Intermolecular Interactions in Conjugated Oligothiophenes. 3. Optical and Photophysical Properties of Quaterthiophene and Substituted Quaterthiophenes in Various Environments

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A detailed analysis of the optical and photophysical properties of 2,2′:5′:2″:5″,2‴-quaterthiophene (QT), 3,3‴-dimethoxy-2,2′:5′:2″:5″,2‴-quaterthiophene (DMOQT), 3,3‴-dimethyl-2,2′:5′:2″:5″,2‴-quaterthiophene (DMQT) and 3′,4″-didecyl-2,2′:5′:2″:5″,2‴-quaterthiophene (DDQT) in various environments is reported. In solution at room temperature, the optical properties of the free molecules are obtained and discussed in terms of the effect of the substitution on the conformation adopted by each derivative in the electronic ground and first excited states. In a tetradecane matrix at 77 K, the optical properties are obtained for the isolated molecules in this rigid medium where the oligothiophenes adopt conformations similar to those found in the solid state. The optical properties of the quaterthiophene derivatives in their aggregated forms and in the solid state are also reported and discussed in terms of the substitutional effect on the intermolecular interactions, which affect the spectral and photophysical properties of the isolated molecules. For the first time, a β,β'-disubstituted oligothiophene (DMQT) showing an excitonic splitting similar to that obtained for QT is reported. All other substituted oligothiophenes presented show a conformational change, following the aggregation process. This difference is explained by more disordered crystalline forms for DMOQT and DDQT. Theoretical calculations using the ZINDO/S semiempirical method are also performed on the crystalline structure of each derivative in an attempt to correlate the optical properties of these molecules in their aggregated forms and in the solid state with the molecular arrangement found in the crystal.

1. Introduction

Polythiophenes have been widely studied in the past few decades because they combine good conductivity and optical and mechanical properties.[1,2] One intriguing and interesting phenomenon is the chromic effects observed for these polymers in the solid state or in solution.[3−5] These optical properties are discussed in terms of conformational changes and intermolecular interactions.[3−5] Oligothiophenes are also very promising for the development of new materials. For instance, the conducting properties of tetramers and hexamers have allowed the development of organic semiconductors and light-emitting diodes.[6,7] Oligothiophenes also show chromic effects similar to those found for the corresponding polymers.[8,9]

Since the polymers exhibit broad and unstructured absorption and fluorescence bands and since the use of polymers is limited to few environments, the use of well-defined oligothiophenes has been found very useful in an attempt to understand the origin of the spectral properties of the polymers. Experimental and theoretical analyses of the effect of the substitution on the conformation of 2,2′-bithiophene[10−14] allow us to understand the effect of the lateral groups on the conformation of oligothiophenes. These studies have also allowed us to obtain a good correlation between the presence (or not) of thermochromism for the substituted polythiophenes and the conformation and rotational barriers of the repetitive units found in the polymer backbone.[15] The spectroscopic properties of unsubstituted oligothiophenes in the solid state (specially the tetramer and the hexamer) have been widely studied in the literature.[16−20] From these results, a better understanding of the effect of intermolecular interactions on the optical properties of these molecules has been achieved. It has been found that the intermolecular interactions present in the solid state cause a Davydov splitting (excitonic splitting) in the absorption spectra of unsubstituted thiophene oligomers. This splitting gives rise to an intense blue-shifted band compared to that observed in room temperature solutions and a weak (weakly allowed) red-shifted band. On the other hand, the fluorescence spectra of these molecules show only one band, which is attributed to the emission from the lowest Frenkel exciton state. The photophysics of these oligothiophenes in their aggregated forms and/or in the solid state is not yet known. Recently, Oelkrug et al. have reported an important decrease in the fluorescence quantum yield and an increase of the fluorescence lifetime of unsubstituted oligothiophenes in their aggregated forms and in the solid state[21,22] compared to these photophysical parameters obtained in dilute solutions at room temperature.[23,24] A reduction of the radiative fluorescence decay constant is responsible for this behavior.

Despite these results on unsubstituted oligothiophenes, surprisingly no data dealing with the relation between the conformation, the intermolecular interactions, and the optical and photophysical properties of substituted oligothiophenes has yet been reported in the literature. Nevertheless, the substitutional effect is very important since the majority of oligothiophenes and polythiophenes developed up to now have lateral chains. To improve our knowledge on these topics, we have first studied

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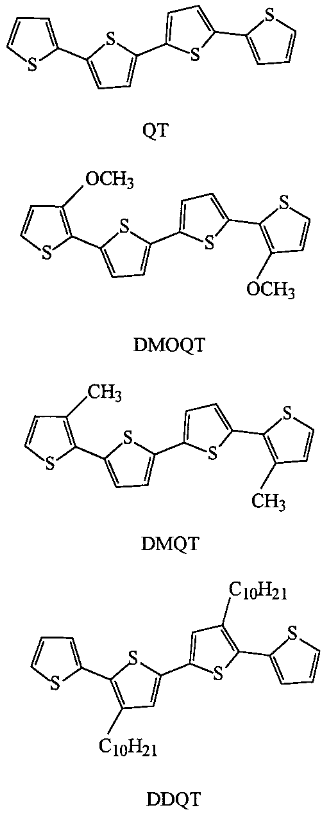

Figure 1. Molecular structures of the quaterthiophenes investigated.

the effect of the substitution on the conformation of model dimers as mentioned above. These results clearly indicated that the conformational changes induced by the lateral groups is important in the description of the optical properties observed for the polythiophenes. Then we have reported for the first time the thermochromism involving substituted oligothiophenes. From these results, it has been concluded that conformational changes play a major role in the optical changes observed. By contrast, chromic properties of unsubstituted oligothiophenes involve intermolecular interactions.[8,9] Finally, it was found that these conclusions are well-correlated with theoretical calculations performed on the crystalline structures of these oligothiophenes.[9]

We present in this paper a continuation of this study with the report of the optical properties of quaterthiophene derivatives in various environments. The photophysical properties of substituted oligothiophenes in aggregated forms will be presented for the first time in this paper. We will also report, for the first time, a substituted oligothiophene in the solid state, which shows an excitonic splitting similar to that observed for some unsubstituted thiophene oligomers. For the other substituted oligothiophenes investigated here, conformational changes are responsible for the optical changes observed following the molecular aggregation or for these molecules in the solid state. These differences are explained by the various conformations adopted by each derivative in their solid state. The molecular structures of the oligothiophenes investigated are displayed in Figure 1.

2. Experimental Section

2.1. Materials. All solvents were purchased from Aldrich Chemical (99+%, anhydrous) and used as received. Prior to use, the solvents were checked for spurious emission in the region of interest and found to be satisfactory. Quaterthiophene (QT),[25] 3,3‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (DMQT),[26] and 3′,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene (DDQT)[25] were prepared according to previously published procedures. 3,3‴-Dimethoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (DMOQT) was prepared according to methods already known.[27]

2.2. Instrumentation. Room-temperature absorption spectra were recorded on a Varian spectrometer, model Cary 1 Bio using 1-cm quartz rectangular cells. Room-temperature 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*-tetradecane matrix and isopentane glass), 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. The solid-state absorption measurements were obtained from thin films (evaporation of chloroform solutions of oligothiophenes) deposited on a quartz plate. Room-temperature fluorescence quantum yields were determined in argon-saturated solutions of the substrates at 298 K against anthracene in ethanol ($\phi_f = 0.27$) or 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.90$) as standards.[28]

Fluorescence lifetimes were measured on a multiplexed time-correlated single-photon counting fluorimeter (Edinburgh Instruments, model 299T). Details on the instrument have been published elsewhere.[29] The instrument incorporates an all-metal coaxial hydrogen flashlamp. The reconvolution analysis was performed by fitting over all the fluorescence decay including the rising edge. The kinetic interpretation of the goodness-of-fit was assessed using plots of weighted residuals, reduced χ^2 values, and Durbin–Watson (DW) parameters. Room-temperature lifetimes were taken in a 1-cm rectangular quartz cell. Low-temperature measurements were taken in a quartz cylinder tube of 0.4 mm (i.d.) immersed in a dewar filled with liquid nitrogen.

2.3. Theoretical Method. The crystalline structures of quaterthiophene (QT),[30] 3,3‴-dimethoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (DMOQT),[27] 3,3‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (DMQT),[26] and of 3′,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene[31] have been built according to X-ray data reported in the literature.

Theoretical calculations were performed using the Hyperchem package, release 5.0, for Windows 95 from Hypercube, Inc on a Pentium computer. The electronic transition energies have been calculated within the framework of the ZINDO/S (Zerner intermediate neglect differential overlap/spectroscopy) semi-empirical method including configuration interaction (CI). ZINDO/S is a modified INDO method parametrized to reproduce UV/visible spectroscopic transitions.[32,33] The electron-repulsion integrals were evaluated using the Mataga–Nishimoto formula. CI is chosen in a way to ensure the absence of changes in the spectroscopic parameters when increasing the size of the CI for the size of clusters studied in this paper (1 to 4 molecules).

TABLE 1: Spectroscopic Parameters of the Molecules Investigated in *n*-Tetradecane at Room Temperature

molecule	$\lambda_A{}^a$ (nm)	$\bar{\nu}_A{}^a$ (cm^{-1})	ϵ^b (mol^{-1} cm^{-1})	fwhm$_A{}^c$ (cm^{-1})	$\lambda_F{}^d$ (nm)	$\bar{\nu}_F{}^d$ (cm^{-1})	fwhm$_F{}^e$ (cm^{-1})	Δ^f (cm^{-1})
QT	391	25600	25500	4800	474	21100	3300	4500
DMOQT	409	24500	32500	4700	483	20700	3400	3800
DMQT	382	26200	22700	5300	473	21150	3300	5050
DDQT	380	26300	26000	5400	481	20800	3300	5500

[a] Taken at the maximum of the absorption bands. [b] Absorption coefficient of the absorption bands, measured at the bands' maxima. [c] Full width at half-maximum (fwhm$_A$) of the absorption bands. [d] Taken at the second vibronic peak, which corresponds to the maxima of the fluorescence bands. [e] Full width at half-maximum (fwhm$_F$) of the fluorescence bands. [f] Stokes shifts (difference between the maxima of the absorption and fluorescence bands).

3. Results and Discussion

3.1. Spectroscopic Analysis of Isolated Molecules at 298 K and 77 K. The spectroscopic parameters of quaterthiophene derivatives in tetradecane at room temperature are listed in Table 1 and can be visualized in Figures 2−5. QT shows a broad and unstructured absorption band, which is a spectral characteristic of a molecule having a nonplanar conformation but with a relatively low rotational barrier against planarity. A detailed spectroscopic and conformational analysis of QT and DDQT has been published previously.[25] The absorption band of DMOQT is red-shifted and more structured compared to that of QT, suggesting a more planar and rigid conformation for the former molecule. This is due to the electron donor properties of the methoxy groups, which improve the electronic delocalization along the molecular frame as described previously for methoxy-substituted bithiophenes[12] and terthiophenes.[9,14] On the other hand, the absorption bands of DMQT and DDQT show a blue shift and an increase in their respective bandwidth suggesting that these alkyl-substituted derivatives are more twisted. This is due to the steric hindrance caused by the presence of the alkyl groups as discussed previously.[10,11,25]

Recently, we have performed a conformational analysis of QT and DDQT using the AM1 semiempirical method.[25] The results have shown that the length of the oligomer has almost no effect on the local rotational barriers between thiophene rings.[25,34] The minima obtained were close to those calculated for the corresponding bithiophenes using ab initio calculations.[11] Ab initio calculations performed on terthiophene derivatives lead to the same conclusion.[14] From these results, one can assume that QT has dihedral angles of ∼150° (all-anti rotamer) between adjacent thiophene rings.[11,14,25] In the case of DDQT, thiophene rings substituted with a decyl group are twisted to about 120° with their neighbors and to ∼150° with each other.[11,25] Since methyl and longer alkyl groups cause similar steric effects,[11,35,36] the dihedral angles present in the molecular frame of DMQT should be close to those observed for DDQT. From ab initio calculations performed on methoxy-substituted bithiophenes[12] and terthiophenes,[14] it was observed that thiophene rings having one methoxy group in the 3 position form a twisting angle of ∼170° with their neighbors. A similar behavior is thus expected for DMOQT, while the inner thiophene rings should be twisted by about the same amount as that of QT. It is worth mentioning that the potential energy surfaces of these relatively long oligomers are expected to be complex and should possess many local minima. This should allow for a wider distribution of rotamers compared to that observed for the shorter oligomers studied until now.[11−14]

On the other hand, the room-temperature fluorescence spectra are much similar. Indeed, a better vibronic resolution is observed in all of the spectra, and the various vibronic peaks appear at similar wavenumbers. These results strongly suggest that all of the molecules adopt a more planar conformation in their first excited singlet state as observed before for other thiophene derivatives.[10,14,25,34] From Table 1, one can see that alkyl-substituted derivatives possess larger Stokes shifts because these molecules are more twisted in their ground state, while in the excited state, their conformations are similar to those of the other oligothiophenes as suggested by identical fwhm$_F$.

The optical spectra of the quaterthiophenes investigated in a tetradecane matrix at 77 K are shown in Figures 2−5. This solvent was used because it has the same molecular length as the long axis of the tetramers. This allows for the formation of a substitutional matrix, which can isolate the solute in the matrix at 77 K.[37] This method was used successfully to obtain the full vibronic resolution of the excitation and fluorescence spectra of QT at 4 K.[38] For all of the derivatives, the excitation spectra recorded in the tetradecane matrix at 77 K show a red shift compared to the absorption spectra measured in tetradecane at room temperature. Thus, one can conclude that the molecules adopt an almost planar conformation in the tetradecane matrix at 77 K as demonstrated for terthiophenes.[9] The increase in the ground-state planarity observed in the tetradecane matrix is not surprising since almost planar conformations are obtained for these molecules.[26,27,30−31] For DMOQT and DMQT, the vibronic resolution obtained in the matrix is better but not as good as that observed for QT. It is quite possible that the substitutional matrix obtained for these derivatives is not as good due to the presence of the lateral chains. Indeed, DDQT, which possesses a very long alkyl chain, exhibits a poor vibronic resolution in the tetradecane matrix at 77 K.

3.2. Spectroscopic Analysis of Aggregated Forms. In an attempt to study the effect of the intermolecular interactions on the optical properties of the quaterthiophene derivatives investigated, the optical spectra of these molecules in their aggregated forms and in the solid state (thin films) have been recorded and are displayed in Figures 2−5. To create the aggregated forms, high concentrations of the solute in isopentane at 77 K (glassy medium) have been used. As in the isopentane glass, there is no formation of a substitutional matrix; the aggregation process is more favored in isopentane than in *n*-tetradecane despite the fact that the concentration used in isopentane (QT) is smaller than or similar to (DMOQT) that in *n*-tetradecane. All compounds except DMQT have shown the formation of aggregates using this method. For the latter molecule, even methanol/water mixtures have failed to show any aggregates.[9] Thus, only the absorption spectrum of DMQT in the solid state is reported in this paper. Moreover, no fluorescence has been detected for these compounds in the solid state because the films formed by the evaporation of chloroform solutions are too thin.

The excitation spectrum of QT in its aggregated form shows an intense band near 30 000 cm^{-1}, which is blue-shifted compared to the absorption band of the free molecules in dilute solutions (see Figure 2A). One can also observe a weak band near 22 000 cm^{-1}, which is red-shifted compared to the absorption band of the free molecules in dilute solutions and to the excitation band of the isolated molecules in the tetradecane

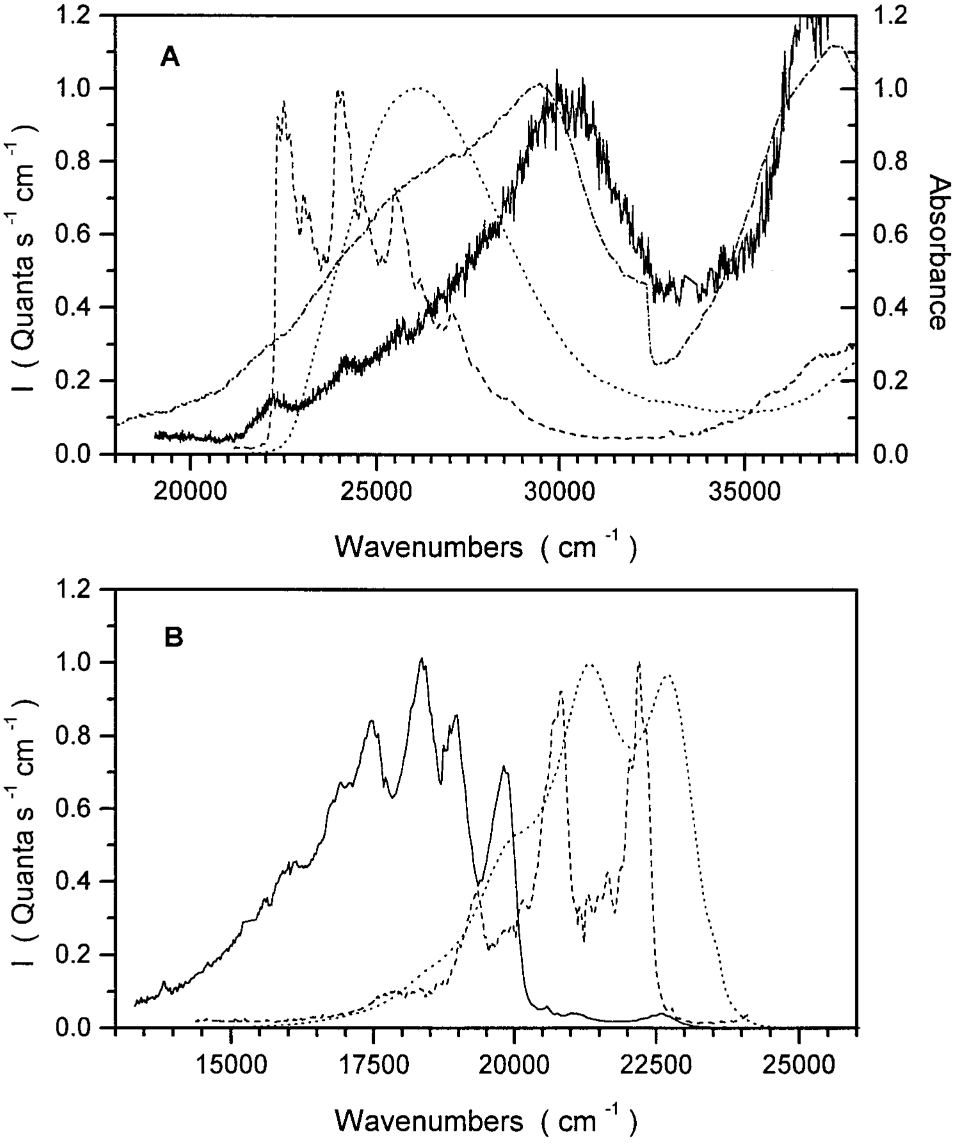

Figure 2. Optical spectra of QT in various environments. (A) (···) Absorption spectrum in isopentane at 298 K, (- - -) excitation spectrum (λ_{em} = 500 nm) in *n*-tetradecane at 77 K, (—) excitation spectrum (λ_{em} = 600 nm) in isopentane at 77 K and (- • - • - •) absorption spectrum in the solid state (thin film). (B) Fluorescence spectra: (···) in isopentane at 298 K (λ_{ex} = 400 nm), (- - -) in *n*-tetradecane at 77 K (λ_{ex} = 400 nm) and (—) in isopentane at 77 K (λ_{ex} = 325 nm). The concentrations used were 1×10^{-5} and 2.1×10^{-5} mol dm^{-3} in isopentane and in *n*-tetradecane, respectively at 298 K.

matrix at 77 K. The absorption spectrum of QT in the solid state exhibits approximately the same features as those observed for the aggregates. However, an intense shoulder is observed near 25 000 cm^{-1}, suggesting that more disorder is probably present in the solid state. These spectral properties have been reported in the literature for QT[16,22] and for other unsubstituted oligothiophenes[9,17−21,39,40] and have been well explained using the excitonic model, which predicts a splitting in the absorption spectra. The excitonic model has been fully described by Kasha.[41] The fluorescence spectrum of the aggregated forms of QT shows one intense electronic band centered at ~17 650 cm^{-1}, which is red-shifted by a large amount compared to that of the free and isolated molecules. This emission has its origin from the lowest Frenkel excited state.[16−18,20−22]

From Figure 3, one can see that the excitation spectrum of DMOQT in its aggregated form exhibits a small red shift as well as an increase of its vibronic resolution compared to the absorption spectrum of the free molecule at room temperature. These optical changes are very similar to those observed for the isolated molecules at 77 K. This might be explained by the fact that the aggregation process does not occur in this environment, but the fluorescence spectrum (see below) clearly indicates that it is not the case. The absorption spectrum of DMOQT in the solid state is very similar to that of the aggregated form. These spectral properties strongly suggest that the intermolecular interactions induce a conformational change similar to that observed in the tetradecane matrix at 77 K. It thus seems that the excitonic splitting, as observed for QT, is very small or absent in the case of DMOQT. The conformational change is not surprising since a more planar conformation is observed in the crystal compared to that expected in solution. However the relatively small red shift induced by intermolecular interactions emphasizes the nearly planar conformation expected for the free molecules. Following the aggregation process, the change of conformation is probably induced through an improved cohesional energy between the molecules. The absence of any observable excitonic splitting for DMOQT might be due to a lower symmetry crystalline arrangement caused by the presence of the methoxy groups (see below). Indeed, these substituents should decrease the intermolecular cohesion energy

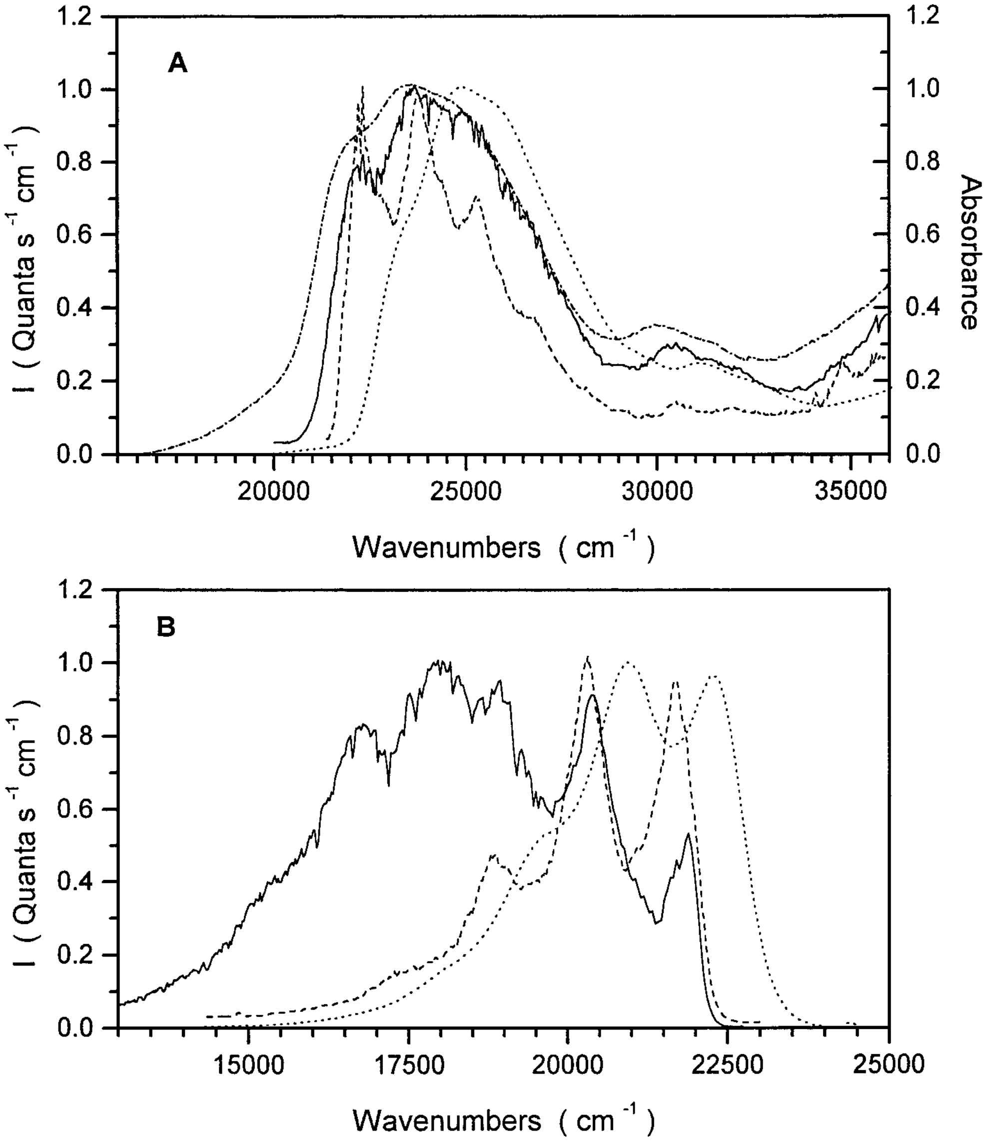

Figure 3. Optical spectra of DMOQT in various environments. (A) (···) Absorption spectrum in isopentane at 298 K, (- - -) excitation spectrum (λ_{em} = 485 nm) in *n*-tetradecane at 77 K, (—) excitation spectrum (λ_{em} = 555 nm) in isopentane at 77 K and (- • - • - •) absorption spectrum in the solid state (thin film). (B) Fluorescence spectra: (···) in isopentane at 298 K (λ_{ex} = 410 nm), (- - -) in *n*-tetradecane at 77 K (λ_{ex} = 410 nm) and (—) in isopentane at 77 K (λ_{ex} = 425 nm). Concentrations used were 3.1×10^{-5} and 1.4×10^{-5} mol dm^{-3} in isopentane and in *n*-tetradecane, respectively at 298 K.

as observed for quaterthiophene. Recently, a similar behavior was reported for β,β'-didecyl-sexithiophene[40] and for substituted terthiophenes.[9]

By contrast to the absorption or excitation spectra, the fluorescence spectrum of the aggregated forms of DMOQT exhibits a part which is red-shifted and centered at ~17 600 cm^{-1}, similar to that observed for QT and much different than that found for the isolated molecules in the tetradecane matrix at 77 K. The occurrence of an important relaxation process, after the excitation of the aggregates, could explain these results. However, another explanation could involve the emission from a trap (physical defaults in the aggregated forms) dispersed in the aggregate. On the other hand, from Figure 3B, one can see that the fluorescence band of the isolated molecules (having the conformation as found in the crystal) is still present.

The absorption spectrum of DMQT, which is displayed in Figure 4, exhibits an important Davydov splitting similar to that observed for QT. To the best of our knowledge, it is the first time that an excitonic splitting is reported for a β,β'-disubstituted oligothiophene. Up to now, oligothiophenes having side chains have only shown conformational changes induced by the aggregation process.[8,9] Since the methyl groups are located in the same positions as those of the methoxy groups in DMOQT, these results are quite unexpected. But, as discussed below, DMQT possesses a much different crystalline structure, giving rise to a very good π-stacking which probably promotes a good excitonic splitting. One important point to mention here is that the presence of substituents is not the sole reason for the absence of any observable excitonic splitting in oligothiophenes. Indeed, the nature and the position of the substituents play also an important role in the optical changes caused by the intermolecular interactions for this kind of molecules.

Figure 5 shows the optical spectra of DDQT in its aggregated form and in the solid state as well as those of the free and the isolated molecules. The excitation spectrum of the aggregated form is red-shifted and is more structured, giving a band very similar to that obtained for the isolated molecule in a tetradecane matrix at 77 K. As discussed before for DMOQT, one can conclude that a conformational change is induced by the aggregation and is responsible for the optical changes. Moreover

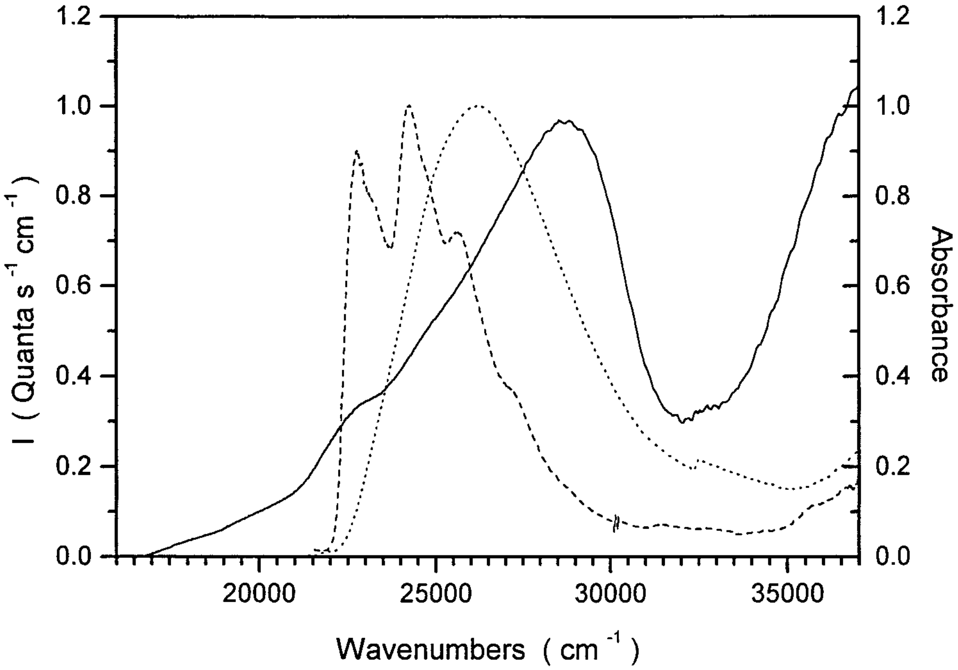

Figure 4. Optical spectra of DMQT in various environments. (···) Absorption spectrum in *n*-tetradecane at 298 K, (- - -) excitation spectrum (λ_{em} = 480 nm) in *n*-tetradecane at 77 K and (—) absorption spectrum in the solid state (thin film). Concentration used was 1.8 × 10^{-5} mol dm^{-3} in *n*-tetradecane at 298 K.

this red shift is larger than that obtained for DMOQT since a more twisted conformation is expected for the free molecule of DDQT. The absence of any observable excitonic splitting for DDQT is due to the presence of the long alkyl chains, which hinders the formation of a good π-stacking in the solid state. A similar behavior has been reported for β,β'-didecyl-sexithiophene in the solid state.[40]

The fluorescence spectrum of the aggregated forms of DDQT shows a large red shift, which cannot be induced by any conformational changes. This behavior is also observable in low-temperature fluid solutions where a clear isoemissive point is found similar to the isosbestic point observed in the absorption spectra.[8] As discussed above for DMOQT, the emission is expected to come from the aggregated forms in their relaxed S_1 state or from a trap, which is different from the absorbing species.

3.3. Photophysical Analysis of Isolated and Aggregated Molecules. The photophysical parameters of the quaterthiophenes investigated in isopentane for the free molecules and for the aggregated forms are listed in Table 2. For the reason mentioned previously, the fluorescence quantum yield and lifetime for DMQT in its aggregated form are not reported. Room-temperature fluorescence quantum yields and lifetimes have been obtained in the linear region of the I_F vs C curve (C = 3.1−3.9 × 10^{-6} mol dm^{-3}) using the procedure described in the Experimental Section. For the fluorescence quantum yields of the aggregated forms, the absorption and fluorescence spectra have been taken in isopentane at 298 K and 77 K using a 1-mm pathway quartz cell in order to reduce the reabsorption and inner filter effects. Moreover, the fluorescence spectra have been recorded using the front face arrangement of the instrument. Concentrations used were 4.7 × 10^{-5}, 2.9 × 10^{-5}, and 1.1 × 10^{-5} mol dm^{-3} for QT, DDQT, and DMOQT, respectively, giving absorbances near 0.1 for QT and DDQT and an absorbance of 0.25 for DMOQT at the absorption peak maxima. Fluorescence quantum yields for the aggregates at 77 K have been obtained using the room temperature quantum yield of each quaterthiophene derivative as a standard. The change of the refractive index of isopentane from 298 K to 77 K has been neglected. It is worth mentioning that the fluorescence quantum yields obtained at 77 K are less accurate than those measured at 298 K because the concentrations used to form the aggregated forms are relatively high and also because absorbances measured at 77 K are less precise.

From Table 2, one can see that room-temperature quantum yields (ϕ_F) and lifetimes (τ_F) are smaller for alkyl-substituted derivatives that are greatly twisted in their ground states, giving rise to larger values of their nonradiative decay rate constants (k_{nr}). On the other hand, the fluorescence decay rate constants (k_F) of these molecules are very close to that of DMOQT, which is expected to be almost planar in its ground state. Apparently, the radiationless process involved in these quaterthiophene derivatives seems related to their ground-state conformations. Even if almost planar conformations are expected for oligothiophenes in the relaxed S_1 state, greatly twisted molecules in their ground-state might remain slightly twisted after the relaxation of the excited singlet state. Since it is well-known that the major deactivation pathway of the S_1 state of unsubstituted oligothiophenes involves an intersystem crossing process,[24,42] it is possible that this mechanism is influenced by the conformation of the molecules in the S_1 state. Indeed, the relative energetic positions of the singlet and triplet states may be affected in such a way that the triplet quantum yield might be higher for molecules that are slightly twisted in their relaxed S_1 state.

Table 2 shows that an important decrease in the ϕ_F values are observed for compounds in their aggregated forms. For instance, the fluorescence quantum yield of QT aggregates is more than twenty times smaller than the ϕ_F value of the free molecule obtained at room temperature, in agreement with the data reported by Oelkrug et al.[21,22] This decrease in ϕ_F combined with an important increase in the fluorescence lifetimes leads to a huge decrease in the radiative rate constant (k_F). This strongly suggests that the emission has its origin from a weakly allowed transition that might involve the first Frenkel excited state as discussed above. However, these results do not refute the mechanism involving a trap dispersed in the aggregated

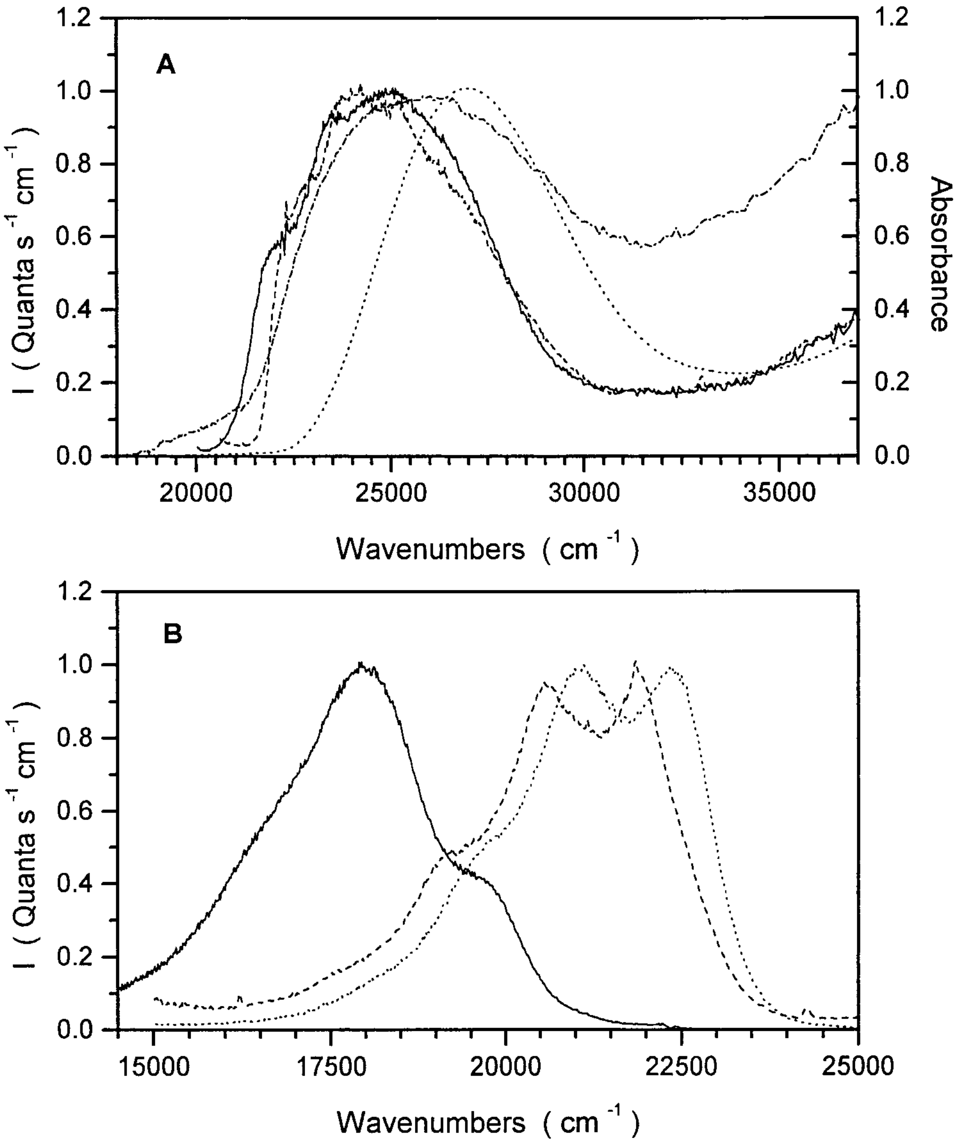

Figure 5. Optical spectra of DDQT in various environments. (A) (···) Absorption spectrum in isopentane at 298 K, (- - -) excitation spectrum (λ_{em} = 500 nm) in *n*-tetradecane at 77 K, (—) excitation spectrum (λ_{em} = 500 nm) in isopentane at 77 K and (- • - • - •) absorption spectrum in the solid state (thin film). (B) Fluorescence spectra: (···) in isopentane at 298 K (λ_{ex} = 375 nm), (- - -) in *n*-tetradecane at 77 K (λ_{ex} = 375 nm) and (—) in isopentane at 77 K (λ_{ex} = 450 nm). Concentrations used were 2.3×10^{-4} and 2.1×10^{-5} mol dm^{-3} in isopentane and in tetradecane, respectively at 298 K.

TABLE 2: Photophysical Parameters of the Free (298 K) and Aggregated Forms (77 K) of the Molecules Investigated in Isopentane

molecule	ϕ_F[a]	τ_1[b] (ns)	τ_2[b] (ns)	B_1[c]	B_2[c]	$\langle\tau_F\rangle$[d] (ns)	k_F[e] ($\times 10^{-8}$ s^{-1})	k_{nr}[f] ($\times 10^{-8}$ s^{-1})
298 K								
QT	0.27	0.52					5.2	14.1
DMOQT	0.25	0.61					4.1	12.3
DMQT	0.19	0.43					4.4	18.8
DDQT	0.16	0.38					4.2	22.1
77 K								
QT	0.014	1.03	5.92	0.94	0.06	2.42	0.058	4.1
DMOQT	0.038	0.78	3.13	0.93	0.07	1.32	0.29	7.3
DDQT	0.070	1.31	8.11	0.75	0.25	5.85	0.12	1.6

[a] Fluorescence quantum yields. [b] Obtained from the reconvolution fit: $A + B_1(\exp(-t/\tau_1)) + B_2(\exp(-t/\tau_2))$. [c] Normalized preexponential factor. [d] Average lifetime calculated from the expression: $\langle\tau_F\rangle = \sum B_i\tau_i^2/\sum B_i\tau_i$. [e] Radiative fluorescence decay rate constant obtained from: $k_F = \phi_F/\tau_F$. [f] Nonradiative fluorescence decay rate constant obtained from: $k_{nr} = k_F\ ((1 - \phi_F)/\phi_F)$.

forms. For DMOQT and DDQT, the decrease in ϕ_F and k_F values of the aggregates is less important than that found for QT. Since the excitation spectra of DMOQT and DDQT in their aggregated forms do not show any weak red-shifted bands such as that observed for QT and DMQT (see Figures 2 and 4), one may think that the model of a trap dispersed in the aggregated forms applies here. But we will show below that weakly allowed bands could also be present for these two derivatives.

3.4. ZINDO/S Calculations on Crystalline Structures of the Molecules Investigated. Figure 6 shows the crystalline

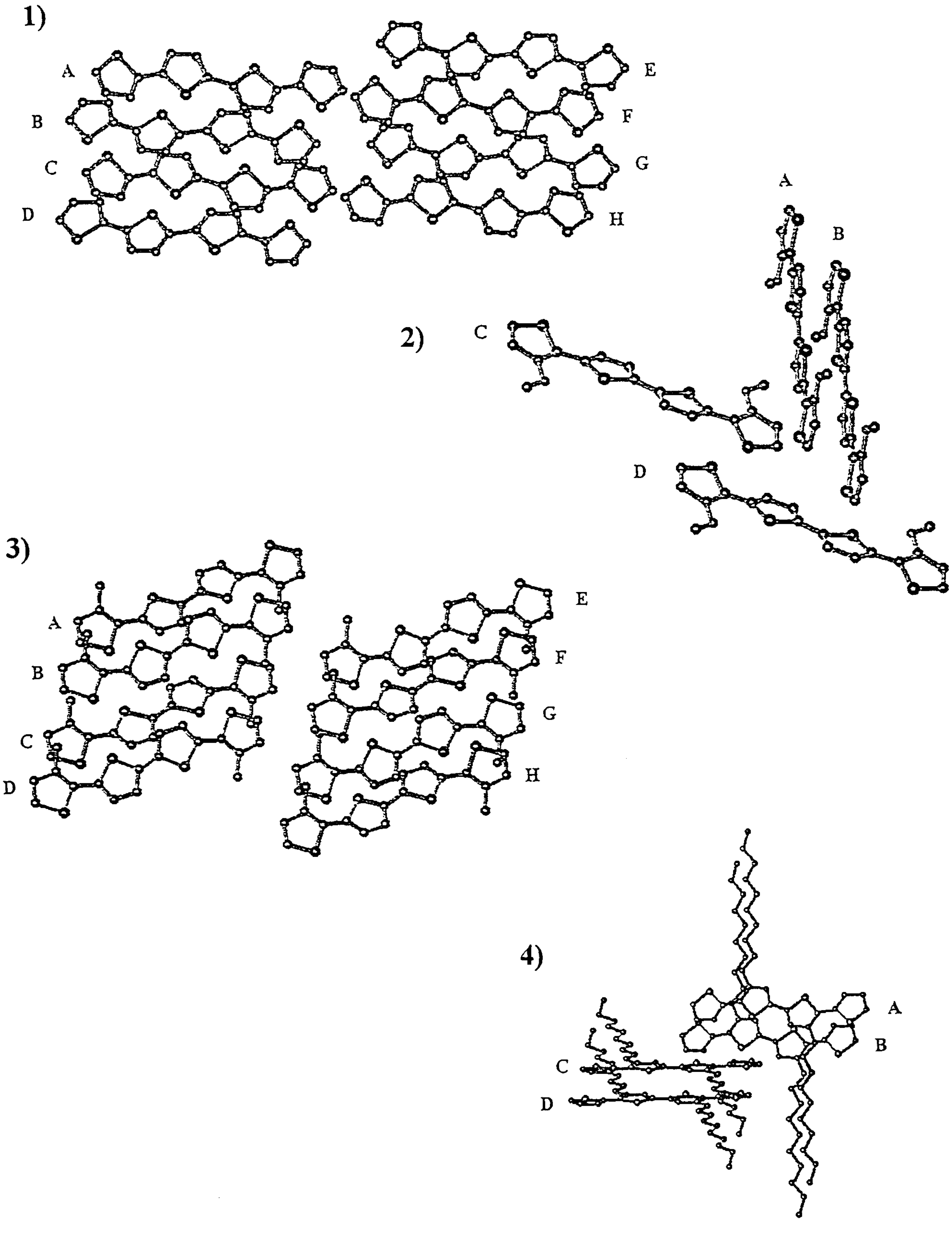

Figure 6. Crystalline structure of QT (1), DMOQT (2), DMQT (3), and DDQT (4). The letters correspond to the molecules involved in the ZINDO/S calculations.

structures of QT,[30] DMOQT,[27] DMQT,[26] and DDQT.[31] Each molecule of QT in the crystal is almost planar. Molecules A, C, E, and G are in planes parallel to each other, while the four other molecules are also in planes parallel to each other, which are oriented at quasi-45° with the first ones. The crystalline structure is a quasi-sandwich-type giving rise to good π-interactions, which are responsible for the conformational change observed for QT in the solid state and in aggregated forms.

The crystalline structure of DMOQT shows two distinct conformations and arrangements: molecules A and B, which are nearly planar, and molecules C and D, which are more twisted (see Figure 6-2). Molecules A and B are in parallel planes giving rise to a good stacking (sandwich-type). Molecules C and D are also in parallel planes, which are perpendicular to those including molecules A and B, giving rise to a very small overlap between these two types of molecules. Thus, the π-interactions found in the crystalline structure of DMOQT is more reduced compared to those observed for the crystalline structure of QT. One can see that insertion of relatively small methoxy groups in the molecular frame is sufficient to drastically change the crystalline structure.

Figure 6-3 shows that the crystalline structure of DMQT is very similar to that of QT. But the molecules are more twisted due to the steric effects caused by the presence of the methyl substituents. All molecules are located in relatively parallel planes (sandwich-type) such that the intermolecular overlap is good. Thus, the presence of methyl groups creates a totally different molecular arrangement compared to that of the methoxy groups. In other words, as mentioned above, the crystalline structure of each quaterthiophene derivative is more dependent on the nature and the position of the substitution. A similar behavior has been observed before for terthiophene derivatives.[9]

In contrast to the molecules present in the DMQT crystal, all molecules in the crystalline structure of DDQT are perfectly planar. This is surprising because relatively similar rotational barriers against planarity exist for DMQT and DDQT.[11,14,25] Moreover, the crystalline structure of DDQT is less ordered than that of DMQT giving rise to weaker intermolecular interactions, which are responsible for the conformation adopted by the molecules in the crystal (see Figure 6-4). This shows again that the crystalline structure of each oligothiophene is unique and rather hard to predict. In the crystal, DDQT molecules form two distinct arrangements: (1) molecules A and B, which are parallel and form a sandwich-type of interaction, (2) molecules C and D, which are also parallel, the mirror plane of which is oriented almost perpendicularly with the one formed by molecules A and B. The π-molecular overlap between molecules A and C or B and D is weak.

To evaluate the effect of the intermolecular interactions on the optical spectra of quaterthiophenes, the electronic transitions of the isolated molecules having the structural parameters found in the crystal and those of small crystalline clusters (four molecules) have been calculated using the ZINDO/S semiempirical method. The calculated electronic transitions of the isolated molecules will be compared with the absorption spectra measured in the tetradecane matrix at 77 K, whereas the spectral properties of the aggregates will be correlated to the electronic transitions predicted for the clusters. ZINDO/S calculations have also been performed on the most stable conformations expected in solution (see above). These results will be correlated with the optical spectra of the free molecules at room temperature. This methodology has also been applied for terthiophene derivatives.[9]

TABLE 3: Singlet−Singlet Electronic Transitions and Their Oscillator Strengths Obtained Using ZINDO/S Calculations Performed on Free, Isolated, and Crystalline Clusters of the Molecules Investigated

molecule	label[a]	transition	transition energy (cm^{-1})	f[b]	expt[c] (cm^{-1})
QT	"free"[d]	$S_0 \rightarrow S_1$	25 747.3	1.395	25 600
	A	$S_0 \rightarrow S_1$	24 000.3	1.508	24 000
	A,B,C,D	$S_0 \rightarrow S_1$	24 190.2	0.0232	22 000
		$S_0 \rightarrow S_2$	24 437.9	0.0076	
		$S_0 \rightarrow S_3$	25 132.6	0.0034	
		$S_0 \rightarrow S_4$	27 606.0	5.82	30 000
DMOQT	"free"[e]	$S_0 \rightarrow S_1$	23 769.9	1.514	24 500
	A	$S_0 \rightarrow S_1$	23 668.6	1.451	23 700
	A,B,C,D	$S_0 \rightarrow S_1$	23 412.1	0.014	
		$S_0 \rightarrow S_2$	24 759.8	1.476	
		$S_0 \rightarrow S_3$	25 186.4	1.989	23 700
		$S_0 \rightarrow S_4$	25 597.1	2.049	
DMQT	"free"[f]	$S_0 \rightarrow S_1$	26 799.0	1.253	26 200
	A	$S_0 \rightarrow S_1$	22 810.0	1.542	24 200
	A,B,C,D	$S_0 \rightarrow S_1$	22 836.3	0.0597	
		$S_0 \rightarrow S_2$	23 674.2	0.216	22 500
		$S_0 \rightarrow S_3$	24 588.1	0.0029	
		$S_0 \rightarrow S_4$	26 232.9	5.595	29 000
DDQT	"free"[g]	$S_0 \rightarrow S_1$	27 042.0	1.194	26 300
	A	$S_0 \rightarrow S_1$	22 706.6	1.517	24 100
	A,B,C,D	$S_0 \rightarrow S_1$	23 153.5	0.0003	
		$S_0 \rightarrow S_2$	23 299.2	0.0142	
		$S_0 \rightarrow S_3$	24 764.7	5.656	24 100
		$S_0 \rightarrow S_4$	24 993.8	0.0053	

[a] Label of the molecules involved in the calculations (see Figure 7). [b] Oscillator strength. [c] Experimental transition energy (see text). [d] Conformation expected in solution (dihedral angles between adjacent thiophene rings = 150°, see section 3.1). [e] Conformation expected in solution (dihedral angles between successive thiophene rings = 170°, 150°, 170°, see section 3.1). [f] Conformation expected in solution (dihedral angles between successive thiophene rings = 120°, 150°, 120°, see section 3.1. [g] Conformation expected in solution (dihedral angles between successive thiophene rings = 120°, 150°, 120°), see section 3.1.

The simulated absorption spectra are displayed in Figure 7, and the parameters of the first singlet−singlet transitions of the various structures are listed in Table 3. For QT, the first singlet−singlet transition of the isolated molecule in the crystal is calculated at 24 000 cm^{-1}. On the other hand, the most stable conformer of the free molecule (dihedral angles of 150° between adjacent thiophene rings) has a singlet−singlet energy transition of 25 747 cm^{-1} with a smaller oscillator strength. This blue shift is induced by a reduction in the π-orbital overlap as the torsions increase in the molecular frame. The above values are close to the excitation maximum of the isolated molecules in the tetradecane matrix at 77 K (24 000 cm^{-1}) and to the absorption maximum in solution for the free molecules (25 600 cm^{-1}). The more intense singlet−singlet transition of the cluster (molecules A,B,C,D, see Figure 6-1) appears at 27 606 cm^{-1}, which represents an important blue shift compared with the energy transition of the free and isolated molecules. ZINDO/S calculations also predict a low energy transition (24 190 cm^{-1}), which is forbidden (or weakly allowed). This electronic transition is red-shifted compared to the energy transition calculated for the free molecule and appears at about the same energy as that of the isolated molecule in the crystal. These calculations are in relatively good agreement with the absorption spectra of QT in the aggregated forms and that of QT in the solid state displayed in Figure 2. Indeed, an intense blue-shifted band is observed near 30 000 cm^{-1} and a weak red-shifted band appears near 22 000 cm^{-1}. Compared to the absorption spectrum of the isolated molecules in the tetradecane matrix, the blue shift of the absorption band of the aggregated forms is about 6000 cm^{-1}, which is much higher than the blue shift predicted by ZINDO/S calculations (~3500 cm^{-1}). We believe that this difference might involve the size of the clusters used in the calculations (four molecules here), which is probably smaller than the real aggregates. Indeed, the importance of the Davydov splitting is expected to increase with the size of the cluster. It is worth mentioning that other molecular combinations have been considered. For instance, the intermolecular interactions involved between molecules A and B (sandwich-type dimer) lead to similar spectral effects, but to a lesser extent, than those

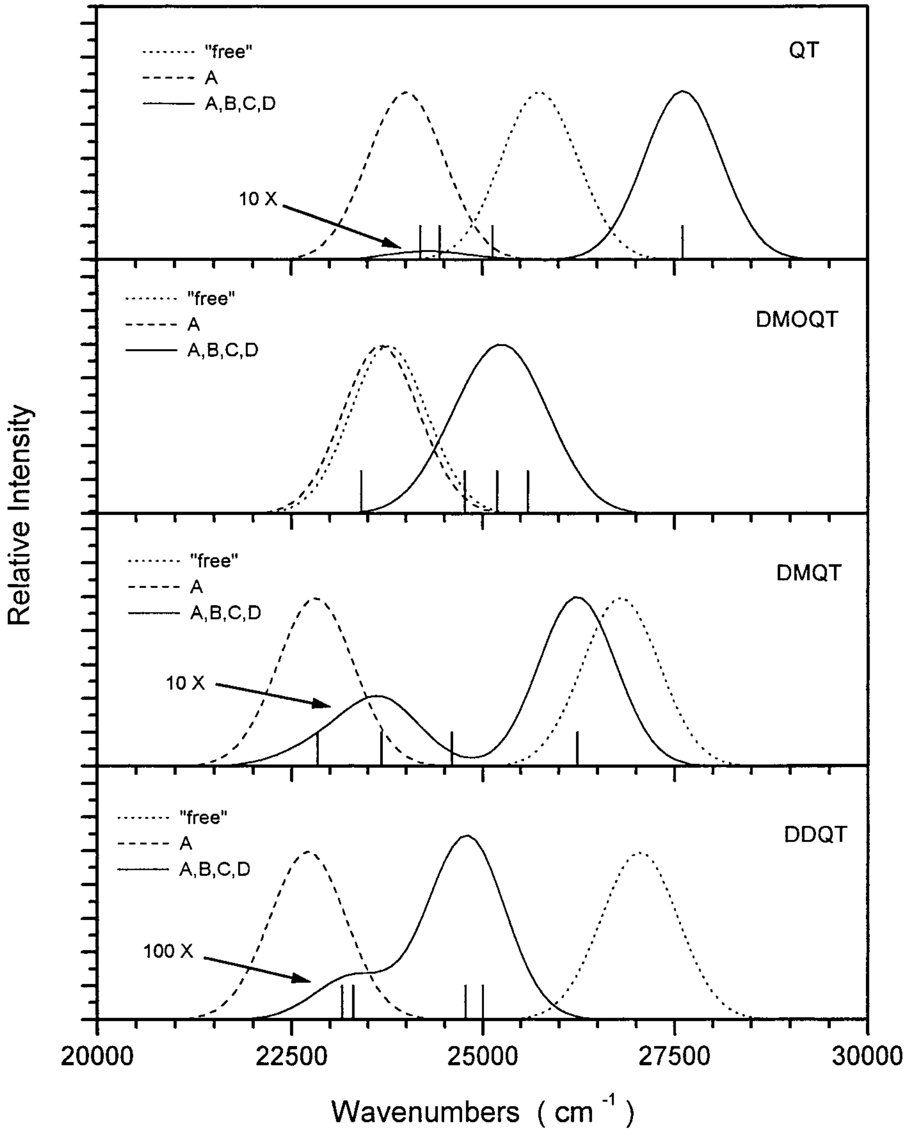

Figure 7. Simulated absorption spectra of the compounds investigated. Letters in the legend represent the molecules involved in the crystalline form calculated (see Figure 6). The spectra of the free molecules are obtained as discussed in the text. The vertical lines indicate the normalized transition energies of the tetramers.

discussed above for the four molecular cluster. On the other hand, the intermolecular interactions present between molecules A and E (head-to-tail dimer) do not significantly affect the transition energy of the molecules isolated in the crystal, showing the small overlapping in this molecular arrangement. Finally, the transition energies of the tetramer formed by the molecules A,B,E,F are close to those found for the dimer A,B, showing that the sandwich-type interaction is by far the more important interaction in this crystalline structure.

Figure 7 and Table 3 show that the simulated absorption spectra of DMOQT for the free (23 770 cm^{-1}) and isolated molecules (23 669 cm^{-1}) appear at about the same energetic position. This is not surprising since the most stable conformation of the free molecules in the gas phase (or in dilute solution) is very close to that of the molecules isolated in the crystal. These values are in good agreement with the absorption maxima measured in solution (24 500 cm^{-1}) and in the tetradecane matrix (23 700 cm^{-1}) for the free and isolated molecules, respectively. Various dimers have been considered in the clusters. Intermolecular interactions involved between molecules C and D do not induce any significant changes in the first singlet−singlet transition energy of the isolated molecules. This clearly indicates that the π-molecular overlapping between these molecules is very small. A similar behavior has been observed in the case of the dimer A,C. On the other hand, the intermolecular interactions present in the dimer A,B induce an excitonic splitting resulting from a much larger π-molecular overlapping between molecules A and B. The theoretical results obtained for the tetramer displayed in Figure 6-2 are shown in Figure 7. ZINDO/S calculations performed on this cluster predict that three intense singlet−singlet transitions appear within 1000 cm^{-1} (see Table 3), giving an overall blue shift of about 1500 cm^{-1} compared to that of the isolated molecules in the crystal. This shift is much smaller than that calculated above for the cluster of QT (3500 cm^{-1}). Experimentally, we do not observe any blue shift. However, a blue shift of 1500 cm^{-1} might be difficult to detect since the bandwidths of the optical spectra are about 4000−5000 cm^{-1}. Moreover, it is possible that the molecular structure of the aggregates is slightly different than that of the single crystal such that more disorder is present in the aggregates. It is worth pointing out that the excitonic splittings calculated here are upper limits for a given cluster. Experimentally, we expect that the effect of the intermolecular interactions on the optical spectra would be smaller (assuming that the aggregates have the same size as that of the clusters investigated). But it is clear that the intermolecular interactions involved for DMOQT in the solid state are weaker than those found in the QT crystal, giving rise to weaker effects on the optical properties of DMOQT. This is surely due to a higher molecular disorder in the crystalline structure of DMOQT caused by the presence of the methoxy groups.

The calculated electronic transitions for the free and isolated molecules of DMQT are also similar to those observed experimentally. As predicted for QT, the intermolecular interactions involved in the dimer A,B induce an excitonic splitting while those found in dimer A,E do not cause any significant effect. The tetramer A,B,C,D shows an intense singlet–singlet transition ($f = 5.595$) located at 26 233 cm^{-1}, which is blue-shifted by about 3500 cm^{-1} compared to that of the isolated molecules (see Table 3). This blue shift is identical to that calculated for QT. A weak electronic transition is also predicted at about the same energy as that of the isolated molecules. Table 3 shows that these theoretical results are in relatively good agreement with the experimental data. However, as observed for QT, the calculated blue shift of the allowed transition is smaller than that measured experimentally (4800 cm^{-1}). As discussed for QT, the reason for this behavior might involve the size of the cluster investigated. As a consequence, the allowed transition predicted by ZINDO/S calculations is slightly red-shifted compared to that calculated for the free molecule. Experimentally, a blue shift of 2000 cm^{-1} is observed for the free molecule in comparison with the isolated one (see Table 3). Apart from the size of the cluster investigated, this difference could also be explained in part by a more planar conformation than theoretically expected for the free molecule (a blue shift of 3989 cm^{-1} is predicted theoretically).

Table 3 shows that the calculated electronic transitions for the free and isolate molecules of DDQT are in relatively good agreement with the experimental data. The interaction between molecules which are mutually perpendicular (e.g., A and C, see Figure 6-4) is very weak and has no significant influence on the optical properties of the isolated molecules. On the other hand, the interaction between two parallel molecules (e.g., A and B) is more important, giving rise to a Davydov splitting. A similar behavior is obtained for the cluster A,B,C,D as shown in Figure 7. The blue-shift calculated following the aggregation for the allowed transition is 2000 cm^{-1}, which is smaller than those calculated for QT and DMQT. Experimentally, no significant blue shift is observed in the absorption spectrum of DDQT in its aggregated form or in the solid state. As discussed above for DMOQT, the absence of any observable blue shift might be explained by the large bandwidth of the optical spectra measured and the fact that the aggregates (or the thin films) are less ordered than in the crystals.

To conclude this part, molecules possessing a good stacking in their crystalline forms (QT and DMQT) show an important excitonic splitting in their absorption spectra caused by strong intermolecular interactions. The incorporation of methoxy and decyl groups to the molecular frame does not lead to a good stacking of the molecules in their crystalline forms. Consequently, weaker intermolecular interactions are present for DMOQT and DDQT, giving rise to smaller excitonic effects. In the case of DDQT, an important change of conformation between the solution and the solid state is found, which is the main cause of the optical changes (red shift) observed. On the other hand, DMOQT is nearly planar in solution and in the solid-state such that small optical changes are observed upon aggregation.

4. Concluding Remarks

Use of well-defined unsubstituted and substituted quaterthiophenes has allowed us to study the effect of substitution and the intermolecular interactions on the optical and photophysical properties of these molecules in various environments. In solution, methoxy groups induce a greater planarity between the thiophene rings while alkyl substituents cause a larger twisting of the molecule. However, after the excitation to the S_1 state, all compounds relax to a nearly planar conformation. For the free molecules isolated in a tetradecane matrix at 77 K, all compounds adopt more planar conformations, similar to those found in the crystals, leading to a red shift of their absorption (or excitation) spectra but no significant shift in their fluorescence spectra.

Following the aggregation or in the solid state, QT exhibits an important Davydov splitting, showing the strong sandwich-type of interactions between the molecules in condensed media. This leads to an important blue shift of the allowed transition. On the other hand, the fluorescence spectrum shows only a red-shifted band, which is most probably attributed to the emission from the lowest Frenkel excited state or to a trap dispersed in the aggregated forms or in the solid state. By contrast, no important optical changes are observed following the aggregation or in the solid state for DMOQT. Indeed, only a small red shift is observed in the absorption (or excitation) spectra, which is caused by small conformational changes, similar to those found for the isolated molecules in the tetradecane matrix at 77 K. This clearly shows that the intermolecular interactions are weak for this compound in condensed media. In the case of DMQT in the solid state, an important Davydov splitting of the absorption spectrum is observed for the first time, showing that the insertion of methyl groups in the molecular frame does not significantly affect the strength of the intermolecular interactions in comparison with QT. This excitation splitting is well explained by the high-symmetry crystalline structure of this derivative. Finally, the optical changes obtained for DDQT in the aggregated forms or in the solid state are induced by important conformational changes, similar to those observed in the tetradecane matrix, suggesting that weak intermolecular interactions exist for this compound in condensed media.

ZINDO/S calculations performed on crystalline clusters are in good agreement with the above spectral evidences. The good π-interactions observed in the crystalline structure of QT and DMQT lead to an important excitonic splitting as observed experimentally. For DMOQT and DDQT, the crystalline structures is less ordered giving rise to weaker intermolecular interactions and thus to smaller excitonic effects in the simulated absorption spectra. For DDQT, the conformational changes induced by the aggregation process are the main reason for the large red shift observed in the excitation spectrum of the aggregates.

Finally, this paper shows the importance of using simulated spectra from X-ray structures to interpret aggregation phenomena and conformational effects in solutions or in solid states.

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