

# Intermolecular Interactions in Conjugated Oligothiophenes. 1. Optical Spectra of Terthiophene and Substituted Terthiophenes Recorded in Various Environments

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The absorption and fluorescence spectra of terthiophene (TT) as well as three substituted terthiophene derivatives, namely 3,3''-dimethoxy-2,2':5',2''-terthiophene (DMOTT), 3,3''-dimethyl-2,2':5',2''-terthiophene (DMTT), and 3',4'-dihexyl-2,2':5',2''-terthiophene (DHTT), isolated in an alkane matrix and in their aggregated forms are reported. The thermochromic properties of substituted oligothiophenes are reported for the first time. The optical changes observed for the isolated molecules in the alkane matrix are interpreted in terms of conformational changes caused by the packing effect. After aggregation, TT exhibits a splitting in the excitation spectrum, which is provoked by an excitonic effect. On the other hand, it is observed that the changes in the optical properties of substituted terthiophenes are close to those found in the alkane matrix. This strongly suggests that the aggregation process does not produce any significant optical change, other than those provoked by conformational changes, in the excitation spectra of these molecules. It is suggested that the presence of the side chains weaken the intermolecular interactions, which are responsible for the excitonic effect. Finally, the fluorescence spectra of all the molecules investigated show a new red-shifted band, when aggregated. The new emission cannot be explained by conformational changes and has its origin in the aggregation process itself.

## 1. Introduction

Electronic and optical properties of organic conjugated polymers have evolved over the past two decades, providing the chemical and physical community with viable tools for probing polymer structures on a molecular scale. By investigating optical phenomena of organic conjugated polymer systems, one can develop an accurate picture of intermolecular interactions taking place in solution and in solid phases. This is indeed in the field of interest of many parts of modern chemistry as organic, bio-, and solid-state chemistry.

Polythiophene is an interesting example of a conjugated polymer because of its high electrical conductivity in its oxidized (doped) state.<sup>1</sup> The high conductivity is ascribed to the movement of delocalized charges and associated structural deformations along and between polymer chains.<sup>2</sup> However, this conducting polymer with a highly conjugated  $\pi$ -system is insoluble and infusible. Although the delocalized electronic structure of polythiophene tends to yield relatively stiff chains with little flexibility, solubility has been achieved by the incorporation of relatively long and flexible side chains.<sup>3–5</sup> Introducing an *n*-alkyl group with a minimum of four carbon atoms at the 3-position of the thiophene ring allows the polymer to be soluble in common organic solvents, fusible, and melt processible, yet retaining a rather high conductivity of about 30–100 S/cm.<sup>6</sup> The physical and chemical properties of poly-(3-alkylthiophene)s have been applied in a number of applications such as batteries, light-emitting devices, photopattern recordings, and photo catalysts.<sup>7–9</sup>

Due to the incorporation of side chains to the backbone, some polythiophene derivatives exhibit interesting reversible thermo-

chromic,<sup>10–14</sup> solvatochromic,<sup>6</sup> and piezochromic<sup>15</sup> properties. These optical phenomena are not unique to polythiophenes and have also been reported for some polysilanes<sup>16</sup> and polydiacetylenes.<sup>17</sup> In most cases, these dramatic color transitions have been associated with conformational changes since, in  $\pi$ -conjugated polymers, there is a strong coupling between the electronic structures and the backbone conformation.<sup>10–14,18</sup> The thermochromism and solvatochromism were considered at a molecular level as a result of the interruption of the conjugation caused by a generation of twists along the main chain. The increased thermal motion of the side chains is believed to be intimately involved in the thermochromic effect by influencing the planarity of the polymer backbone and therefore the electronic structure. For instance, poly(3-alkylthiophene)s are red in the solid state at room temperature and this material becomes yellow at higher temperatures.<sup>14</sup> Crystallographic data for this material show a lamellar structure with a high degree of planarity of the backbone at room temperature.<sup>19–21</sup> As the temperature is increased, the thermal agitation of the lateral chains would induce a larger repulsion between the chains creating a high deviation from planarity in the main chain. It is important to mention here that X-ray data provide information over the crystalline region while the UV–visible absorption spectra are sensitive to electronically conjugated local chain segments and also to the interchain interactions.<sup>21</sup>

Our goal is to better understand how intermolecular interactions affect the optical properties with respect to those observed in isolated molecules and hence to understand the role played by intermolecular interactions in the phenomenon of thermochromism observed in some substituted polythiophenes. However, the polymers are exhibiting a broad and not fully characterized range of conjugation lengths that make difficult the measurement of vibrationally resolved optical spectra. For

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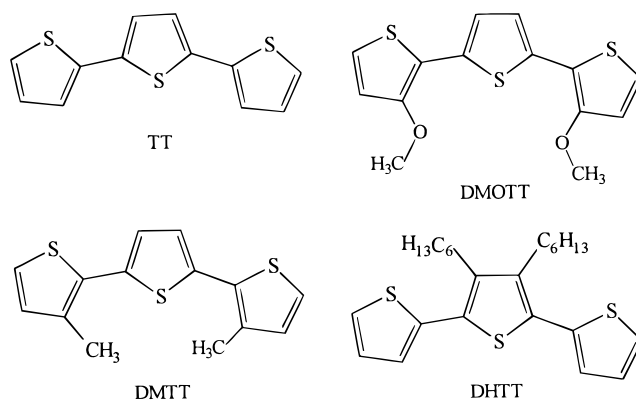
this reason, we have focused our attention on oligothiophenes for which optical properties are better characterized. Indeed, the optical properties of many unsubstituted<sup>22,23</sup> and substituted<sup>24–29</sup> oligothiophene derivatives, in solution at room temperature, are well-known. Despite the fact that the synthesis of many substituted oligothiophenes is reported in the literature, the thermochromic properties of these compounds in solution are still lacking. The only chromic effects reported in the literature deal with unsubstituted oligothiophene derivatives in various environments, such as in thin films,<sup>30–34</sup> in inclusion complexes<sup>34–37</sup> and in aggregated forms.<sup>32,38</sup> In thin films or in aggregated forms, the optical properties have been explained using an excitonic model.<sup>39</sup>

We have recently reported and described the HF/3-21G\* potential energy surfaces of many substituted bithiophenes.<sup>40–42</sup> The unsubstituted bithiophene shows a twisted conformation with a minimum at  $\theta = 150^\circ$  (dihedral angle between thiophene rings).<sup>40</sup> The insertion of methoxy groups in 3 and/or 3' positions favors planar conformations due to the electron donor properties of these substituents.<sup>42</sup> On the other hand, the incorporation of alkyl groups on the same positions induces a greater torsion between thiophene rings with higher rotational energy barriers against planarity.<sup>40</sup> Finally, bithiophenes having thioalkyl groups as well as mixed substituents exhibit a good number of various conformers.<sup>41,42</sup> From these theoretical results, it has been possible to correlate the rotational barriers between the lowest energy conformation and the coplanar conformation of the substituted bithiophenes with the thermochromic properties observed (or not) in the parent polymers.<sup>43</sup> Moreover a new thermochromic polythiophene has been predicted using this correlation.<sup>44</sup> These theoretical results strongly suggest that conformational changes are playing an important role in the thermochromism observed in polymers. In contrast, some authors have recently explained optical changes observed in the absorption spectra of poly(3-alkylthiophene)s on the sole basis of interchain interactions ( $\pi$ -stacking effect) and by neglecting possible conformational changes along the main chain.<sup>45</sup> It will be shown in this paper that this is certainly in disagreement with the origin of the chromic effect observed in substituted oligothiophenes.

In this work, to obtain spectral evidence about the origin of the thermochromic effect, the absorption and fluorescence spectra of four terthiophene derivatives isolated in an *n*-alkyl matrix at 77 K and in aggregated forms (in a glassy medium or in methanol/water mixtures) are reported. Both the packing and the excitonic effects on the optical spectra are analyzed. Results show that the optical changes found for the isolated molecules in a 77 K matrix are associated with conformational changes (packing effect). Conformational changes are also responsible for the main part of the optical changes found in the absorption spectra of the substituted terthiophenes in their aggregated forms. However the formation of parallel H-type excitons may also play a role in these spectra. On the other hand, the fluorescence spectra of the terthiophene derivatives in their aggregated forms cannot be explained by conformational changes and have their origin in the excitonic effect. This study deals with conformational property relationships and  $\pi$ -stacking of conjugated organic oligomers. These are key properties to control in the development of new organic conducting polymers. The molecular structures of the oligothiophenes investigated are displayed in Figure 1.

## 2. Methodology

**2.1. Materials.** Terthiophene (TT, 99%), *n*-decane (99+%), isopentane (99.5+%, HPLC grade), and methanol (99.9%,



**Figure 1.** Molecular structures of the substituted terthiophenes investigated.

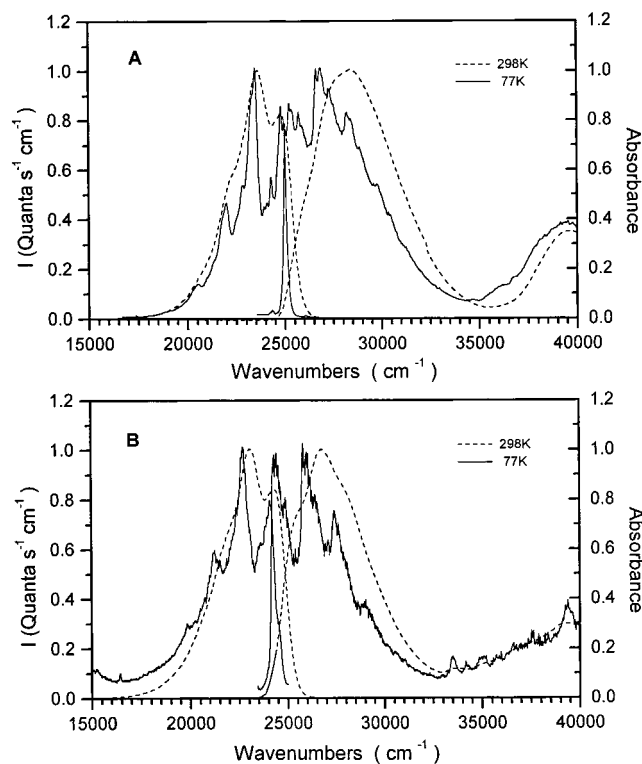
spectrophotometric grade) were purchased from Aldrich Chemicals and used as received. Distilled water was used in the methanol/water mixtures. Prior to use, all the solvents were checked for spurious emissions in the region of interest and found to be satisfactory. 3',4'-Diethyl-2,2':5',2''-terthiophene (DHTT)<sup>24</sup> and 3,3''-dimethyl-2,2':5',2''-terthiophene (DMTT)<sup>46</sup> were prepared according to previously published procedures. 3,3''-Dimethoxy-2,2':5',2''-terthiophene (DMOTT) was prepared by following procedures similar to those previously reported in the literature.<sup>47</sup>

**2.2. Instrumentation.** Room-temperature absorption spectra were recorded on a Varian spectrometer, model Cary 1 Bio, and temperature-dependent absorption spectra were recorded on a Varian spectrometer, model 5E, using 1 cm quartz rectangular cells. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with a F2T11 special configuration (1 cm rectangular quartz cells). The excitation and emission band-passes used were 2.6 and 1.9 nm, respectively. The fluorescence and excitation spectra were found independent of the excitation and emission wavelength, respectively, and the excitation spectra were identical to their respective absorption spectra.

In rigid media at 77 K (*n*-decane matrix, isopentane glass, and methanol/water mixtures), excitation and fluorescence spectra were recorded using the front face arrangement of the instrument to avoid any reabsorption or inner filter effects. Measurements were taken in a quartz cylinder tube of 0.4 mm (i.d.) immersed in a Dewar filled with liquid nitrogen. Excitation and emission band-passes of 0.34 and 3.8 nm, respectively, were used for the recording of the excitation spectra while the fluorescence spectra were recorded using excitation and emission band-passes of 1.10 and 0.75 nm, respectively. Temperature-dependent measurements (in fluid media) were done using 1 cm quartz cells and with excitation and emission band-passes similar to those employed for the room-temperature measurements. Temperatures were varied using a Cryo Industries cryostat, model RC 152, using liquid nitrogen for the cooling gas and monitoring with a thermocouple immersed in the sample solutions.

## 3. Results and Discussion

**3.1. Conformational Analysis.** In a recent paper,<sup>48</sup> we have reported and described the ab initio HF/3-21G\* potential energy surfaces of all terthiophenes investigated here (see Figure 1) as well as their respective absorption and fluorescence spectra recorded at room temperature. The potential energy surface of TT has shown that the most stable conformation is *anti-gauche*, about  $30^\circ$  off planarity. Moreover, the rotational barrier against

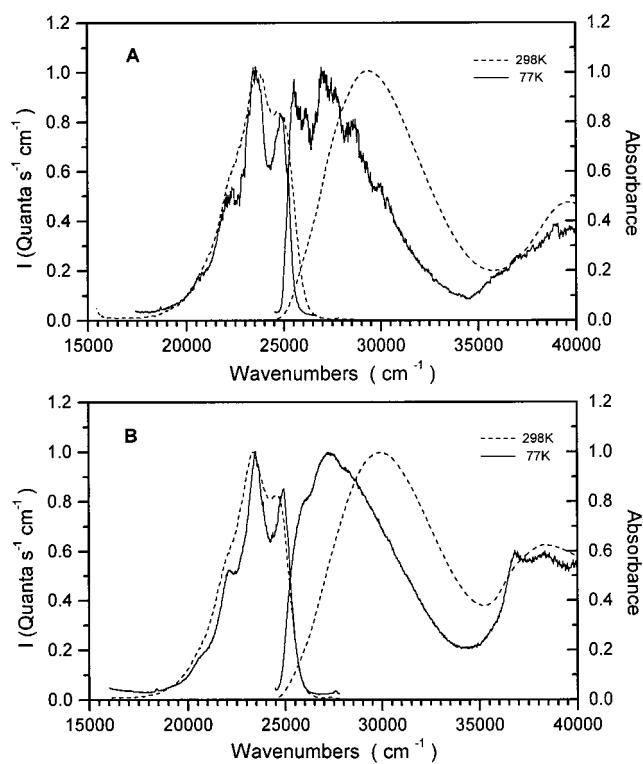


**Figure 2.** Absorption (298 K), excitation (77 K), and fluorescence spectra of TT (A) and DMOTT (B) in *n*-decane. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentration was  $2.5 \times 10^{-5}$  mol dm $^{-3}$  for TT and DMOTT at room temperature.

planarity is relatively small (0.67 kcal mol $^{-1}$ ) allowing for the presence of many conformers at room temperature. The methoxy substituents in the DMOTT compound induces a more planar conformation compared to that of TT. On the other hand, the presence of alkyl substituents (DMTT and 3',4'-diethyl-2,2':5',2''-terthiophene (DETT)) induces a strong twisting between adjacent thiophene rings and a high rotational energy barrier against planarity. Rotational energy barriers and torsional angles of the lowest energy conformers of each derivative are listed in reference.<sup>48</sup>

Absorption spectra, recorded in *n*-decane at room temperature (Figures 2 and 3), are in good agreement with theoretical results. Indeed, the large and nonstructured absorption band of TT suggests that this molecule is not planar and is flexible in agreement with its potential energy surface. On the other hand, the red shifted and more structured absorption band of DMOTT compared to that of TT shows that the molecule is more planar as predicted by the *ab initio* calculations. However, a part of the red shift is also induced by the electron donor properties of the methoxy groups. Finally, compared to the absorption band of TT, the absorption bands of DMTT and DHTT are blue shifted, their absorption coefficients are smaller,<sup>48</sup> and their bandwidths are larger.<sup>48</sup> These optical properties strongly suggest that DMTT and DHTT are much twisted in their ground state as predicted by their respective potential energy surfaces.

Fluorescence spectra of each molecule, recorded in *n*-decane at room temperature (Figures 2 and 3), are more structured and narrower than their respective absorption spectra and rather similar. Moreover, the relatively large Stokes shifts and the poor adherence to the mirror image relationship between absorption and fluorescence spectra indicate a nonnegligible conformational change between these two states. This led to the conclusion that all molecules adopt a more planar conformation in the first



**Figure 3.** Absorption (298 K), excitation (77 K), and fluorescence spectra of DMTT (A) and DHTT (B) in *n*-decane. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentrations were  $5.6 \times 10^{-5}$  (DMTT) and  $5.2 \times 10^{-5}$  (DHTT) mol dm $^{-3}$  at room temperature.

relaxed excited singlet state. The red shift observed for the fluorescence band of DMOTT compared to that of TT is very small and is attributed to the electron donor effect of the methoxy groups. The fluorescence bands of DMTT and DHTT are located at about the same energy as the emission band of TT showing that, after relaxation in their excited state, these three molecules adopt similar conformations. A more detailed analysis of the spectroscopic parameters of all these molecules has been done before.<sup>48</sup>

**3.2. Matrix Isolation of the Terthiophene Derivatives.** The optimum conditions for the appearance of the quasi-linear spectra (Shpol'skii effect) of linear aromatic molecules is obtained when the length of the long axes of the *n*-alkane solvent and the aromatic molecule are matched.<sup>49</sup> For this reason, *n*-decane has been chosen to form a substitutional matrix, which should totally isolate the trimers even at concentrations where aggregates are observed in other solvents.

Figure 2A shows the absorption (or excitation at 77 K) and fluorescence spectra of TT in *n*-decane at room temperature (fluid solution) and isolated in the solvent matrix at 77 K. One can see that, in a *n*-decane matrix at 77 K, the excitation spectrum of TT is red shifted and more structured compared to its absorption spectrum measured at room temperature. By contrast, the fluorescence spectrum of TT recorded at 77 K does not show any significant shift. However, an increase in the vibronic resolution is observed in the *n*-decane matrix. It is also observed that the mirror image relationship is well respected at 77 K so that the Stokes shift is small between the excitation and fluorescence spectra. These observations strongly suggest that, at 77 K, conformations of TT in the ground and in the excited state are very close. Since a nearly planar conformation is expected for TT in its first singlet excited state, in solution



at room temperature,<sup>48</sup> and since, at 77 K, the fluorescence band is not shifted, it can be concluded that TT also adopts a planar ground-state conformation in the *n*-decane matrix. The change of conformation in the ground state between room-temperature solution and 77 K *n*-decane matrix probably occurs due to a better cohesion energy existing between planar molecules and the matrix (packing effect). This is in agreement with X-ray data showing that bithiophene<sup>50,51</sup> and terthiophene<sup>52</sup> are planar in the solid state. The change of conformation adopted by TT is responsible for the red shift observed in the excitation spectrum, relative to the room-temperature one, recorded in the *n*-decane matrix. Birnbaum and Kohler reached the same conclusion from the full vibrational analysis of the excitation and fluorescence spectra of TT in *n*-decane at 4 K.<sup>53</sup> It is important to mention here that this ground-state conformational change between room temperature and 77 K can also be achieved in glassy media (isopentane and *n*-butanol) (figures not shown). These results are also in total agreement with the excitation and fluorescence spectra of unsubstituted oligothiophenes reported by Becker et al. in an ethanol glass at 77 K.<sup>23</sup> The second absorption band, near 40 000 cm<sup>-1</sup>, is not affected by the conformational change since this electronic transition is localized on one thiophene ring.

A red shift of the DMOTT absorption spectrum is also observed in the *n*-decane matrix with a much improved vibronic resolution (see Figure 2B). The low-temperature fluorescence spectrum also shows a better vibronic resolution, but in contrast with TT, a small but detectable red shift of the band is also observed compared to the room-temperature spectrum. The mirror image relationship is relatively good at 77 K, and the Stokes shift is small showing that DMOTT adopts rather similar conformations in the ground and first singlet excited states. Since DMOTT is expected to be almost planar (9° off planarity) in fluid solution,<sup>48</sup> it is a good assumption to consider that DMOTT is nearly planar in the *n*-decane matrix. Thus, one would expect a smaller difference between room- and low-temperature absorption spectra. The red shift of the excitation spectrum recorded at 77 K, though smaller than that observed for TT, might involve both a small conformational change of the backbone combined with a conformational change of the methoxy groups. The latter would also explain the red shift of the fluorescence band recorded in the matrix, which cannot be accounted for by a conformational change of the backbone. The last statement can be correlated with the geometry of alkoxy-substituted oligothiophenes calculated (gas phase) and obtained from crystallographic data (solid state). Indeed HF/3-21G\* ab initio calculations performed on DMOTT<sup>48</sup> and on 3,3'-dimethoxy-2,2'-bithiophene (DMO33BT)<sup>42</sup> predict that the methoxy groups are perpendicularly oriented relative to the plane of the molecule. On the other hand, in the solid state, X-ray data shows that the alkoxy groups of DMO33BT and other alkoxy-substituted bithiophene derivatives are coplanar with the thiophene rings.<sup>54,55</sup> It is expected that, in the solid state, the coplanar arrangement of the alkoxy groups maximize the packing energy.

One can see in Figure 3A that the excitation spectrum of DMTT isolated in the matrix shows a large red shift and an increase of the vibrational structure compared to that measured at room temperature. On the other hand, the fluorescence band recorded at 77 K does not show any significant shift but a better vibronic resolution is observed. According to the above discussion, it can be also concluded that DMTT is more planar in the *n*-decane matrix. However, the excitation band of DMTT in the matrix is slightly blue shifted compared to the excitation

**TABLE 1: Comparison of the Absorption (or Excitation) and Fluorescence Maxima between Room Temperature and 77 K in *n*-Decane**

trimers	$\bar{\nu}_E^a$ (cm <sup>-1</sup> )	$\bar{\nu}_A^b$ (cm <sup>-1</sup> )	$\bar{\nu}_F^c$ (cm <sup>-1</sup> )	
	at 77 K	at 298 K	77 K	298 K
TT	26 800	28 350	23 500	23 600
DMOTT	25 900	26 800	22 750	23 100
DMTT	27 050	29 300	23 550	23 700
DHTT	27 250	29 900	23 500	23 300

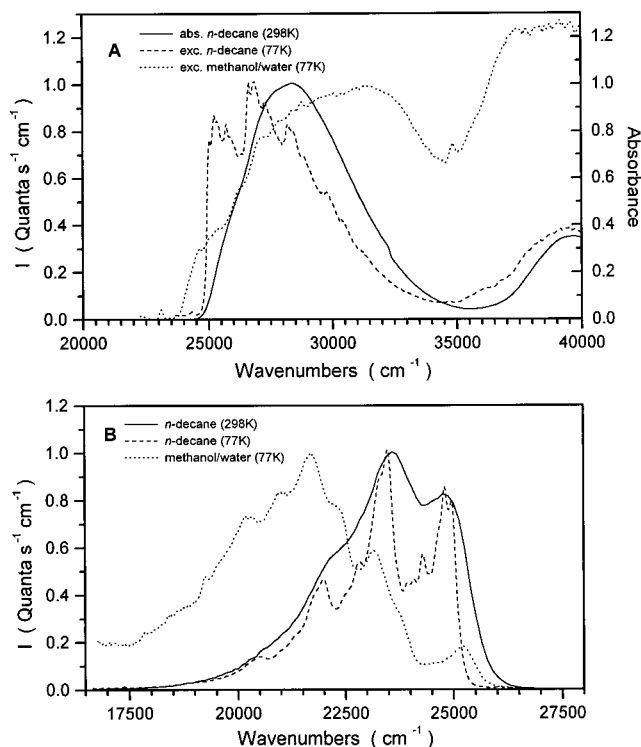
<sup>a</sup> Maxima of the excitation spectra. <sup>b</sup> Maxima of the absorption spectra. <sup>c</sup> Maxima of the fluorescence spectra.

band of TT in the same environment (see Table 1). But, for the same twisting angles between thiophene rings, a red shift of the absorption band should be observed for DMTT compared to TT due to the electron-donating properties of the methyl groups.<sup>56</sup> Moreover, this terthiophene derivative is twisted (about 30° from planarity) in the solid state.<sup>51</sup> According to these observations, it can be concluded that the conformation of DMTT is not as planar as that of TT in rigid matrixes, which explains the blue shifts observed in the excitation and fluorescence spectra of DMTT at 77 K compared to those of TT.

Figure 3B shows that similar optical changes exist between room- and low-temperature spectra of DHTT indicating that, for this molecule, a more planar conformation is also adopted in the *n*-decane matrix at 77 K. As DHTT and DMTT show very similar shifts following the formation of the *n*-decane matrix, it is expected that both molecules adopt very similar conformations in their ground state. However, the vibronic resolution of the 77 K excitation spectrum of DHTT is less pronounced than that found for DMTT. This is probably caused by the presence of the hexyl chains, which preclude the formation of a perfect substitutional matrix and thus allow for a wider distribution of conformers. One can also see that the fluorescence band of DHTT in the matrix is slightly blue shifted compared to that at room temperature. This can also be attributed to the nonuniformity of the matrix, which may trap more twisted conformers.

The spectral properties of the terthiophene derivatives are listed in Table 1. One can see that the shifts between the maxima of the room temperature absorption spectrum and the low-temperature excitation spectrum of these molecules are larger for those molecules which are more twisted in the ground state as suggested theoretically.<sup>48</sup> For the fluorescence bands, the shifts are much less pronounced except for DMOTT where a conformational change of the methoxy groups is expected as discussed above. In conclusion, in a *n*-decane matrix at 77 K, the molecules are well isolated and they adopt conformations similar to those found in the solid state. Thus, by comparing absorption and fluorescence spectra of the terthiophene derivatives in fluid solution with those obtained in the rigid matrix, it has been possible to observe the optical changes induced by the packing effect (giving a conformational change) on isolated molecules. Now, let us see how these optical changes can be compared with those observed for the aggregated forms of these trimers.

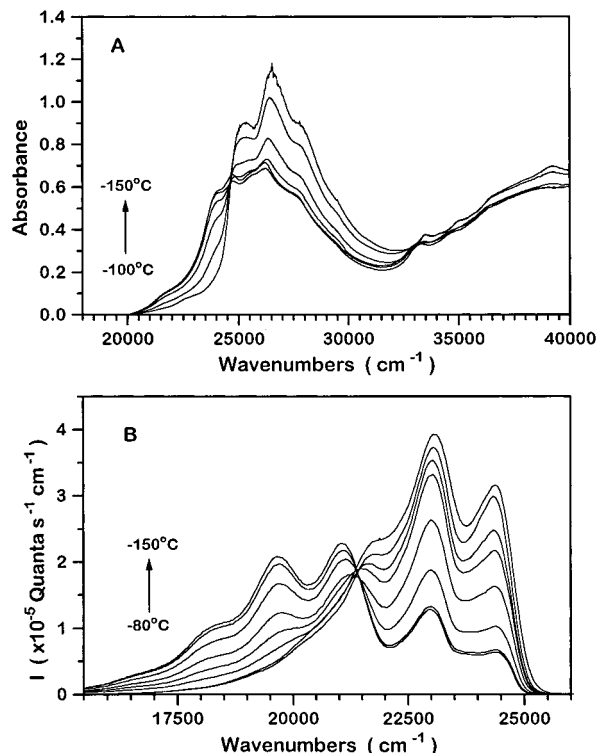
**3.3. Intermolecular Interactions after Aggregation.** To investigate the aggregation phenomenon, high concentrations of the molecules in isopentane or in methanol/water mixtures at 77 K were used. Isopentane instead of *n*-decane is employed because, at 77 K, this solvent forms a glass avoiding the possibility to trap molecules in interstitial and/or substitutional lattices. Moreover, the spectral resolution of DMOTT aggregates is improved in isopentane compared to the methanol/water mixtures at 77 K. Unfortunately, it was observed that the other



**Figure 4.** Absorption (A), excitation (A), and fluorescence (B) spectra of TT in various environments. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentration was  $4.9 \times 10^{-5}$  mol dm $^{-3}$  at room temperature in the methanol/water mixture.

terthiophenes investigated do not form significant amount of aggregates in isopentane. For this reason, since terthiophene derivatives are not soluble in water, methanol/water mixtures have been used for the other compounds. It is important to mention here that, for DMOTT, similar optical changes have been measured in isopentane and in methanol/water mixtures at 77 K.

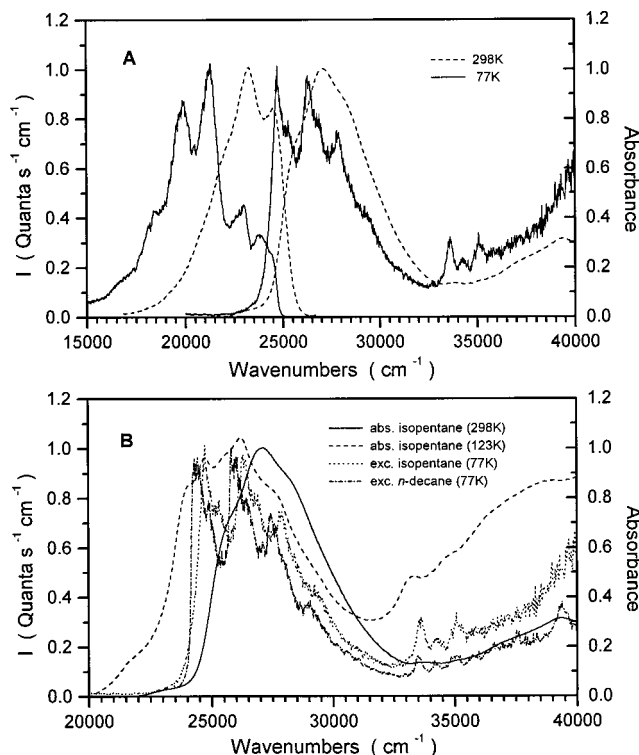
Figure 4 shows the excitation (A) and fluorescence spectra (B) of TT in a methanol/water mixture (25:75) at 77 K. The respective spectra of TT in *n*-decane at room temperature (298 K) and at 77 K (rigid matrix) are also reported in Figure 4. As discussed in the previous section, the red shift observed for the excitation spectrum of TT isolated in the *n*-decane matrix compared to the room-temperature absorption spectrum in the same solvent is caused by conformational changes favoring the planarity of the molecule. On the other hand, the excitation spectra of TT in aggregated forms (methanol/water mixture) show two components, one intense band located at 31 700 cm $^{-1}$  which is blue shifted compared to that recorded at room temperature in *n*-decane and a weak peak near 25 000 cm $^{-1}$  which is red shifted. One can note that the red-shifted part of the excitation spectrum is more red shifted than that of the excitation spectrum of the planar conformation of the isolated molecule in the *n*-decane matrix at 77 K. These spectral properties have been observed for several unsubstituted thiophene derivatives<sup>30–34,38</sup> and have been interpreted on the basis of a parallel excitonic type model.<sup>39</sup> The splitting (Davydov splitting) of the absorption band is induced by the two orientations of the molecular transition dipole moment in the H-aggregated forms. Indeed, the weak red-shifted low-energy band (L) is dipole-forbidden while the intense blue-shifted high-energy band (H) is dipole-allowed. This is a consequence of the formation of a local  $C_{2h}$  symmetry (parallel type) Frenkel exciton, which is later delocalized throughout the microaggregates.



**Figure 5.** Temperature-dependent absorption (A) and fluorescence spectra (B) of DMOTT in isopentane. The excitation wavenumber used for the fluorescence spectra was 27 030 cm $^{-1}$ , and the molar concentrations were  $3.6 \times 10^{-5}$  (for absorption) and  $1.8 \times 10^{-5}$  (for fluorescence) mol dm $^{-3}$  at room temperature.

The fluorescence spectra of TT in the methanol/water mixture recorded at 77 K show some peaks centered at 21 500 cm $^{-1}$ . The peaks located at 25 000 and 23 500 cm $^{-1}$  are very close in energy to those observed in *n*-decane and should correspond to the emission of some free molecules. Indeed, the excitation spectrum monitored at 23 500 cm $^{-1}$  (figure not shown) in the methanol/water mixtures shows a red-shifted band, which is similar to the one observed for the isolated molecules in the *n*-decane matrix. The new red-shifted fluorescence band observed here and for other unsubstituted oligothiophenes has been assigned to the emission from the L energy level of the aggregate.<sup>30–34,38</sup>

Figure 5 shows the temperature-dependent absorption (A) and fluorescence (B) spectra of DMOTT in isopentane. One can see that both absorption and fluorescence spectra exhibit the presence of a new red-shifted band which shows, through the appearance of the isosbestic point, that an equilibrium does exist between two species. In the fluorescence spectra, the formation of the new red-shifted band is spectral evidence that DMOTT can form aggregates in this range of temperature. Indeed, as shown above, the conformational change in the ground state does not induce any significant change in the fluorescence spectrum since the emission always arises from nearly planar conformations at all temperatures. Moreover it will be shown below that the new fluorescence band also appears in the isopentane glass at 77 K with vibrational fine structure ruling out the excimer model since no molecular diffusion should occur in this rigid medium and no vibrational structure is expected in an emission spectrum that involves a ground state with a dissociative energy potential surface. Thus, the new emission is attributed to a certain type of aggregation. The appearance of a new band to the red of the high-temperature absorption spectrum might also be a consequence of the aggregation

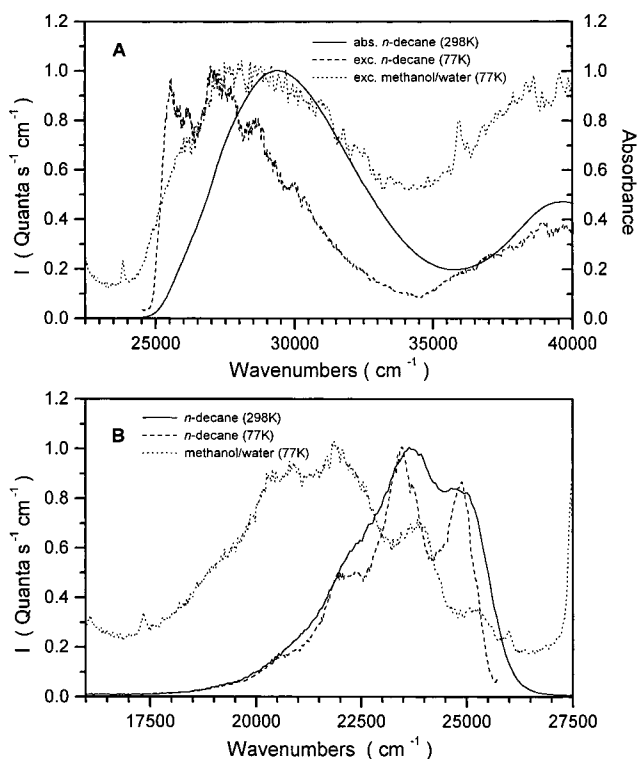


**Figure 6.** (A) Absorption (298 K), excitation (77 K), and fluorescence spectra of DMOTT in isopentane. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentration was  $2.1 \times 10^{-5} \text{ mol dm}^{-3}$  at room temperature. (B) Comparison of absorption and excitation spectra of DMOTT in different environments.

process. But, as discussed above, conformational changes may also induce similar optical changes.

To shed more light on the nature of the process involved, the excitation and fluorescence spectra of DMOTT in isopentane at room temperature and in the glassy medium at 77 K have been recorded and are illustrated in Figure 6A. In the isopentane glass, the excitation spectrum of DMOTT (the second vibrational peak) is slightly red shifted compared to the maximum of the room-temperature spectrum. This spectral shift is similar to that observed for the isolated molecules in the *n*-decane matrix and to the red shift observed in low-temperature fluid solutions in isopentane (see Figure 6B). Moreover, the vibrational fine structure of the spectra in the *n*-decane matrix and in the isopentane glass are identical. Thus, according to the above discussion, small conformational changes involving the dihedral angles between thiophene rings and/or the orientation of the methoxy groups should be mainly responsible for the optical changes observed in the excitation spectrum of DMOTT in the glassy medium.

One can see that the aggregation process induces quite different optical changes in the excitation spectra of TT and DMOTT. Indeed an H-type excitonic effect is responsible for the spectral properties of TT whereas conformational changes might explain the optical changes found in DMOTT (as well as alkyl-substituted terthiophenes; see below). We believe that this difference may involve the intermolecular distance and orientation in the aggregates. Indeed the presence of side chains should increase intermolecular distances and disorder in substituted terthiophenes, which should weaken the ground-state electronic interactions between molecules, interactions that are mainly responsible for the H-type excitonic effect. On the other hand, the good packing of TT molecules should allow for a better intermolecular electronic interaction giving rise to the



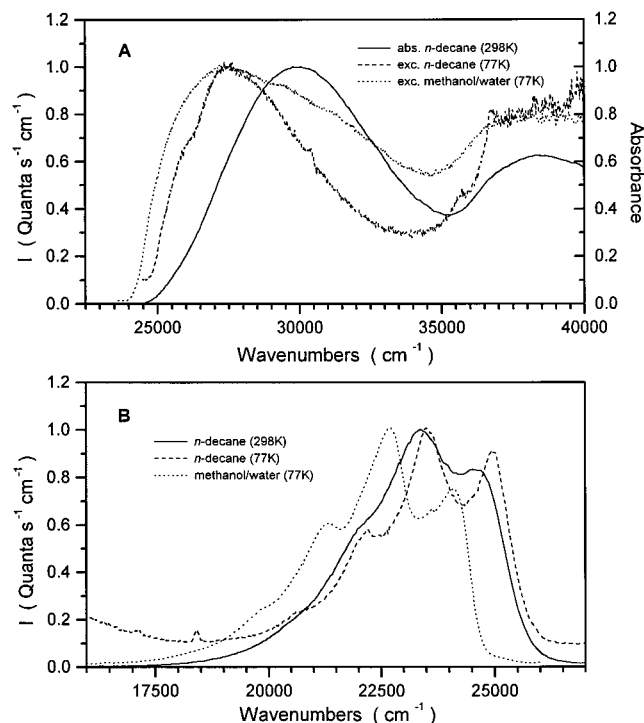
**Figure 7.** (A) Comparison of absorption and excitation spectra of DMTT in various environments. (B) Comparison of fluorescence spectra of DMTT in various environments. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentration was  $\sim 1.6 \times 10^{-5} \text{ mol dm}^{-3}$  at room temperature in the methanol/water mixture.

important splitting of the absorption band. It will be shown in the second part of this series of papers that ZINDO/S calculations performed on the crystalline structures are in good agreement with this statement.

One can see in Figure 6A that the fluorescence spectrum of DMOTT in the isopentane glass shows the appearance of a new band, which presents a large red shift, is structured, and is independent of the excitation wavelength used as reported for the temperature-dependent fluorescence spectra (see Figure 5B). Moreover, the relative ratio between the two fluorescence bands is independent of the excitation energy showing that only one absorbing species is responsible for the two emissions. As discussed above, conformational changes cannot explain such a large red shift observed for the new emission. The electronic interactions involved in the aggregation process should be responsible for the new emission. Work is still underway to determine the nature of this fluorescence emission.

Similar results are obtained for the two other substituted terthiophenes. The excitation spectra of the isolated molecules of DMTT (*n*-decane matrix at 77 K) and of the aggregated forms (methanol/water (25:75) at 77 K) as well as the absorption spectrum at room temperature in *n*-decane are reported in Figure 7A. The respective fluorescence spectra are given in Figure 7B. These results, and the fact that the aggregation process does not induce any optical changes other than conformational changes for DMOTT, strongly suggest that a change in the DMTT conformation might also be responsible for the optical changes found in the aggregated forms. Similar results have also been observed on diluted polymer solutions.<sup>13,14,57,58</sup> Moreover, we also know that going from substituted bithiophenes to substituted sexithiophene does not affect much the conformation of these oligomers.<sup>24-27</sup> All these results are in contradiction





**Figure 8.** (A) Comparison of absorption and excitation spectra of DHTT in various environments. (B) Comparison of fluorescence spectra of DHTT in various environments. The excitation and emission wavenumbers were near the maximum of the absorption (or excitation) and emission spectra, respectively. The molar concentration was  $\sim 3.5$  mol dm $^{-3}$  at room temperature in the methanol/water mixture.

with the assumption that no conformational change could explain the optical changes observed in the absorption spectra of some poly(3-alkylthiophene)s in solution.<sup>45</sup>

The same methodology but in a methanol/water (1:10) mixture to promote the aggregation phenomenon has been applied for DHTT. Results are displayed in Figure 8. As discussed above for DMTT and DMOTT, the red shift observed is attributed to a conformational change toward planarity. Figure 8B shows that the fluorescence spectrum of DHTT in the methanol/water mixture at 77 K is red shifted compared to that found at room temperature in *n*-decane. However this shift is smaller than that observed for DMTT in the same environment. This may be due to the presence of the hexyl chains, which should increase the intermolecular distance and thus should reduce intermolecular electronic interactions in the excited state.

#### 4. Concluding Remarks

This work has shown that well-defined substituted oligomers can be used to study conformation/optical property relationships more efficiently than by using only unsubstituted oligothiophenes. The great variety of substituted oligomers having different conformations and potential energy surfaces allowed us to improve significantly our basic knowledge on these systems by using coupled experimental and theoretical methods. For the first time, the thermochromic properties of substituted oligothiophenes are reported.

It has been observed, in this work, that terthiophene derivatives isolated in an alkane matrix become more planar in their ground electronic states due to the packing effect as observed in the pure solid state. Moreover, the resulting red shifts in the excitation spectra are larger for oligothiophenes which are more twisted in fluid solutions. On the other hand, the fluorescence spectra of the isolated molecules in the rigid matrix are not

significantly shifted indicating that these molecules in fluid solutions are nearly planar in their S<sub>1</sub> relaxed excited states.

Following aggregation, the band in the excitation spectrum of TT is split into two components. This phenomenon has been observed for several unsubstituted oligothiophenes and has been interpreted in terms of a parallel H-type excitonic model. On the other hand, the excitation spectra of the substituted terthiophenes in their aggregated forms are close to those observed for the isolated molecules in an alkane matrix. This indicates that the intermolecular interactions induced by the aggregation process provoke conformational changes, which are similar to those induced by the packing effect in the alkane matrix. We believe that, for the substituted oligothiophenes, the presence of the side chains weakens the intermolecular interactions, which are responsible for the H-type excitonic effect observed in TT. This assumption will be tested in part 2 of this series of studies.

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#### References and Notes

- Schopf, G.; Kossmehl, G. *Adv. Polym. Sci.* **1997**, *127*, 1.
- Chance, R. R.; Boudreau, D. S.; Brédas, J. L.; Silbey, R. in *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.
- Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
- Chen, S. A.; Ni, J. M. *Macromolecules* **1992**, *25*, 6081.
- Hsu, W. P.; Levon, K.; Ho, K. S.; Myerson, A. S.; Kwei, T. K. *Macromolecules* **1993**, *26*, 1318.
- Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.
- Kawai, T.; Kuwabara, T.; Wang, S.; Yoshino, K. *J. Electrochem. Soc.* **1990**, *137*, 3793.
- Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1938.
- Morita, S.; Kawai, T.; Yoshino, K. *J. Appl. Phys.* **1991**, *69*, 4445.
- Inganäs, O.; Salaneck, W. R.; Österholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395.
- Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141.
- Roux, C.; Bergeron, J.-Y.; Leclerc, M. *Makromol. Chem.* **1993**, *194*, 869.
- Faïd, K.; Fréchette, M.; Ranger, M.; Mazerolle, L.; Lévesque, I.; Leclerc, M.; Chen, T.; Rieke, R. D. *Chem. Mater.* **1995**, *7*, 1390.
- Leclerc, M.; Fréchette, M.; Bergeron, J.-Y.; Ranger, M.; Lévesque, I.; Faïd, K. *Macromol. Chem. Phys.* **1996**, *197*, 2077.
- Yoshino, K.; Nakajima, S.; Onada, M.; Sugimoto, R. *Synth. Met.* **1989**, *28*, C349.
- Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Ziegler, J. M. *Adv. Chem. Ser.* **1990**, No. 224, 341.
- Variano, B. F.; Sandroff, C. J.; Baker, G. L.; *Macromolecules* **1991**, *24*, 4376.
- Thémans, B.; Salaneck, W. R.; Brédas, J. *Synth. Met.* **1989**, *28*, C359.
- Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *28*, C419.
- Tashiro, K.; Ono, K.; Minagawa, Y.; Kobuyashi, M.; Kawai, I.; Yoshino, K. *J. Polym. Sci., Polym. Ed.* **1991**, *29*, 1223.
- Mardalen, J.; Samuelson, E. J.; Gautun, O. R.; Carlsen, P. H. *Synth. Met.* **1992**, *48*, 363.
- Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahm, D. U.; Birckner, E.; Naarmann, H. *Synth. Met.* **1993**, *60*, 23.
- Becker, R. S.; de Melo, J. S.; Maçanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683.
- Belletête, M.; Mazerolle, L.; Desrosiers, N.; Leclerc, M.; Durocher, G. *Macromolecules* **1995**, *28*, 8587.
- DiCésaire, N.; Belletête, M.; Raymond, F.; Leclerc, M.; Durocher, D. *J. Phys. Chem. A* **1997**, *101*, 776.
- DiCésaire, N.; Belletête, M.; Donat-Bouillud, A.; Leclerc, M.; Durocher, G. *J. Lumin.*, in press.
- DiCésaire, N.; Belletête, M.; Donat-Bouillud, A.; Leclerc, M.; Durocher, G. *Macromolecules* **1998**, *31*, 6289.
- Van Hutten, P. F.; Gill, R. E.; Herrena, J. K.; Hadziioannou, G. *J. Phys. Chem.* **1995**, *99*, 3218.

- (29) Rossi, R.; Ciofalo, M.; Carpita, A.; Ponterini, G. *J. Photochem. Photobiol. A* **1993**, *70*, 59.
- (30) Fichou, D.; Horowitz, B.; Yu, B.; Garnier, F. *Synth. Met.* **1992**, *48*, 167.
- (31) Oelkrug, D.; Egelhaaf, H.-J.; Worrall, D. R.; Wilkinson, F. *J. Fluoresc.* **1995**, *5*, 165.
- (32) Oelkrug, D.; Egelhaaf, H.-J.; Giersehner, J.; Tompert, A. *Synth. Met.* **1996**, *76*, 249.
- (33) Kanemitsu, Y.; Shimisu, N. *Phys. Rev. B* **1996**, *54*, 2198.
- (34) Bosisio, R.; Botta, C.; Colombo, A.; Destri, S.; Porzio, W.; Grilli, E.; Tubino, R.; Bongiovanni, G.; Mura, A.; DiSilvestro, G. *Synth. Met.* **1997**, *87*, 23.
- (35) Bongiovanni, G.; Botta, C.; Brédas, J. L.; Cornil, J.; Ferro, D. R.; Mura, A.; Pioggi, A.; Tubino, R. *Chem. Phys. Lett.* **1997**, *278*, 146.
- (36) Botta, C.; Bosisio, R.; Bongiovanni, G.; Mura, A.; Tubino, R. *Synth. Met.* **1997**, *84*, 535.
- (37) De Feyter, S.; van Stam, J.; Imans, F.; Viaene, L.; De Schryver, F. C.; Evans, C. H. *Chem. Phys. Lett.* **1997**, *277*, 44.
- (38) Gierschner, J.; Egelhaaf, H.-J.; Oelkrug, D. *Synth. Met.* **1997**, *84*, 529.
- (39) Kasha, M. *Radiat. Res.* **1963**, *20*, 55.
- (40) DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *Synth. Met.* **1998**, *94*, 291.
- (41) DiCésare, N.; Belletête, M.; Raymond, F.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1998**, *102*, 2700.
- (42) DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *J. Mol. Struct. (THEOCHEM)*, accepted for publication.
- (43) DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **1997**, *275*, 533.
- (44) Raymond, F.; DiCésare, N.; Belletête, M.; Durocher, G.; Leclerc, M. *Adv. Mater.* **1998**, *10*, 599.
- (45) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B. L.; Saganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsud, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047.
- (46) Georges, G. Ph.D. Thesis, Université de Montréal, 1997.
- (47) Zotti, G.; Gallazi, M. C.; Zerbi, G.; Meilla, S. V. *Synth. Met.* **1995**, *73*, 217.
- (48) DiCésare, N.; Belletête, M.; Marrano, C.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1998**, *102*, 5142.
- (49) Birks, J. B. *Photophysics of Aromatic Molecules*, Wiley-Interscience: New York, 1970; p 118.
- (50) Pelletier, M.; Brisse, F. *Acta Crystallogr.* **1994**, *C50*, 1942.
- (51) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *Acta Crystallogr.* **1994**, *C50*, 1941.
- (52) Van Bolhuis, F.; Wynberg, H. *Synth. Met.* **1989**, *30*, 381.
- (53) Birnbaum, D.; Kohler, B. E. *J. Chem. Phys.* **1989**, *90*, 3506.
- (54) Paulus, E. F.; Dammel, R.; Kampf, G.; Wegener, P. *Acta Crystallogr.* **1988**, *B44*, 509.
- (55) Pelletier, M.; Brisse, F.; Cloutier, R.; Leclerc, M. *Acta Crystallogr.* **1995**, *C51*, 1394.
- (56) ZINDO/S calculations, unpublished results.
- (57) Roux, C.; Leclerc, M. *Chem. Mater.* **1994**, *6*, 620.
- (58) Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843.