Electronic coupling responsible for energy transfer in columnar liquid crystals

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Abstract

Electronic coupling is the driving force for energy transfer in molecular materials and consists of several components. We determine the strength of dipolar/multipolar coupling and coupling due to orbital overlap for excitation transport in triphenylene columnar liquid crystals. We use time-resolved fluorescence spectroscopy and computer simulations. The fit of the experimental and simulated fluorescence decays reveals that the transfer process is dominated by short range interactions (multipolar and orbital overlap) but the contribution of long range dipolar interactions cannot be neglected. © 1999 Elsevier Science B.V. All rights reserved.

Electronic energy transfer is a basic function of photosynthetic antennas and could be used as a mode of signal transmission in molecular electronics. From this point of view, systems characterized effectively by one-dimensional structures are quite appealing. Most of the relevant features of molecular energy guides, such as, for example, dimensionality, velocity and propagation distance, depend on the electronic coupling which is responsible for transport. Therefore, it is important to determine its various

components, which depend both on the electronic structure of the molecular units and on their arrangement.

Electronic coupling is divided into two classes, Coulombic interactions and interactions due to intermolecular orbital overlap. Coulombic interactions are composed of long range dipolar interactions and short range multipolar interactions [1]. Interactions due to intermolecular orbital overlap are only short range and include electron exchange [2] and charge resonance interactions [3,4]. Triplet energy transfer is due only to orbital overlap whereas all types of interactions may be responsible for singlet transfer. Although the simultaneous action of all types of interactions for singlet energy transfer involving weakly allowed transitions has been known for a

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long time [1,5], no experimental study provided a quantitative picture of this problem.

For large molecules, interactions due to intermolecular orbital overlap are difficult to reliably calculate by quantum chemistry methods, contrary to Coulombic interactions. They can be obtained from an analysis of low temperature absorption spectra via appropriate models [6]. Since the mode of energy transport is strongly temperature dependent [7], it is important to determine the effective coupling at room temperature, corresponding to the operating conditions of molecular devices. Here, we propose a new method to determine the orbital overlap interactions using columnar liquid crystals as a model (Fig. 1A). We take advantage of the simple molecular arrangement of these columnar mesophases to model excitation transport. The fit of the experimental fluorescence decays with decays simulated by the Monte Carlo method, associated to quantum chemistry calculations, provides the strength of the dipolar/multipolar interactions and of the interactions due to orbital overlap. We discuss the role of charge reso-

nance interactions, related to excimer fluorescence and we illustrate the spatio-temporal evolution of the excitation.

We recorded the fluorescence decays of the mesophases doped with different concentrations of energy traps using the single photon counting technique. The mesophase was formed by an oligomeric triphenylene derivative consisting of four hexapentyloxytriphenylene units (Fig. 1B). The interest in studying this compound is that its hexagonal columnar mesophase can be studied at room temperature [8]. The triphenylene aromatic cores are stacked in columns of 3.6 Å; the intercolumnar distance is 20.7 Å [9]. The energy trap is 2,4,7-trinitrofluorenone. The experimental procedure is described in Ref. [10].

The properties of the singlet electronic transitions of the tetrameric triphenylene are identical to those of the mononomeric analogue [10,11]. The $S_0 \rightarrow S_1$ electronic transition associated with the experimentally detected fluorescence is symmetry forbidden but weakly allowed through vibronic coupling. Thus the coupling is expected to be small compared to the bandwidth of the electronic transition. Therefore, it is reasonable to consider that excitation transport takes place via a hopping mechanism. The probability density per unit time w_i for the energy to hop from an excited molecule to a molecule i is calculated from Fermi's golden rule:

$$w_i = \frac{\partial P_i}{\partial t} = \frac{4\pi^2}{h} T_{\text{vib}} V_i^2$$

where the vibronic terms T_{vib} are identical for all molecules. This is a reasonable assumption since all the molecules are chemically identical and have the same environment; it is corroborated by the fact that the fluorescence maximum does not show any important shift (< 200 cm^{-1}) as a function of time. Under these conditions, the probability density w, for the excitation to leave a given molecule, is independent of this molecule. The quantity w is the reciprocal of an average 'residence time' t_{h} also called the 'hopping time':

$$w = \Sigma w_i = 1/t_h.$$

In our simulations, the excitation performs a random walk on a three-dimensional lattice (10^6 sites) having the structure of the columnar mesophases.
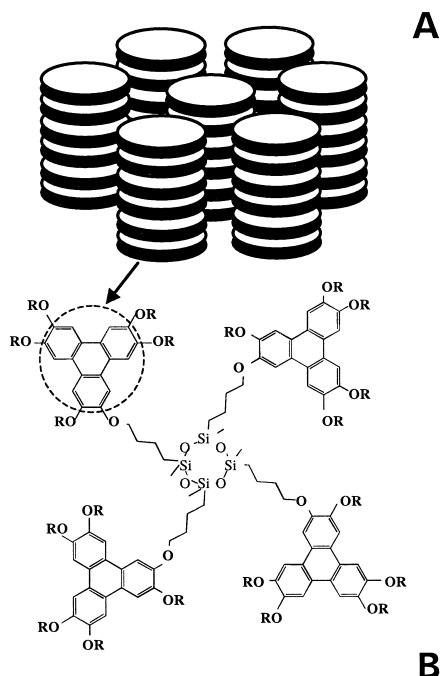

Fig. 1. Schematic representation of the hexagonal columnar mesophase (A) and the studied tetrameric triphenylene derivative (B). Each disk corresponds to an aromatic triphenylene core.

The transition moments are orthogonal to the column axis and randomly oriented around it. The energy traps are randomly distributed on the lattice and their concentration ranges from 1‰ to 1%. When the excitation reaches a trap, it disappears, as found experimentally [10]. The normalized probability P_i that excitation hops to a molecule i is calculated by:

$$P_i = w_i / \sum_{j=1}^{j=N} w_j = V_i^2 / \sum_{j=1}^{j=N} V_j^2$$

where N is the number of sites. This process lasts one Monte Carlo step.

The modeling of the distance dependence of the electronic coupling plays a key role in the simulation of the energy transport. For the two nearest neighbors within a column (3.6 Å) dipolar (V_{dip}) and short range (V_{sh}) interactions are operative; the total coupling is $V_{tot} = V_{dip} + V_{sh}$, where V_{sh} is taken as identical for all the molecular pairs [2] and includes both intermolecular orbital overlap and multipolar interactions. In contrast, for further neighbors, we consider only dipolar interactions, $V_{tot} = V_{dip}$.

The dipolar interactions V_{dip} were calculated from a semi-empirical quantum chemistry method providing a representation of the transition dipole in the form of an atomic transition charge distribution [11]. The transition monopoles of the symmetry forbidden $S_0 \rightarrow S_1$ transition were determined from the transition monopoles of the first allowed transition $S_0 \rightarrow S_3$ from which $S_0 \rightarrow S_1$ borrows its oscillator strength [10]. Each atomic transition charge describing the $S_0 \rightarrow S_3$ transition is multiplied by 0.8/5.6, in order to adjust [11] the calculated $S_0 \rightarrow S_3$ transition moment ($\mu = 5.6$ D) to the experimental $S_0 \rightarrow S_1$ dipole moment ($\mu = 0.8$ D) determined from the absorption spectrum of the mesophase. The distance dependence of the dipolar coupling calculated from the atomic transition charges is perfectly described by the extended dipole model [13] with a dipole length l of 7.2 Å. Consequently, the calculation of the hopping probabilities P_i with the extended dipole model and $l = 7.2$ Å is strictly equivalent to the calculation of

the P_i from the atomic transition charge distribution. For convenience, we use the extended dipole model in the simulations.

In order to compare the relative strength of short range and long range interactions acting between nearest neighbors, we use the ratio $K = V_{sh}/V_{dip}^{II}$ where V_{dip}^{II} denotes the dipolar coupling between parallel transition dipoles at 3.6 Å. When the transition moment and the extended dipole length are constant, V_{dip}^{II} is constant. Fig. 2 shows that upon increasing K up to 20, the decay of the survival probability is slowed down. This happens because an increase in K favors hops to the nearest neighbors in comparison with all the other possible hops and thus enhances the one-dimensional character of the transport. Consequently, the number of distinct visited sites decreases and the probability to encounter a trap diminishes.

We determine the K value which gives the best agreement between experimental and simulated fluorescence decays. For a given K, which is the first fitting parameter, the simulated fluorescence decays are obtained from the survival probability Φ multiplied by $\exp(-t/\tau_f)$, where τ_f is the fluorescence lifetime recorded in absence of traps. For each K value, the parametric adjustment between experimental and simulated decays leads to the hopping time which is the second fitting parameter (Fig. 3A). The quality of the fit is evaluated with the least-squares method by calculating the reduced χ^2 value (Fig. 3B). The χ^2 plot obtained for the highest trap
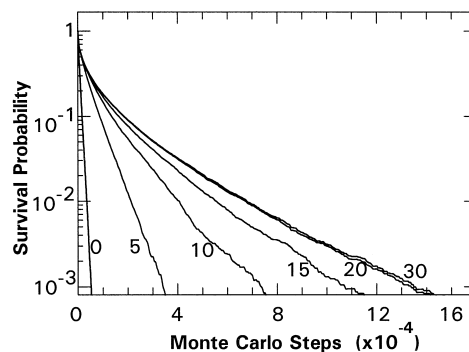

Fig. 2. Influence of the relative strength of the short range and dipolar interactions ($K = V_{sh} / V_{dip}^{II}$) acting between nearest neighbors on the simulated survival probability of the excitation. K ranges from 0 to 30. The trap molar fraction is 10^{-2}.

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[2] V_{sh} is considered to be the same for all the molecular pairs because of the C_3 symmetry axis of the chromophore and the staggered configuration adopted in the columnar mesophase [12].

concentration (1%) presents a minimum around $K = 8$ corresponding to a hopping time of 1.2 ps. The fit of the experimental decays recorded for lower trap concentrations gives similar K and t_h values, i.e. 8 ± 2 and 1.2 ± 0.2 ps, respectively.

The simulated decays obtained for three typical K values, 0, 8 and ∞, are presented in Fig. 3C–E
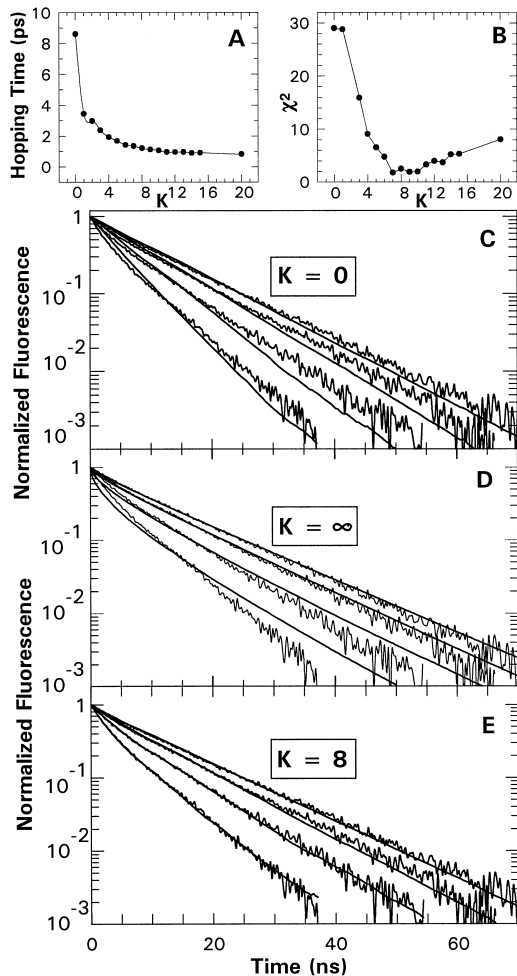

Fig. 3. Fit of the experimental and simulated fluorescence decays of the mesophase doped with energy traps. Hopping time (A) and the corresponding reduced χ^2 (B) obtained as a function of the relative strength of short range and dipolar interactions ($K = V_{sh} / V_{dip}^{II}$) acting between nearest neighbors for 10^{-2} trap molar fraction. The experimental curves (noisy) are compared to simulated curves (smooth) for $K = 0$ (C), $K = \infty$ (D) and $K = 8$ (E). The trap molar fractions are 10^{-3}, 2×10^{-3}, 5×10^{-3} and 10^{-2}; the highest concentration corresponds to the most rapid decay; $\lambda_{ex} = 300$ nm; $\lambda_{fl} = 380$ nm.
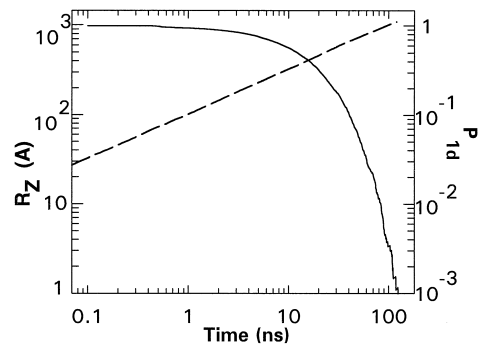

Fig. 4. Spatio-temporal evolution of the excitation in the studied mesophase with $K = V_{sh} / V_{dip}^{II} = 8$ and $t_h = 1.2$ ps. Root mean square displacement along the column axis (R_z) (dashed line) and probability for the excitation to remain in the column in which it was initially created (P_{1d}) (solid line).

together with the experimental ones. The model with $K = 0$, i.e. when all the long range dipolar interactions are operative but $V_{sh} = 0$, corresponds to the Förster mechanism, widely used in the analysis of singlet excitation hopping. When $K = \infty$, only short range interactions are included but $V_{dip} = 0$. This model corresponds to the well-known model of a one-dimensional random walk with hops only to nearest neighbors [14]. The fit obtained with $K = 0$ (Fig. 3C) or with $K = \infty$ (Fig. 3D) are both of poor quality compared to those obtained with $K = 8$ giving the best fit (Fig. 3E). Thus we assert that energy transfer is controlled by two types of coupling. First, all the long range dipolar interactions have to be considered since the model with $K = \infty$ is not good enough. Secondly, the energy transfer is dominated by short range interactions as indicated by the high K value leading to the best fit [3].

The spatio-temporal evolution of the excitation is illustrated by calculating the root-mean-square displacement of the excitation along the column axis (R_z) and the probability for the excitation to remain in the column in which it was initially created (P_{1d}) using $K = 8$ and $t_h = 1.2$ ps. At 14 ns (fluorescence lifetime at 20°C) R_z is 400 Å (Fig. 4). This R_z value

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[3] In [10] we reported results of fits using a crude model. The main weak points were the use of (i) only dipolar coupling, (ii) unique intercolumnar hopping probability, and (iii) distance dependent hopping time.

is small compared to the monodomain size (> 1 μm), explaining why the experimental fluorescence decays are not affected by the mesophase alignment. Our results show that the transport is initially one-dimensional and becomes three-dimensional after 1 ns. At 14 ns, 55% of the excitations have quitted the column where they were created (Fig. 4).

The fit of the simulated and experimental fluorescence decays provides the relative strength of short range and dipolar interactions ($V_{sh}/V_{dip}^{II} = 8 \pm 2$). Below, we quantify the various interactions acting between nearest neighbors. The dipolar coupling V_{dip}^{II} associated to a transition moment of 0.8 D and calculated according to the atomic transition charge distribution model is 19 cm^{-1}. Consequently, the short range coupling is $V_{sh} = 152 \pm 38$ cm^{-1}. The maximum total coupling $V_{sh} + V_{dip}^{II}$ is 171 ± 38 cm^{-1}, which is smaller than the absorption bandwidth (800 cm^{-1}), in agreement with our assumption of a hopping mechanism. The multipolar interactions strength, calculated by a quantum chemistry method is 18 cm^{-1} [10]. Thus, the coupling due to intermolecular orbital overlap is 134 ± 38 cm^{-1}. This value, which is close to that calculated by ab initio methods (190 cm^{-1}) for polyene dimers at 3.6 Å [15], is at least one order of magnitude larger than exchange interactions [6]. Consequently, charge resonance interactions should play a dominant role in the excitation hopping, in agreement with the formation of weakly bound excimers in the triphenylene columnar mesophases [11].

The model presented in this report takes into account many factors commonly ignored in the analysis of experimental results, i.e. the electronic structure, the molecular arrangement and the simultaneous action of long range dipolar and short range (multipolar and orbital overlap) interactions. Our methodology, combining an experimental and numerical approach, allows the quantification of the various components of the electronic coupling and the determination of the relevant features of energy transport in molecular materials.

Acknowledgements

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