
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Extended Oligothiophenes : New Materials for Molecular Electronics

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Version of record first published: 04 Oct 2006.

To cite this article: Denis Fichou , Gilles Horowitz & Francis Garnier (1992): Extended Oligothiophenes : New Materials for Molecular Electronics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 193-196

To link to this article: http://dx.doi.org/10.1080/10587259208046899

*Mol. Cryst. Liq. Cryst.* 1992, Vol. 217, pp. 193–196
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Printed in the United States of America



# EXTENDED OLIGOTHIOPHENES : NEW MATERIALS FOR MOLECULAR ELECTRONICS

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Abstract - Thiophene oligomers with extended π-systems can be considered as linear polyenes. They are stable and processible low molecular solids with electronic properties close to those of polythiophene. We report in this paper on the optical properties of vacuum evaporated oligothiophene thin films and their use as molecular semiconductors in the fabrication of "all-organic" field-effect transistors.

## INTRODUCTION

Organic semiconductors are the key compounds of a number of molecular devices such as photovoltaic cells, light emitting diodes and field-effect transistors [1]. The high purity and crystallinity that can be achieved with low-molecular solids is counterbalanced by their modest π-π orbital overlap. This is the opposite situation in conjugated polymers whose expected transport properties are ruined by disorder and impurities. The design of new molecular semiconductors would then consist in realizing a compromise between traditional small organics on one side and an extended polymer-like π-system on the other side.

We have recently synthesized a series of alpha-conjugated thiophene oligomers α-nT (with n=3 to 10 repeat units) [2]. These low-molecular compounds are highly conjugated because of pure α-coupling between consecutive rings and a nearly planar structure in the

solid state [3]. The energy of the fundamental $\pi$-$\pi^*$ transition is essentially controlled by the chain length n and decreases with increasing n to level-off at approximately n=8. Thiophene oligomers can be considered as linear polyenes, with a mixed cis-trans conjugated system due to an anti-parallel chain conformation. We used them as model molecules towards a better understanding of doped polythiophene [4]. Furthermore, they are thermally stable and can be evaporated to form polycrystalline thin films with high optical and electrical quality. Their linear and nonlinear optical properties have been investigated, revealing well-resolved features usually met in molecular crystals [5]. Just as polythiophene, they behave as p-type semiconductors and form with metals either rectifying or ohmic junctions [6]. Finally, we built $\alpha$-nT based field-effect transistors and studied the influence of various parameters on the device performances [7,8].

## OPTICAL PROPERTIES OF $\alpha$-nT THIN FILMS

Thin solid films of $\alpha$-nT (thickness = 100-150 nm) are prepared by evaporation under reduced pressure ($5x10^{-3}$ Pa) of the powdered oligomers onto sapphire substrates.

At room temperature, the absorption spectra show two or three bands and a broad $\pi$-$\pi^*$ absorption in the visible range with characteristics side-peaks on the low-energy side. Lowering the temperature down to 14 K improve considerably the optical resolution of the $\pi$-$\pi^*$ bands of the spectrum which exhibits narrow peaks further split into hyperfine satellites (Figure 1). Peaks labelled A, B and C have a constant energy spacing $\Delta E$ of 0.192 eV for $\alpha$-6T. Similar spectra are obtained with the tetramer $\alpha$-4T and the octamer $\alpha$-8T, the energy spacing between successive side-bands being respectively 0.199 eV and 0.196 eV. It can also be observed that $\Delta E$ is independent on the chain length.

Additional hyperfine structures are observed at 14 K on band A of the $\pi$-$\pi^*$ transition of $\alpha$-6T (Figure 2). Band A appears extremely well-resolved and exhibits a symmetrical feature according to a central vertical axis. On each side of this axis stand four equally spaced absorption peaks with a $\Delta E$ spacing of 0.018 eV.

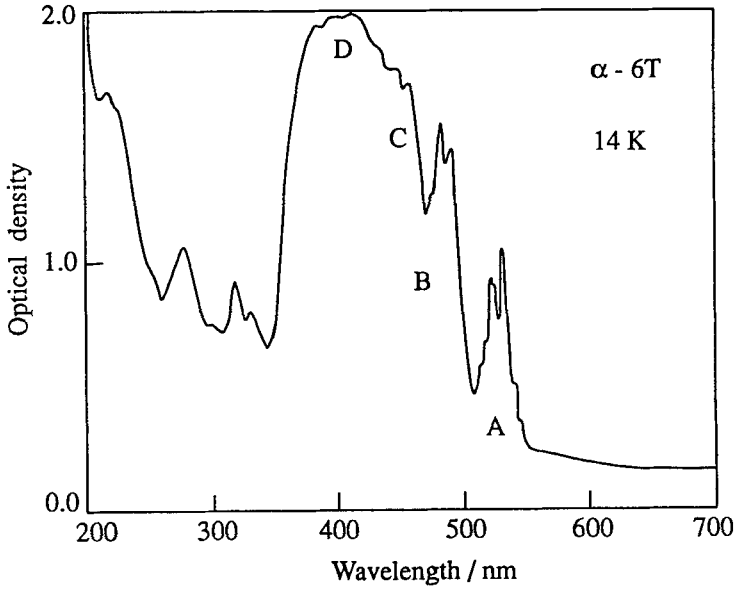


Figure 1 - Optical absorption spectrum of a α-6T evaporated thin film at 14K.

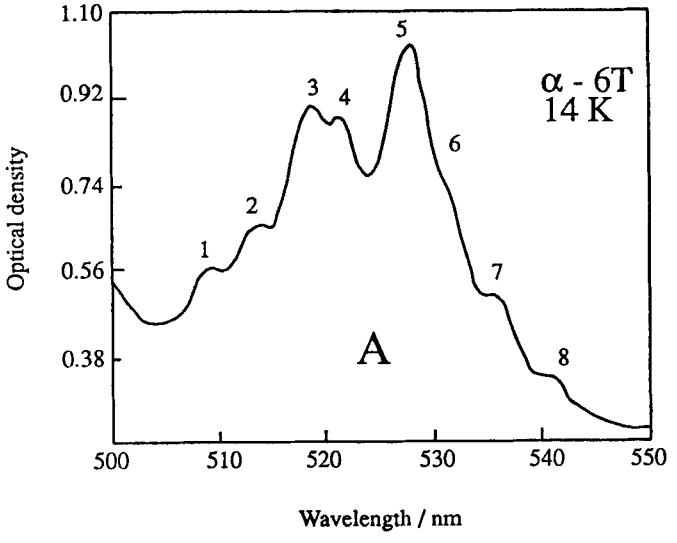


Figure 2 - Hyperfine absorption structure of band A of α-6T at 14 K.

These unusual optical features are observed for the very first time on thiophene derivatives in the solid state and are discussed in terms of couplings with the fundamental electronic transition.

## ALL-ORGANIC α-6T BASED FIELD-EFFECT TRANSISTORS

The good optical quality of these highly crystalline oligothiophene films appears as very promising towards efficient charge transport properties. We prepared field-effect transistors using α-6T as the semiconductor and various inorganic and organic insulators [7].

When an organic insulator with high dielectric constant such as cyanoethylpullulane (ε=18) is used, field-effect carrier mobilities as high as $\mu_{FE}=10^{-1}$ $cm^2$ $V^{-1}$ $s^{-1}$ are routinely obtained [8]. These relatively high values are in the range of those currently found with a-SiH in MISFETs and must be compared with the low mobilities of various polythiophenes or polyacetylene.

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