

## Conjugated Oligomers Combining Fluorene and Thiophene Units : Towards Supramolecular Electronics

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### Introduction

For the past two decades, conjugated oligomers and polymers have been a major topic of interest due to their outstanding optoelectronic properties, offering new opportunities in a number of technologies, such as light-emitting diodes (LEDs),<sup>[1]</sup> field-effect transistors (FETs),<sup>[2]</sup> photovoltaic diodes,<sup>[3]</sup> or sensory systems.<sup>[4]</sup> In particular, oligo- and poly-thiophenes and derivatives are of considerable interest, thanks to their charge transport properties that have directed their use as active layers in organic FETs. The performances of thiophene-based FET (threshold voltage, charge mobility and current on/off ratio) are dramatically influenced by the purity, the structural order and the morphology of the active layer, particularly within the first layers near the dielectric interface. In this context, the fine control of the organization of the conjugated molecules (and therefore the control of the intermolecular interactions), via molecular engineering (e.g., via end-substitution of oligothiophenes or control of regioregularity in poly(3-alkylthiophene)s) has produced FET performances approaching those of amorphous silicon. However, polythiophene compounds suffer from their high HOMO energy (-4.8 eV), a feature that leads to easy oxidation by environmental oxygen, which reduces the lifetime and efficiency of the devices.

One way to overcome this problem is to combine the thiophene moieties with other conjugated monomers with lower-lying HOMOs, such as phenylene, thiazole, or fluorene.<sup>[5]</sup> In particular, fluorene derivatives seem to be promising partners to thiophene derivatives, since polyfluorenes (PFs) are stable compounds and possess lower-lying HOMO energies (around -5.7 eV).<sup>[6]</sup> Indeed, various (un)soluble thiophene-fluorene co-oligomers were recently synthesized and tested, with outstanding FET characteristics (mobility and on/off ratio on the order of 0.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 10<sup>5</sup>, respectively).<sup>[7]</sup> Alternating polymers of fluorene derivatives and bithiophene were also tested as active layers in all-polymer transistor circuits prepared by ink-jet printing, where the liquid crystallinity of the compounds has allowed to orient the chains onto a rubbed substrate, giving rise to interesting circuit properties in combination with easy processing. Another major interest of combining fluorene and thiophene units is the fact that PFs possess high luminescence efficiency in the blue spectral region. Several groups have therefore copolymerized fluorene with thiophene oligomer derivatives to tune the band gap of the material, with the purpose of producing LEDs of distinct colors for full color-display applications. This combination has also been shown to improve the thermal stability, and is a step forward towards better device performances. Recently, we have shown that the molecular architecture of alternating copolymers of (indeno)fluorene and oligothiophene governs the chain self-assembling properties, which in turn strongly influences the transport properties in FETs.<sup>[8]</sup> In particular, comparing the microscopic morphology of thin copolymer deposits and the results of molecular simulations, we concluded that the major factor driving the chain assembly towards highly-regular semiconducting nanostructures is the efficiency of the "mixed" intermolecular interactions (*i.e.*, between fluorene and oligothiophene units). In this context, model oligomer compounds have been designed in order to gain further understanding on the importance of the

fluorene/thiophene interactions on the supramolecular assembly in the solid-state.

This paper reports on the synthesis, the relationship between the structural ordering and the microscopic morphology, and the optical properties of those co-oligomers, combining fluorene and thiophene units, used as models for the corresponding copolymers. The first compound is made of a terthiophene central unit, surrounded by octyl-substituted fluorene units (F-T3-F) while the second one is based on a fluorene trimer, end-capped by thiophene units (T-F3-T).

### Results and discussion

Using well-defined oligomers for alternating fluorene/thiophene copolymers allows for a detailed investigation of the relationship between the microscopic morphology, the optical properties, and the solid-state organization. The sequence of the fluorene and thiophene units along the backbone is the major factor controlling the optoelectronic properties of those systems: for T-F3-T, the  $\pi$ - $\pi$  interactions between molecules are probably weak, which precludes the formation of highly-ordered structures. As a consequence, an untextured microscopic morphology is observed. In strong contrast, the microscopic morphology of F-T3-F is made of extended strip-like 2D-crystals with long-range order, which can be related to the existence of  $\pi$ - $\pi$  interactions. For this compound, confocal microscopy also shows that the structural order leads to a polarized emission along the long axis of the strip-like structures, with red-shifted emission originating from well-defined aggregates. Since these structures show polarized emission along the long axis of the crystallites, their alignment would lead to the spatial control of the polarized emission. Along the same line, we have recently used the self-assembly of F-T3-F oligomers in combination with an original lithographic approach, in order to fabricate FET made of aligned, hundred of nm-wide stripes.<sup>[9]</sup> We have shown that this process leads to improved charge transport properties when relevant 1-D alignment of the stripes is achieved (perpendicularly to the electrodes), compared to uniform films. Therefore, F-T3-F appears as a promising, long-range ordered, soluble molecular material with anisotropic optoelectronic properties.

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