Growth and Characterization of Sexithiophene Single Crystals

Gilles Horowitz,* Bernard Bachet,† Abderrahim Yassar, Philippe Lang,
Frédéric Demanze, Jean-Louis Fave,‡ and Francis Garnier

Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry-Dunant, 94320 Thiais, France

Received January 11, 1995. Revised Manuscript Received April 12, 1995®

Single crystals of unsubstituted sexithiophene (6T) were produced by a sublimation technique. X-ray structure shows that the molecule has a quasi-planar all-trans configuration, the torsional angles between adjacent rings being lower than their respective standard deviation. The unit cell belongs to space group $P2_1/n$ and presents the herringbone packing common to a great deal of planar molecules. Owing to the well-defined orientation of the molecules in single crystals, the polarization of vibration modes and coupling due to crystal-field effects could be unambiguously determined from polarized light IR spectroscopy. Raman spectra of the single crystals are also presented and compared to that of polycrystalline evaporated films.

Introduction

Fifty years have passed since the first thiophene oligomers (*n*T, where *n* stands for the number of thiophene rings) have been synthetized.[1,2] Later works showed that terthiophene (3T) is a natural insecticide,[3] acting through a phototoxic mechanism.[4] More recently, oligothiophenes have been used in electronic devices, such as field-effect transistors (FETs)[5–7] and light-emitting diodes (LEDs).[8–10] It is worth pointing out that FETs made of sexithiophene (6T) derivatives present to date the highest reported field-effect mobility for organic-based devices.[5c,d,7b] Studies of the physical and chemical properties of *n*Ts are generally carried out either in solution or on polycrystalline thin films that can be obtained by spin coating (when the compound is soluble) or vacuum evaporation. For a complete characterization of oligothiophenes in the solid state, single crystals are of course highly desirable. As such crystals are generally grown from solutions, they have been up to now limited to short oligomers, up to the unsubstituted terthiophene,[11] although single crystals of sexithiophene substituted by solubilizing groups, namely pendent alkyl chains[12] and silyl derivatives at end position,[12,13] have been described recently.

We report here on the growth of 6T single crystals by the sublimation technique described by Lipsett.[14] Single crystals were obtained as plates a few tens of micrometers thick, that could be some millimeters long. They were characterized by X ray diffraction (XRD) and IR and Raman spectroscopy.

Experimental Section

Sexithiophene was synthesized according to the method of Kagan and Aora,[15] where the commercially available terthiophene is lithiated and oxidatively coupled with copper chloride as a catalyst.

The apparatus used to produce sublimation crystals consists of a 30 cm long 5 cm Pyrex tubing, closed at one end, and fitted at the other to a top assembly through a ground cone. This top assembly is equipped with a vacuum stopcock, which is used to pump out the vessel. In operation, we place in the tube a collecting assembly, which consists of a glass rod equipped with a collecting cup and a centering system. The tubing is placed into a vertical tube furnace (Thermolyne, type 21100), its elevation being adjusted so that the collecting cup is about 1 cm above the top of the furnace. The temperature of the furnace was monitored with a chromel–alumel (K-type) thermocouple and a Digi-Sense (Cole-Parmer) temperature controller. The crystal growth is conducted under a reduced pressure of a few millibars of argon and at a temperature ranging between 220 and 240 °C. This temperature is

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[†] Laboratoire de Minéralogie et Cristallographie, CNRS, Universités Paris 6 Pierre et Marie Curie et Paris 7 Denis Diderot, 75252 Paris Cedex 05, France.

[‡] Groupe de Physique des Solides, Universités Paris 6 Pierre et Marie Curie et Paris 7 Denis Diderot, 75251 Paris Cedex 05, France.

® Abstract published in *Advance ACS Abstracts,* June 1, 1995.

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Table 1. Crystal Data and Structural Results of Sexithiophene

	Crystal Data
formula	$C_{24}H_{14}S_6$
formula wt (g mol^{-1})	494.76
crystal system	monoclinic
space group	$P2_1/n$ (14)
Z	4
a (Å)	44.708 (6)
b (Å)	7.851 (3)
c (Å)	6.029 (2)
α (deg)	90.0
β (deg)	90.76 (2)
γ (deg)	90.0
vol (Å^3)	2116.5
μ (Cu Kα) (mm^{-1})	5.97
density calc (g cm^{-3})	1.553
crystal size (mm^3)	0.4 × 0.2 × 0.02
crystal color	orange
crystal shape	flat plate
F(000)	1016.0
temp (K)	292
	Data Collection
2θ limit (deg)	128
range of h, k, l	$-51 \rightarrow +52$; $0 \rightarrow +9$, $0 \rightarrow +6$
total no. of reflns	3342
independent reflns ($I > 3\sigma(I)$)	2142
	Structure and Refinement
weighting scheme	Tukey and Prince, $w = w'[1 - (\Delta F/6\sigma F)^2]^2$
no. of parameters	273
S	1.103
R	0.054
weighted R	0.066
absorption correction method (DIFABS)	empirical, $T_{min} = 0.8537$, $T_{max} = 1.0956$

Table 2. Fractional Atomic Coordinates, with Estimated Standard Deviation in Parentheses, and Equivalent Isotropic Displacement Parameter U_{eq} (Å^2) ($U_{eq} = {}^1/_3\Sigma_{ij}U_{ij}a^*_ia^*_ja_ia_j$)

atom	x/a	y/b	z/c	U_{eq}
S(5)	0.04369(2)	0.1311(1)	0.4705(2)	0.0522
S(10)	0.13886(2)	0.0005(1)	0.4724(1)	0.0409
S(15)	0.20301(2)	0.1350(1)	0.9986(1)	0.0402
S(20)	0.29814(2)	0.0015(1)	1.0061(1)	0.0408
S(25)	0.36226(2)	0.1337(1)	1.5342(1)	0.0409
S(30)	0.45691(2)	−0.0079(1)	1.5400(2)	0.0523
C(1)	0.02754(8)	0.0503(5)	0.2346(7)	0.0538
C(2)	0.04728(9)	−0.0324(4)	0.1080(7)	0.0515
C(3)	0.07643(7)	−0.0326(4)	0.1994(6)	0.0432
C(4)	0.07842(7)	0.0516(4)	0.4015(5)	0.0370
C(6)	0.10404(6)	0.0797(4)	0.5437(5)	0.0347
C(7)	0.10575(7)	0.1616(4)	0.7431(5)	0.0403
C(8)	0.13459(7)	0.1628(4)	0.8386(5)	0.0393
C(9)	0.15529(7)	0.0812(3)	0.7130(5)	0.0341
C(11)	0.18675(7)	0.0550(4)	0.7582(5)	0.0345
C(12)	0.20760(7)	−0.0272(4)	0.6328(5)	0.0382
C(13)	0.23633(7)	−0.0275(4)	0.7283(6)	0.0390
C(14)	0.23783(7)	0.0548(3)	0.9303(5)	0.0342
C(16)	0.26341(6)	0.0821(3)	1.0746(5)	0.0339
C(17)	0.26489(7)	0.1648(4)	1.2740(6)	0.0392
C(18)	0.29352(7)	0.1659(4)	1.3722(5)	0.0385
C(19)	0.31440(7)	0.0822(4)	1.2467(5)	0.0353
C(21)	0.34574(7)	0.0551(4)	1.2929(5)	0.0360
C(22)	0.36652(8)	−0.0281(4)	1.1680(6)	0.0406
C(23)	0.39537(7)	−0.0300(4)	1.2631(5)	0.0402
C(24)	0.39694(7)	0.0514(4)	1.4652(5)	0.0376
C(26)	0.42271(7)	0.0767(4)	1.6074(5)	0.0354
C(27)	0.42469(7)	0.1635(4)	1.8103(5)	0.0408
C(28)	0.45404(8)	0.1574(4)	1.9009(6)	0.0496
C(29)	0.47353(8)	0.0708(5)	1.7755(6)	0.0530

maintained for several days, during which crystals form as thin plates on the rim of the collecting cup and on the central rod. The sublimation is stopped by lifting the system off the furnace and letting it cool down. The crystals can then be collected directly from the central rod.

The crystallographic data was collected at 19 °C on a Philips PW 1100 diffractometer, using Cu Kα (λ = 1.541 80 Å) radiation. The structure was solved using SHELXS86[16] and refined with CRYSTALS.[17] Data were weighted according to the scheme by Tukey and Prince. Absorption was corrected by DIFABS.[18] Other experimental details are summarized in Table 1.

IR spectra were recorded with a Brucker IFS 48 FTIR spectrometer equipped with a Specac wire grid polarizer.

The Raman spectra set up includes an excitation in the blue by an argon ion laser and in the NIR by an ion-pumped Titane-Sapphire tunable laser, a Ramanor Jobin-Yvon U1000 monochromator, and a GaAs photocathode photomultiplier. Samples were held at 12 K in a closed-cycle helium cryostat (Air Product) equipped with two quartz windows.

Results and Discussion

X-ray Diffraction. A crystal structure of 6T has already been reported by Porzio and co-workers by using the Rietvield analysis on polycrystalline samples.[19] However, the diffractometer gave us straight away a nearly shoe box cell, which was more convenient for further graphical manipulations. Moreover, we found the space group to be $P2_1/n$ rather than the $P2_1/a$ group reported by our Italian colleagues. The crystal data are gathered in Table 1. As the molecule is centrosymmetric, we tried to find out a noncrystallographic center of symmetry. We indeed found it at 0.25, 0.0674, 1.003 (fractional coordinates), which corresponds to the pseudosymmetry operator $0.50 - X$, $0.13 - Y$, $2.01 - Z$. This operator is based only on the symmetry of the molecule and not on that of the cell. Even in the case where the cell was of higher symmetry (e.g., orthorombic), there is no group with a crystallographic operator at $0.13 - Y$.

Table 2 gives the fractional coordinates of nonhydrogen atoms, and Figure 1 the molecular structure and numbering scheme of 6T. The unit cell, shown in Figure 2, presents the herringbone packing common to most planar molecules. The molecular long axis is at an angle of 23.5° with the a axis, and the molecule is practically planar, the dihedral angles between adjacent rings being lower than their estimated standard deviations (esd's). We note that these esd's mainly come from a small deviation from planarity of the rings themselves. Our crystal structure can be compared to that obtained by Porzio and co-workers[19] (Table 3). The cell parameters b and c are quite identical, and the difference in a and β is merely due to the choice of the setting. We note that they correspond to nearly identical interlayer spacing $a \sin \beta$ (44.82 and 44.71 Å for polycrystalline film and single crystal, respectively). However, the planarity of the molecule is much more pronounced in the single crystal. We also note that the molecule of 6T single crystal is more planar than that of 3T single crystal (the longest unsubstituted nT single crystal reported to date), in which the dihedral torsion angles vary between 6 and 9°.[11] A similar trend has been observed on p-phenylene oligomers: the torsion angles

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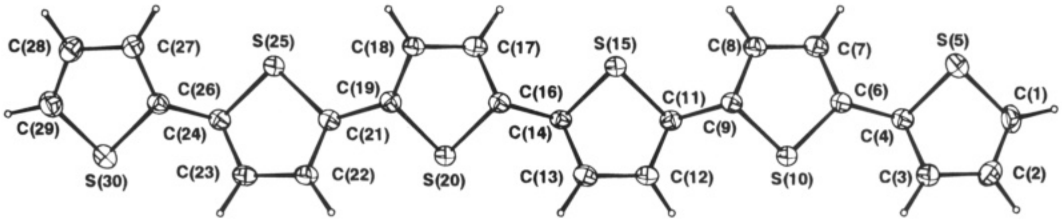

Figure 1. Molecular structure and numbering of sexithiophene (6T).

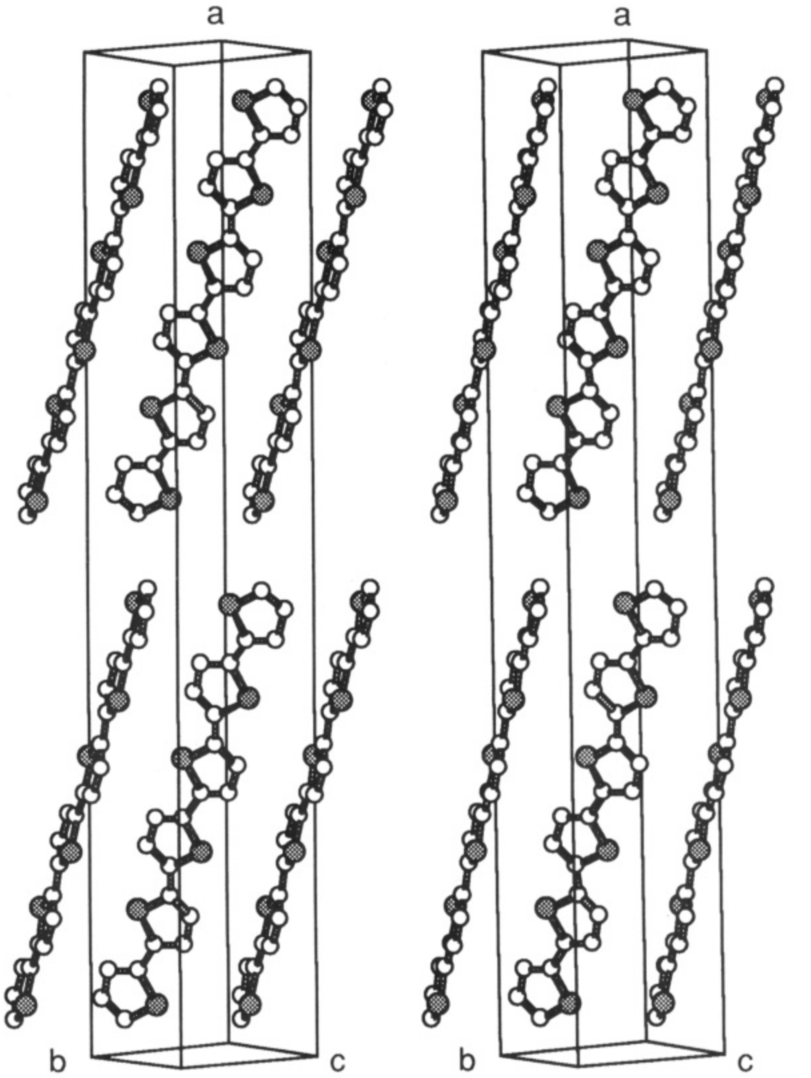

Figure 2. Stereographic view of the sexithiophene unit cell.

in *p*-sexiphenyl crystals have been reported to range between 3.3 and 3.6°.[20]

Table 4 gives the bond distances and angles. It is worth noting that all the six thiophene rings have practically identical geometry, except for the two external C=C double bonds which are shorter than all the others (1.32 and 1.37 Å, respectively). This is also true, though to a smaller extent, for the two external S−C bonds (1.71 against 1.73 Å). We note that in both cases, the differences are significantly higher than the esd's. Figure 3 compares the bond lengths and angles of the four central thiophene rings of 6T with those of the middle ring of terthiophene (3T), as reported in ref 11. The agreement between the two sets of data is remarkable and leads us to conclude that the geometry of the inner thiophene rings is not affected by the oligothiophene length.

The distances between atoms of nearest molecules are all longer than the sum of the van der Walls radii; for molecules in the same layer, the shortest C−C, C−S, and S−S distances are 3.67, 3.91, and 4.18 Å, respectively. The distance between the centers of nearest-neighbor molecules is 4.95 Å. The shortest C−C distance between nearest molecules in adjacent layers is 3.82 Å. It is worth noting that, owing to their tilt angle with the *a* axis, these molecules are nearly coplanar.

We have determined that the flat surface of the 6T single crystals corresponds to a *bc* plane. Since the unique axis *b* is also an optical axis, the crystals are easily oriented relative to this axis by observing their extinction under a crossed-polarized microscope.

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Table 3. Comparison of Structural Parameters of 6T Polycrystalline Films (Porzio et al.,[19]) and Single Crystals (This Work)

	ref 19	this work
τ^a (deg)	67	66
μ^a (deg)	−9	0.1 (15)
	12	0.0 (8)
	−4	−0.3 (11)
	5	0.3 (5)
	−3	−1.2 (13)
ϕ^a (deg)	30	23.5
$D_c{}^a$ (g/cm^3)	1.54	1.55
a (Å)	45.38	44.71
b (Å)	7.86	7.85
c (Å)	6.03	6.03
β (deg)	99.0	90.8
space group	$P2_1/a$	$P2_1/n$

[a] τ, herringbone angle; μ, torsion dihadral angle between adjacent thiophene rings; ϕ, tilt angle of the long molecular axis L with a; D_c, calculated density.

Table 4. Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviation in Parentheses

S(5)−C(1)	1.709(4)	C(8)−C(9)	1.364(4)
S(5)−C(4)	1.730(3)	C(9)−C(11)	1.444(4)
S(10)−C(6)	1.736(3)	C(11)−C(12)	1.370(4)
S(10)−C(9)	1.738(3)	C(12)−C(13)	1.400(5)
S(15)−C(11)	1.731(3)	C(13)−C(14)	1.380(4)
S(15)−C(14)	1.734(3)	C(14)−C(16)	1.444(4)
S(20)−C(16)	1.732(3)	C(16)−C(17)	1.367(4)
S(20)−C(19)	1.734(3)	C(17)−C(18)	1.403(5)
S(25)−C(21)	1.736(3)	C(18)−C(19)	1.376(4)
S(25)−C(24)	1.735(3)	C(19)−C(21)	1.441(4)
S(30)−C(26)	1.721(3)	C(21)−C(22)	1.370(5)
S(30)−C(29)	1.710(4)	C(22)−C(23)	1.405(5)
C(1)−C(2)	1.342(6)	C(23)−C(24)	1.377(4)
C(2)−C(3)	1.408(5)	C(24)−C(26)	1.441(4)
C(3)−C(4)	1.388(5)	C(26)−C(27)	1.402(4)
C(4)−C(6)	1.439(4)	C(27)−C(28)	1.416(5)
C(6)−C(7)	1.365(4)	C(28)−C(29)	1.346(5)
C(7)−C(8)	1.405(5)		
C(1)−S(5)−C(4)	92.1(2)	S(15)−C(14)−C(13)	110.3(2)
C(6)−S(10)−C(9)	91.9(1)	S(15)−C(14)−C(16)	120.6(2)
C(11)−S(15)−C(14)	92.2(1)	C(13)−C(14)−C(16)	129.1(3)
C(16)−S(20)−C(19)	92.0(1)	S(20)−C(16)−C(14)	120.5(2)
C(21)−S(25)−C(24)	92.2(2)	S(20)−C(16)−C(17)	110.5(2)
C(26)−S(30)−C(29)	92.4(2)	C(14)−C(16)−C(17)	129.0(3)
S(5)−C(1)−C(2)	112.3(3)	C(16)−C(17)−C(18)	114.0(3)
C(1)−C(2)−C(3)	112.9(3)	C(17)−C(18)−C(19)	112.7(3)
C(2)−C(3)−C(4)	113.1(3)	S(20)−C(19)−C(18)	110.8(2)
S(5)−C(4)−C(3)	109.6(2)	S(20)−C(19)−C(21)	120.2(2)
S(5)−C(4)−C(6)	120.8(2)	C(18)−C(19)−C(21)	129.0(3)
C(3)−C(4)−C(6)	129.6(3)	S(25)−C(21)−C(19)	120.8(2)
S(10)−C(6)−C(4)	120.5(2)	S(25)−C(21)−C(22)	110.3(2)
S(10)−C(6)−C(7)	110.3(2)	C(19)−C(21)−C(22)	129.0(3)
C(4)−C(6)−C(7)	129.2(3)	C(21)−C(22)−C(23)	114.0(3)
C(6)−C(7)−C(8)	113.9(3)	C(22)−C(23)−C(24)	113.1(3)
C(7)−C(8)−C(9)	113.3(3)	S(25)−C(24)−C(23)	110.5(2)
S(10)−C(9)−C(8)	110.6(2)	S(25)−C(24)−C(26)	121.1(2)
S(10)−C(9)−C(11)	120.4(2)	C(23)−C(24)−C(26)	128.4(3)
C(8)−C(9)−C(11)	129.0(3)	S(30)−C(26)−C(24)	120.8(2)
S(15)−C(11)−C(9)	120.2(2)	S(30)−C(26)−C(27)	110.4(2)
S(15)−C(11)−C(12)	110.6(2)	C(24)−C(26)−C(27)	128.8(3)
C(9)−C(11)−C(12)	129.2(3)	C(26)−C(27)−C(28)	111.6(3)
C(11)−C(12)−C(13)	113.6(3)	C(27)−C(28)−C(29)	113.8(3)
C(12)−C(13)−C(14)	113.3(3)	S(30)−C(29)−C(28)	111.8(3)

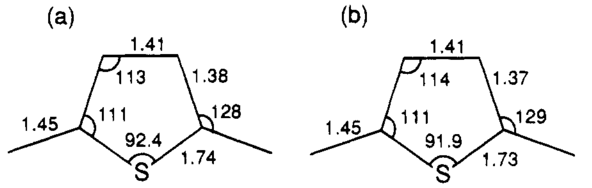

Figure 3. Bond lengths and angles of the central ring(s) of (a) terthiophene (3T) and (b) sexithiophene (6T). Data on 3T taken from ref 11.

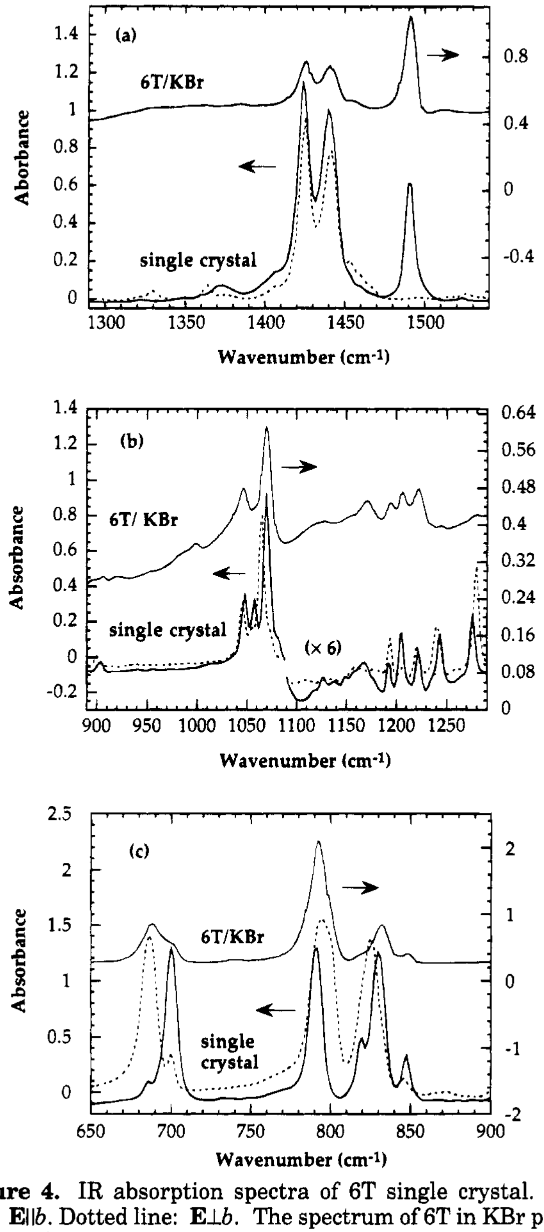

Figure 4. IR absorption spectra of 6T single crystal. Full line: **E**∥b. Dotted line: **E**⊥b. The spectrum of 6T in KBr pellet is given for comparison.

IR Spectroscopy. The vibration modes of the 6T molecule are polarized along one of its three axes, namely, the long axis L, the in-plane short axis M, and the axis perpendicular to the plane of the molecule N. To determine the polarization axis of the vibration modes of 6T and the effect of crystal field, we have carried out IR absorption measurements in two ways. First, the flat surface of the crystal was set perpendicular to the incident light, and spectra were recorded with light-polarized parallel and perpendicular to b (Figure 4). Second, the crystal was rotated around the b axis, and IR absorption measured under a light-polarized perpendicular to this axis. The L-polarized modes are characterized by the quenching of their absorption both under **E** ⊥ b polarized light at normal incidence, and when the crystal is rotated by an angle of about 50−55° around the b axis. This incidence angle corresponds to a refractive angle close to 24°, where, owing to the tilt angle of the molecules, **E** is perpendicular to L. According to previously reported assignments,[21−23] the bands at 1491 cm^{-1} (antisymmetric C=C stretching), 1372 cm^{-1} (intra-ring C$-$C stretching) and 1205 cm^{-1} (inter-ring C$-$C stretching) are L-polarized (Figure 4a). Similarly, the bands at 1440 and 1426 cm^{-1} (symmetric C=C stretching) and 1048 cm^{-1} (C$-$H bending) are *M*-polarized.

Some bands split into doublets, one component of which is polarized parallel to *b* and the other perpendicular to *b* (i.e., *c*-polarized, or polarized along an axis close to *c*). A large splitting is thus resolved for the bands assigned to the vibration of the terminal C$-$H bonds, at 686 (polarized $\parallel b$) and 698 cm^{-1} (polarized $\perp b$). It could come from a strong coupling between closest (and nearly coplanar) molecules in two adjacent layers. The inner C$-$H deformation mode is more complex. The band polarized $\parallel b$ (791 cm^{-1}) is very broad and hides the one at 795 cm^{-1} (polarized $\perp b$). A splitting is also observed for the C$-$S stretching mode at 825 (polarized $\parallel b$) and 830 cm^{-1} (polarized $\perp b$).[21,23] When the crystal is rotated, the behavior of the bands located at 791 and 795 cm^{-1} is different from that of the bands at 686 and 698 cm^{-1} and 825 and 830 cm^{-1}, as already reported in ref 22. By comparing their behavior to that of the bands at 1426 and 1440 cm^{-1}, which are *M*-polarized, we can conclude that the band at 790 cm^{-1} is *N*-polarized, whereas those at 690 and 830 cm^{-1} are *M*-polarized. Such an assignment agrees with ref 23, but not with ref 22.

Raman Spectroscopy. The Raman spectrum in the C=C stretching mode region is shown in Figure 5. For the single crystal, the choice of an excitation in the near-IR, largely beyond the absorption threshold, allows us to observe Raman emission in preresonance conditions, without any excitation of the photoluminescence; the sharp lines (1460, 1473 and 1506 cm^{-1}, fwhm $\approx$ 3.5 cm^{-1}) can be safely expected to be typical of the bulk. For the polycrystalline thin film, the excitation is in the blue, approximately in the middle of the singlet exciton absorption band, and the Raman spectrum was recorded below the onset of photoluminescence. At such high excitation, however, it is difficult to exclude an additional resonant contribution of distorted molecules at grain boundaries, and this can account for the larger width of the lines (1460, 1473 and 1501 cm^{-1}, fwhm $\approx$ 17 cm^{-1}).

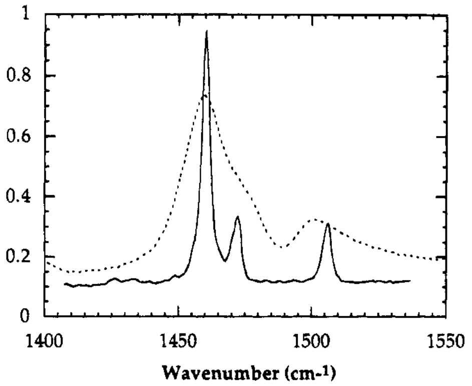

Figure 5. Raman spectra of 6T polycrystalline film (dotted line, λ_{exc} = 488.07 nm) and single crystal (full line, λ_{exc} = 701.24 nm).

Conclusions

By a sublimation technique, we have produced sexithiophene single crystals in the shape of flat plates a few hundredths of a millimeter thick, the lateral dimensions of which can reach a few millimeters. The structure of these crystals is close to that already resolved from polycrystalline films, except for the fact that the molecules in single crystals are strongly planar, the torsion angles between adjacent rings being less than 1°. As expected, IR spectra of the single crystals are much more resolved than those of polycrystalline films or powders. Moreover, Raman spectra could be obtained in the nonresonant mode, which resulted in an enhancement of the resolution. Previous determinations of the polarization of IR modes have been unambiguously confirmed. Moreover, crystal field effects on the terminal C$-$H deformation mode has been evidenced. Further works on the UV$-$visible and fluorescence properties of 6T single crystals are presently under way.

Acknowledgment. Our thanks to Dr. Habib Bouchriha (Faculté des Sciences de Tunis, Tunisia) for his help in the Raman spectroscopy measurements.

Supporting Information Available: List of anisotropic thermal parameters (1 page). Listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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