

Synthesis of a Thermally Stable Hybrid Acene-Thiophene Organic Semiconductor via a Soluble Precursor

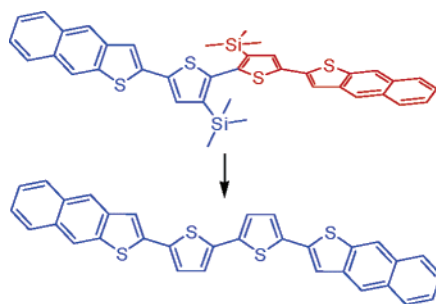
Yohann Nicolas,[†] Philippe Blanchard,^{*,†} Jean Roncali,[†] Magali Allain,[‡]
Nicolas Mercier,[‡] Anne-Laure Deman,[§] and Jacques Tardy[§]

Groupe Systèmes Conjugués Linéaires, CIMMA, UMR CNRS 6200, Université
d'Angers, 2 Bd Lavoisier, F-49045 Angers, France, and Ecole Centrale de Lyon,
LEOM, UMR CNRS 5512, 36 Av. Guy de Collongue, F-69134 Ecully Cedex, France

philippe.blanchard@univ-angers.fr

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ABSTRACT



An acene fused-thiophene hybrid *p*-semiconductor exhibiting high thermal stability has been synthesized via a soluble precursor bearing sterically interacting trimethylsilyl groups.

The synthesis of organic semiconductors has been extensively developed in recent years as a result of the opportunity to fabricate low-cost and/or large-area electronic components.¹ In this context, acenes^{1,2} and thiophene^{1,3} oligomers represent two of the most widely investigated classes of *p*-type organic semiconductors. Several examples of hybrid acene-thiophene conjugated systems have recently been reported in the literature.⁴ However, because of their strong π -stacking interactions, these conjugated systems are in general insoluble, which limits their purification to vacuum sublimation

methods. Owing to the major impact of impurity on the performance of electronic organic devices, the definition of synthetic methods allowing simple and straightforward purification of organic semiconductors appears as a key issue for future development of the field.

Several groups have already reported the preparation of soluble thermally or photochemically sensitive precursors allowing the direct formation of active films of pentacene or sexithiophene derivatives.^{5,6}

We report here the synthesis of a novel hybrid thiophene-acene molecule **1** consisting of a 2,2':5',2'':5'',2'''-quater-

[†] Groupe Systèmes Conjugués Linéaires, CIMMA.

[‡] CIMMA.

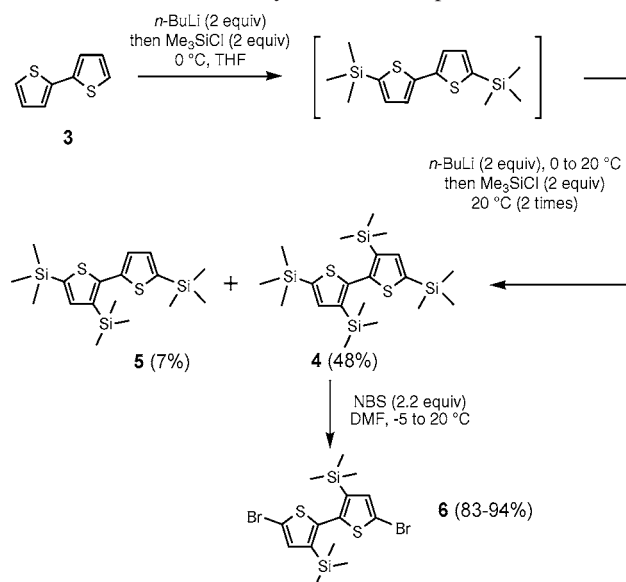
[§] Ecole Centrale de Lyon.

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Scheme 1. Synthesis of Compound 6

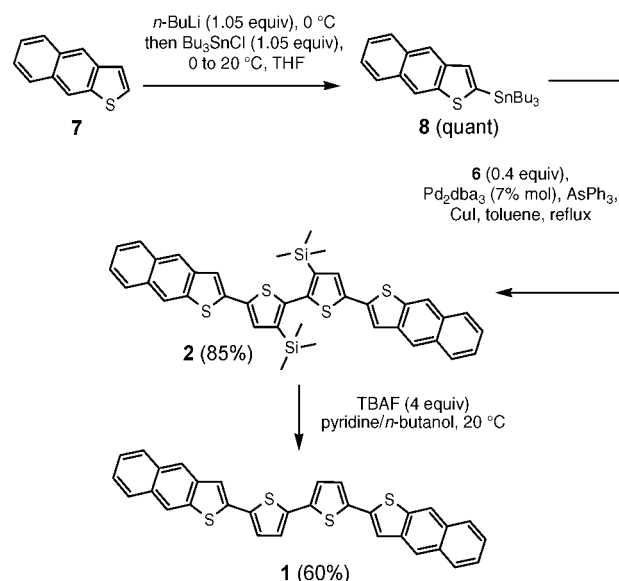


thiophene structure end-capped with fused-naphthalene groups and a first evaluation of its potentialities for the realization of field-effect transistor.

The practically insoluble compound **1** material has been prepared by elimination of the trimethylsilyl groups of a soluble precursor **2**, which can be easily purified by silica gel chromatography. This procedure avoids the use of organometallic catalyst for C–C coupling reactions in the last step of the synthesis, whose presence, even as traces, may alter the electronic properties of the organic semiconductor.^{3b,4a,7}

The synthesis of the target compound **1** is depicted in Schemes 1 and 2. Reaction of 2 equiv of *n*-BuLi with 2,2'-bithiophene **3** in THF at 0 °C followed by addition of 2 equiv of chlorotrimethylsilane led to the 5,5'-disilylated intermediate. The reaction mixture was further subjected to two sequences of successive treatments by *n*-BuLi (2 equiv) and chlorotrimethylsilane (2 equiv) at 20 °C. This one-pot

Scheme 2. Synthesis of Compound 1 via the Soluble Precursor 2



procedure afforded the tetrasilylated compound **4** in 48% yield together with 7% of compound **5** resulting from incomplete silylation.

Although ¹H and ¹³C NMR spectra were consistent with the symmetrical structure of compound **4**, the isomeric structure corresponding to the 4,4',5,5'-tetrakis(trimethylsilyl)-2,2'-bithiophene could not be completely ruled out for **4**. Therefore, single crystals, grown by slow evaporation of a solution of **4** in ethanol, have been analyzed by X-ray diffraction. The crystallographic structure of compound **4** (Figure 1) definitively confirms the expected structure and the regioselectivity of the silylation reaction at the 5,5' and 3,3' positions of bithiophene **3**.

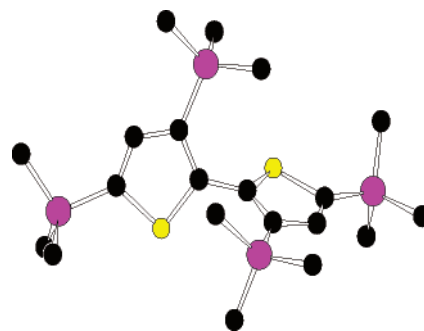


Figure 1. Crystallographic structure of **4** (molecule A).

As expected, steric interactions between the sulfur atoms and the trimethylsilyl groups generate a twisted locked structure with a large dihedral angle between the two thiophene rings. This result can explain the presence of two independent molecules **A** and **B** in the crystal structure

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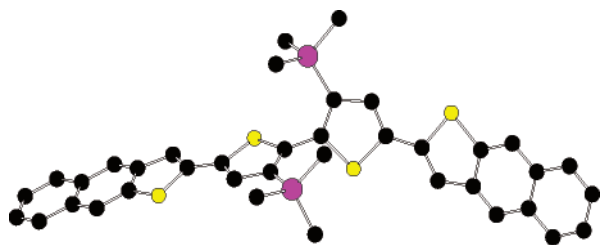


Figure 2. Crystallographic structure of **2**.

corresponding to two atropoisomers (see Supporting Information). Thus, molecules **A** and **B** show a highly distorted conformation associated with a S–C–C–S dihedral angle between the two thiophene rings of ca. 108° and 90°, respectively.

Compound **6**, namely, 3,3'-bis(trimethylsilyl)-5,5'-dibromo-2,2'-bithiophene, was prepared by a 2-fold regioselective bromodesilylation reaction with 2.2 equiv of NBS. The stannyl derivative **8** was obtained by regioselective deprotonation at the 2-position of naphtho[2,3-*b*]thiophene **7**⁸ using *n*-BuLi at 0 °C followed by quenching with Bu₃SnCl. An excess of **8** was then reacted with 1 equiv of dibromo compound **6** under the conditions of the Stille reaction in the presence of a catalytic amount of Pd₂dba₃ to give the key compound **2** in 85% yield (Scheme 2).⁹

Compound **2** shows a good solubility in dichloromethane and can thus be purified by chromatography on silica gel. Yellow plates were also obtained by slow diffusion of a chloroform solution of **2** into ethanol. As for **4**, the crystal structure of compound **2** shows a twisted conformation with a dihedral angle of 118° between the two halves of the molecule, each part adopting a practically planar geometry (Figure 2).

The target compound **1** was then obtained by elimination of the two trimethylsilyl groups of **2** using tetrabutylammonium fluoride in pyridine.

Figure 3 shows the UV–vis absorption spectra of compounds **1** and **2**. Because of the extremely low solubility of compound **1**, the spectrum has been recorded in *o*-dichlorobenzene, in which the compound was sparingly soluble. The spectrum of compound **2** shows an absorption maximum at 372 nm. This relatively blue-shifted λ_{max} agrees well with the restricted conjugation imposed by the twisted structure of the molecule. In contrast, the spectrum of compound **1** shows a maximum at 428 nm, which confirms that the planarization of the structure after elimination of the trimethylsilyl groups makes it possible to restore an extended effective conjugation. The presence of a long absorption tail in the long wavelength region suggests possible formation of aggregates, as might be expected from the low solubility

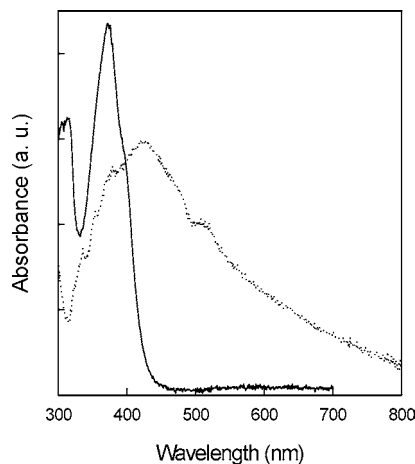


Figure 3. UV–vis spectra of molecules **1** in *o*-dichlorobenzene (dotted line) and **2** in dichloromethane (solid line).

of the molecule and the strong propensity of acenic compound to stack.

Compound **2** shows fluorescence emission properties with an emission maximum at 504 nm and a quantum yield of 15% (against anthracene as standard). The spectrum of a solution cast film shows an emission maximum at 512 nm. The persistence of luminescence properties in the solid state suggests poor intermolecular interactions due to the twisted conformation of the molecule. In contrast, compound **1** does not show any fluorescence properties in solution, a result consistent with the occurrence of strong π -stacking interactions already present in solution as suggested by the UV–vis spectrum.

The thermal stability of compound **1** has been investigated by thermogravimetric analysis under a nitrogen atmosphere at a heating rate of 10 °C/min. By comparison with 2,2':5',2'':5'',2''':5'''-quaterthiophene¹⁰ (**T₄**) used as reference compound, the fusion of two naphtho groups to the terminal thiophene rings of **T₄** leads to a considerable enhancement of the decomposition temperature (corresponding to 5% loss of weight) from 225 to 455 °C.

This result associated with the electronic properties of **1** and its planar conformation incites us to realize field-effect transistors using **1** as active semiconducting layer.

Organic field-effect transistors (OFETs) were processed by vacuum evaporation of compound **1** or **T₄** onto a bilayer of PMMA/Ta₂O₅ as dielectric.¹¹ The schematic diagram of the OFET and details of fabrication are described in Supporting Information. The drain current versus drain-source voltage characteristics of **1** show that the drain current increases with increasing negative gate voltage, indicating that the OFETs based on **1** or **T₄** function as *p*-type transistors. The field effect mobility μ was evaluated in the

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saturation regime. The measured mobility of **1** was $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a drain voltage of -12 V , whereas that of reference compound **T₄** was measured to be $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a drain voltage of -15 V . These results show that replacement of the two terminal thiophene rings of **T₄** by two naphtho[2,3-*b*]thiophene groups leads to a significant increase in mobility.

To summarize, a hybrid thiophene-acene conjugated system has been synthesized using a soluble precursor in which solubility originates from the presence of trimethylsilyl groups that induce a considerable distortion of the π -conjugated system and hence prevent π -stacking.

Consequently, the key precursor can be easily purified and the straightforward elimination of the trimethylsilyl groups led to the planarization of the π -conjugated system.

An OFET based on the target compound has been realized, and it has been shown that this compound associates promising hole mobility value with high thermal stability. Finally, our approach offers the possibility to envisage the synthesis of other *a priori* insoluble π -conjugated systems.

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Supporting Information Available: Synthetic procedures, structural characterization of all compounds, X-ray data for compounds **2** and **4** in CIF format, and details of fabrication of OFETs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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