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Exciton Coupling Effects in the Absorption and Photoluminescence of Sexithiophene Derivatives

A. Yassar,* G. Horowitz, P. Valat, V. Wintgens, M. Hmyene, F. Deloffre,† P. Srivastava, P. Lang, and F. Garnier

Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry Dunant 94320 Thiais, France

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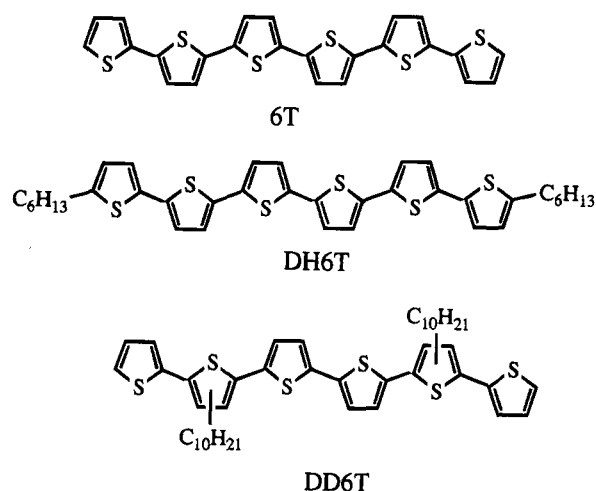
Absorption and photoluminescence properties in thiophene oligomers can be controlled through chemical engineering of the molecules. In the case of sexithiophene, the end or side disubstitution with hexyl groups modulates the absorption, emission, and photoluminescence characteristics. These effects are discussed in terms of structural data on the molecular organization in thin films obtained from X-ray diffraction spectra. The low quantum yields of photoluminescence observed in thin films are associated with the close-packed arrangement of the molecules in the solid state. Such an arrangement leads to the splitting of the excited level into two exciton bands, according to Davydov's rule, and the lowest energy transition becomes forbidden. On the other hand, when hexyl groups are substituted as pendent substituents, the spreading out of the oligomer molecules in the solid state leads to higher photoluminescence yields.

Introduction

The use of conjugated polymers and oligomers in electroluminescent devices has stimulated wide interest in recent years, with the goal of understanding the mechanisms of charge injection, transport, and radiative recombination in these materials, an understanding that should allow the control of their emission spectrum and quantum yield.¹ For this long-term goal, one could consider these materials as molecular assemblies and try to analyze their properties using a rational approach that involves (i) a detailed knowledge of the electronic and optical properties of the isolated molecules, (ii) the determination of the structural organization of these molecules in their molecular assemblies, and (iii) the analysis of the modification of the electronic and optical properties appearing in the solid state upon material formation, and primarily those associated with molecular interactions. As a matter of fact, absorption and emission properties of conjugated materials have been shown to depend highly on their structural organization and on their regioregularity, as for instance in the case of poly(3-hexylthiophene) where steric interactions between "head to tail" substitutions largely govern the fluorescence spectrum and quantum yield.² This dependence, in turn, can also be used for tuning the spectral properties of these materials, as shown in the case of copolymers derived from poly(phenylenevinylene), where various substitutions on segments of the polymer induce a significant shift of the emission wavelength.³

Thin oligothiophene films have raised increasing interest as potential candidates for future use in molecular electronic, photonic, or electroluminescent diodes. Furthermore, oligothiophenes are interesting models of the parent polythiophenes. Whereas polythiophenes present a large distribution of conjugation lengths and high structural disorder, the well-defined conjugation length and chemical structure of oligothiophenes have already allowed a better understanding of the parameters controlling the charge transport and optical properties in conjugated materials. X-ray structural characterization of these oligomers has shown that structural order is a key parameter. Though the electrical and structural properties of these oligomers

SCHEME 1: Chemical Structure of Sexithiophene Derivatives



have been widely discussed in the literature, and particularly in the case of sexithiophene (6T), very little work has been carried out on the optical characteristics of 6T, and the energetic diagram of this compound is still an object of debate. From photoluminescence measurements under one- and two-photon excitation on a polycrystalline thin film of 6T, an electronic level ordering has been proposed by Taliani et al. in which it is suggested that the lowest A_g exciton level lies at 898 cm^{-1} above the lowest one-photon-allowed $1B_u$ exciton level.⁴ Athouel et al. have reported that the $\pi-\pi^*$ transition in *p*-sexiphenyl is affected by orientation of these molecules in a thin film.⁵ Hamano et al. have fabricated molecular oriented thin films of 6T by organic molecular beam deposition. The molecular orientation was determined from the electronic spectra. In films deposited at a low deposition rate and under ultrahigh vacuum (10^{-9} Torr), the 6T molecules are aligned almost perpendicular to the surface.⁶

In this paper, we report on the absorption, photoluminescence, and excitation spectrum of 6T and show that these characteristics can be modulated by the chemical modification of sexithiophene with alkyl groups, substituted either as pendent groups in β position or as terminal groups in α,ω position; see Scheme 1.

* Schneider Electric, Direction Recherche et Développement, 33 Avenue du Maréchal Joffre, 92002 Nanterre, France.

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TABLE 1: Crystallographic Data of Sexithiophene and Derivatives

| compound | 6T | | DH6T | DB6T |
|--|----------|----------|----------|--------|
| | ref 10 | ref 11 | ref 7 | ref 9d |
| crystal system | $P2_1/c$ | $P2_1/a$ | $P2_1/c$ | $C2/c$ |
| a (Å) | 5.980 | 45.38 | 5.88 | 32.532 |
| b (Å) | 7.798 | 7.86 | 7.88 | 5.651 |
| c (Å) | 50.276 | 6.03 | 71.2 | 22.104 |
| β (deg) | 111.3 | 99.0 | 111.3 | 131.35 |
| Z | 4 | 4 | 4 | 4 |
| D_{calc} (g cm^{-3}) | 1.504 | 1.54 | 1.435 | 1.325 |
| herringbone angle (deg) | 62 | 67 | | |
| tilt angle (deg) | 0 | 30 | 0 | 28.7 |
| torsion angles (deg) | | 0–12 | | 9–11 |

Absorption and emission spectra of the isolated molecules and of solid films are presented and discussed in terms of the structural organization of the films, as obtained from X-ray diffraction (XRD) measurements. The final object of this structure–property study is the a priori control, through chemical modification of the oligomer, of its optical and electro-optical properties.

Experimental Section

The thiophene oligomers, sexithiophene (6T), β,β' -didecylsexithiophene (DD6T), and α,ω -dihexylsexithiophene (DH6T) were synthesized according to a previously described procedure.⁷ The solvents, spectrograde from Aldrich, were used without further purification. Thin films are prepared by evaporation under reduced pressure of the powdered compounds on sapphire substrates. UV–vis spectra at low temperature are obtained, under reduced pressure in an Air Products close-cycle cryostat equipped with quartz optical windows, using a Varian Cary spectrophotometer, Model 2415. The fluorescence and excitation spectra were obtained using a Perkin-Elmer Model MPF-44B apparatus, equipped with a DCSU-2 spectral correction unit and an Aminco SLM 8000 apparatus.

Results

Structural Characterization. In agreement with the theoretically predicted high-density lattices, the herringbone packing is probably the most widely encountered structure among linear conjugated molecules.⁸ This is particularly the case for the few thiophene oligomers on which a complete crystallographic study has been achieved so far: terthiophene,^{9a} dimethylquaterthiophene,^{9b} tetramethylquaterthiophene,^{9c} and more recently a stereoregular β -substituted dibutylsexithiophene (DB6T)^{9d} very similar to β,β' -didecylsexithiophene (DD6T). XRD characterization has also been carried out on polycrystalline evaporated thin films of 6T and α,ω -dihexylsexithiophene (DH6T). All sexithiophenes reported so far crystallize in a monoclinic system, the parameters of which are presented in Table 1. The molecules are in an almost planar trans configuration, with dihedral angles between adjacent rings less than 12° .

Two crystalline structures have been reported for the unsubstituted molecule (6T),^{10,11} one in which the long axis of the molecules is rigorously aligned with that of the crystal¹⁰ and the second in which an angle of around 30° is found between the two axes.¹¹ We note, however, that in both cases, the angle between the molecular axis and the normal to the shortest crystal plane is 21° , leading to the same value for the monolayer thickness, 23.4 Å .¹⁰

The crystalline structure of DH6T⁵ is very similar to that of 6T, the elongation of the long axis being related to that of the molecule. We note that in both 6T and DH6T, the distance between nearest molecular axes is about 4.9 Å , which corre-

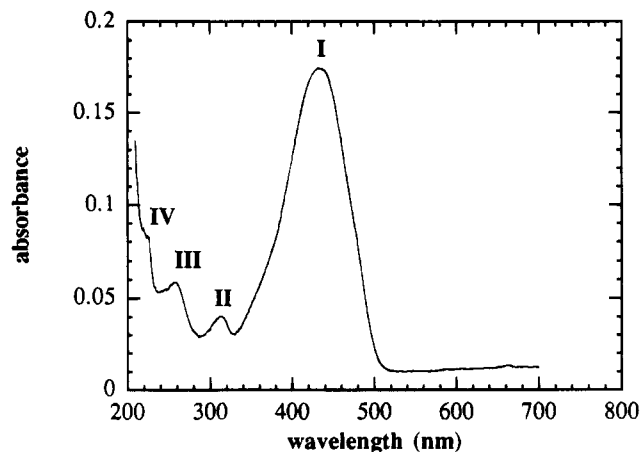


Figure 1. Absorption spectrum of sexithiophene in dioxane.

sponds to the closest intermolecular approach between conjugated systems and suggests a close packing of the thiophene backbones.

Substitution of alkyl chains as pendent groups in the β position leads to a considerable increase of the a parameter in the unit cell, which mirrors the greater separation of the thiophene backbones. It is worth noting that intermolecular distances in the stereoregular DB6T^{9d} "are all longer than the van der Waals radii".

The orientation of crystal grains has been determined from pole figure analysis in 6T¹⁰ and DH6T⁷ evaporated films. Two orientations are found in 6T, with the long crystal (and molecular) axis either parallel or perpendicular to the substrate plane. By contrast, DH6T films are highly oriented, with all the long axes perpendicular to the substrate. Finally, we have not found any difference between the X-ray diffractogram of DD6T films and that of the powdered material, which indicates that films of this compound are largely isotropic.

Optical Absorption and Emission of Isolated Molecules.

The absorption spectrum of sexithiophenes in dioxane at room temperature is characterized by four unstructured broad bands in the UV–vis region (see Figure 1). The position of the strongest absorption band, I, is weakly dependent on the chemical structure of the molecule: 428 nm for DD6T, 432 nm for 6T, and 444 nm for DH6T. This shows that the effective conjugation length of the substituted molecules nearly equals that of the unsubstituted sexithiophene. The position of absorption maximum, λ_{max} = 432 nm, appears lower than that observed for fully coplanar 6T molecules obtained in the solid state, in which $\lambda = 513 \text{ nm}$.¹² These results can be explained by intramolecular free rotation existing in solution for these thiophene oligomers, occurring along the σ bonds between the thiophene moieties. The resulting lowering of the effective conjugation length of 6T is expected to lead to an increase of the corresponding transition energy. This interpretation is confirmed by recent results on terthiophene, where it has been shown that rigidification of this molecule by an interthiophene methylene bridge increases the absorption maximum in solution from 350 to 372 nm.¹³ The introduction of an alkyl group in the β position, DD6T, induces a small hypsochromic shift of 216 cm^{-1} , which can be associated to some torsion of the molecule along its long axis, due to steric interactions induced by the pendent alkyl groups. In the terminal α,ω position, the same alkyl groups lead to a bathochromic shift of 420 cm^{-1} , which can be related to a better coplanarity of the molecule and to the electron-donating effect of the hexyl groups. As already widely described in the literature, the optical transition associated with band I is polarized parallel to the long axis of

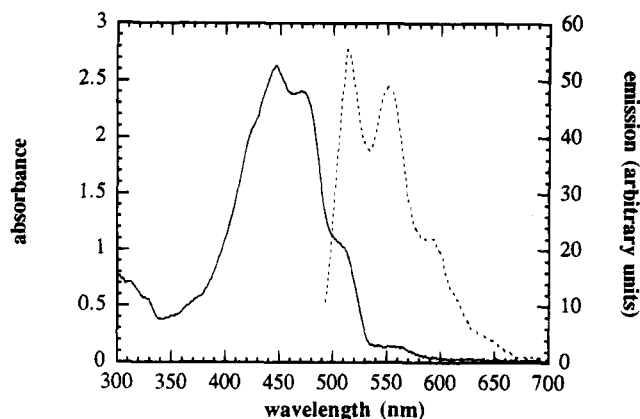


Figure 2. Absorption (solid line) and fluorescence (dotted line) spectra of DD6T in EPA glass at 77 K.

the molecule. The second, weaker band II, located at 315 nm, has also been assigned in the literature to a transition polarized parallel to the long molecular axis.¹⁴ On the other hand, absorption bands III and IV appear rigorously at the same energy for the three sexithiophenes, at 259 and 220 nm, respectively. Interestingly, literature data on unsubstituted and variously substituted oligothiophenes, ranging from bithiophene to dodecithiophene,¹⁵ all present these two absorption bands at the same energy in the UV range, whatever the conjugation length. Orientational studies underdone in the literature by means of polarization fluorescence on stretched thin films of thiophene oligomers have shown that, whereas transition I shows a degree of polarization close to unity over its whole vibrational progression, transition III shows a polarization close to zero or even negative.^{16,17} These results suggest thus that the transition dipole associated with transitions III and IV is oriented almost perpendicular to the long molecular axis of these oligomers, making these transitions largely independent of conjugation length n .

As noted above, the structureless spectrum of 6T and its alkylated derivatives at room temperature can be explained by the intramolecular free rotation of the sexithiophene molecules and also by interactions between their ground state and the solvent, which result in the collapse of the spectrum into a single, broad, and featureless band. When the temperature is lowered, the decrease of the ground state–solvent interactions leads to the existence of preferential conformations of the molecules and therefore to a more structured spectrum than the one obtained at room temperature. Thus, the absorption spectrum of DD6T becomes structured in diethyl oxide–isopentane–alcohol (EPA) glass at 77 K (Figure 2), which can be attributed to a Franck–Condon vibronic structure, as will be discussed in more detail in the case of solid films where these vibronic structures are more precisely defined. The well-defined low-temperature absorption spectrum shows a shoulder at 513 nm (2.42 eV), which we assign to the (0–0) fundamental transition of the DD6T molecule in its isolated state.

In solution, oligothiophenes are strongly fluorescent. Both the fluorescence yield and the maximum emission wavelength depend on the conjugation length of the oligomer and on the substituent introduced on the chain. In the case of unsubstituted sexithiophene, the emission spectrum presents two peaks, at 516 and 552 nm, and a shoulder at longer wavelength. The shape of the fluorescence excitation spectrum matches rigorously that of the absorption spectrum. The Stokes shift has been measured at room temperature on the structureless spectrum between the lowest energy absorption band and the highest energy emission band. The small energy change of observed Stokes shift, 3985, 3768, and 3143 cm^{-1} for DD6T, 6T, and DH6T, respectively,

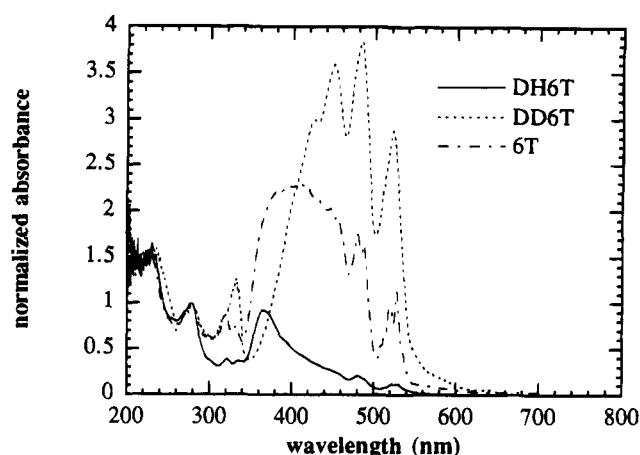


Figure 3. UV–vis absorption spectra of 6T, DD6T, and DH6T thin films recorded at 13 K.

can be attributed to a decrease in geometric changes between the fundamental and the excited state in the order DD6T > 6T > DH6T. It must be pointed out, however, that these values correspond to apparent Stokes shifts, which can also be explained by a greater energy migration of the excitons following excitation in this series of sexithiophenes, in agreement also with a decrease in geometric changes in the order DD6T > 6T > DH6T. The fluorescence spectrum of DD6T at 77 K in diethyl oxide glass, Figure 2, presents a shape very similar to that obtained at room temperature. Absorption and emission spectra at 77 K, Figure 2, follow the classical image rule, the band at 513 nm corresponding to the (0–0) transition. The shoulders in the emission spectra correspond to those observed in the absorption spectra and originate from vibronic coupling, as will be discussed later. The fluorescence quantum yield, determined in CH_2Cl_2 is only slightly dependent on the structure of the molecule and ranges from 35 to 45%. It increases when the temperature decreases, which agrees with the expected rigidification of the molecule.

UV–Visible Absorption and Photoluminescence of Thin Films. Figure 3 shows the UV–vis absorption spectra of 6T, DD6T, and DH6T thin films recorded at 13 K. The spectra were normalized for presenting the same absorption at the two high-energy peaks. These peaks are found in the spectra of all oligothiophenes and can be understood to originate from the thiophene rings. One can therefore expect that the normalized spectra of Figure 3 correspond to roughly the same amount of sexithiophene. We note a well-marked difference between the spectra of DD6T and DH6T. In the former case, the spectrum presents an intense peak at 523 nm (2.37 eV), followed by two peaks at 484 and 452 nm (2.56 and 2.75 eV), respectively. These three peaks are located at almost the same energy as those of DD6T isolated molecules in a glass matrix (see above). The constant interval on the order of 0.19 eV (1504 cm^{-1}) is close to the frequency of the C=C stretching mode. These peaks can therefore be attributed to the (0–0) transition of the isolated molecule, together with their vibronic replica. These peaks are still present in the spectrum of DH6T, although considerably attenuated and slightly red shifted. We also note a splitting of each peak into two components. However, the most remarkable feature of this last spectrum is an intense peak at 364 nm (3.40 eV).

The absorption spectrum of 6T seems to combine the features of both DD6T and DH6T. The peaks corresponding to the (S_0 – S_1) transition are well-marked, though less intense than that for DD6T. Furthermore, the peaks are split in two and also present a fine structure. These two features have already been discussed

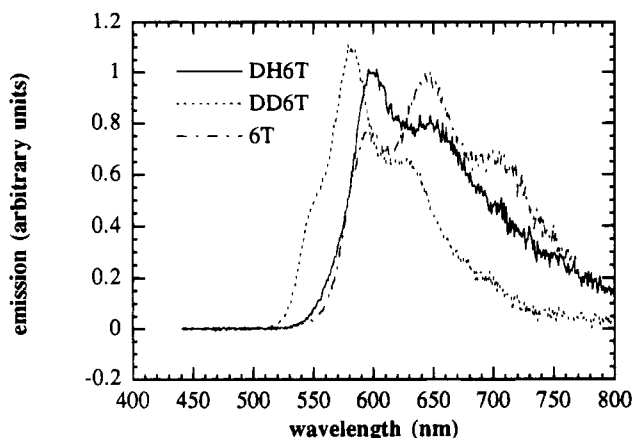


Figure 4. Photoluminescence spectra of 6T, DD6T, and DH6T in thin film at 293 K.

in a previous paper.¹⁸ It is also worth noting that the rest of the spectrum extends toward high energies up to the intense peak of DH6T, thus forming a broad featureless massif that contrasts with the spectra of the substituted molecules.

The photoluminescence (PL) spectra of 6T, DD6T, and DH6T in thin film are shown in Figure 4. They all present a maximum, which depends on the molecular structure, and two or three shoulders. For DD6T the PL spectrum consists of three shoulders at 550, 630, and 700 nm, together with a peak at 582 nm. The emission spectrum of 6T presents shoulders at 600 and 700 nm and a maximum at 640 nm. The same shape is observed on DH6T, with a maximum at 600 nm and two shoulders. The mean separation between shoulders is about 1410 cm^{-1} and can be attributed to a coupling with the C=C stretching mode. The determination of the quantum yield of the solid films has not been achieved. However, we have observed that the emission intensity of films of similar optical absorbance is several times smaller for DH6T and 6T than for DD6T, although in solution the three molecules exhibit the same quantum yield. The PL excitation spectrum of DD6T slightly differs from its absorption spectrum. By contrast, the PL excitation spectra of DH6T and 6T do not match their absorption spectra and present a maximum at the low-energy side (513 nm), which corresponds to the (0–0) transition of the absorption of the isolated molecule, in agreement with results reported by Dippel et al.¹⁹

Discussion

The similarity between the absorption spectra of DD6T solid films and that of the isolated molecule rigidified in a glass matrix shows that molecular interactions in the solid state are weak, in agreement with the crystallographic data, which indicate that the intermolecular distances are longer than those in a close-packed arrangement.

In contrast, the intense peak at 3.40 eV of DH6T can be attributed to exciton interactions between nearest neighbor molecules in a close-packed organization. A consequence of the herringbone structure is that the unit cell presents at least two different sites. The coupling between the transition dipole of molecules at nonequivalent sites leads, in the case of a rigid infinite lattice, to the well-known Davydov's splitting.²⁰ When the dipoles are all parallel, the transition between the ground state and the lower crystalline excited state is completely forbidden, thus accounting for the unique intense peak of DH6T. According to the molecular exciton model developed by El Bayouni and Kasha,²¹ the shift of the transition as compared to that of the free isolated molecule in solution is given to a first approximation by

$$\Delta\nu = \left(\frac{2}{hc}\right) \left(\frac{N-1}{N}\right) \left(\frac{\mu^2}{r^3}\right) (1 - 3 \cos^2 \gamma) \quad (1)$$

where h is the Planck constant, c the velocity of light, N the number of molecules in the aggregate, μ the dipole moment of the transition in the monomeric molecule, r the distance between molecular centers, and γ the tilt angle between the line of the molecule centers and the direction of the transition dipole moment.

The dipole moment μ is related to the molar extinction by

$$\mu^2 = 9.185 \times 10^{-39} \frac{1}{\bar{\nu}} \int \epsilon \, d\bar{\nu} \quad (2)$$

For DH6T, the application of Kasha's rule, with $\mu^2 = 9.48 \times 10^{-35} \text{ erg}\cdot\text{cm}^2$, $\Delta\nu = 4875 \text{ cm}^{-1}$, and $r = 4.916 \text{ \AA}$, leads to an angle γ of 69° . This value appears in close agreement with that deduced from X-ray diffraction data. The same theory, Kasha's rule, was applied for the assignment of the molecular-oriented thin films of sexithiophene by Hamano et al.⁶ The molecular exciton model has also been used by Egelhaaf et al.^{14,16} for the assignment of thin films, of mono- and multilayers of 5T and 6T, prepared by gas phase deposition.

From the above discussion, two energy level diagrams can be put forward for DD6T and DH6T, respectively (see Figure 5). In the case of DD6T, the diagram in the solid state is very similar to that of the isolated molecule, with only a slight shift of both the ground and the excited levels. As for DH6T, the close-packed arrangement of the molecules in the solid state leads to a splitting of the excited level into two exciton bands. The small absorption peak at 520 nm and its vibronic replica originate from disordered domains, e.g., grain boundaries, where the misalignment of the molecules leads to an energy diagram similar to that of DD6T, with no splitting of the excited level. We note that such a description can also account for the excitation spectrum of 6T and DH6T films, the photoluminescence of which would only originate from misaligned domains.

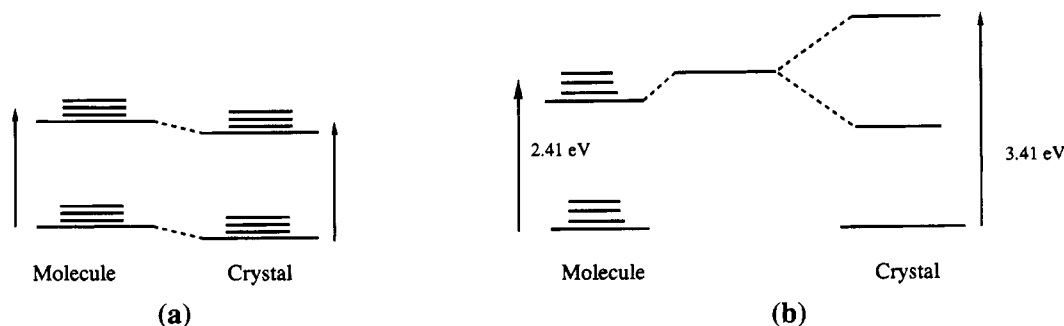


Figure 5. Energy-level diagram of molecular and crystalline DD6T (a) and DH6T (b).

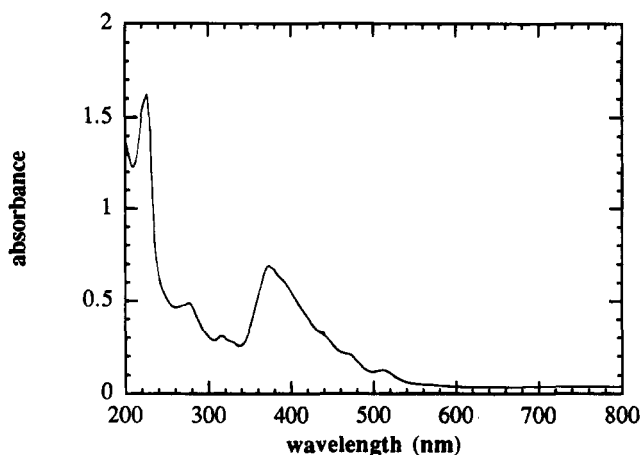


Figure 6. Absorption spectrum of a 6T film deposited on a substrate cooled down to 77 K.

The broad absorption massif of 6T has probably a different origin. As stated above, X-ray pole figure measurements have shown that the crystal grains in 6T films, evaporated on substrates held at room temperature, present at least two orientations, with the crystal long axis parallel or perpendicular to the substrate.¹⁰ This feature can be changed by varying the substrate temperature. On a heated substrate, the crystal grains are mainly perpendicular to the substrate,^{6,22} whereas they are parallel to a substrate evaporated on a substrate cooled down to liquid nitrogen.²² In both cases, the massif tends to disappear and be replaced by a narrow peak at about 360 nm, similar to the one observed on DH6T, as shown in Figure 6 for the case of a film deposited at 77 K. The massif can therefore be associated with the multiple orientation of crystal grains in 6T films deposited at room temperature. To date, we do not have any further explanation to rationalize such behavior.

Conclusion

In this work, a new approach has been developed for understanding the light absorption and emission properties of oligothiophene (e.g., sexithiophene). The optical properties and electronic level ordering of these molecules are largely determined by the structural organization of molecules in the film. Unsubstituted and α,ω -disubstituted sexithiophenes show a tendency to self-organize, with their long axes parallel to each other and perpendicular to the substrate plane. The photoluminescence yield of these films is very low. On the other hand, the introduction of an alkyl group in the β position leads

to materials that possess a larger quantum yield of photoluminescence and are thus potentially of interest for electroluminescent devices.

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