

# Tuning of the Electronic and Optical Properties of Oligothiophenes via Cyano Substitution: A Joint Experimental and Theoretical Study

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Cyano-substituted bi- and terthiophene derivatives have been synthesized and characterized both electrochemically and optically. The experimental data are compared to the results of quantum-chemical calculations in order to rationalize the evolution of the frontier levels of the thiophene oligomers as a function of the number and position of the cyano substituents. This issue is of particular relevance in the context of organic light-emitting diodes and field-effect transistors to determine the substitution pattern required for the design of efficient electron-transporting (n-type) oligothiophene derivatives. The experimental and theoretical results demonstrate that the cyano functionalization allows for a fine-tuning of the electronic and optical properties of the thiophene compounds.

## 1. Introduction

Organic light-emitting diodes (OLEDs) are emerging as a potential short-term application of organic semiconductors. Two classes of organic materials are used in OLEDs: conjugated polymers—mainly poly(paraphenylenevinylene), PPV, and its derivatives, which were initially reported by the Cambridge group<sup>1</sup>—and low molecular weight molecules.<sup>2</sup> The generally accepted mechanism of organic electroluminescence involves a double injection of electrons and holes<sup>3</sup> that recombine to form excitons followed by the radiative deactivation of these excitons. Since most of the early emitting materials were p-type (hole transporting), electron injection was the major limiting step. A major breakthrough was achieved by using multilayered structures that combine hole- and electron-transporting materials, first in the case of small molecules<sup>2,4</sup> and then with conjugated polymers.<sup>5</sup> In the latter case, cyano substitution of PPV appeared very encouraging, and comparative experimental and theoretical studies proved to be powerful in the search for suitable compounds.<sup>6</sup>

Oligomers stand between these two classes of materials. Although oligothiophenes ( $T_n$ ,  $n$  being the number of thiophene rings) have been demonstrated to be among the best candidates for making organic field-effect transistors (OFETs),<sup>7–10</sup> which constitute another variety of organic-based electronic devices, they do not compete at present in OLEDs (the reported electroluminescence quantum yield of sexithiophene is between  $5 \times 10^{-4}\%$ <sup>11</sup> and  $10^{-3}\%$ <sup>12</sup>). This is in part due to the fact that unsubstituted  $T_n$ 's are essentially hole transporting, which considerably limits electron injection in single or even double layer oligothiophene-based OLEDs. Moreover, the energy separation between the  $1B_u$  and  $2A_g$  excited states decreases as the oligomer length is increased (the  $1B_u$  state being around 0.9 eV lower in energy than the  $2A_g$  state in bithiophene<sup>13</sup>) and the two states are expected to have similar energy in the six-ring oligomer.<sup>14,15</sup> Therefore, this could also be the reason for the poor quantum efficiency reported for sexithiophene. The use of n-type (electron-transporting) material is also of interest

in OFETs; it would allow the making of complementary type devices (known in silicon electronics as CMOS technology). Encouraging results have been reported with fullerene ( $C_{60}$ ) as an n-type semiconductor.<sup>16</sup> However, this compound suffers from a large instability toward oxygen. The need for stable n-type materials is therefore one of the most important challenges for the development of organic electronic devices. As exemplified by the case of cyano-derivatized PPVs,<sup>6</sup> n-type conductivity (i.e., electron transport ability) in organic semiconductors requires a high electron affinity to allow an easy electron injection. It can therefore be expected that n-type oligothiophenes may be realized by substituting the oligomer with electron acceptors such as cyano groups.

The work reported here was initiated by the synthesis of bi- and terthiophenes substituted by cyano groups at either terminal or lateral positions. In all cases, the substitution pattern is such that there is full conjugation between the cyano moieties and the carbon backbone. The electrochemical characterization of the compounds have already been described.<sup>17</sup> In this work, we compare the relative locations of the molecular levels, as deduced from both electrochemical and optical measurements, to those provided by quantum chemistry calculations. We dwell on the influence of the position and number of the cyano substituents. The theoretical approach is detailed in the next section. In the following two sections, we report on the electrochemical and optical measurements, respectively, and compare the results to the theoretical calculations.

## 2. Theoretical Modeling

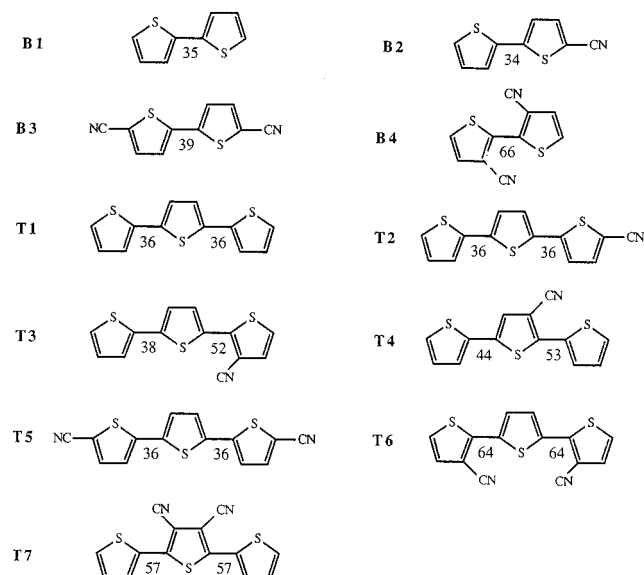
We focus on the cyano-substituted oligothiophenes that have been investigated experimentally (see Figure 1) in order (i) to analyze how the locations of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels are affected when the number and position of the substituents are varied and (ii) to determine the resulting changes in the lowest transition energy. These two theoretical aspects are tested by cyclic voltammetry and optical absorption measurements, respectively.

We have first carried out geometry optimizations on the oligothiophenes at the ab initio Hartree–Fock 3-21G\* level. In

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**Figure 1.** Molecular scheme of the substituted bi- and terthiophene series. The AM1-calculated dihedral torsion angles (in degrees) are indicated below each inter-ring bond.

our theoretical approach, the bond angles and bond lengths involving carbon and sulfur atoms are initially optimized for the various dimers in their planar conformation. The choice of a 3-21G\* basis set is validated by the close agreement observed for the unsubstituted oligomers between the calculated C—C bond length alternation and C—S bond lengths and X-ray diffraction data, as well as earlier *ab initio* calculations including a larger basis set.<sup>18</sup> Since the results obtained on the dimers indicate that the cyano substitution does not modify significantly the values of the bond angles, these parameters are kept frozen during the optimization procedure of the planar cyano-substituted trimers and have been extracted from the geometry of the unsubstituted trimer.

The geometry characterizations have been extended to a qualitative study of the evolution of the torsion angle between adjacent thiophene units as a function of substituent positions. Since it would be most difficult to treat accurately the solvent effects that influence the experimental data, we have adopted a very simple approach. It consists of optimizing the torsion angles with the help of the semiempirical Hartree–Fock Austin Model 1<sup>19</sup> calculations performed within a rigid rotor approximation, i.e., by keeping the bond lengths and bond angles frozen at the *ab initio* values. We emphasize that our main goal in performing such gas-phase calculations is to provide simple trends for the connection between the amplitude of the torsion angles and the substitution patterns. The choice of the AM1 formalism is validated in the case of bithiophene by the close agreement obtained between the AM1-optimized torsion angle and the results from post-Hartree–Fock *ab initio* and density functional calculations, around 35°. <sup>20</sup> This approach is also validated by the fact that the inter-ring C—C bond is hardly affected within the range of torsion angles considered in the following.<sup>21</sup>

The 3-21G\* calculations indicate that cyano substituents in the  $\alpha$  position affect the geometry of the thiophene ring to which they are connected without altering the length of the C—C inter-ring bond. We note that these geometric deformations are stronger than those previously reported for cyano-substituted phenylenevinylene oligomers<sup>6</sup> because of the weaker aromatic character of the thiophene units. The presence of cyano groups in the  $\beta$  position is found to affect also the C—C bonds of the neighboring ring, in such a way as to minimize the steric

**TABLE 1: Oxidation and Reduction Potentials of Cyano Thiophene Derivatives (in V vs SCE)<sup>a</sup>**

compound	$E_{\text{ox}}^{\circ}$	$E_{\text{red}}^{\circ}$	$E_g$
<b>B2</b>	1.64 <sub>6</sub>	−1.77 <sub>6</sub>	3.42
<b>B3</b>	1.98 <sub>0</sub>	−1.40 <sub>9</sub>	3.39
<b>B4</b>		−1.46 <sub>0</sub>	
<b>T1</b>	1.10 <sub>9</sub>	−2.06 <sub>4</sub>	3.17
<b>T2</b>	1.29 <sub>6</sub>	−1.62 <sub>6</sub>	2.92
<b>T3</b>	1.30 <sub>6</sub>	−1.66 <sub>7</sub>	2.97
<b>T4</b>	1.37 <sub>8</sub>	−1.68 <sub>6</sub>	3.06
<b>T5</b>	1.50 <sub>6</sub>	−1.41 <sub>2</sub>	2.92
<b>T6</b>	1.53 <sub>0</sub>	−1.40 <sub>8</sub>	2.94
<b>T7</b>	1.66 <sub>0</sub>	−1.40 <sub>6</sub>	3.07

<sup>a</sup> The energy gap  $E_g$  (in eV) is taken as the absolute difference between  $E_{\text{ox}}^{\circ}$  and  $E_{\text{red}}^{\circ}$ . Data are taken from ref 17.

hindrance, without any modification of the inter-ring distance. These geometry deformations are driven by both the  $\pi$ -acceptor nature of the cyano group and inductive effects within the  $\sigma$ -backbone resulting from the higher electronegativity of the nitrogen atoms.

In a second step, we determine the one-electron structure of the oligomers using the semiempirical Hartree–Fock intermediate neglect of differential overlap (INDO) method. The INDO formalism is then coupled to a single configuration interaction (INDO/SCI)<sup>22</sup> scheme to calculate the lowest transition energies and related oscillator strengths of the investigated compounds. The electron–electron repulsion term used in the INDO calculations is expressed by means of the Mataga–Nishimoto potential.

### 3. Electronic Properties

**3.1. Experimental Results.** The electrochemical properties of the cyano oligothiophene derivatives have been detailed previously.<sup>17</sup> The main results are gathered in Table 1. The following trends should be emphasized. First, the oxidation potential increases with (i) the lowering of the oligomer chain length, (ii) the number of substituted sites, and (iii) a central substitution compared to a terminal one. Second, although the reduction potential follows a similar behavior, the evolution with the chain size and position of the cyano groups is much less important. For instance, in the twice substituted terthiophenes, the reduction potential is found to be nearly independent of the substitution pattern. Third, the electrochemical gap decreases as the number of thiophene subunits increases and is larger with a central than with a terminal substitution. Surprisingly, the electrochemical gap of the terthiophene series does not change significantly with the number of substituted sites.

**3.2. Theoretical Results.** We report in Table 2 the INDO-calculated locations of the HOMO and LUMO levels of the substituted oligomers when they are forced to remain in a planar conformation. These calculations demonstrate that substitution with acceptor groups leads to an overall stabilization of the frontier levels whose amplitude intimately depends on the number and position of the cyano groups. Note that this stabilization is asymmetric in the sense that the energy of the LUMO level is more affected than that of the HOMO level, a feature that has been amply documented earlier.<sup>6</sup> We also note that the shifts of the frontier levels are much larger in the disubstituted compounds.

Despite the fairly good agreement observed between the theoretical and experimental results (see Table 2), a detailed analysis of the theoretical results indicates that calculations performed on planar conformations fail to rationalize simultaneously the experimental evolution of the reduction and oxidation potentials among the series of oligomers. For

**TABLE 2: Energy (in eV) of the HOMO and LUMO Levels, Lowest Transition Energy ( $E_g$ , in eV), and Related Oscillator Strength (O.S. in arbitrary units) of the Cyano Oligothiophenes in a Planar Conformation, As Provided by the INDO/SCI Calculations<sup>a</sup>**

compound	HOMO	LUMO	$E_g$ (O.S.)
<b>B2</b>	-7.69	-0.86	3.59 (0.86)
<b>B3</b>	-7.94 (-0.25/- <b>0.32</b> )	-1.30 (-0.44/- <b>0.36</b> )	3.48 (1.04)
<b>B4</b>	-7.92 (-0.23)	-1.27 (-0.41/- <b>0.32</b> )	3.45 (0.67)
<b>T1</b>	-7.02	-0.61	3.26 (1.04)
<b>T2</b>	-7.25 (-0.23/- <b>0.19</b> )	-1.03 (-0.42/- <b>0.43</b> )	3.17 (1.25)
<b>T3</b>	-7.19 (-0.17/- <b>0.20</b> )	-0.99 (-0.38/- <b>0.39</b> )	3.12 (0.98)
<b>T4</b>	-7.27 (-0.25/- <b>0.27</b> )	-0.99 (-0.38/- <b>0.38</b> )	3.22 (0.96)
<b>T5</b>	-7.47 (-0.45/- <b>0.41</b> )	-1.35 (-0.74/- <b>0.65</b> )	3.10 (1.44)
<b>T6</b>	-7.36 (-0.34/- <b>0.42</b> )	-1.27 (-0.66/- <b>0.65</b> )	3.03 (0.96)
<b>T7</b>	-7.48 (-0.46/- <b>0.55</b> )	-1.27 (-0.66/- <b>0.65</b> )	3.15 (0.89)

<sup>a</sup> We present in parentheses the INDO shifts of the frontier levels (with respect to compounds **B1** and **T1** in the bithiophene and terthiophene series, respectively) that are compared to the corresponding experimental values appearing in bold.

instance, the fact that the oxidation potential is larger when the cyano group occupies a more central position in the trimer (as observed in the **T5** → **T6** → **T7** series) cannot be accounted for by our data. However, we observe that the relative positions of the frontier orbitals are well-reproduced when addressing separately derivatives **T3**, **T4**, **T6**, and **T7**, where the cyano groups are located in the inner part of the molecule, and derivatives **T2** and **T5** where the substituents are found on the outer  $\alpha$  carbons. Furthermore, we note that the larger discrepancy between theory and experiment is obtained for derivatives **T6** and **T7**, which have two substituents at the  $\beta$  position of the thiophene rings. This indicates that the substituted molecules of a given group are characterized in solution by similar torsion angles between adjacent thiophene units and that the absolute values of these angles differ within the two groups.

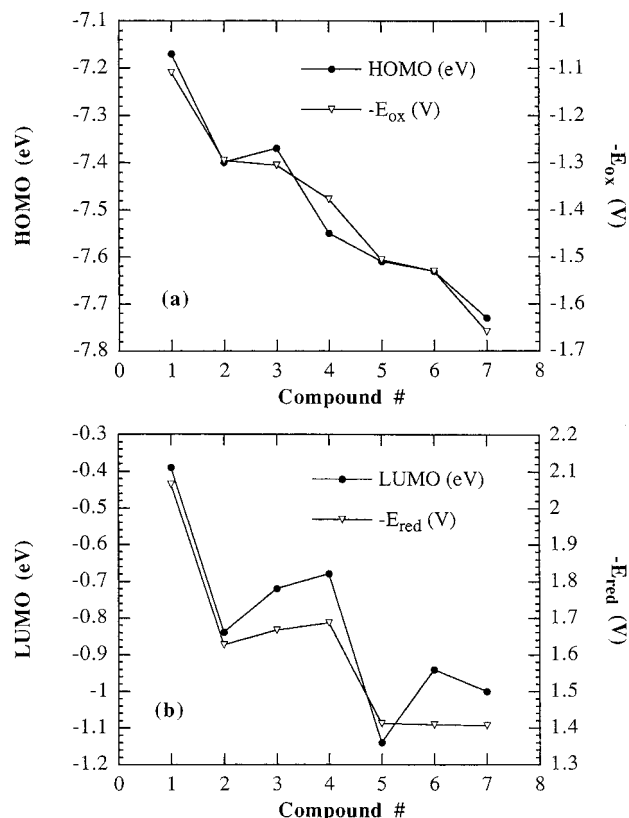
As mentioned above, to check on the validity of these assumptions, we have simply optimized the torsion angles between adjacent rings by means of AM1 calculations on the isolated molecules. These optimizations show (see Figure 1) that the torsion angle between two adjacent thiophene units is on the order of  $35^\circ$  in situations where the rings are either unsubstituted or the cyano groups are connected in  $\alpha$  positions. In contrast, derivatives with cyano groups in  $\beta$  positions are characterized by larger dihedral angles between the substituted ring and the adjacent unit. Since the measurements are carried out in solution, we are led to the conclusion that it is necessary to deal explicitly with twisted conformations to rationalize the experimental data.

On the basis of the previous considerations, we have calculated the INDO positions of the frontier levels in the trimer derivatives within a simple model. First, we assume that the torsion angle between unsubstituted rings in weakly polar solvents is as large as that calculated for the isolated molecule,  $\sim 35^\circ$  (this approach is validated by the results of recent self-consistent reaction field (SCRF) calculations, taking explicit account of the dielectric constant of the medium during the optimization procedure<sup>23</sup>). Second, a similar value is adopted in the case of thiophene units substituted by cyano groups in the  $\alpha$  position. Third, we have determined the value of the torsion angle, between an unsubstituted ring and a ring involving a cyano substituent in the  $\beta$  position, that provides the best match to the experimental evolution of the oxidation potential. We find this value to be close to  $45^\circ$ . In this context where we only take account of two values for the torsion angles, we obtain an excellent agreement between the theoretical and experimental evolution of the oxidation potentials (see Table 3 and Figure 2a). The agreement confirms the need for torsion angles to be considered in our model.

**TABLE 3: Energy (in eV) of the HOMO and LUMO Levels, Lowest Transition Energy ( $E_g$ , in eV), and Related Oscillator Strength (O.S. in arbitrary units) of the Trimers with Torsion Angles Defined by Our Model, As Provided by the INDO/SCI Calculations<sup>a</sup>**

compound	HOMO	LUMO	$E_g$ (O.S.)
<b>T1</b>	-7.17	-0.39	3.50 (0.95)
<b>T2</b>	-7.40 (-0.23/- <b>0.19</b> )	-0.84 (-0.45/- <b>0.43</b> )	3.43 (1.17)
<b>T3</b>	-7.37 (-0.20/- <b>0.20</b> )	-0.72 (-0.33/- <b>0.39</b> )	3.41 (0.85)
<b>T4</b>	-7.55 (-0.38/- <b>0.27</b> )	-0.68 (-0.29/- <b>0.38</b> )	3.58 (0.79)
<b>T5</b>	-7.61 (-0.44/- <b>0.41</b> )	-1.14 (-0.75/- <b>0.65</b> )	3.32 (1.31)
<b>T6</b>	-7.63 (-0.46/- <b>0.42</b> )	-0.94 (-0.55/- <b>0.65</b> )	3.41 (0.82)
<b>T7</b>	-7.73 (-0.56/- <b>0.55</b> )	-1.00 (-0.61/- <b>0.65</b> )	3.48 (0.72)

<sup>a</sup> We present in parentheses the INDO shifts of the frontier levels (with respect to compound **T1**) that are compared to the corresponding experimental values appearing in bold.

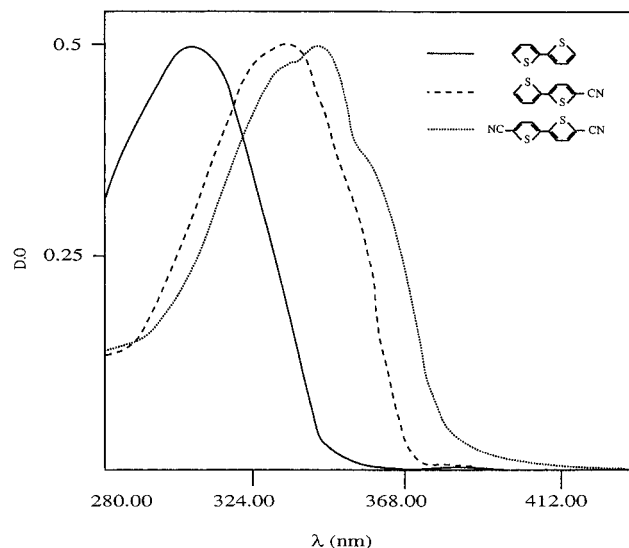


**Figure 2.** Measured (open symbols) and calculated (filled symbols) HOMO (a) and LUMO (b) levels in the terthiophene series. The measured levels correspond to the (negative) oxidation and reduction potential, respectively. The different energy scales for the measured and calculated levels are due to the different reference levels.

We emphasize that the ionization potential values are governed by the position and number of substituents and by the amplitude of the torsion angles, with substitution and torsion both leading to a stabilization of the HOMO level. In contrast, the position of the LUMO level results from a compromise between the stabilization induced by the cyano substituents and the destabilization associated with larger torsion angles. Note that the changes occurring in the lowest transition energy calculated within the same model are also consistent with the experimental results, as described in a following section.

#### 4. Optical Properties

**4.1. Experimental Results.** All the spectra presented here have been measured in toluene. Cyano-substituted bithiophenes and terthiophenes present a very weak solvatochromism, as was verified by their absorption in dichloromethane, acetonitrile, and



**Figure 3.** UV-visible absorption spectra of cyano-substituted bithiophenes **B1**, **B2**, and **B3**. The spectrum of **B4**, which is very close to that of **B2**, is not shown for clarity.

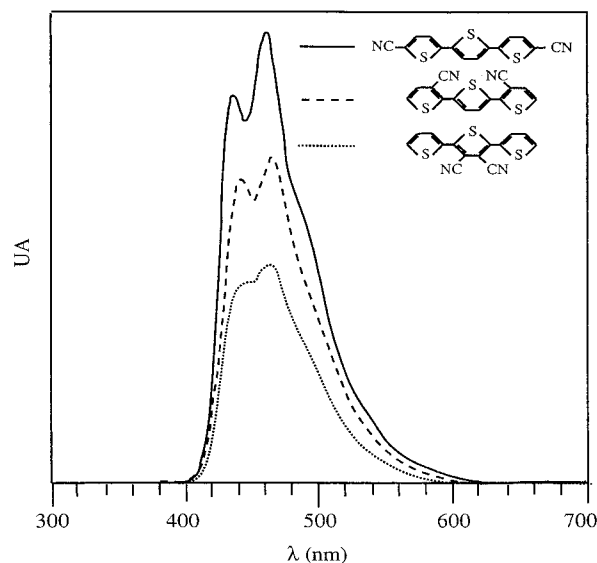
**TABLE 4: Maximum Absorption and Emission  $\lambda_{\text{max}}$  (in nm; in eV for Values in Parentheses), Molar Extinction Coefficient  $\epsilon$  (in  $\text{cm}^{-1} \text{M}^{-1} \text{L}^{-1}$ ), Fluorescence Quantum Yield  $\Phi$ , and Optical Gap  $E_{00}$  (in eV) of the Cyano-Substituted Bithiophene and Terthiophene Series**

compound	$\lambda_{\text{max abs}}$	$\lambda_{\text{max emis}}$	$\epsilon$	$\Phi$	$E_{00}$
<b>B1</b>	305 (4.07)	365 (3.40)	9850	0.019	3.68
<b>B2</b>	331 (3.75)	390 (3.18)	17000	0.081	3.43
<b>B3</b>	341 (3.64)	396 (3.13)	16900	0.052	3.37
<b>B4</b>	333 (3.72)	410 (3.02)	7200	0.995	3.32
<b>T1</b>	354 (3.50)	411, 435 (3.02, 2.85)	17625	0.055	3.11
<b>T2</b>	378 (3.28)	457 (2.71)	23100	0.116	2.98
<b>T3</b>	377 (3.29)	459 (2.70)	20900	0.115	2.96
<b>T4</b>	369 (3.36)	454 (2.73)	15900	0.072	3.02
<b>T5</b>	383 (3.24)	436, 461 (2.84, 2.69)	29000	0.154	2.94
<b>T6</b>	379 (3.27)	440, 464 (2.82, 2.67)	11100	0.125	2.95
<b>T7</b>	374 (3.31)	434, 453 (2.86, 2.74)	8200	0.082	3.00

hexane; the shift of the peaks was always less than 10 nm (and often much less). Accordingly, the position of the peaks can be directly compared to the redox potentials, regardless of the fact that the redox potentials were measured in acetonitrile.

**4.1.1. UV-Visible Absorption.** The UV-vis absorption spectra of terthiophene derivatives are not structured except for the  $\alpha,\omega$ -disubstituted terthiophene **T5**, which has a weak shoulder at long wavelength. In contrast, bithiophene derivatives in solution show a more structured absorption with a shoulder at both sides of the main peak, which corresponds to the 0–1 vibronic feature (Figure 3). In the case of single substitution, or when the cyano substituents are grafted at the  $\beta$  position, the shoulder at the short wavelength side disappears and that at long wavelength decreases.

The following remarks can be made about the location of UV-visible absorption bands (Table 4). The main absorption peak is red-shifted when bithiophene is substituted at the terminal position, first by one cyano group, then by a second one (the shifts are 26 and 36 nm, respectively). The spectrum of **B4** is very similar to that of **B2** (Table 4) and is not shown in Figure 3 for the sake of clarity. Its blue shift compared to that of **B3** is a good indication that oligomers substituted at the end positions are more conjugated than those substituted at lateral positions. Accordingly, the torsion angle between the two substituted rings is expected to be greater in **B4** than in **B3**, in agreement with the theoretical results. A similar trend is found on the terthiophene series, namely, a bathochromic shift



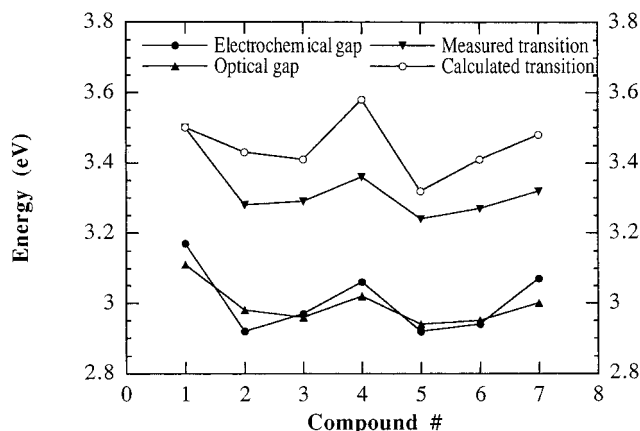
**Figure 4.** Fluorescence emission (in arbitrary units) of cyano-substituted terthiophenes **T5**, **T6**, and **T7**. The spectra are drawn with different heights for clarity.

of the peak when the number of substituted sites increases and a hypsochromic shift in the mono- or disubstituted series when the substituent moves from the terminal to the central position. The latter evolution is fully consistent with the results of the theoretical calculations, as emphasized below.

**4.1.2. Photoluminescence.** Unlike in absorption, the emission spectra of all terthiophene derivatives are structured. This can be attributed to the more planar conformation in the excited state of the oligothiophenes.<sup>24</sup> The structure is better resolved when compounds are disubstituted but tends to smear out when the substituents move from terminal to central positions (Figure 4). This can be related to the torsion angle of the ground-state conformation, which is higher with central substitution (see Figure 1). In the  $\alpha,\omega$ -disubstituted derivative **T5**, we expect light emission to take place from a fully planar conformation,<sup>24</sup> or from a conformation close to the equilibrium geometry in the excited state. This gives rise to a line narrowing, which could be limited in derivatives **T6** and **T7** because of a strong influence of steric effects induced by the presence of high torsion angles in the ground state of these derivatives.

As in absorption, the position of the emission peaks is red-shifted when bithiophene is substituted at a terminal position, first by one cyano group, then by a second one (the shifts are 25 and 31 nm, respectively). Likewise, a bathochromic shift is recorded between compounds **B3** and **B4**. A bathochromic shift of the emission peaks is also found in the terthiophene series when the number of substituted sites increases. However, the hypsochromic shift of the mono- and disubstituted series when going from terminal to central positions is not as clear as in absorption.

**4.1.3. Fluorescence Quantum Yield and Optical Gap.** The optical gap, as defined by the 0–0 transition energy  $E_{00}$ , was estimated from the intersection of the excitation and emission spectra, regarded as mirrors of the 0–0 transition. The influence of possible Stokes shifts is therefore neglected in these estimates. We report in Table 4 the optical gap measured for the various derivatives and illustrate in Figure 5 that these data compare very well to the values of electrochemical gap previously discussed. For both bithiophene and terthiophene derivatives,  $E_{00}$  tends to slightly decrease with the number of substituted sites. Accordingly, the optical gap decreases from 3.11 eV for the unsubstituted compound **T1** to 2.94 eV for **T5**, passing by 2.98 eV for **T2**. In fact, we find very similar gaps for the



**Figure 5.** Measured energy gap and theoretical and experimental lowest transition energy of the terthiophene series.

terthiophene series **T2**, **T3**, **T5**, and **T6**, where the central thiophene subunit is not substituted. They range from 2.94 to 2.97 eV and thus show a weak influence of the number of substituted sites. The terthiophene derivatives substituted at the central thiophene subunit present similar optical gaps (3.02 and 3.00 eV for **T4** and **T7**, respectively), which are higher than those of the other derivatives. This is also the case for the theoretical calculations (see Table 3.)

The substitution of terthiophene by one or two cyano groups increases the fluorescence quantum yield, which is lower for monosubstituted terthiophenes than for their disubstituted homologs. For example, the fluorescence yield of **T1** and **T2** is 5.5% and 11.8%, respectively. When a second cyano group is introduced (compound **T5**),  $\Phi$  increases to 15.4%. For both the bi- and terthiophene series, we observe a lowering of the fluorescence quantum yield when the substituents move from terminal to lateral positions. Substituted bithiophenes have an unusual behavior; the substitution with strong electroaccepting cyano groups increases the fluorescence quantum yield, but in contrast to the case of terthiophenes, we do not find any correlation between the yield and the substitution pattern. Moreover, compound **B4**, which has two cyano groups in lateral positions, presents a fluorescence yield close to 100%, which is truly remarkable for an oligothiophene compound. This modulation of the quantum efficiency by the substitution pattern has to be intimately related to changes in the relative positions of the lowest excited states within the singlet and triplet manifolds and, hence, to changes in the decay rate of efficient nonradiative routes, such as intersystem-crossing processes.<sup>24</sup>

**4.2. Theoretical Results.** In all systems, the lowest energy transition is mainly described by an electronic excitation between the HOMO and LUMO levels (with an additional contribution arising from the  $H - 1 \rightarrow L + 1$  excitation). Considering the oligothiophenes in their planar conformation (Table 2), we observe that the cyano substitution leads to a red shift of the lowest optical transition due to the fact that the derivatization gives rise to an asymmetric stabilization of the frontier orbitals. Since the largest red shift calculated among the three-ring oligomers amounts to  $\sim 0.2$  eV (in the case of derivative **T6**), we thus expect significant changes in the color of the light emitted by a LED to occur upon cyano substitution. However, the transition energies and related oscillator strengths calculated for the planar oligomers (see Table 2) fail to reproduce the experimental data, which indicate that the energy of the first optical transition gradually diminishes as the cyano group gets located closer to the chain end. In other words, the measured transition energy is found to decrease along the sequences **T4/T3/T2** and **T7/T6/T5**. This discrepancy is again corrected when

involving the torsion aspects in our calculations (see Table 3 to be compared with the  $\lambda_{\max}$  values reported in Table 4). As a matter of fact, the use of the simple model described in the previous section allows us to reproduce the experimental evolution of the lowest transition energy. This is shown in Figure 5, where a very good agreement is obtained between the experimental and theoretical values. It is also of interest to note that the calculated oscillator strength associated with the lowest optical transition (see Table 3) nicely correlates with the measured molar extinction coefficients (reported in Table 4).

## 5. Conclusion

As in the case of poly(paraphenylenevinylene), the effect of substituting cyano groups on bithiophene and terthiophene is to stabilize (lower) both the HOMO and LUMO levels. Theoretical calculations, taking explicit consideration of the torsion angles between thiophene units, are fully consistent with oxidation potential data: The HOMO level is found to have a larger stabilization when the number of substituents is increased and when the substituent moves toward the center of the molecule. Despite the fact that the quantitative agreement is less satisfactory for the LUMO level vs reduction potential data, both theory and experiment indicate that the stabilization of the LUMO level is stronger for the monosubstituted terthiophenes when the cyano group is at the terminal position. Although a similar behavior is expected for the disubstituted compounds on the basis of the calculations, this is not the case experimentally, since the reduction potential is observed to be nearly independent of the substitution pattern. A crucial point for electron-transporting materials is the position of the LUMO level; this discrepancy requires further studies in order to determine the most favorable position of the substituents. Finally, it is found that the evolution of the calculated lowest optical transitions compares well to the experimental data ( $\lambda_{\max}$ ).

Because of the low melting point of bi- and terthiophene, the realization of practical devices, on which the n-type character of the oligomer could be actually checked, relies on the synthesis of longer substituted oligothiophenes. A first step toward this goal has already been achieved with the electrochemical synthesis of small amounts of substituted sexithiophenes.<sup>25</sup> Note that the  $1B_u$  excited state of this compound is expected to lie at a lower energy than the  $2A_g$  state when electron-acceptor groups are attached to the conjugated backbone and when high torsion angles are observed between adjacent thiophene rings (the  $2A_g$  state is then strongly destabilized because of the more pronounced quinoid character of its wave function).<sup>26</sup>

## 6. Experimental Section

Oligothiophenes **B3** and **B4**, substituted at the terminal position by one and two cyano groups, respectively, were synthesized via direct functionalization of terthiophene through the addition of chlorosulfonyl isocyanate in dichloromethane, followed by solvolysis in dimethylformamide.<sup>27</sup> The general procedure for cyanothiophenes **T2**, **T3**, **T4**, and **T5** involves the coupling between the halogeno derivatives of thiophene or bithiophene and the organozinc derivative of 3-cyanothiophene (compounds **T2**, **T3**, and **T4**) or 3,4-dicyanothiophene (compound **T5**) in presence of a catalytic amount of  $Pd^0(dppp)$ .<sup>28</sup> All products were purified by column chromatography.

Absorption spectra were recorded with a CARY 2415 (Varian) spectrophotometer. All spectra were corrected for the solvent absorption and the concentration adjusted in order to get a maximum optical density of 0.5. Emission and excitation

spectra were obtained with a SLM Aminco spectrofluorometer. The concentration of the solution was adjusted to a maximum optical density of 0.05. The quantum yields are measured in toluene, with the unsubstituted terthiophene as reference. The efficiency of the latter (0.065) has been previously measured at Thiais<sup>29</sup> and elsewhere.<sup>30,31</sup>

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