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Structure of Thiophene-Based Regioregular Polymers and Block Copolymers and Its Influence on Luminescence Spectra

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Two approaches toward control of the luminescence wavelength of polythiophenes have been explored: (i) block copolymers in which oligothiophene blocks alternate with oligosilanylene blocks and (ii) regioregular polythiophenes in which oligothiophene sequences are delimited by *n*-octyl substituents placed in a "head-to-head" fashion on adjacent rings. Both methods aim at restricting the π-conjugation to the oligothiophene sequences. The block copolymer approach is very effective, whereas the (solution) luminescence spectra of the regioregular polymers are strongly red-shifted with respect to absorption and confined to a narrow range of wavelengths. This is due to the quinoid character of the excited singlet state, in which there is a strong electronic driving force toward coplanarity of adjacent thiophene rings, which offsets the steric hindrance of the octyl substituents and increases the size of the conjugating π-system. This explanation is supported by calculations and by spectral data of substituted bithiophenes.

Introduction

The growing need for miniaturization of devices has stimulated fundamental materials research also in the field of organics. Several classes of organic polymers have been found to be promising, in terms of both stability and efficiency, for the generation of light by means of electron/hole injection (electroluminescence), notably poly(*p*-phenylenevinylene),[1,2] poly(*p*-phenylene),[3] and polythiophene.[4−6] This is relevant for the application of these polymers in small devices such as light-emitting diodes. There is particular interest in the emission of blue light, which has been difficult to realize efficiently with classical semiconductor materials. In display applications, of course, luminescent materials are required for the primary colors and it would be attractive to span the entire range of the visible spectrum with one type of material. Light-emitting polymers based on thiophene are the subject of our current research.[7−9] The electroluminescence spectrum of a conjugated thiophene-based block copolymer has been found to be largely identical to its photoluminescence (fluorescence) spectrum,[5,8] which has led us to conclude that the same bound exciton states are at the origin of both types of luminescence.

In a series of thiophene oligomers, there is a steady progression of the wavelengths of maximum absorption with the number of rings, showing asymptotic behavior, and a similar trend is found for the fluorescence (Figures 1 and 2). From a chemical viewpoint, this is explained by increasing length of conjugation of the π-electronic system, resulting in a lowering of the HOMO−LUMO gap. Fluorescence wavelengths are longer than those of absorption because of geometry relaxations in both the ground state and the excited state. The conformational changes that accompany the relaxation of the excited state are quite pronounced and will be the subject of our current discussion.

A challenge for today's chemist is the incorporation of the above-mentioned functionality of "color-tunable" luminescence in a processable material, i.e., one which is soluble and film-forming. The obvious approach is to synthesize polymer molecules having well-defined sequences of conjugated units, with interruption of the conjugation between these sequences. Several ways to achieve this have been explored, among which are (i) copolymerization with chemically distinct blocks[7,8,10,11] and (ii) stereochemically induced conjugation breaks.[9,12,13]

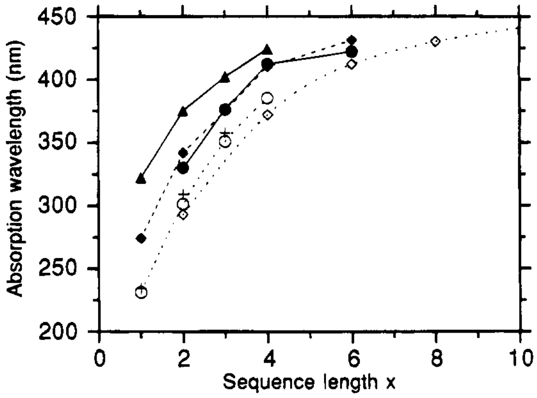

Figure 1. Wavelengths of absorption maxima for thiophene-based compounds (see Table 1): (○) oligomers, T$_x$; (◇) oligomers with *n*-octyl side chains, T$_x$Oct$_y$; (+) oligomers with trimethylsilyl end groups, T$_x$SiMe$_3$; (●) poly(di-*n*-butylsilanylene-*block*-thiophene)s, *p*-T$_x$SiBu$_2$ and *p*-T$_6$Oct$_2$SiBu$_2$; (◆) poly(tetra-*n*-butyldisilanylene-*block*-thiophene)s, *p*-T$_x$Si$_2$Bu$_4$ and *p*-T$_6$Oct$_2$Si$_2$Bu$_4$; (▲) regioregular poly(dioctyl oligothiophene)s, *p*-T$_x$Oct$_2$.

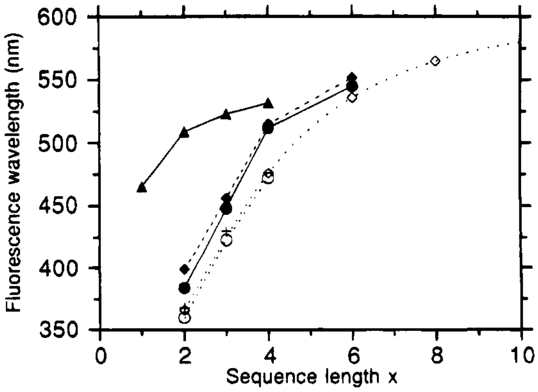

Figure 2. Wavelengths of fluorescence maxima for thiophene-based compounds (see Table 1): (○) oligomers, T$_x$; (◇) oligomers with *n*-octyl side chains, T$_x$Oct$_y$; (+) oligomers with trimethylsilyl end groups, T$_x$SiMe$_3$; (●) poly(di-*n*-butylsilanylene-*block*-thiophene)s, *p*-T$_x$SiBu$_2$ and *p*-T$_6$Oct$_2$SiBu$_2$; (◆) poly(tetra-*n*-butyldisilanylene-*block*-thiophene)s, *p*-T$_x$Si$_2$Bu$_4$ and *p*-T$_6$Oct$_2$Si$_2$Bu$_4$; (▲) regioregular poly(dioctyl oligothiophene)s, *p*-T$_x$Oct$_2$.

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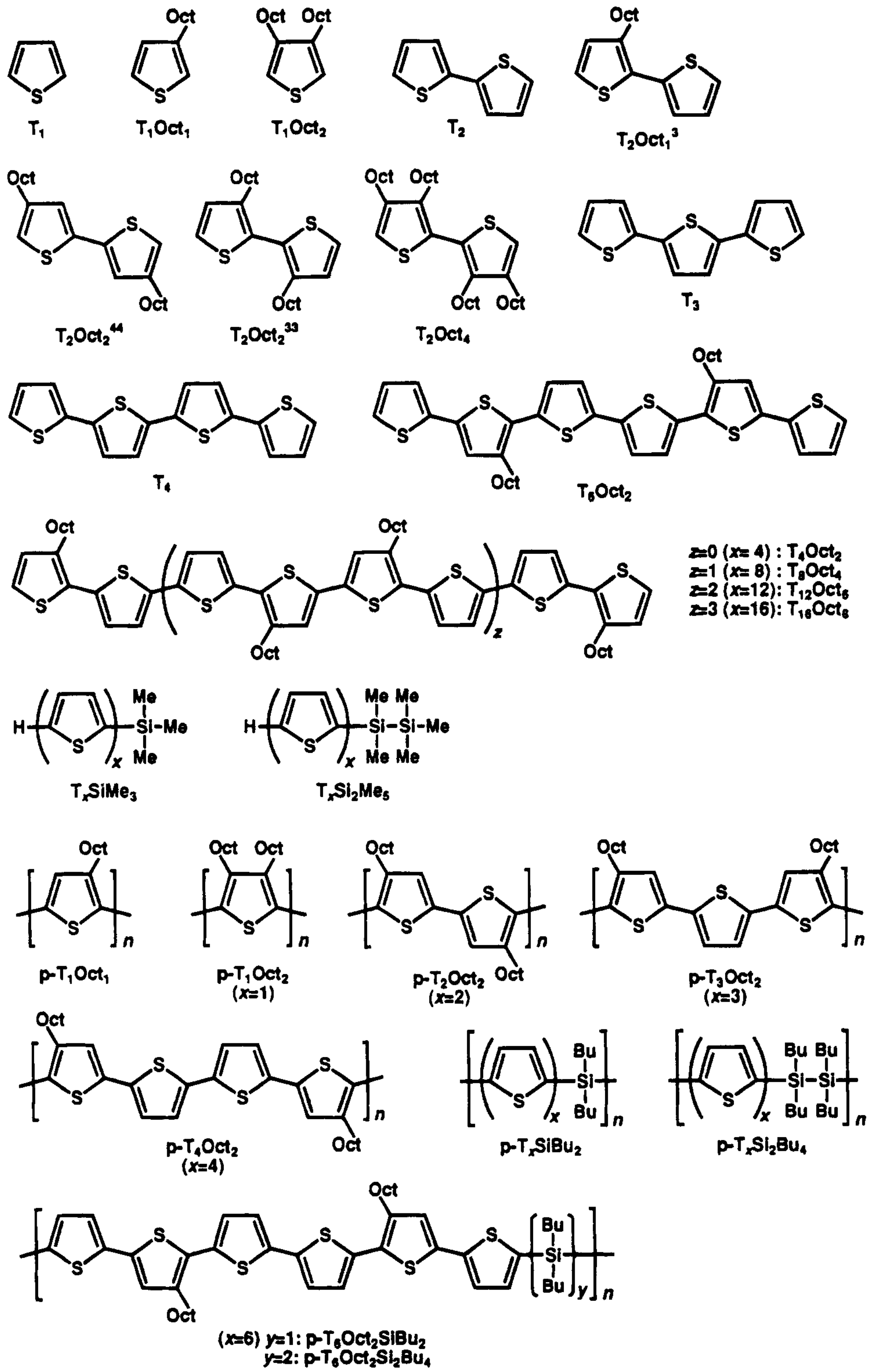

Figure 3. Overview of the compounds studied and the nomenclature used.

In this paper, we will deal with thiophene-based compounds, and we will discuss spectroscopic results obtained for both approaches, the poly(silanylene-*block*-thiophene)s and the regioregularly substituted polymers, respectively. In the latter case, long *n*-alkyl substituents are introduced at facing positions on two adjacent thiophene rings (both ortho with respect to the interring bond: head-to-head) at regular intervals in order to force these rings out of coplanarity. The chemical constitution of all molecules is given in Figure 3, which also serves to introduce the notation used and to indicate the meaning of the quantity *x*, the thiophene sequence length, in each case.

Materials and Methods

3-Octylthiophene (T_1Oct_1) and 3,4-dioctylthiophene (T_1Oct_2) were prepared from 3-bromothiophene and 3,4-dibromothiophene, respectively, by a Ni-catalyzed Grignard coupling.[14] 4,4′-Dioctyl-2,2′-bithiophene (T_2Oct_2[44]) and 3,3′,4,4′-tetraoctyl-2,2′-bithiophene (T_2Oct_4) were prepared by the oxidative coupling of the monolithio compound of T_1Oct_1 and T_1Oct_2, respectively. 3,3′-Dioctyl-2,2′-bithiophene (T_2Oct_2[33]) was prepared from 2-bromo-3-octylthiophene via a Grignard coupling. The synthesis of the octyl-substituted oligomers T_4Oct_2 and T_6Oct_2 is described in ref 15. Regioselective oligothiophenes T_8Oct_4 and

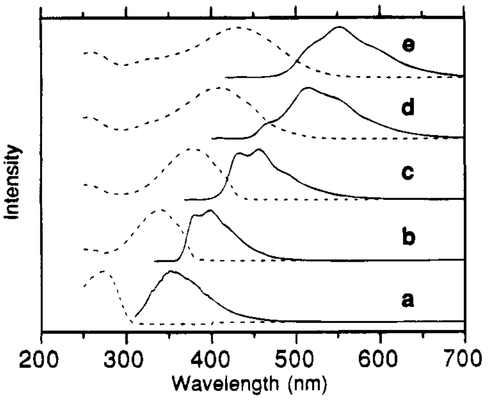

Figure 4. Absorption (- - -) and fluorescence (—) spectra of poly(tetrabutyldisilanylene-*block*-thiophene)s: (a) p-$T_1Si_2Bu_4$; (b) p-$T_2Si_2Bu_4$; (c) p-$T_3Si_2Bu_4$; (d) p-$T_4Si_2Bu_4$; (e) p-$T_6Oct_2Si_2Bu_4$.

$T_{16}Oct_8$ were prepared by oxidative coupling of the monolithio compounds of T_4Oct_2 and T_8Oct_4, respectively. $T_{12}Oct_6$ was isolated as a byproduct. Full details of the synthesis and characterization will be published elsewhere. Trimethylsilyl- and pentamethyldisilanyl-substituted oligothiophenes were prepared by monolithiation of thiophene, bithiophene, and terthiophene, followed by condensation with monochlorosilane or -disilane. The synthesis of some of the poly(silanylene-*block*-thiophene)s is described in ref 7 and that of the regioregular polythiophenes in ref 9. Poly(3-octylthiophene) was prepared according to a Ni-catalyzed regioselective polymerization described in the literature.[16]

UV–vis spectra were obtained on a SLM Aminco 3000 Array spectrophotometer from solutions in spectral grade *n*-hexane. Fluorescence spectra were recorded on a SLM Aminco SPF-500 spectrofluorometer. The optical density of each solution was below 0.1 at its absorption maximum.

For the calculation of optimized geometries, we used the AM1 Hamiltonian implemented in the MOPAC6 package.[17] The geometries obtained were input to the INDO/S-based program ZINDO,[18] in which a configuration interaction (CI) can be carried out on the molecular oribtals in order to produce ground- and excited-state energies. We employed the spectroscopic parametrization (Mataga-Nishimoto gamma's) within ZINDO.

Results and Discussion

Spectral Data. As an example of color tuning, Figure 4 shows absorption and fluorescence spectra for silanylene–thiophene block copolymers in *n*-hexane solution. The positions of the spectral maxima are listed in Table 1 and plotted in Figures 1 and 2, along with the data for the regioregular polymers and for the thiophene oligomers, which will be used for comparison. The data obtained for $T_{12}Oct_6$ and $T_{16}Oct_8$ show that the limiting conjugation length has not yet been attained at these oligomer lengths (Table 1). For reasons of solubility, some of the rings in the longer oligothiophenes and in the block copolymers have one *n*-octyl substituent. One would expect a small red shift to result because of the electron-pushing character of an alkyl chain (inductive effect). Interestingly, this is indeed found in fluorescence, but in absorption, a blue shift is noted (*cf.* T_4 and T_4Oct_2 oligomers). We rationalize this by considering that although these octyls are not head-to-head on adjacent rings, the substitution still yields a slightly larger preference for a noncoplanar geometry,[19,20] which only shows up in the ground electronic state, as will be explained below. The same behavior is found for 3-octyl-2,2′-bithiophene ($T_2Oct_1{}^3$) with respect to 2,2′-bithiophene: a blue shift in absorption and a red shift in fluorescence (see also Figure 5).

TABLE 1: Absorption and Fluorescence Wavelengths at Peak Maxima of Thiophene-Based Oligomers and Polymers, Measured in *n*-Hexane at Room Temperature

oligomer	λ_{Abs}, nm	λ_{Fl}, nm	polymer	λ_{Abs}, nm	λ_{Fl}, nm
T_1	231		p-T_2SiBu_2	330	360/384
T_1Oct_1	235		p-T_3SiBu_2	376	422/448
T_1Oct_2	242		p-T_4SiBu_2	412	512
T_2	301	360	p-$T_6Oct_2SiBu_2$	422	545
$T_2Oct_1{}^3$	293	366			
$T_2Oct_2{}^{44}$	310	372			
$T_2Oct_2{}^{33}$	280[a]	353/379	p-$T_1Si_2Bu_4$	274	354[b]
T_2Oct_4	280[a]	353/380	p-$T_2Si_2Bu_4$	342	380/399
T_3	351	406/423	p-$T_3Si_2Bu_4$	375	432/456
T_4	385	444/472	p-$T_4Si_2Bu_4$	410	515
T_4Oct_2	372	449/476	p-$T_6Oct_2Si_2Bu_4$	431	552
T_6Oct_2	412	503/536			
T_8Oct_4	430	531/565			
$T_{12}Oct_6$	447	548/587	p-T_1Oct_2	322	465
$T_{16}Oct_8$	452	552/590	p-T_2Oct_2	375	509
			p-T_3Oct_2	402	523
T_1SiMe_3	234		p-T_4Oct_2	424	532
T_2SiMe_3	309	368			
T_3SiMe_3	358	413/430			
			p-T_1Oct_1	430	561
$T_1Si_2Me_5$	242				
$T_2Si_2Me_5$	314	374			
$T_3Si_2Me_5$	360	416/437			

[a] Approximate position of a faint shoulder. The absorption maximum is found at *ca.* 250 nm; it is attributed to the "local" excitation.[25] [b] This peak is to be attributed to excimer fluorescence.

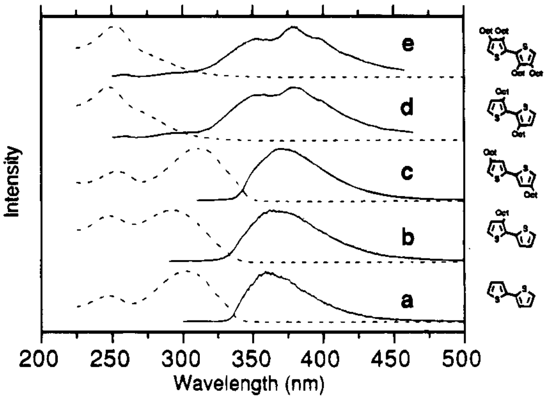

Figure 5. Absorption (- - -) and fluorescence (—) spectra of 2,2′-bithiophenes: (a) T_2; (b) $T_2Oct_1{}^3$; (c) $T_2Oct_2{}^{44}$; (d) $T_2Oct_2{}^{33}$; (e) T_2Oct_4.

In order to demonstrate the effects of the substitution patterns more clearly, we have synthesized and studied the series of substituted bithiophenes listed in Figure 3. The results will be discussed at appropriate places. A study of the absorption wavelengths of bi-, ter-, and quaterthiophenes bearing ethyl and methyl substituents was published by Van Pham *et al.*[21]

Figures 1 and 2 show that in both absorption and fluorescence, the silanylene–thiophene block copolymers are considerably closer to the oligomers than the regioregular polymers are. This indicates that the presence of one or two silicon atoms between thiophene sequences results in a stronger interruption of the conjugation than the one caused by the stereochemically induced kinks. Moreover, it seems safe to conclude that with respect to breaking the conjugation in thiophene-based polymers, one silicon atom is at least as effective as two. Nonetheless, a certain through-conjugation apparently exists in the silanylene-interrupted polymers, since the spectra of the polymers are red-shifted with respect to those of sil(an)yl-substituted oligomers, which we have studied for comparison. The introduction of a trimethylsilyl end group into an oligomer results in a slight red shift, followed by another small shift when going to two silicon atoms in the case of pentamethyldisilanyl substitution (Table 1; Figures 1 and 2 show data for trimethylsilyl substitution only). This is due to the participation of empty silicon d orbitals in the π-system of the ring (back-bonding), which results in an increase of the conjugation length. This phenomenon has been analyzed for analogous benzene derivatives.[22,23]

The pure oligomers of thiophene show a considerable Stokes shift of approximately 5×10^3 cm^{-1}. This is suggested to be due, in part, to noncoplanarity of the oligomer rings in the ground state, whereas the excited molecule is essentially planar.[24] This point will be elaborated on in more detail below, with the help of quantum chemical calculations. The shift decreases moderately with increasing length of the oligomer and is systematically higher for the octyl-substituted oligomers for the reasons discussed above. For the block copolymers p-$T_xSi_2Bu_4$, the Stokes shift follows an irregular pattern. For $x = 1$, it is very large, 8250 cm^{-1}, goes down to 4180 cm^{-1} for $x = 2$, and then steadily increases with increasing thiophene block length to ca. 5090 cm^{-1} for $x = 6$. From a study of model compounds not mentioned in this paper, we have obtained indications that in the case of p-$T_1Si_2Bu_4$ ($x = 1$), the fluorescence originates from an intramolecular excimer; this is currently under investigation. The presence of several overlapping peaks in the fluorescence spectra (Figure 4) complicates the analyses; we have taken the lowest-energy peaks. In the case of p-T_xSiBu_2, we only have data for $x = 2-6$, which are similar to those for p-$T_xSi_2Bu_4$.

The behavior of the regioregular polythiophenes is quite different: the Stokes shift is approximately 9600 cm^{-1} for $x = 1$ and decreases strongly for higher x down to 4800 cm^{-1} for $x = 4$. As in the case of the oligomers, the explanation will be that excitation is followed by a relaxation to a much more planar conformation, the difference being that in the polymer molecules the conjugation can extend over distances exceeding the formal sequence length x. For the excited state, the value of x loses its meaning and small differences distinguish $x = 2$, 3, and 4 in fluorescence: these polymers are found to become almost equivalent. The $x = 1$ polymer clearly has a shorter conjugation length: this is due to the presence of two substituents on each ring. As a result, the barrier to interring rotation is higher than for adjacent singly substituted rings. It is important to note that with respect to poly(3-octylthiophene) (p-T_1Oct_1), the regioregular polymers display a significant blue shift, in fluorescence as well as in absorption. The effect of head-to-head couplings is therefore unmistakably present.

The effects of substituents on interring rotation barriers are clearly demonstrated by the series of bithiophenes studied (Table 1; Figure 5). Single substitution at the 3-position ($T_2Oct_1{}^3$) leads to an 8-nm blue shift in absorption (reduced coplanarity) and to a 6-nm red shift in fluorescence (inductive effect in a coplanar excited state). With two substituents, at the 4- and 4′-positions ($T_2Oct_2{}^{44}$), there is no steric interaction, only an inductive effect yielding red shifts of approximately 10 nm in both absorption and fluorescence. In $T_2Oct_2{}^{33}$, the 3,3′-substitution leads to a strong blue shift of approximately 20 nm in absorption due to considerable noncoplanarity (the absorption maximum is now at 250 nm, but this is the "local" excitation;[25] the faint shoulder at 280 nm probably corresponds to the maximum found at 300 nm for T_2, which is ascribed to a charge-transfer excitation). The fluorescence is particularly interesting, because it shows two peaks, one at 353 nm and one at 380 nm. Since the latter peak is stronger, the average fluorescence energy is still comparable with that of 4,4′-substituted bithiophene and red-shifted with respect to bithiophene. The appearance of two peaks is strong support for our assertion that fluorescence occurs from essentially coplanar states: in the case of $T_2Oct_2{}^{33}$, the excited *syn* and *anti* states have sufficiently different energies to be distinguished in the spectrum, while the two peaks will be much closer for the other bithiophenes. Since the peak at 353 nm is blue-shifted with respect to T_2, the *syn* geometry is probably not fully coplanar or it may show significant ring distortions caused by the interaction of the substituents.

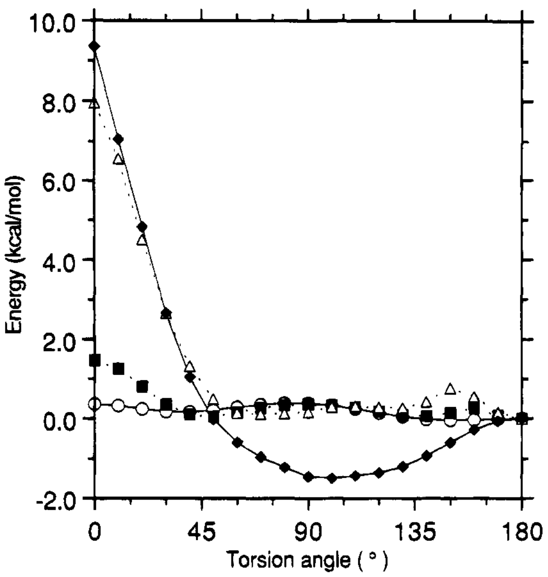

Figure 6. Potential energy curves for rotation around the interring bond (torsion) of bithiophenes, obtained from AM1 heats of formation: (○) 2,2′-bithiophene; (■) 3-propyl-2,2′-bithiophene: (△) 3,3′-dipropyl-2,2′-bithiophene; (◆) 3,3′,4,4′-tetrapropyl-2,2′-bithiophene. For each compound, the energy of its *anti* conformer was taken to be zero in order to have a common reference point.

Calculations. In what follows, a number of quantum chemical calculations will serve to illustrate the foregoing considerations, regarding torsional potentials between thiophene rings, whether substituted or unsubstituted, in the ground or excited state, and regarding the dependence of the wavelengths of absorption on this torsion angle. We have used the AM1 parametrization[17] for the generation of geometries. It underestimates C−S bond lengths in the thiophene rings (1.68 Å calculated vs 1.73 Å found in several structural studies, including ours[15]), and the interring bond is also 0.05 Å below the experimental value. Excited-state geometries were also generated by AM1; this may have to be regarded as a severe extrapolation, but it served its purpose of supplying quinoid-like geometries. Excitation energies were calculated by means of a CI procedure implemented in the program ZINDO.[18] The appropriate recipe for the CI remains to be found, however, and has been the subject of a recent study.[26]

Several authors[19,20,26−35] have already addressed the issue of interring torsion potential and the existence of conformers in thiophene oligomers, by means of both molecular mechanics and quantum chemistry methods. For unsubstituted bithiophene, the results show a flat potential curve with barriers of about 1 kcal/mol (in one case, STO-3G *ab initio* yielded 4 kcal/mol[30]), although there is disagreement on the position of the absolute minimum. Substitution significantly changes this picture only when both rings bear substituents in a "head-to-head" fashion.

Figure 6 compares potential energy curves for rotation around the interring bond, obtained from heats of formation of AM1 energy-minimized geometries at a given torsion angle, for unsubstituted, 3-propyl-substituted, and 3,3′-dipropyl-substituted 2,2′-bithiophenes. The barriers calculated for pure bithiophene are within 0.45 kcal/mol, and rotation is essentially free at room

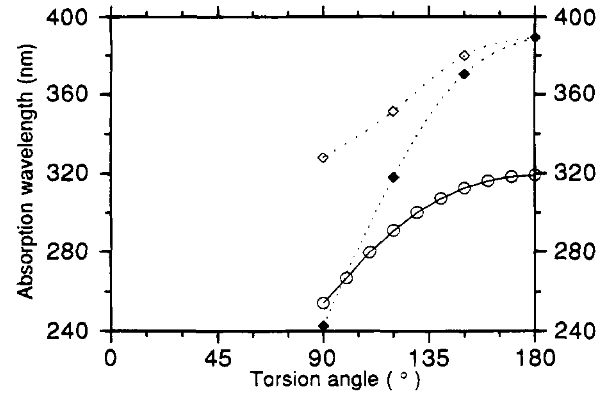

Figure 7. Calculated absorption wavelengths as a function of the interring torsion angle(s) in 2,2′-bithiophene (○) and in 2,2′:5′,2″-terthiophene: (◇) rotation around one interring bond, the other fixed at 180°; (◆) rotation around both interring bonds with C_2 symmetry imposed. (Single and double configuration interaction for HOMO → LUMO excitations.)

temperature ($NkT = 0.6$ kcal/mol). AM1, however, has been found to strongly underestimate rotational barriers, while the general shape of the potential energy curve agrees satisfactorily with experimental or *ab initio* results in many cases.[36] In the 3- and 3,3′-substituted bithiophenes, steric hindrance is evident around 0° (*syn* conformation); beyond 60°, the energy curve is flat with a minor hump at 150°. In each case, the minimum is at 180° (*anti* conformation). The calculation does not indicate that adjacent thiophene rings, substituted in a head-to-head fashion, preferentially assume a noncoplanar conformation. The results suggest that, for both unsubstituted and 3,3′-substituted bithiophene, an ensemble of molecules will show a multitude of different rotamers. These rotamers will have quite different absorption maxima (Figure 7) as a result of the strong dependence of the interring π-conjugation on the torsion angle. The absorption spectra will therefore be inhomogeneously broadened.

Statistically, however, coplanarity is more likely for unsubstituted rings, since the region around the *syn* rotamer is excluded in the case of 3,3′-substitution. The "average" coplanarity decreases with the fraction of rings bearing substituents, and this explains how the spectral properties of the regioregular polymers depend on the sequence length x (x is the inverse degree of substitution). Since the torsion potential energy curve of consecutive monosubstituted rings still allows many almost coplanar (*anti*) rotamers to exist, the effective conjugation length in a polymer can be larger than the sequence length x, i.e., larger than the conjugation length in an oligomer of x rings.

Does the actual size of the substituents (octyl instead of propyl) enforce noncoplanarity? We have limited the calculations to propyl substitution, since it is found that in a fully equilibrated geometry, the ultimate carbon atom of a propyl chain is sufficiently remote from the neighboring ring that extending the chain will have no influence on the potential curve. It would lead to much more time-consuming calculations, however. Still it is to be expected that in a real system, a longer alkyl chain would experience more collisions with the adjacent ring and coplanarity would be less probable because of the dynamics of the molecule, an entropy aspect that cannot be represented by the equilibrium torsion potential energy.

What is the situation for fluorescence? We consider it to correspond to a low-energy vertical electronic transition in a relaxed excited-state geometry. Figure 8 shows the torsion potential energy curve calculated (AM1) for the excited state of bithiophene. This state has quinoid character with a shortened interring bond in the coplanar arrangements. *Anti* and *syn* conformations clearly correspond to potential energy minima. A similar result is found for the excited state of 3,3′-dipropylbithiophene, but in this case, steric hindrance around 0° causes the minimum at 180° to be the deeper one (Figure 9). Such a difference in energy between *syn* and *anti* excited states was also suggested by the appearance of distinct peaks in the fluorescence spectrum of T_2Oct_2[33] (Figure 5). The calculations clearly indicate that there is an electronic driving force toward coplanarity of the rings. This result explains the considerable Stokes shifts found experimentally for the pure oligomers as well as for the regioregular polymers, where the shifts are even larger. In saying so, we extrapolate our findings from bithiophene to oligothiophenes. The situation for the excited state is analogous to that for charged states occurring in doped oligothiophenes: there is an increased contribution from electronic levels that are bonding across the interring bond, viz. LUMO or HOMO-1. Doping, therefore, also induces coplanarity of the rings, which is favorable for conduction.

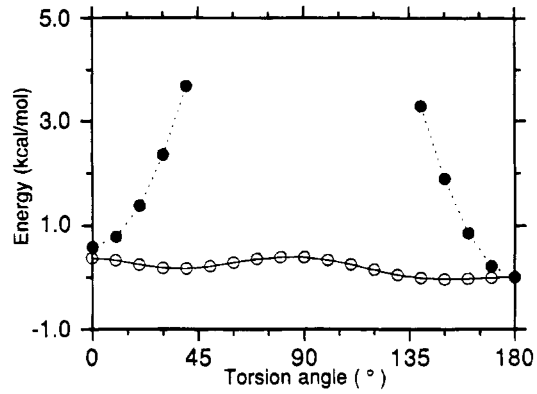

Figure 8. Torsion potential energies calculated for 2,2′-bithiophene in the ground (○) and excited (●) states. For each state, the *anti* conformer was assigned an energy value of zero in order to have a common reference point.

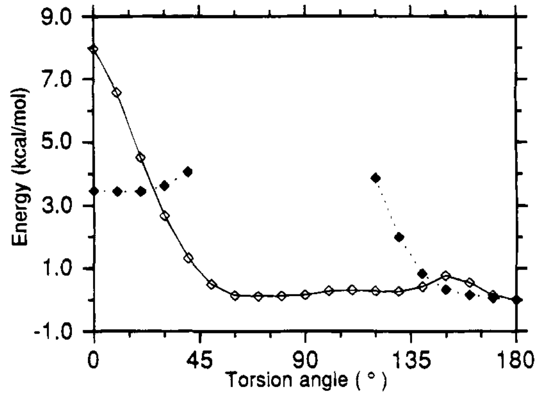

Figure 9. Torsion potential energies calculated for 3,3′-dipropyl-2,2′-bithiophene in the ground (◇) and excited (◆) states. For each state, the *anti* conformer was assigned an energy value of zero in order to have a common reference point.

Doubly Substituted Rings. A similar reasoning tells us why the regioregular polymer with $x = 1$ (p-T_1Oct_2) behaves differently in that it does not attain such a high degree of coplanarity on excitation, as inferred from the fluorescence wavelength. In this $x = 1$ polymer, the rings are all doubly substituted, and our calculations on 3,3′,4,4′-tetrasubstituted bithiophene show that a propyl group on the 4-position forces the propyl on the 3-position out of the ring plane, which results in more pronounced steric interaction between the latter propyl and the other ring. 3,3′,4,4′-Substitution leads to a higher energy of the *syn* geometry and a well-defined minimum in the torsion

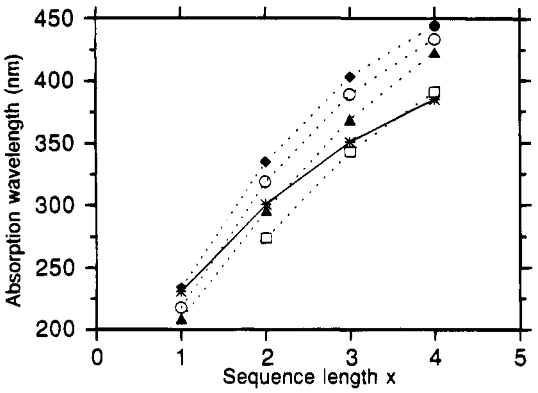

Figure 10. Comparison of experimental (*) absorption wavelengths of thiophene oligomers, T_x, with wavelengths calculated at various levels of configuration interaction: (◆) SCI HOMO → LUMO; (○) SDCI HOMO → LUMO; (▲) SDCI HOMO-1 → LUMO+1; (□) SDCI HOMO-2 → LUMO+2.

potential curve at ca. 95°, although it is still only 1.5 kcal/mol below the *anti* conformation (Figure 6). This simple result tells us that stronger and more well-defined kinks in polythiophene could be obtained by introducing doubly substituted rings at both ends of the sequences of length *x*.

We have supplemented this by an experimental study of the model compound 3,3′,4,4′-tetraoctyl-2,2′-bithiophene (T_2Oct_4 in Table 1 and Figure 5). The absorption spectrum is very similar to that of $T_2Oct_2{}^{33}$. The main maximum is the "local" excitation around 250 nm;[25] it is slightly red-shifted. The shoulder at approximately 280 nm which we attribute to the interring charge-transfer excitation is again visible. The fluorescence spectrum is not very different from that of $T_2Oct_2{}^{33}$ either: the two maxima are still located at 353 and 380 nm (and the shoulder at approximately 400 nm is more clearly observable). This similarity suggests that the excited-state geometry is the same as that of $T_2Oct_2{}^{33}$. We note, however, that this would imply a red shift induced by the two additional substituents. This shift is not observed, and we think that the inductive effect is just cancelled by a small (average) deviation from coplanarity. The results for the model compound do not fully account for the differences observed in the regioregular polymers, and probably the dynamic aspects of the geometry relaxation after excitation play a role.

Comparison of Experimental and Calculated Excitations. A calculation of excitation energies as a function of interring torsion, as presented in Figure 7, in principle allows one to estimate the effective average interring torsion angle in an ensemble of oligothiophene rotamers. The results shown have been obtained through CI of single and double HOMO → LUMO excitations in a set of molecular orbitals produced by an INDO/S calculation.[18] The size of the CI expansion is of some concern, however. Figure 10 shows absorption maxima calculated through single-excitation CI (SCI) and through single and double CI (SDCI) for a varying number of π-levels involved, as well as experimental data. For thiophene ($x = 1$), the simple SCI approach produces the closest value (234 nm from SCI *vs* 231 nm experimentally), but the calculated increase of the wavelength with *x* is stronger than the experimental trend; this holds true for any CI procedure in which a fixed number of π-levels is used. Lower wavelengths are found when more π-levels are involved in the CI. Instead of taking the size of the actual π-system into account when allowing for electron correlation,[26] we might consider the question to what extent the interring torsions determine the evolution of the absorption wavelength with increasing oligomer length.

For bithiophene, according to Figure 7, an absorption wavelength of 300 nm corresponds to an interring dihedral angle of approximately 130°. Proceeding along this line, we calculate the excitation for terthiophene having both interring dihedrals at 130° (C_2 symmetry) and we find 342 nm. This is already somewhat below the experimental value of 351 nm, but a slightly smaller torsion (dihedrals approximately 135°) is adequate. In order to maintain the agreement, we have to increase the dihedrals up to 140−145° for quaterthiophene. There is no obvious reason why the average angle should change, but it has been found that the interring bonds are slightly shorter (have stronger double-bond character) in longer oligomers.[33] We emphasize that our approach is crude and that the angle calculated is only an effective average one for the ensemble of rotamers, based on absorption peak positions. Some scaling of the size of the CI expansion with the length of the oligomer may still be justifiable for a more exact description of the evolution of absorption wavelengths.

Conclusion

We have discussed aspects relevant to color tuning of the spectral properties of thiophene-based polymers. The key factor is the effective average degree of coplanarity of the rings, which can be quite different in ground and excited states. In the excited state, which is relevant to light emission, there is a strong electronic driving force toward coplanarity of the rings. This electronic force largely cancels any conformational features (that would result in interruption of the π-conjugation) induced by substituents on the rings. Conjugation is broken more efficiently by a single silicon atom between sequences of thiophene rings.

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