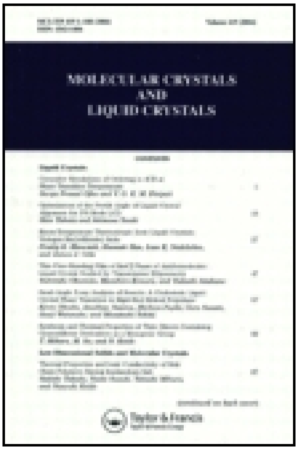

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# Energy Transport in Columnar Mesophases

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# ENERGY TRANSPORT IN COLUMNAR MESOPHASES

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*An overview of the various aspects related to the transport of electronic excitation energy in columnar liquid crystals is presented. The different modes of transport (hopping or intrabande scattering) and their dependence on the type of electronic excited states (localised on single molecular discs or delocalised over a large number of them) are discussed. The influence of the structural disorder is examined. Some conclusions regarding the electronic structure of the molecular discs necessary to obtain efficient transport are drawn.*

*Keywords*: energy transport; excition states; columnar mesophases

## 1. INTRODUCTION

Discotic columnar liquid crystals attracted attention as potential energy guides for signal transmission in the field of molecular electronics because electronic excitation transport in these molecular materials is expected to be one-dimensional due to their highly anisotropic structure. The first publications reporting one-dimensional energy migration in triphenylene and phthalocyanine columnar mesophases were published in 1987 [1–2]. However, as investigations went on, it appeared that both experimental and conceptual problems could lead to an erroneous picture of energy transport in these molecular materials. Thus it became evident that special caution is needed to avoid experimental artefacts, such as those arising from local phase transitions induced by a laser beam [3], photo-degradation leading to

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the formation of fluorescent products [4], or distortion of absorption spectra of macroscopically aligned mesophases [5]. Moreover, it was shown that the conclusions regarding the transport properties highly depend on the models which are used to analyse the experimental data [3]. Thus, a subtle combination of experiments and modelling is necessary in order to get a good understanding of the transport process in columnar liquid crystals.

The present communication is a critical synthesis of the research I have carried out in this field for the past fifteen years. Its objective is threefold. First, to make a general survey of the various factors which govern the transport process in columnar mesophases. Second, to outline a methodology allowing a quantitative description of the spatio-temporal evolution of the excitation in a given mesophase. And finally, to point out some characteristics of discotic molecules which can lead to efficient energy guides.

In Section 2, I discuss the relation between type of excited states (localised/delocalised) and mode of transport (hopping/intraband scattering). Then, I examine two key factors, excitation energy (§3) and electronic coupling which is the driving force for the energy transport (§4). The behaviour of delocalised excited states is outlined in Section 5 whereas excitation hopping is described in Section 6. Conclusions are drawn in Section 7.

## 2. EXCITED STATES AND MODES OF TRANSPORT

The mode of energy transport depends on whether the excited states involved are localised on single molecular discs or delocalised on a certain number of them (Figure 1). In the former case, excitation hops from disc to disc performing a random walk (hopping mechanism). In the latter, the excited states of the system are described in the frame of the exciton theory. They form the exciton band and energy migration is viewed as internal conversion among these states (intraband scattering). Although theories unifying the two modes of transport have been developed, in practice the analysis of experimental data obtained with a given columnar phase necessitates to determine whether its excited states are localised or delocalised.

The formation of delocalised excited states depends on the one hand on the relative magnitude of the dispersion of the excitation energy and on the other hand on the electronic coupling. For simplicity's sake, let's consider two neighbouring discotic molecules A and B within a column having excitation energies $E_A$ and $E_B$, respectively. The excitation will be delocalised over these two molecules if the electronic coupling $V_{AB}$ is larger than the absolute value of the energy difference $\Delta E = |E_A - E_B|$.

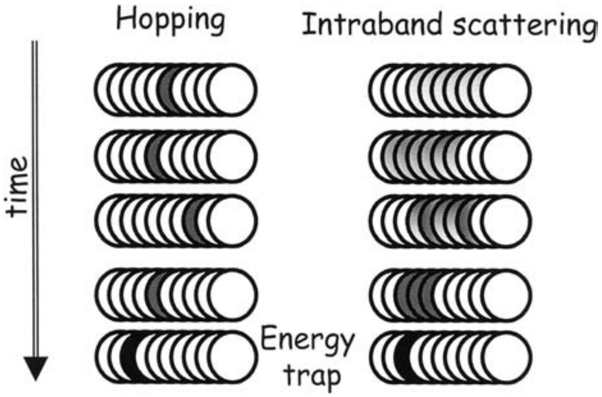

**FIGURE 1** Illustration of the modes of energy transport within a column, hopping and intraband scattering, involving localised and delocalised excited states, respectively.

Remark 1. The term "exciton" is usually associated to both excitation hopping and intraband scattering whereas the term "exciton states" designates the delocalised excited states which are also called collective states or Frenkel excitons.

Remark 2. Photon absorption and excitation transport in columnar mesophases involve only the aromatic moiety of the discotic molecules which is the "chromophore" . Nevertheless, the lateral chains play an indirect role in these processes because they contribute to the geometrical arrangement of the chromophores.

## 3. EXCITATION ENERGY

The discotic molecules forming a columnar mesophase are, in general, identical. However, the energy of a given electronic transition is not strictly the same for all the molecules. Such a dispersion arises partly from intramolecular vibrations. At a given temperature T, the Boltzman factor kT represents a lower limit to $\Delta E$. Another origin of the variations of excitation energy is inherent to the structure of the columnar phases which are not perfectly ordered. Consequently, the excitation energy corresponding to each molecular disc, which is the difference between the energy of the ground state and that of the excited state, depends on its relative position with respect to the neighbouring discs which determine the intermolecular interactions.

The intermolecular interaction energy both in the ground state and the excited state can be calculated by quantum chemistry methods as a sum of electrostatic, polarisation, repulsion and dispersion terms. This type of calculation has been performed for columnar stacks of triarylpyrylium [6] and triphenylene [3] discotic moieties. An important conclusion of these studies is that insertion of a chromophore within the column lowers its excitation energy. As a result, the ends of the monodomains will behave as reflecting barriers for the excitation energy. Similarly, molecules located partly out of the column will tend to transfer their energy to those which are well-stacked.

The absence of helical arrangement around the column axes may induce further fluctuations of the excitation energy, particularly in the case of molecules with low symmetry for which the atomic charge distribution in the excited state is very different from that in the ground state resulting in different electrostatic interactions. Such a behaviour is encountered, for example, for mesophases formed by triarylpyrylium derivatives. As a matter of fact, numerical simulations have revealed that fluctuations as large as $3000\,\mathrm{cm}^{-1}$ may occur along the column stacks of triarylpyrylium salts [6]. In contrast, for triphenylene derivatives characterised by a three-fold symmetry axis and presenting only a weak photo-induced charge transfer, the excitation energy is not affected by the rotation of the molecular discs around the column axis [3]. This point has been checked experimentally by recording time-resolved fluorescence spectra which did not present any significant shift as a function of time [3].

## 4. ELECTRONIC COUPLING

The electronic coupling is composed of various components which depend on both the electronic structure of the molecular units and their arrangement. It 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. Interactions due to intermolecular orbital overlap are only short range and include electron exchange and charge resonance interactions. Charge resonance interactions are responsible for excimer formation. The short range terms act mainly between neighbouring discs within the columns. The long range dipolar term may operate also between neighbouring columns. All types of interactions may be responsible for singlet transfer whereas triplet energy transfer is only due to orbital overlap. Therefore, triplet migration is an intracolumnar one-dimensional process. In contrast, singlet migration, may involve intercolumnar transfer.

It is useful to have in mind an order of magnitude for the various coupling terms acting between neighbouring discs within a column. The strength of exchange interactions is $\sim 1\,\mathrm{cm}^{-1}$. Multipolar interactions may be one order of magnitude larger ($\sim$10 cm$^{-1}$). Charge resonance interactions reach $\sim$100 cm$^{-1}$; such values correspond to the formation of weakly bound excimers. However, even higher values may be encountered when fully developed excimers are formed, but so far, this situation has not been detected for columnar mesophases. Finally, dipolar coupling ranges from zero to 1000–2000 cm$^{-1}$. As thermal fluctuations at room temperature are $\sim$ 200 cm$^{-1}$, it is unlikely that short range interactions can induce significant delocalisation of the excitation. Thus, the formation of delocalised states in columnar mesophases greatly depends on the strength of the dipolar coupling. The latter is proportional to the square of the transition moment of the dipolar transition which has to be determined for each type of discotic molecule.

The transition moment of a given dipolar transition is determined from the area absorption spectrum of the "isolated" discotic molecule obtained for solutions in some inert solvent (alkanes if possible) in low concentration, typically $10^{-5}$ M. A serious difficulty at this step is that the absorption spectra of large aromatic molecules are composed of several overlapping bands corresponding to several dipolar transitions. A spectral decomposition has to be made on the basis of a quantum chemical determination of the properties of the electronic transitions, possibly accompanied by fluorescence anisotropy measurements [3,7].

Knowing the dipole moment of the electronic transitions and the relative position of two chromophores, the dipolar coupling can be calculated at various levels of approximation. The simplest one, the so-called point dipole approximation, has been proved to be completely erroneous in the case of columnar mesophases where the stacking distance is smaller than the "diameter" of the molecular discs [8]. A correct determination of the dipolar coupling is provided by the atomic charge distribution model which necessitates semi-empirical quantum chemistry calculations. An alternative is the use of the analytical formula corresponding to the extended dipole approximation, the delicate point being the determination of the extended dipole length. In the case of triphenylene derivatives, the extended dipole length, adjusted via a comparison with the coupling values obtained by the atomic charge distribution model, has been found to be 7.2 Å, that is roughly equal to the "diameter" of the molecular disc [8].

## 5. BEHAVIOUR OF DELOCALISED STATES

The formation of delocalised excited states is usually evidenced by a blueshift in the absorption spectrum of the mesophase as compared to that of dilute solutions. Such spectral modifications have been observed for phthalocyanine [9] and triphenylene mesophases [3,7]. We recall that a simple “solvation” effect without delocalisation of the excitation lowers the energy of the electronic transition, thus inducing a red shift of the absorption spectrum. In this respect, the spectrum of alkoxytriphenylenes mesophases is very informative. The absorption band corresponding to the lowest in energy weak transition (1 Debye) and related to fluorescence emission is red shifted by 200 cm$^{-1}$, whereas that corresponding to the absorption maximum ($S_0 \rightarrow S_4$ transition: 10 Debyes) is blue shifted by 2000 cm$^{-1}$ [3,8]. It has to be stressed that stabilisation of the molecular transitions takes place even when collective states are formed. These two antagonistic trends are schematically represented in Figure 2. The shift observed in the experimental absorption spectra of columnar mesophases is in fact the combined effect of stabilisation and delocalisation. Consequently, if the absorption maximum of the mesophase is the same as that of dilute solutions, it does not necessarily mean that the excited states are localised.

In columnar phases in which the intercolumnar distance is at least 18 Å, delocalisation of the excitation is essentially limited within the columns [8]. Thus, the properties of the exciton states can be modelled by simply

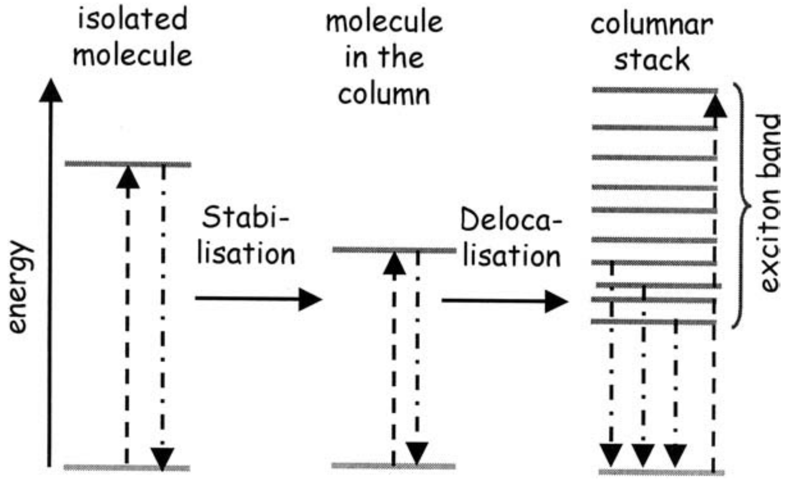

**FIGURE 2** Schematic representation of the modification of the energy levels going from the isolated discotic molecule to the columnar phase. When the molecule is inserted within the stack its excitation energy decreases due to intermolecular interactions (solvation effect). The electronic coupling acting among the various pairs of molecules in the stack induces a delocalisation of the excitation resulting in a blue-shift of the absorption spectrum (- - - - >) and a red shift of the fluorescence spectrum (-.-.- >). The experimental shift of the absorption maximum depends on the relative magnitude of stabilisation and delocalisation.

considering columnar aggregates having the structural characteristics of the mesophase. The properties of the exciton states (transition energy, transition moments, polarisation, degree of delocalisation . . . ) are obtained by diagonalising the exciton matrix in which the diagonal terms represent the excitation energy of each molecule within the aggregate and the off-diagonal terms represent the dipolar coupling acting for all pairs of molecules in the column [3,6,8,10]. The precision of the calculated quantities depends on the way that the various terms of the exciton matrix are calculated. In this respect, a methodology combining the exciton theory and quantum chemistry methods was developed for the study of the exciton states of triarylpyrylium mesophases [6] and, later, it was further improved by studying those of hexa-substituted triphenylenes [3,8]. In this methodology the discotic molecules are represented atom by atom. The diagonal and off-diagonal terms of the exciton matrix are calculated by taking into account both the electronic structure of the chromophores and their coordinates within the aggregate. The above methodology gives the possibility to examine precise molecular arrangements and take into account structural defects.

It was shown that small random variations of the stacking distance do not seriously affect the properties of the exciton states [8]. In contrast, rotation of the molecules around the column axis may have a drastic influence on them, most importantly, reducing the degree of delocalisation in a significant way [8,10]. However, localisation of the excitation can be avoided if the exciton states of columnar phases are built on two electronic states of the individual chromophores instead of a single one. This happens when the discotic chromophores have two electronic transitions doubly degenerate, as for example triphenylenes triphenylenes, metal phthalocyanines, porphyrins, benzenes and coronenes, or even two orthogonal transitions close in energy (*i.e.* metal free phthalocyanines, triarylpyrylium cations).

Intraband scattering was exemplified by studying the fluorescence of triarylpyrylium mesophases [5,11]. It was found that the profile of the fluorescence decays depends on the detection wavelength. Upon increasing wavelength (e.g. upon decreasing excitation energy), the rise-time of the signal increases from 200 ps (time-resolution of the experiment) up to 1 ns. Simultaneously, the signal decays more and more slowly. The time-resolved fluorescence spectra shift progressively to lower energy. The total shift detected was 1400 $\text{cm}^{-1}$. A temperature increase results in a shortening of both the rise-time and the decay of the fluorescence signal. These experimental observations were interpreted modelled as follows. Laser excitation initially forms exciton states which are delocalised practically over the whole length of the columns. Then, the coupling with the thermal bath leads to an internal conversion towards states of the exciton band with lower energy (Fig. 1), associated to nearly forbidden transitions, and consequently having a longer radiative lifetime. At shorter times, fluorescence arises from high energy delocalised states whereas at longer time, emission originates from states with lower energy localised around the structural defects. The longest rise-time detected (1 ns) corresponds to the time needed for the internal conversion to be completed. The initial part of the transport process, involving internal conversion among the high energy collective states, is very rapid ($< 200$ ps) and could not be detected with the time resolution of the experimental set-up.

## 6. EXCITATION HOPPING

The most complete investigation of excitation hopping was performed for triphenylene columnar liquid crystals and, in particular, for a mesophase formed by a tetrameric derivative which is stable at room temperature [12,13]. In the latter system, a comparative investigation of singlet and triplet migration was made using as energy traps trinitrofluorenone molecules which can be inserted into the columnar stacks and form charge transfer complexes with the triphenylene cores [14]. Singlet migration was studied by means of time-resolved fluorescence spectroscopy whereas transient absorption provided evidence for triplet transport.

For both singlet and triplet transport, transient signals corresponding to excited state populations were fitted with model curves obtained considering a random walk process among identical molecules. The average hopping time, defined as the reciprocal of the probability density for the excitation to leave a given molecule, was a fitting parameter. As triplet excitation is transferred only via interactions due to orbital overlap, the transport was considered to be one-dimensional with hops only to nearest neighbours; for such a pattern, the survival probability of the excited state population is given by analytical formulas which were adapted to describe the experimental data. In contrast, for singlet transport for which all types of coupling may operate, giving rise to short and long range hops, both intracolumnar and intercolumnar, Monte Carlo simulations were used. In the simulations, the excitation was considered to perform a random walk on a three-dimensional lattice ($10^6$ sites) having the structure of the columnar mesophase. The transition moments were taken orthogonal to the column axis and randomly oriented around it.

The hopping time value found for triplet migration ($2 \pm 1$ ps) is very close to that determined for singlet excitons ($1.2 \pm 0.2$ ps). This happens because the electronic coupling responsible for singlet transport, related to a symmetry forbidden electronic transition, is dominated by interactions due to orbital overlap between neighbouring chromophores in the stacks.

Those interactions are the only operative in the case of triplet transport which is hindered by the existence of structural defects. The average length of well ordered columnar segments delimited by such defects was evaluated at 200 ± 100 aromatic cores, that is somewhat larger compared to the migration length of the singlet exciton (*ca.*100 aromatic cores) during its lifetime (14 ns). Triplet excitations remain imprisoned within the columnar segment in which they are created whereas singlet excitations can escape due to the weak but non negligible long range dipolar interactions. In the case of singlets, the transport is practically one-dimensional at times shorter than 1 ns, but afterwards it becomes three-dimensional.

It is worth-noticing that the hopping time value of triplet excitons determined for the ordered hexagonal mesophase of the above-mentioned triphenylene derivative is somewhat longer than that found for the same type of mesophase formed by a zinc phthalocyanine (0.4 ps) [9]. A faster transport process in the phthalocyanine mesophase is explained by a better interchromophore orbital overlap due to the larger size of the aromatic cores and the existence of the axial d orbitals of the zinc atoms. For the latter mesophase, it was also demonstrated that the hopping time is one order of magnitude shorter than in the corresponding crystalline phase.

## 7. CONCLUSIONS

After having examined the various factors affecting the transport of electronic excitation energy in columnar liquid crystals, the question arises whether these molecular materials can be used as energy guides for signal transmission in the field of molecular electronics. To answer this question one needs to define the requirements for building efficient energy guides. Although their characteristics would highly depend on the precise technological application and such studies have not been carried out so far, it is reasonable to consider that ultrafast one-dimensional transport is a minimum requirement.

To this end, columnar mesophases giving rise to delocalised excited states are preferable. Such mesophases are formed by molecules whose lowest in energy transition is a strong one. Consequently, discotic moieties having a $C_3$ or $C_6$ symmetry axis must be ruled out because their lowest in energy transitions are forbidden by symmetry. Moreover, orientation of the molecules around the column axis should not induce localisation of the excitation. For this purpose, chromophores having a doubly degenerate transition are preferable because, in this case, the electronic coupling is not affected by orientational disorder. To avoid self-trapping of the exciton due to large fluctuations of the electronic energy along the column axis, the chromophores have to be symmetric and present only a weak photo-induced charge transfer. These requirements may be encountered in chromophores having a $C_4$ symmetry axis. For example, mesophases formed by symmetric zinc phthalocyanine derivatives would be promising candidates.

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