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Functionalized Oligothiophenes for Optoelectronic Applications: 3′,4′,3‴,4‴-Tetra [(methoxycarbonyl)methyl]-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquithiophene and Related Polymers

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We present the optical properties and LED performance of single-layer devices of a tetra-ester of α-quinquithiophene (**TET5**) and of two related polymers (**PTET5** and **PDET3**) and discuss them in connection with the crystal structure features of this oligomer. The solution photoluminescence quantum yield (PLQY) of **TET5** is smaller than that of the corresponding unsubstituted oligomer, while its value in the solid state is appreciable. Molecular packing, consisting of a sequence of molecular stacks linked by relatively strong polar hydrogen-bond-like interactions, favors PL quenching and hence accounts for the limited quantum efficiency of LED devices built by a single-layer film displaying substantial order ($\eta_{\mathrm{ext}} \geq 5 \cdot 10^{-3}\%$). Films of the corresponding **PTET5** polymer are amorphous, morphologically homogeneous, and behave differently, with LED devices showing over 500 cd/m^2 at 15 V. The probable reason for the difference between **TET5** and **PTET5** is to be found in molecular aggregation and orientation with respect to the substrate, implying that PLQY in this class of materials is substantially influenced by self-assembly. This is confirmed by the poor efficiency of the **PDET3** polymer, the films of which are substantially more ordered than those of **PTET5**.

Introduction

The ability to synthesize a variety of functionalized conjugated oligomers and polymers based on thiophene residues, particularly those carrying heteroatoms in the side chains, has greatly advanced in recent years. We have also witnessed significant progress in our understanding of the correlation between solid-state aggregation and optoelectronic properties in molecular crystals and macromolecules.[1,2] Fine-tuning of the material properties has been shown to be crucial for the development and optimization of optoelectronic devices such as electroluminescent diodes (LED), field effect transistors (FET), optical waveguides, etc.[1,2] In fact, the performance of a particular compound is strongly dependent on its molecular organization in the actual device prototype.[3−5] For example, proper working of an LED demands a balance between molecular separation, avoiding PL quenching, and a good charge transfer, i.e., appreciable mobility favoring exciton recombination.[3] In this respect, relevant results have been recently reported concerning oligomeric or polymeric thiophene derivatives.[6−10] The preparation of thiophene−fluorene and of other copolymers has significantly widened the choice of materials, allowing better tuning of the usable window.[11−13] Another important and stimulating advance is the development of devices exploiting phosphorescence, which maximizes the quantum yield, both in polymers[3] and in transition metal complexes.[14]

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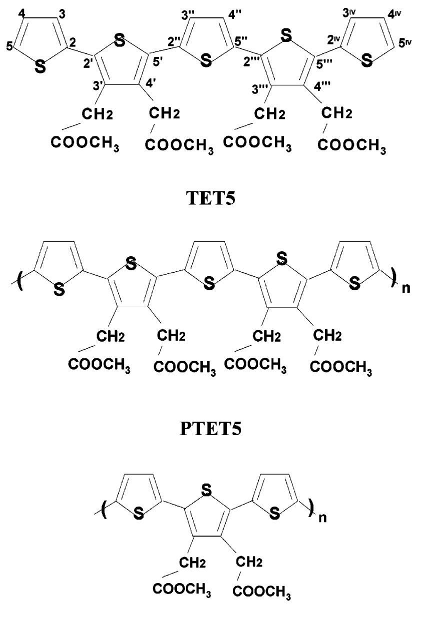
Scheme 1



TET5

PTET5

PDET3

With the improvement of our general understanding of these materials, we have also witnessed the emergence of a more rational approach to material design, whereby appropriate substitution patterns are proposed as a function of the desired properties. The introduction of carboxylate side-chains has contributed to expanding the variety of applications that can be envisaged for oligo- and polythiophenes, with the additional bonus of permitting the modification of important features of the substitution pattern even after the preparation of the oligomers and polymer.[15] Examples of applications for this new class of derivatives are LED fabrication with thiophene−esters polymers[16,17] and near-infrared emitters based on Er-salts of oligothiophene carboxylic acids.[18]

With the aim to prepare lanthanide complexes based on thiophenic polymers, we have considered 3′,4′,3‴,4‴-tetra[(methoxycarbonyl)methyl]-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquithiophene, sketched in Scheme 1 and labeled henceforth as **TET5**. Its lateral substitution involves (a) some hindrance leading to separation of adjacent molecules and (b) sufficient polarity to produce strong and specific intermolecular interactions. In a recent paper, interesting LED devices were obtained using a related polymer obtained by electropolymerization of a terthienylderivative (**PDET3** in Scheme 1).[17] However, due to the scarce degree of order attained, no clear indication on the role of ester derivatives in LED functioning could be evinced.

The aim of the present investigation is to clarify this role using **TET5** and the corresponding polymer (**PTET5**) obtained by electrosynthesis from **TET5**. Optical characterization is carried out and correlated to information resulting from the crystal structure analysis of **TET5**. Key electrical properties of LED prototypes based on both **TET5** and **PTET5** are also reported.

Experimental Section

TET5 was prepared according to ref 19, and crystals suitable for XRD analysis were crystallized from ethanol. The corresponding macromolecule **PTET5** was obtained by electrochemical polymerization under the conditions detailed below.

Experiments were performed at room temperature under nitrogen in three-electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm indium−tin-oxide (ITO) sheet (ca 20 ohm/square resistance, from Balzers, Liechtenstein) was used.

The molecular weights of **PTET5** were determined by gel permeation analysis (GPC) relative to polystyrene standards and by matrix-assisted laser desorption ionization (MALDI) mass spectroscopy. The measurements were carried out using a Waters GPCV 2000 SEC System apparatus equipped with a 410 differential-refractometer on-line detector and Waters Styragel columns at room temperature using THF as eluent. MALDI mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as matrix.

Monodimensional ^1H and bidimensional heteronuclear spectra of both oligomer and polymers have been acquired employing a 939 T Bruker DRX spectrometer equipped with a z gradient reverse probe. Gradient enhanced heteronuclear experiments (HSQC and HMBC) have been performed by acquiring a bidimensional matrix consisting of 256 × 2048 points with a window of 27 000 and 6000 Hz, respectively, for ^{13}C and ^1H nuclei. A repetition time of 5 s and 128 scans for each experiment have been used.

Optical transmission measurements for both solutions and films were performed with a Lamba 900 Perkin-Elmer spectrometer. CW photoluminescence spectra were recorded using a SPEX 270M monochromator equipped with a N_2 cooled CCD detector, by exciting with a monochromated Xe lamp. Solution PLQY measurementss were performed using a quinine sulfate solution (10^{-4} M sulfuric acid) as reference and exciting at 350 nm ($\Phi = 54.6\%$). Solid-state PLQY were carried out using an integrating sphere exciting the sample with a He−Cd laser ($\lambda = 325$ nm).

XRD experiments were carried out on both powders and films of the materials at room temperature using a computer-controlled Siemens D-500 diffractometer equipped with Soller slits and a graphite-monochromator, in Bragg−Brentano geometry. Transmission spectra of polymer powders were also recorded using a Bruker P4 diffractometer and a Hi-Star 2D detector.

Single-Crystal Data of TET5. $C_{32}H_{28}O_8S_5$, $M_w = 700.84$, monoclinic, space group $C2/c$, $a = 34.980(5)$ Å, $b = 11.332(1)$ Å, $c = 35.075(6)$ Å, $\beta = 115.483(9)°$, $V = 12551(2)$, $Z = 16$, $D_c = 1.584$ Mg m^{-3}, $\mu = 3.847$ mm^{-1}. A total of 10 727 reflections (9035 unique, $R_{int} = 0.088$) were collected on a Bruker P4 diffractometer. The structure was solved by direct methods using the SIR97 program and refined by full-matrix least squares using SHELXL97.

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Table 1. Attribution of Both ^{1}H and ^{13}C NMR Spectra of TET5

proton	OCH_3	CH_2	H_4	$H_{3''}$	H_3	H_5
ppm	3.73 3.74	3.79 3.82	7.10 dd	7.21 s	7.23 d	7.34 d

carbon	CH_2	OCH_3	C_4	C_3''	C_3	C_5	$C_3';C_4'$	C_5'	C_2'	C_2	C_2''	C=O
ppm	33.8 33.9	52.2 52.3	126.7	127.4	127.76	127.81	131.5	132.9	133.8	134.7	135.8	170.9 171.0

The final values of R1 and wR2 were 0.126 and 0.298, respectively, for the 5442 reflection with $I > 2\sigma(I)$ and 0.172 and 0.348 for all data.

Ab initio calculations were performed with the Gaussian 03 program, revision B.04.[20] Molecular geometries of the tetra-ester of the thiophene trimer (**TET3**, analogous to **TET5** but with the two outer rings replaced by hydrogens for computational convenience) were optimized with no symmetry restrictions at the B3LYP/6-31G** level. The effect of the surrounding environment was included in an average way by a conductor-like polarizable continuum model (C-PCM or COSMO),[21] with the relative dielectric constant of the surrounding medium set to $\epsilon_r = 5$ (a typical value for several organic esters).[22]

Spin-coated films suitable for LED device tests were prepared by using a P6700 PI-KEM apparatus in air. Indium–tin-oxide (ITO) glasses were etched and subsequently ultrasonically cleaned in H_2O for 15 min, in $CHCl_3$ for 15 min, and in methanol for 15 min. LED devices were prepared by spin-coating PEDOT-PSS and the polymer successively onto an ITO-coated glass substrate. In LED fabrication the average thickness of the PEDOT-PSS layer was approximately 90 nm, obtained by spinning at 500 rpm, while the emitting polymer monolayer was spun at 2000 rpm from a $CHCl_3$ solution of 8 $mg\cdot cm^{-3}$, giving a film with an absorbance of 0.3. Al or Ca/Al (30/100 nm) electrodes were thermally evaporated in a vacuum ($\cong 10^{-7}$ mBar) onto films. Current–voltage (I–V) characteristics were measured using a HP voltameter 6634B and a HP multimeter 34401A. Light emitted from displays was measured by a photodiode Centronic OSD100-7 and a picoamperometer. The I–L–V measurements were carried out under nitrogen at room temperature.

Synthesis of Bulk PTET5 Polymer. A suspension of 37 mg of **TET5** in 25 mL of acetonitrile + 0.1 M $NaClO_4$ was electrolyzed at 0.9 V with the passage of 2.5 F mol^{-1}. The obtained black suspension was reduced with hydrazine to a red precipitate which was filtered, washed with water, and dried. The polymer was then extracted with chloroform and dried (ca 31 mg, 84% yield).

^{1}H NMR (deuterated tetrachloroethane, δ ppm) 7.48–6.98 aromatic region containing inner, 7.28–7.21, and end molecular units, 3.82 (s,8H, CH_2), 3.75 (s,12H, $O-CH_3$). ^{13}C NMR (deuterated tetrachloethane, δ ppm): 170.8 (C=O), 137.6, 135.5, 133.7, 133.1, 132.9, 131.7, 128.0, 127.8, 124.7, 52.4, 33.7. Elemental analysis. Calcd for ($C_{32}H_{26}O_8S_5$): C, 55.00; H, 3.75; S, 22.94. Found: C, 54.79; H, 3.85; S, 22.75.

Results and Discussions

Molecular Characterization. To completely assign resonances of polymer **PTET5**, ^{1}H ^{13}C NMR HMBC and HSQC spectra on monomer **TET5** have been carried out. The chemical shift values of proton and carbon atoms of **TET5** are reported in Table 1 following the labeling of Scheme 1 and considering its molecular symmetry. Two distinct aromatic regions, i.e., from 126 to 128 ppm and from 131 to 136 ppm in the monomer carbon spectrum, are recognized; the former is related to tertiary carbons, while the latter is related to quaternary ones. The same fingerprint is observed in the ^{13}C spectrum of **PTET5**, in particular the signal due to the C5 aromatic carbon has been shifted from the former to the latter region, while in the side-chain carbon region a single resonance is observed for each carbon. A total of twelve peaks have been evidenced.

Resolution enhancement functions applied on the ^{1}H spectrum of **PTET5** revealed the presence of main-chain resonances, centered at 7.2 ppm, and of a chain end signal, $4/4^{IV}$ at 7.1 ppm and $5/5^{\ IV}$ at 7.35–7.4 ppm, respectively. The integral ratio between these signals indicates a ratio of ~1:10 for main-chain end proton signals. These results match well with SEC analysis findings, i.e., $M_w < 19\,000$, M_w/M_n 2.05, corresponding to ~12 units. In contrast, MALDI mass spectroscopy of the polymer shows a wide distribution from the dimer up to the dodecamer, centered on tetramer. However, for polymers displaying polydispersity >1.4, it has been recently shown that MALDI techniques may severely underestimate molecular weights.[23]

Single-Crystal Structural Characterization. A view of just one of the two molecules forming the asymmetric unit in the crystal structure of **TET5** is presented in Figure 1, with the atomic labeling used in the discussion. Figure 2 provides an overall view of the unit cell. Bond lengths and angles are all in the expected ranges and do not warrant a detailed discussion. Selected main- and side-chain torsion angles are given in Table 2. As apparent from these data, the conformation of the second molecule is very similar to the one shown in Figure 1. Four of the five thiophene rings in each molecule are nearly anti-coplanar, with the inter-ring torsion angles alternating between values close to +5°

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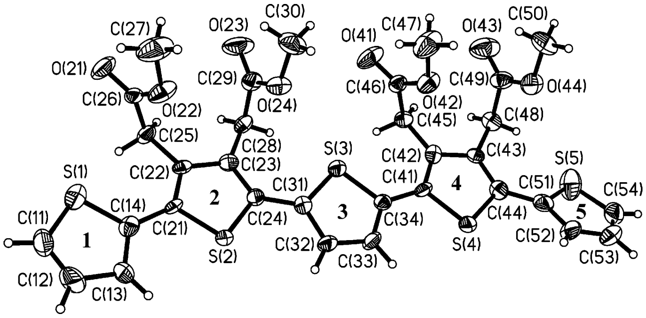

Figure 1. View of a molecule of **TET5** with the numbering scheme used in the text.

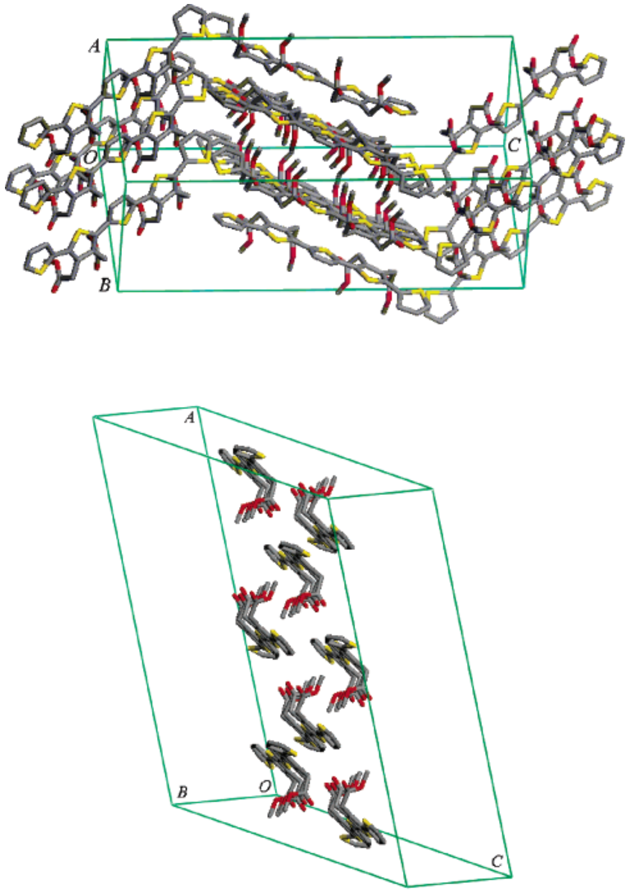

Figure 2. Two views of the crystal packing of **TET5**. In the first view, two layers of very nearly parallel molecules that develop in the c direction are evidenced. The second view shows one of the two layers with the quinquithiophene molecular planes roughly perpendicular to the paper.

and −5°. The angles π_{45} between the planes of the fourth and last thiophene ring measures 24.5(4)° and 31.5(5)° in the two molecules. These values are significantly different, as the two molecules are only approximately related by a noncrystallographic center of symmetry. The substantial deviation from main-chain coplanarity at these terminal rings and the arrangement of the side chains imply that neither molecule allows for a 2-fold symmetry axis through the central sulfur atom S(3).

The side-chain conformations appear to play a major role in determining the complex crystal architecture of **TET5**. To a first approximation, the side-chains are arranged in planes roughly perpendicular to the quinquithiophene backbone, approaching a symmetry involving a mirror plane running through S(3) and perpendicular to the molecular plane. Consistently with conformational energy calculations (see below), the absolute values of the torsion angles on carbon−carbon bonds adjacent to the rings, namely φ_2, φ_{2*}, φ_4, and φ_{4*}, are all close to 90° (see Table 2). The signs of these angles alternate, however, between positive and negative values. As apparent in Figure 2B, this implies an arrangement of all four side-chains on the same side with respect to the main chain, quite probably as a result of packing energy optimization. For all side-chains the carboxymethyl group shows very modest deviations from planarity with the terminal methyl group practically eclipsed with the carbonyl oxygen (see Figure 2). The values of the angles χ show that the methoxyl oxygen is also not too far from eclipsed to the ring carbon atom from which the side-chain originates (see Table 2). More in detail, the angles χ alternate between values rather close to 0° and with the same sign of the corresponding φ angle, and nearly gauche and with opposite sign of the neighboring φ angle.

According to our ab initio calculations, there is one minimum-energy conformation of the **TET3** trimer which resembles the one observed in the **TET5** crystal (see the “Theory” column in Table 2, and the picture in the Supporting Information). The main-chain torsions are in a distorted trans conformation, in disagreeement with the mostly planar conformation of the crystal, which must be evidently the result of packing forces. Interestingly, however, the calculated torsion angles roughly agree with those of the distorted terminal ring (π_{45} in Table 2). The side-chain torsion angles are mostly within 15° degrees from the experimental ones. The molecular conformation is not symmetric, although this would be allowed in principle (i.e., the point group is C_1, instead of C_s). This also agrees with the experimental structure, at a qualitative level. The explanation is that, by breaking symmetry, the molecule effectively minimizes repulsion between the C═O dipoles. Repulsion is only partially compensated or “screened” by interaction with the external dielectric medium. In fact, we have also found a lower-energy minimum (by 2.2 kcal/mol, with the present set of parameters for the dielectric), which is characterized by antiparallel alignment of adjacent C═O groups (see picture in the Supporting Information). Presumably, the “correct” crystal-like conformation is further stabilized by more specific intermolecular interactions, which are not accounted for by the continuum dielectric model. Indeed, an important feature of the molecular packing shown in Figure 2 is the antiparallel arrangement of the carbonyls belonging to facing molecules.

As anticipated, the arrangement of **TET5** in the crystal appears to be largely determined by packing interactions, which evidence significant segregation of the rigid, scarcely polar oligothiophene component from the more flexible and polar side chains. Stacking planes are roughly 100 with the stacking direction corresponding to [010] (see Figure 2). The *a* and *c* lattice directions, which are in essence metrically identical, are thus very different with respect to packing. As already mentioned side-chains of neighboring stacks of **TET5** organize efficiently with a number of short, attractive intermolecular interactions occurring essentially between the carbonyl oxygen and different, favorably located hydrogens

Table 2. Conformational Features of the Two Independent Molecules (A and B) of TET5 in the Crystal

angles between ring (least−squares planes)	symbol	molecule A (deg)	molecule B (deg)	theory[a]
ring 1−ring 2	π_{12}	6.2 (6)	6.0 (5)	
ring 2−ring 3	π_{23}	5.6 (5)	4.9 (5)	41
ring 3−ring 4	π_{34}	4.9 (5)	4.1 (5)	30
ring 4−ring 5	π_{45}	24.0 (4)	31.4 (4)	
selected torsion angles				
C(13)−C(14)−C(21)−C(22)		173.5 (8)	−175.9 (7)	
C(23)−C(24)−C(31)−C(32)		−174.4 (8)	173.9 (8)	137.0
C(33)−C(34)−C(41)−C(42)		175.2 (8)	−175.9 (7)	−150.6
C(43)−C(44)−C(51)−C(52)		150.5 (9)	−146.1 (10)	
C(21)−C(22)−C(25)−C(26)	φ_2	88.3 (9)	−88.4 (9)	−103.8
C(22)−C(25)−C(26)−O(22)	χ_2	8.3 (10)	−8.3 (10)	−32.9
C(24)−C(23)−C(28)−C(29)	φ_{2^*}	−99.5 (9)	98.8 (9)	99.9
C(23)−C(28)−C(29)−O(24)	χ_{2^*}	49.2(10)	−50.9 (10)	−46.8
C(41)−C(42)−C(45)−C(46)	φ_4	82.1 (10)	−80.7 (10)	−92.2
C(42)−C(45)−C(46)−O(42)	χ_4	15.6 (10)	−15.1(10)	−0.9
C(44)−C(43)−C(48)−C(49)	φ_{4^*}	−104.5 (9)	109.4 (9)	104.5
C(43)−C(48)−C(49)−O(44)	χ_{4^*}	58.8 (10)	−63.4(10)	−76.5

[a] Quantum-chemical optimized values of the **TET3** molecule.

(see the Supporting Information). Molecular planes tilted by about 20° with respect to each other can be identified also in the [001] direction, corresponding roughly to the axial molecular direction. Short, plausibly attractive S···S and S···O intermolecular interactions[24] can be found between the S(5) of the first independent molecule and the S(1) and O(21) atom of the second. Note that the reverse does not occur, pointing out once more the difference between the two independent molecules, despite the remarkable conformational similarities between them.

The crystals of **TET5** adopt a lamellar morphology with the [001] direction coinciding with the lamellar normal, while the lateral sides are more difficult to identify with acceptable confidence due to substantial irregularities. These observations and the analysis of the packing suggest that the quinquithiophene systems tend to stand on the substrate in a tilted arrangement reminiscent of other crystalline oligothiophenes. Bulk and thin film diffraction patterns are discussed below.

Diffraction from Powders and Thin Films. Diffraction spectra on thin films (100−300 nm thick) of **TET5** (Figure 3 trace A) onto polar substrates indicate the presence, along with some disordered regions, of crystalline areas with an orientation along the [001] direction (i.e., c^*), consistent with the lamellar habit found in the single crystals. This is independent of the precise nature of the polar substrate (silica, ITO, etc.) and of the deposition techniques, i.e., cast or spin-coating. In fact, both the 002 and 004 peaks, which are expected to be relatively strong on the basis of the crystal structure analysis, are detectable in the spectrum (Figure 3, trace A). Note that the 200 and the 400 reflections, which would occur at the same 2θ value as the 002 and 004 reflections, have calculated intensities which are practically 0 in the former case and quite weak in the second.

Films of **PTET5**, either cast or spin-coated, exhibit very limited, at most nematic order. This is evidenced by the two broad observed peaks, with the sharper one at $2\theta = 10.2°$ corresponding to a $d = 8.7$ Å (Figure 3, trace B). Similar considerations apply to powders of **PTET5** (Figure 3, trace C), although in this instance the lower angle peak presents a weak but sharp feature at $2\theta \approx 11°$, suggesting the presence of some more ordered domains. On the other hand, powders of **PDET3** (Figure 3, trace D) show clear indications of crystallinity, implying higher degrees of 3D order as compared to powders of **PTET5**, suggesting a higher charge mobility for the former. It is furthermore plausible that the solid-state organization of **PDET3** will present stacking interactions involving the thiophene backbone and some aggregation of the polar side chains, reminiscent of features discussed for **TET5**.

With respect to molecular orientation, there is no experimental evidence suggesting the very unlikely arrangement of polymer molecules of either **PDET3** or **PTET5** "head on" on the substrate, as found for **TET5** and quite often for thiophene oligomers. On the other hand we note that, while it is possible and efficient to organize the side chains on the same side of the molecule in the case of **TET5**, such an arrangement cannot be achieved with an anti-main chain conformation in the case of both **PDET3** and **PTET5**. These differences are likely to promote remarkable differences in the solid-state aggregation patterns in the three cases.

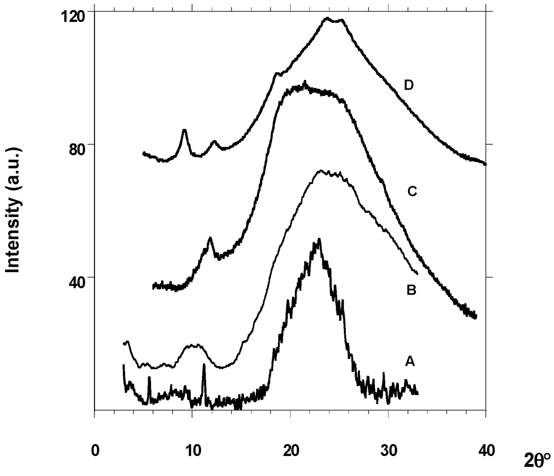

Figure 3. XRD patterns of spin-coated films of **TET5** (A) and of **PTET5** (B) on silica (the diffraction of which corresponds to the broad peak around 20°), and of powders of **PTET5** (C) and **PDET3** (D).

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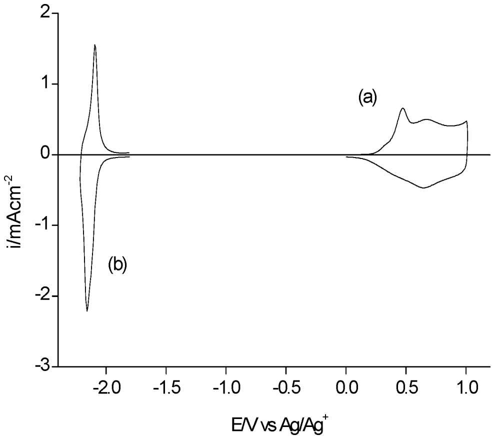

Figure 4. Cyclic voltammogram of **PTET5** in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 Vs^{-1}. Reversible oxidation charge: 2.5 mC cm^{-2}.

Furthermore, the axial periodicity of **PTET5** is 10 thiophene units or about 37.8 Å, as opposed to 6 units and ca. 22.7 Å for **PDET3**. Considering rigidity, polydispersity, features of intermolecular interactions etc., the ability to crystallize displayed by **PDET3** is unexpected.

Electrochemical Characterization. The cyclic voltammogram (CV) of **TET5** in acetonitrile + 0.1 M Bu_4NClO_4 shows an irreversible oxidation process at $E_0 \approx 0.8$ V, while a reversible reduction process occurs at $E_0 \approx -2.5$ V. Potential cycling beyond this oxidation process produces a fast build-up of polymer. From the above data an IP and EA of 5.44 and 2.19 eV, respectively, were derived by adding 4.4 to E_0s.[25]

The **PTET5** film shows a twin reversible oxidation process at $E° = 0.30$ and 0.65 V (Figure 4a) and a reversible reduction process at $E° = -2.2$ V (see Figure 4b). Onsets are 0.2 V for oxidation and −2.0 V for reduction, hence an electrochemical onset-based gap of 2.2 eV is calculated. Moreover IP and EA values of 4.89 and 2.69 eV, respectively, are derived. From the difference of oxidation and reduction E° values (2.68 V) the optical gap of the polymer is calculated as 460 nm. The spectrum of the neutral polymer, performed directly onto the film at the electrode, shows a maximum at 450 nm, close to the expected value, and an onset at 600 nm, i.e., 2.05 eV, to be compared with 2.2 eV.

The polymer is soluble in chloroform and in THF where it displays a solvatochromic shift to 410 and 420 nm, respectively; this effect has be to attributed to esteric group presence. Polymer films are electrochromic with the usual change from orange (neutral) to blue (oxidized). In situ conductivity measurement gives an approximate value of 10^{-3} S cm^{-1} for the p-doped polymer.

Exhaustive electrolysis at 0.8 V (see below) requires ca. 3 F mol^{-1} with production of a black suspension which becomes immediately bright red upon reduction with hydrazine.

Table 3. Features of the Electronic Absorption and Emission Spectra (λ_{max}, in nm)

	THF solution		film	
	absorption	emission	absorption	emission
TET5	365	495	377	510
T5[a]	419	520	420	517
PTET5	420	550	448	600

[a] From ref 13.

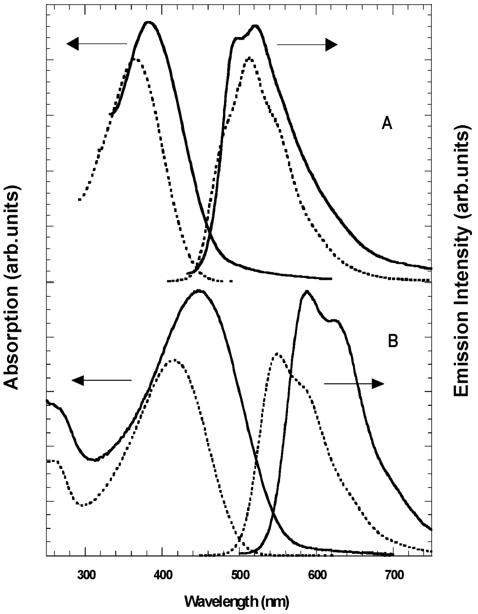

Figure 5. Electronic absorption and emission spectra of **TET5** (a) and **PTET5** (b) in THF solution (dotted line) and in spin-coated film (solid line).

Optical Characterization. All the relevant optical features of the studied materials are reported in Table 3. The electronic absorption and emission spectra of **TET5** are given in Figure 5, both in THF solution and as solid films. Comparison with the unsubstituted **T5** molecule[26] reveals a larger Stokes shift for **TET5**, due to larger deviation of thiophene rings from the mean molecular plane, possibly related to solvent−molecule interactions in solution and side-chain perturbed stacking interactions in the films. In fact, the relatively planar conformation in the crystal of **TET5** plausibly arises essentially to stacking interactions, see above. In contrast, the PL spectra of the two molecules can be almost superimposed, indicating a similar degree of planarity achievable by both the compounds in the excited states.

PLQY values in THF solution ($<10^{-5}$ M) are 35% and 39% for **TET5** and **T5** molecules, respectively. This weak difference can be accounted for by the quite feeble electron-donor effect, i.e., hole-injection availability of carboxymethyl groups, already detected in **PDET3** prepared by electrosynthesis from the trimer.[17] Conversely, in the solid state the commonly observed value for **T5** films [27] is lower than the one measured for **TET5**, which is close to 5%. This is attributed to the different crystal packing; in fact, the former displays the typical herringbone arrangement, while the latter adopts a stacked layer organization where adjacent stacks are separated by side-chain layers (Figure 2). Although spin-coated films of **TET5** are not fully crystalline, the basic local features of the molecular organization appear to correspond

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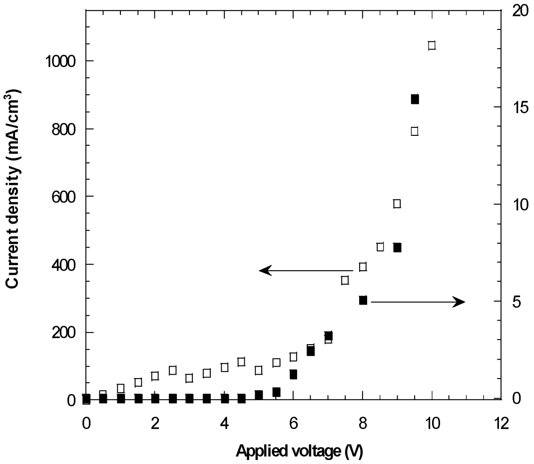

Figure 6. I−L−V curves of an ITO/PEDOT/**TET5**/Ca/Al device.

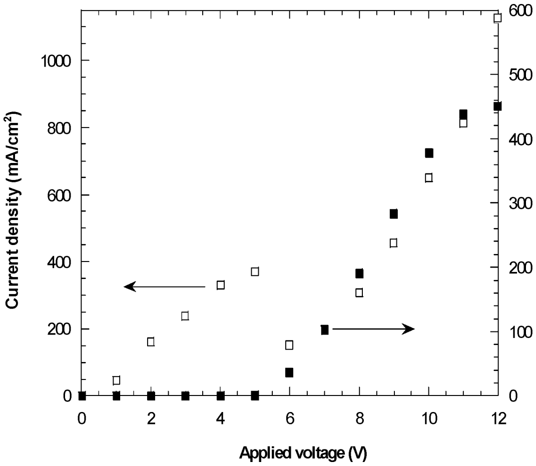

Figure 7. I−L−V curves of an ITO/PEDOT/**PTET5**/Ca/Al device.

to the crystalline organization. PL quenching should thus be more favored in **T5** rather than **TET5** suggesting for the latter the use as active layer in LED devices.

The absorption and emission spectra of **PTET5** in THF solution and as spin-coated films are also given in Figure 5 and Table 3. The comparison with profiles pertaining to **TET5** films reveals that the average conjugation length is larger in the macromolecule, in fact a red-shift of about 70 nm in absorption and of 80 nm in PL spectra, are detected. **PDET3** film displays a quite similar conjugation length,[17] resulting from a similar persistence length despite a lower M_w.

The energy-gap value derived from electrochemical characterization is higher than the one obtained from optical investigations, see above, as already observed in polymeric systems. This difference has been attributed to interface barrier to charge injections.[28]

Electrical Characterization. ITO/PEDOT/**TET5**/Ca/Al devices were built up and the I−L−V curves are reported in Figure 6; the onset, both in light and in current regimes, is ∼5 V, indicating a good carrier balance. The I−L−V curve of corresponding device with **PTET5** as active layer is shown in Figure 7.

Moreover, the examination of the energy levels of the constituents, shown in the inset of Figure 8, showing the photo and electroluminescence of **TET5**, suggests an appropriate situation to charge injection both for holes at the ITO side, and for electrons at the Ca side. The external quantum efficiency (η_{ext}) of the devices is, however, rather poor, 0.005%.

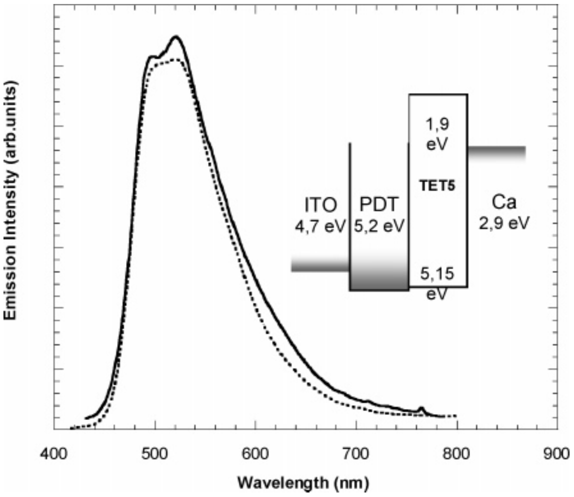

Figure 8. Photoluminescence (solid line) and electro-luminescence spectra (dotted line) of **TET5**; in the inset, the energy levels of the constituents are shown.

Crystallization of spin-coated films favors the carrier mobility, but the limited quantum efficiency of PL results in a low η_{ext}, i.e., about 20 cd/m^2 at 10 V. The EL spectrum is in good agreement with the related PL spectrum, indicating that the EL originates from the electronically excited single state of the molecule. No voltage dependence of EL spectrum is observed. The CIE 1931 coordinates are (0,267;0,491); the color remains stable during the device lifetime.

To evaluate the behavior of **TET5** as FET material, preliminary electrical measurements onto spin-coated films were performed yielding insufficient mobility values. The presence of some amorphous regions and the inhomogeneous morphology of the films are responsible for the scarce charge mobility. Substantial improvement could be envisaged if ordered films could be prepared, e.g., from high-vacuum evaporation.

PTET5 gave more promising results as active layers in LED prototypes, in fact a single active layer device with a Ca/Al cathode gave an external quantum efficiency about an order magnitude larger than that in the case of **TET5** (0.05%). This can be readily accounted for by comparing electronic levels of the two systems (insets of Figures 8 and 9), and also the onsets, 5 V and less than 2 V for **TET5** and **PTET5,** respectively. This observation is clearly related to the fact that the spin-coated polymer is poorly ordered, possibly with a nematic structure, see above, hence preventing efficient orbital overlap among adjacent macromolecules. The maximum luminance is detected as 506 cd/m^2 at 15 V with CIE 1931 coordinates of (0.543; 0.445). In terms of efficiency, the best result (>0.13%) is obtained by using the ITO/PEDOT:PSS/**PTET5**/LiF/Al architecture.

It has been shown that the LiF layer enhances the performance of OLED based on both polyarylene and polyphenylenevinylene derivatives,[29,30] while a significant improvement with respect to Ca/Al cathode, in the case of

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(28) Lim, E.; Jung, B.; Shim, H. *Macromolecules* **2003**, *36*, 4288.

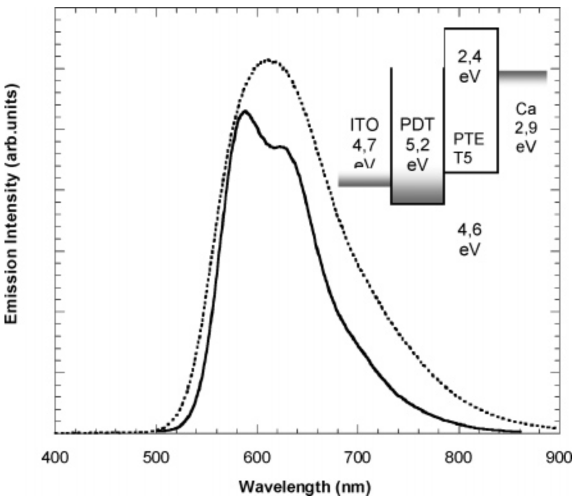

Figure 9. Photoluminescence (solid line) and electro-luminescence spectra (dotted line) of **PTET5**; in the inset, the energy levels of the constituents are shown.

poly(thiophene-*co*-fluorene)s was observed by Leclerc et al.[31] Without entering in the debate on LiF-layer action in LEDs, we would like to note that Ca can react with esteric groups, while LiF is inert.

LED prototypes based on **PDET3**[17] exhibit an order of magnitude lower efficiency (i.e., comparable to that based on **TET5**) despite quite similar onset values (∼2 V). Various factors should be taken into account to understand such a difference. The ratio of the esteric functions *per* thiophene ring in the two polymers (4:5 for **PTET5** and 2:3 for **PDET3**) has a negligible effect on the electronic levels. Differences in the IP and EA are within 0.1 eV, a value which cannot account for the observed performances. Also, the morphology of the two films is comparable at micrometer scale, hence the contacts with the electrodes and interfacial features are likely to be similar. GPC results indicate a larger M_w for the former (∼55 versus ∼21 thiophene rings for **PTET5** and **PDET3,** respectively), while a polydispersity close to 2 was observed for both **PTET5** and **PDET3**.[17] These values can hardly explain the different performance levels in OLED devices. In this view, solid-state organization can probably be singled out as the most important factor. While **PTET5** reveals at most nematic order, **PDET3** shows some crystallinity and a higher degree of 3D order. A significant difference between the two polymers consists of the syndiotactic versus disyndiotactic enchainments for **PDET3** and **PTET5**, respectively, allowing for a easier aggregation for the former. Indeed, we have already mentioned that the solid-state aggregation of **PDET3** is likely resemble that of **TET5**, implying a reduction of radiative recombinations as compared to **PTET5**.

All in all the comparison reveals that, despite some ordered aggregation of **TET5** and **PDET3** in thin films which plausibly enhances the charge mobility, **PTET5** shows better properties in terms of PLQY and LED performance because the augmented chain separation and overall disorder reduce the PL quenching resulting from interactions between adjacent molecules facing each other with parallel molecular axes.[32] The above observations indicate that the insertion of side chains containing esteric functions onto thiophenic backbones can favor the emission, especially when the chain separation is effective.

Conclusions

The structural and optical properties related to the electrical performance in LED prototypes of the ester-substituted quinquithiophene **TET5** and of the electro-synthesized polymers **PTET5** and **PDET3** have been studied and compared. In principle, the insertion of esteric functions in the oligomer and in **PDET3** has two effects, namely to promote (i) molecular separation, which can prevent non-radiative recombination, and (ii) strong polar interactions, i.e., aggregate formation, inducing emission quenching, despite the amorphous component present in the films. The second effect appears to be prominent in the present case. The peculiar backbone enchainment found in **PTET5** allows relatively modest degrees of order and, more significantly, it does not allow periodic, strong, short-range interactions among adjacent chains. Efficiency values of single-layer-based LEDs of **PTET5** are among the highest of substituted thiophene based molecules,[8,14,15,33] presumably due to these features. The possibility to use **PTET5** to form Er complexes appears a plausible attractive development as the emission window of such compounds would be shifted to the near-infrared region, as recently found in a related ter-thiophene salt.[18]

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Supporting Information Available: Table of short intermolecular contacts; tables of crystal parameters, atomic positions, and crystallographic data; ^{1}H NMR spectrum of PTET5; MALDI mass spectroscopy spectrum of **PTET5**; view of minimum-energy ab initio conformations of the tetra-substituted thiophene trimer (**TET3**); view of the two independent molecules of **TET5**; spectroelectrochemistry figure of **PTET5**; I−L−V curves of LED devices of both **TET5** and **PTET5**, with the insertion of thin LiF films, and of **PTET5** device with different thickness (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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