hamamatsu optical sampling oscilloscope with 20 ps time resolution. The emission was excited by the second harmonic of a mode locked Ti:Sapphire with typical pulse width of 150 fs tuned at 810 nm.

## 3. Results

In Fig. 1 the optical absorption spectra of T3 and T5 are shown for the powders, evaporated films, and inclusion compounds. The strong spectral variations observed in aggregated molecules with respect to the weakly interacting Tn-IC molecules, are consistent with the fact that strong inter-molecular interactions spread the excited state molecular levels into an exciton band, whose position and width depend on the strength of the interactions [16,17]. These decrease with the inter-molecular distances  $d$  and depend on the relative orientation of the transition moments, yielding strong excited state interactions for H-type aggregation (parallel-dipole-orientation) [18], as generally encountered in thin evaporated films [3].

Differently from aggregated molecules, in the inclusion compounds, thiophene molecules display optical absorptions very similar to those of frozen solutions indicating that inter-molecular interactions are weak for the large distances  $d = 14$  Å between molecules in the PHTP chan-

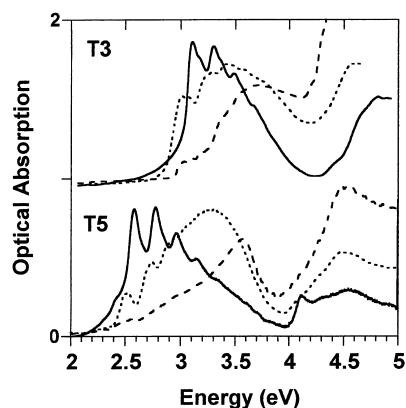


Fig. 1. Optical absorption of T3 and T5 powders (dotted lines), evaporated films (dashed lines) and inclusion compounds (solid lines) at 80 K.

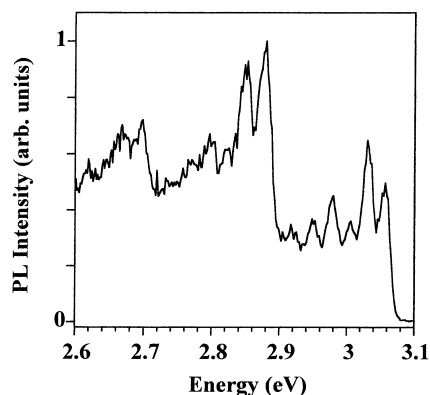


Fig. 2. Photoluminescence of T3-IC at 9 K. Excitation wavelength 363 nm.

nels and excited state interactions are suppressed. At low temperature, the PL spectrum of T3-IC (see Fig. 2) displays well resolved vibronic structures, resembling the data obtained by Kohler and coworkers on frozen solutions [19], while for T5-IC the coexistence of different conformers [9] leads to broader and more complex PL spectra.

In Fig. 3 the optical absorption and PL of T3:T5 coinclusion compounds are reported for different T5 molar concentrations. The two samples show both the emissions of T3 and T5, with origins at 3.07 and 2.54 eV, respectively. For the higher T5 concentration (1) the absorption of both the oligomers are seen, while for the low T5 concentration, the T5 absorption is hindered below the low energy tail of the T3 absorption.

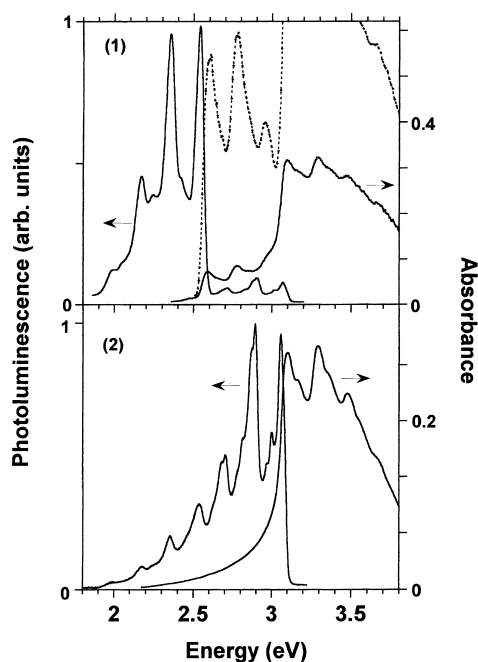


Fig. 3. Absorption, photoluminescence and PL excitation profile (dotted line) of T3:T5-IC at different molar concentrations 6:1 (1) and 250:1 (2).  $T = 80$  K, excitation wavelength 340 nm, emission 560 nm.

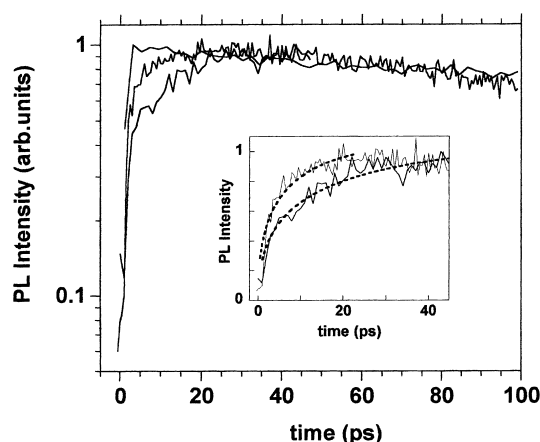


Fig. 4. PL decay of the T5 emission obtained by exciting at 405 nm the T3:T5 inclusion compound with nominal concentration 70:1, for different sample positions. In the inset, the curves are fits from Eq. (4).

Even with the lower T5 molar concentration of 250:1 of T3:T5 in PHTP, by exciting within the T3 absorption, the PL emission from T5 is observed with intensity of about 1/3 with respect to T3. Taking into account the different PL quantum yields of the molecules, it follows that about 1 T5 molecule over 15 T3 molecules contributes to the PL emission in this sample, indicating unambiguously that most of the excitation is transferred from T3 to T5 in the PHTP crystal. This demonstrates that efficient ET processes take place among molecules included in the channels of PHTP. The relative intensity of T5 and T3 emissions does not depend on the exciting wavelength or on the temperature.

In Fig. 4 the time-resolved PL emission from T5 is shown for the coinclusion compound T3:T5. From these data it is evident that the presence of a rise time for the T5 emission is obtained by exciting within the absorption of the T3 molecules, although the decay dynamics changes considerably with sample position, indicating an inhomogeneity in the T5 molar concentration.

#### 4. Discussion

The data reported are clearly indicative of energy transfer processes taking place from the higher energy T3 (donor) to the lower energy T5 (acceptor) oligomer. Since these molecules are included in the channels of the PHTP crystal, the minimum distance between neighboring molecules situated in different channels is  $R = 12\text{--}14$  Å, while the distance of the baricentres of the molecules in the same channel are higher than 16 Å. As described by the Foerster theory, for such inter-molecular distances, long range resonant energy transfers from a donor (D) to an acceptor (A) can occur, provided that their relative distance does not exceed a critical value. This critical distance  $R_0$  is defined as the distance between donor and acceptor for which the donor has the same probability to recombine radiatively or to

transfer its energy to the acceptor.  $R_0$  depends on the degree of spectral overlap between the donor fluorescence and the acceptor absorption, according to [20]

$$R_0^6 = \frac{9000 \ln 10 \Gamma^2 \eta_D}{128 \pi^5 n^4 N_0} \int_0^\infty \frac{F_D(\omega) \varepsilon_A(\omega) d\omega}{\omega^4} \quad (1)$$

where  $\Gamma^2$  is a factor dependent on the relative orientation of the dipoles,  $n$  the refractive index of the medium,  $N_0$  the Avogadro number and  $F_D(\omega)$  the normalized donor fluorescence. By assuming the same values for the acceptor (T5) extinction coefficient  $\varepsilon_A$  [21] and the donor (T3) PL quantum efficiency  $\eta_D$  [22] as measured in solution, for random dipole orientation we obtain  $R_0 = 36$  Å. This value considerably increases by considering the ideal situation of molecules included in the parallel channels of the PHTP crystal, yielding values of  $R_0 = 39$  and 49 Å for inter- and intra-channel energy transfers, respectively. These theoretical results predict efficient ET from T3 molecules to T5, not only if T3 and T5 are in adjacent channels, but also when a channel containing T3 molecules is surrounded by neighboring channels containing only T3 molecules, provided that at least one of the next neighboring channels contains a T5 molecule. Moreover, ET processes can take place within the same channel from T3 to T5 molecules separated by one T3 molecule. These ET steps are schematically represented in Fig. 5.

The observation of a rise time in the T5 PL of the coinclusion compound demonstrates that the T5 excited state is not directly populated by photon absorption, but its population, and hence PL emission originates from an energy transfer from the excited T3 molecules. The fast rise times observed, rule out a trivial absorption–emission pro-

cess. Following the Foerster analysis, the rate equations [23] governing the donor and acceptor population are

$$\frac{dn_D}{dt} = -\frac{n_D}{\tau_D} - \beta \frac{n_D}{\sqrt{t}} \quad \frac{dn_A}{dt} = -\frac{n_A}{\tau_A} + \beta \frac{n_D}{\sqrt{t}} \quad (2)$$

where

$$\beta = \frac{1}{2} \frac{4\pi R_0^3}{3} N_A \sqrt{\frac{\pi}{\tau_D}} \quad (3)$$

The rate equations contain a quenching (gain) term for the donor (acceptor) accounting for the nonradiative transfer from D to A, neglecting donor–donor transfers. This term is proportional to the parameter  $\beta$  and decreases with time, since the probability to have an acceptor at distances below the critical radius decreases as donors are depleted.

By considering times much shorter than the lifetimes of both the donor and acceptor, the rise dynamic in the acceptor population obtained from Eq. (2) yields

$$n_A(t) \approx N_D(1 - e^{-2\beta\sqrt{t}}) \quad (4)$$

The fit of the data, obtained by analyzing different samples with nominal concentration of 1:70 of T3:T5, and different sample positions, gives a minimum value for  $\beta$  of about  $1.4 \times 10^{-7} \text{ s}^{-1/2}$ , corresponding to the slower transfer rate observed. The value of  $\beta$  obtained with Eq. (3) with the calculated critical distance and the T3 fluorescence lifetime measured in solution [22], yields  $\beta$  of about  $0.2 \times 10^{-7} \text{ s}^{-1/2}$ , if the nominal acceptor concentration is assumed. This small value, lower than the minimum  $\beta$  measured, cannot be explained only by considering the inhomogeneity of the samples. We think that such a discrepancy is an indication of the fact that ET processes among donor guest species (T3) cannot be neglected in PHTP host. Indeed, a sizeable spectral overlap in the absorption–emission spectra of the T3 chromophore is present, due to the rather small Stokes shift. Such a contribution should give fast energy transfers, due to the short distance (14 Å) among T3 molecules, thus, accounting for the extremely fast transfer observed from T3 to T5 in PHTP. Preliminary results indicate that, including both donor–acceptor and donor–donor transfers, our data would be fully explained in the frame of the Foerster energy transfer theory. Work is in progress to improve the sample homogeneity in order to define more accurately the relation between the time-resolved data and the Foerster parameters.

Finally, we note that transfer rates faster than those predicted by a simple Foerster treatment, as that here considered, have been already reported also for host–guest polymers and molecularly doped polymers in blend matrixes [11,24].

## 5. Conclusion

The optical properties of terthiophene and quinquethiophene inclusion compounds in perhydrotriphenylene are

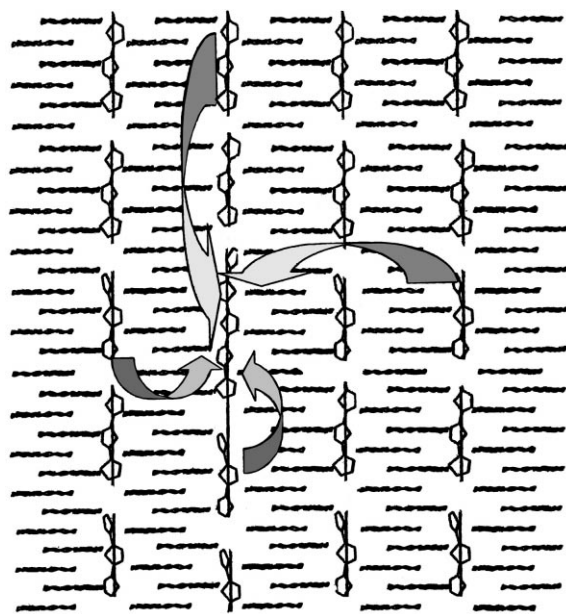


Fig. 5. Schematic structure of T3:T5-IC. Some possible energy transfer steps are represented by arrows.

reported. Excitonic effects are suppressed in PHTP, due to the large inter-molecular distances (14 Å) imposed by the host crystal. In a mixture of quinquethiophene and terthiophene inclusion compounds we observe a very efficient energy transfers from the short to the long oligomer. The analysis of the data in the frame of the Foerster theory indicates that quite large critical radius (39–49 Å) are involved in this system, thanks to the parallel relative orientation of the molecules within the channels of the PHTP crystal. The fast rise times (shorter than 40 ps) in the quinquethiophene excited state population, observed by time-resolved photoluminescence studies, cannot be fully described by a simple Foerster treatment only by T3–T5 transfers, but also the contribution of energy transfers among T3 molecules must be involved.

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