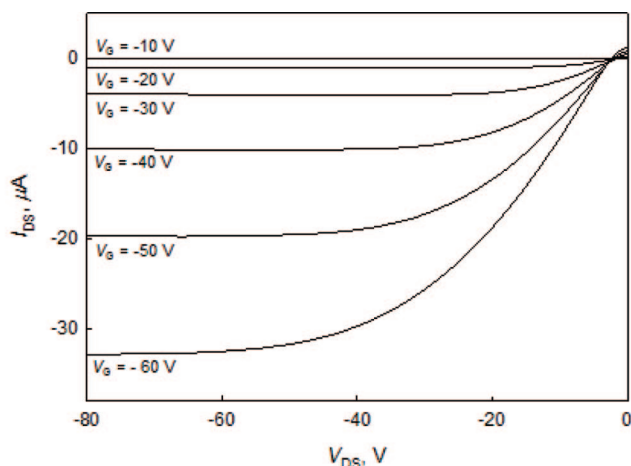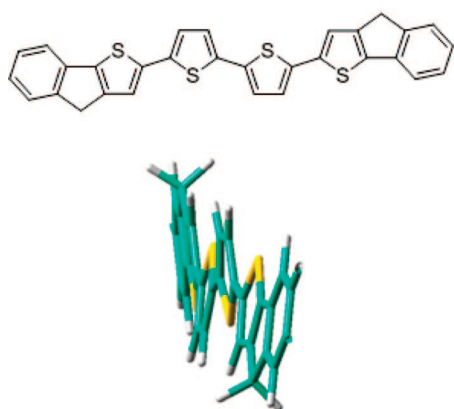# Quaterthiophenes with Terminal Indeno[1,2-*b*]thiophene Units as *p*-Type Organic Semiconductors

Laurent Pouchain, Olivier Alévêque, Yohann Nicolas,[†] Agathe Oger, Charles-Henri Le Régent, Magali Allain, Philippe Blanchard,* and Jean Roncali

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Quaterthiophenes **4T**, **Oct-4T**, and **Tol-4T** based on a central 2,2′-bithiophene core α,ω-terminated with 4,4-unsubstituted and 4,4-disubstituted *n*-octyl or *p*-tolyl indeno[1,2-*b*]thiophene have been synthesized by Stille or Miyaura−Suzuki couplings. Compound **4T** was also synthesized by an alternative route involving a soluble precursor bearing solubilizing trimethylsilyl groups which have been eliminated in the last step. The electronic properties of the compounds have been analyzed by cyclic voltammetry, UV−vis absorption and fluorescence emission spectroscopy. Thermal evaporation of **4T** and **Oct-4T** leads to crystalline thin films and UV−vis absorption and X-ray diffraction data for these films suggest that the molecules adopt a quasi-vertical orientation onto the substrate. Strong π-π intermolecular interactions have been observed for **4T** but not for molecules **Oct-4T** due to the presence of *n*-octyl chains. Sublimed thin films of **Tol-4T** show an amorphous character. The characterization of field-effect transistors fabricated from these three materials gave a hole-mobility of 2.2×10^{-2} cm^2 V^{-1} s^{-1} with an on/off ratio of 2.2×10^4 for **4T** while no field-effect was observed for **Oct-4T** and **Tol-4T**.

Introduction

Organic field-effect transistors (OFETs) are intensively investigated in view of their potential applications in active matrix displays, RFID, and sensors.[1−9] In this context, materials derived from linear π-conjugated systems are a focus of intense research effort.[5,10−16] Whereas acenes[1,10,17,18] and thiophene[1,19−22]

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oligomers still represent some of the most widely investigated classes of organic semiconductors, recent years have witnessed the emergence of various classes of hybrid conjugated systems.[20,23]

Thiophene-phenylene hybrid oligomers have attracted special interest due to a combination of high hole-mobility and synthetic accessibility.[24] However, the conjugated backbone of thiophene-phenylene oligomers presents a deviation from planarity due to steric interactions between thienyl and phenyl units. Theoretical[25] and experimental results[17,23,26−32] have shown that planar π-conjugated systems present better electronic couplings of π-orbitals in the solid state and hence lead to higher charge-carrier mobilities. It has been already shown that rigidification of π-conjugated systems by covalent bridging[33−35] or by using fused ring building blocks[27,36] leads to planar π-systems with enhanced π-electron delocalization and improved thermal stability. Thus, thiophene-based π-conjugated systems incorporating fluorene (**A**) or cyclopentadithiophene (**C**), have demonstrated a high potential as organic semiconductors.[30,37−41] Indeno-[1,2-*b*]thiophene (**B**) represents an intermediate case between **A** and **C** (Chart 1). Compared to fluorene, replacement of one

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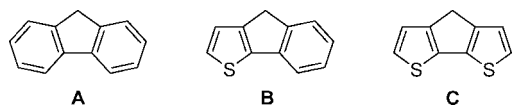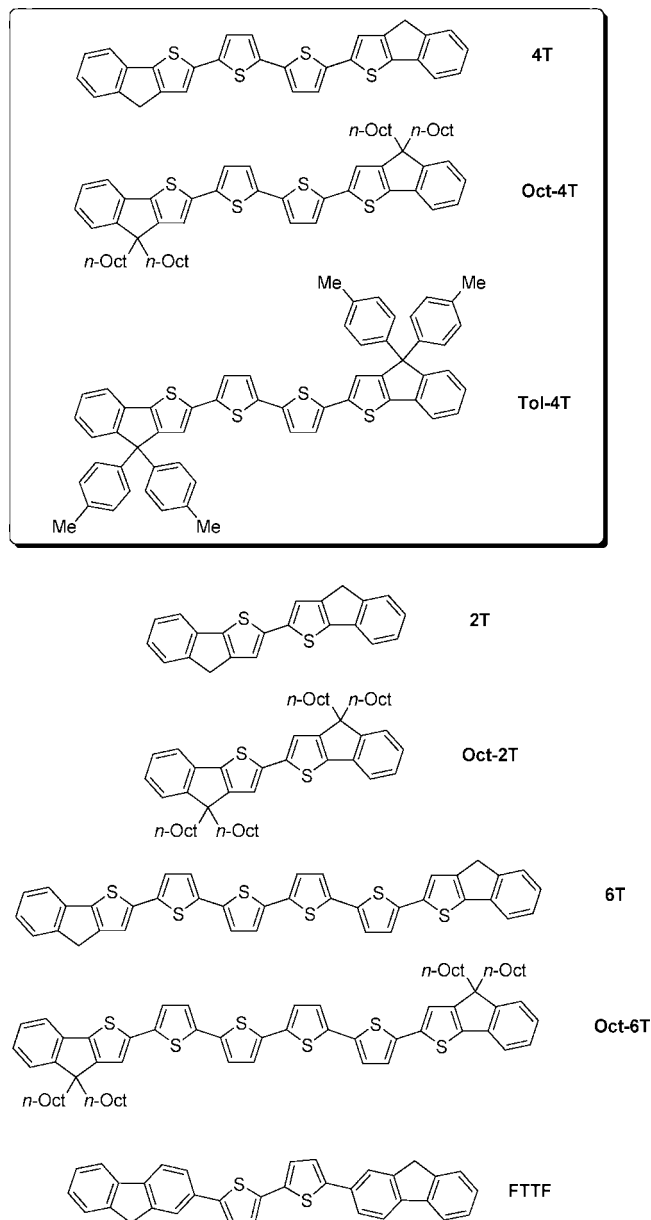
CHART 1

A   B   C

CHART 2

4T

Oct-4T

Tol-4T

2T

Oct-2T

6T

Oct-6T

FTTF

phenyl ring by a thiophene will limit steric interactions on one side and contribute to reduce the overall aromaticity of the system and thus the HOMO−LUMO gap.[34]

We report here the synthesis of a series of quaterthiophenes **4T**, **Oct-4T** and **Tol-4T** bearing α,ω-terminal 4,4-unsubstituted or 4,4-disubstituted indeno[1,2-*b*]thiophene as well as parent oligomers obtained as side product of the synthesis (Chart 2). The electronic properties of the new compounds have been analyzed by cyclic voltammetry, UV−vis and fluorescence emission spectroscopy. Thin films of **4T**, **Oct-4T** and **Tol-4T** prepared by thermal evaporation have been characterized by UV−vis and fluorescence emission spectroscopy and X-ray diffraction and preliminary results on the use of these compounds in OFETs are presented.

Results and Discussion

Synthesis. Compounds **4T**, **Oct-4T** and **Tol-4T** have been synthesized by Stille[42] or Miyaura−Suzuki[43] coupling of appropriate 2,2′-bithiophenes and 2-halogeno or 2-trialkylstannyl derivatives of indeno[1,2-*b*]thiophene. The synthesis of the latter compounds is shown in Scheme 1. Indeno[1,2-*b*]thiophene **5** was prepared according to the McDowell procedure.[44] The synthesis of **2** has been significantly improved by reacting methyl 2-bromobenzoate **1** with 2-tributylstannylthiophene in the presence of a Pd(0) catalyst. Saponification of ester **2** followed by acidification led to acid **3**, which was subsequently converted into acid chloride. Further intramolecular Friedel−Crafts acylation afforded ketone **4**. Compound **5** was obtained after a Wolf−Kishner reduction of ketone **4** and was then selectively iodinated or brominated at the 2-position by 1 equiv of *N*-iodosuccinimide or *N*-bromosuccinimide in DMF to give compounds **6** and **7**, respectively.[45] Owing to the relative acidity of the protons of the methylene bridge of **5**, the 2-tributylstannyl derivative **8** was synthesized by lithium−bromine exchange on compound **7** and reaction with tributylstannyl chloride.

The synthesis of the unsubstituted quaterthiophene **4T** has been carried out in different conditions summarized in Scheme 2. A Miyaura−Suzuki coupling between 2 equiv of iodo derivative **6** and pinacolato boronic ester **9**[46] led to **4T** in 32% yield. Alternatively, Stille couplings between bromo derivative **7** (2.5 equiv) and 5,5′-bis(tributylstannyl)-2,2′-bithiophene **10**[47] or stannyl derivative **8** (2.5 equiv) and 5,5′-dibromo-2,2′-bithiophene **11**[48] gave **4T** in comparable yields close to 45%.

As a result of its low solubility in THF or toluene, **4T** precipitated in the reaction mixture and was recovered by filtration. Purification of **4T** consisted of successive washings with different solvents and further Soxhlet extractions with solvents in the following order: hexane, acetone, dichloromethane, toluene, and finally chlorobenzene. The major part of **4T** was extracted with chlorobenzene while some amount of **4T** was recovered from toluenic extracts. The lack of solubility in common deuterated organic solvents (see Experimental Section and Supporting Information) did not allow for NMR analysis at room temperature. The identity of **4T** was confirmed by the MALDI-TOF mass spectrum of the chlorobenzene extracts, which essentially showed one main peak at $m/z = 506$ (100%, M[+•]), associated with the related less intense isotope peaks at $m/z = 507$ (35%) and 508 (19%) (Figure S2, Supporting Information). However, another system of weak intensity was also observed with the main peak at $m/z = 670$ (6% relative to the peak at $m/z = 506$) assigned to the presence of a small amount of sexithiophene derivative **6T**. This byproduct results

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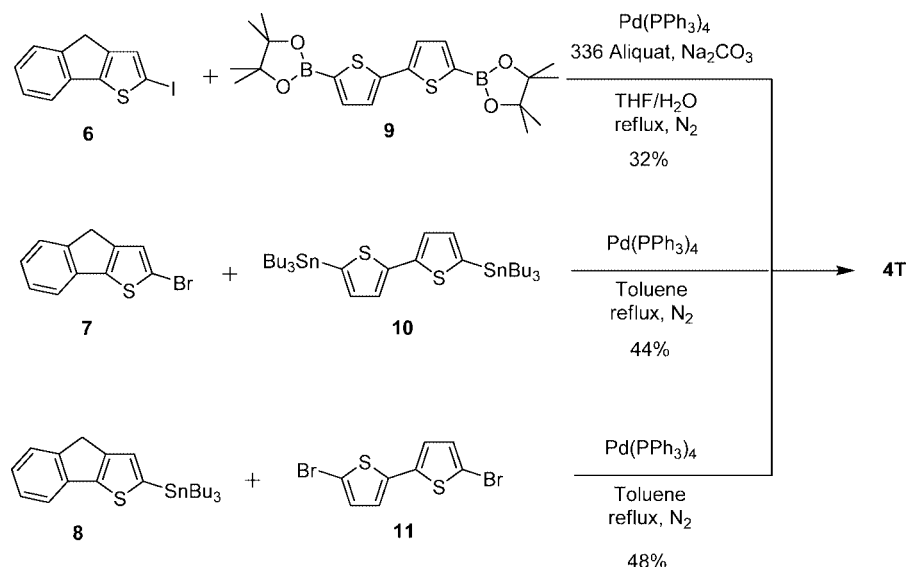(47) (a) Wie, Y.; Yang, Y.; Yeh, J.-M. *Chem. Mater.* **1996**, *8*, 2659–2666. (b) Jousselme, B.; Blanchard, P.; Levillain, E.; Delaunay, J.; Allain, M.; Richomme, P.; Rondeau, D.; Gallego-Planas, N.; Roncali, J. *J. Am. Chem. Soc.* **2003**, *125*, 1363–1370.
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SCHEME 1
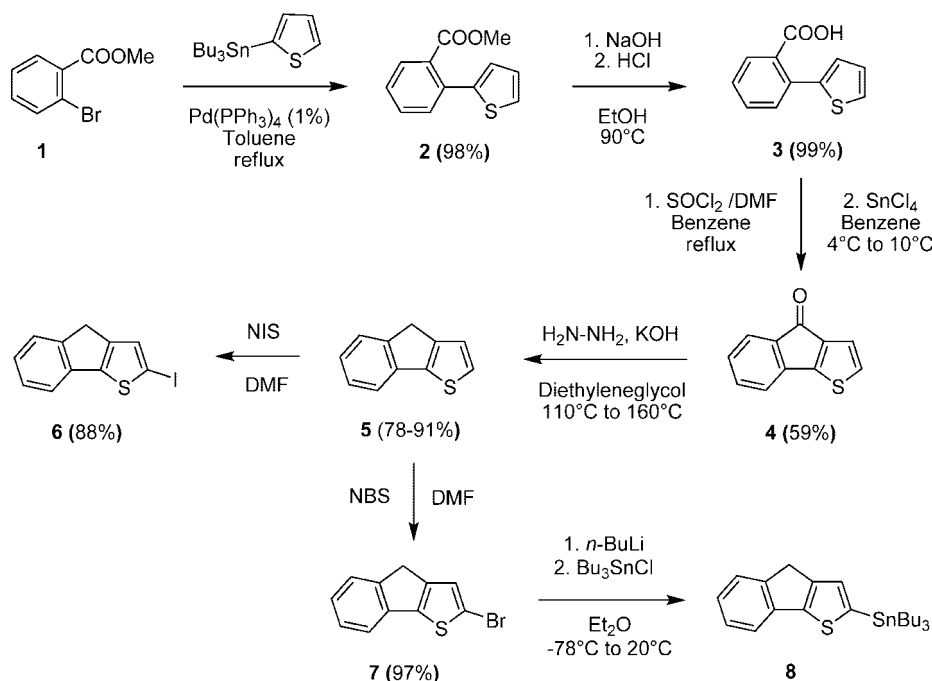
SCHEME 2

from an initial homocoupling of bithiophene derivatives **9**−**11** during Stille or Miyaura−Suzuki reaction. Such Stille homocoupling has already been observed during the synthesis of other oligothiophenes.[49] Interestingly the MALDI-TOF data of the toluenic extracts show the presence of only **4T** (Figure S2, Supporting Information). Similarly, the indenothiophene compounds **6**−**8** used in the synthesis of **4T** were also subjected to homocouplings leading to the formation of bithiophene **2T**.

With the aim of developing an alternative route to **4T** free of **6T**, the soluble precursor **13** was synthesized by reacting 2.5 equiv of stannyl compound **8** with 1 equiv of 3,3′-bis(trimethylsilyl)-5,5′-dibromo-2,2′-bithiophene **12**[23h] (Scheme 3). As recently reported,[23h] the bulky trimethylsilyl groups of

these intermediate compounds strongly enhance their solubility. Purification of **13** was performed by successive silica gel column chromatography and preparative thick layer chromatography to get rid of sexithiophene traces. The subsequent cleavage of the trimethylsilyl groups of **13** in the presence of fluoride anions led to pure **4T**, which was recovered by simple filtration. As expected, the MALDI-TOF spectrum of **4T** confirmed the absence of **6T**. Moreover, the mass spectrum recorded between $m/z = 0$ and 1500 shows only the presence of the molecular ion peak at $m/z = 506$ with the corresponding isotope peaks, thus suggesting a good purity for this sample (Figure S3, Supporting Information). The ^{1}H NMR spectrum of **4T** recorded in CDCl$_3$ at 55 °C or in DMSO-d_6 at 90 °C (Figures S18 and S19, Supporting Information), respectively, shows a very weak singlet at 3.72 or 3.80 ppm corresponding to the protons of the two methylene bridges, suggesting that compound **4T** is pure.
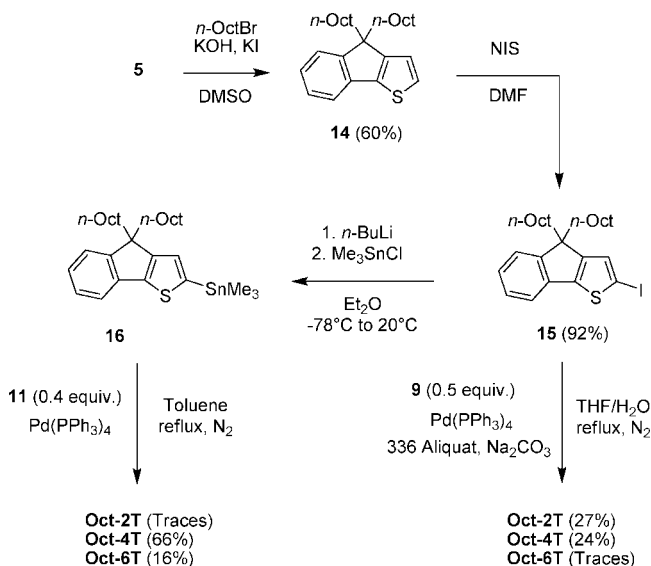
(49) Van Hal, P. A.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J.; Jousselme, B.; Blanchard, P.; Roncali, J. *Chem. Eur. J.* **2002**, *8*, 5415–5429.

SCHEME 3
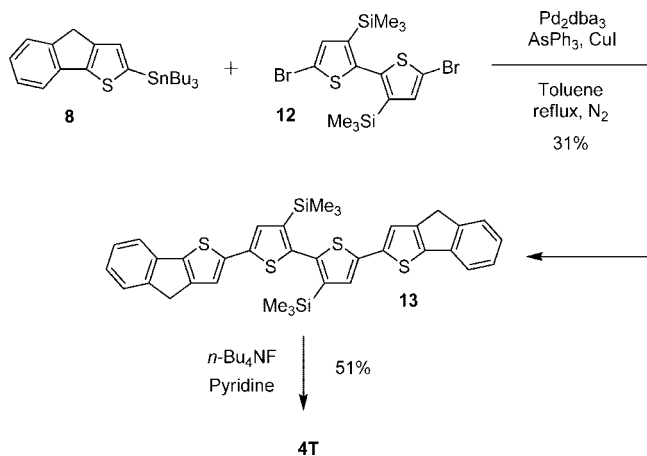
SCHEME 4

However, assignment of the aromatic protons is still prevented by the weakness of the NMR signals.

Analogs more soluble than **4T** have been obtained by substitution at the methylene bridges by *n*-octyl chains and *p*-tolyl groups leading to compounds **Oct-4T** and **Tol-4T**, respectively. Compound **Oct-4T** was prepared either by Miyaura−Suzuki coupling of iodinated compound **15** with pinacolato boronic ester **9** or by Stille coupling of stannyl derivative **16** with 5,5′-dibromo 2,2′-bithiophene **11** (Scheme 4). Compound **16** was obtained from **15** after successive lithium−iodine exchange and reaction with trimethylstannyl chloride. Compound **15** was prepared from **5** by double alkylation with *n*-octylbromide in basic conditions leading to the 4,4-substituted indenothiophene **14**, which was then iodinated using *N*-iodosuccinimide.

In the case of the Suzuki coupling, **Oct-4T** was obtained in modest yield (24%), whereas the main product was 2,2′-bithiophene **Oct-2T** (27%). Only traces of sexithiophene **Oct-6T** were observed. The use of Stille conditions improved the yield of **Oct-4T** to 66%, while 16% yield of sexithiophene **Oct-6T** and traces of bithiophene **Oct-2T** were obtained.

Based on the preceding results, compound **Tol-4T** was prepared in 53% yield by Stille reaction between 5,5′-dibromo-2,2′-bithiophene **11** and the stannyl derivative **19** in the presence
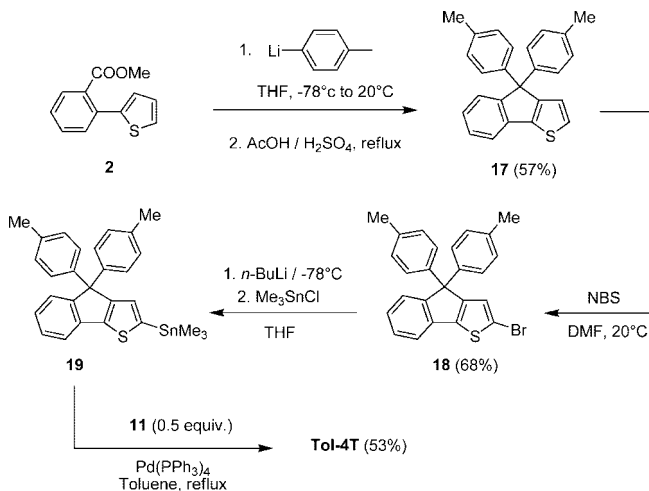
SCHEME 5

TABLE 1. UV−vis Absorption, Fluorescence Emission, and Cyclic Voltammetric Data for Oligothiophenes

| compd	λ_{max}, nm[a]	λ_{em}, nm[b]	Φ, %	E_{pa}^1, V[c]	E_{pa}^2, V[c]
2T	380, **397**, 417	**440**, 466, 495	6	0.85	1.33 (irr)
4T	442	512, 545, 595	26		
Oct-2T	391, **408**, 427	**451**, 477, 510	4	0.84	1.30 (irr)
Oct-4T	450	516, 550, 600	31	0.75	0.93
Oct-6T	470	544, 582, 640	18	0.68	0.82
Tol-4T	452	517, 550, 600	27	0.79	1.00

[a] Absorption maxima in CH_2Cl_2. [b] Emission maxima in CH_2Cl_2 with perylene ($\Phi = 92\%$ in EtOH) as standard. Bold numbers represent the more intense absorption or emission bands. [c] 1 mM substrate in 0.10 M *n*-Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV s^{-1}, Pt working electrode, ref SCE.

of Pd(PPh$_3$)$_4$ (Scheme 5). Compound **19** was obtained from **18** by lithium−bromine exchange and reaction with trimethylstannyl chloride. Bromination of compound **17** with *N*-bromosuccinimide in DMF gave the bromo derivative **18**.[50] Compound **17** was prepared by reacting *p*-tolyllithium, generated by reaction of *n*-BuLi on *p*-bromotoluene, with ester **2** to give an intermediate alcohol which was then cyclized into **17** in acidic conditions.

Electrochemical and Optical Properties. The electrochemical properties of new compounds have been analyzed by cyclic voltammetry (CV) in dichloromethane in the presence of tetrabutylammonium hexafluorophosphate as supporting electrolyte. Table 1 lists CV, UV−vis absorption, and fluorescence emission data for oligothiophenes derivatives. The CV of **4T** could not be recorded because of insufficient solubility. The CV of **2T** presents a one-electron reversible oxidation peak at $E_{pa}^1 = 0.85$ V corresponding to the generation of a stable radical cation followed by an irreversible oxidation peak at more positive potential (Figure S4, Supporting Information).

Figure S5 in Supporting Information shows the CV traces of **Oct-2T**, **Oct-4T**, and **Oct-6T**. Compound **Oct-2T** exhibits a one-electron reversible oxidation peak at $E_{pa}^1 = 0.84$ V and an ill-defined irreversible oxidation wave around 1.30 V (not shown). The CV of **Oct-4T** shows two reversible one-electron oxidation peaks at $E_{pa}^1 = 0.75$ V and $E_{pa}^2 = 0.93$ V, associated with the formation of stable radical cation and dication. As expected, insertion of additional thiophene rings from **Oct-2T** to **Oct-4T** and **Oct-6T** produces a negative shift of E_{pa}^1 and

(50) Wong, K.-T.; Hwu, T.-Y.; Balaiah, A.; Chao, T.-C.; Fang, F.-C.; Lee, C.-T.; Peng, Y.-C. *Org. Lett.* **2006**, *8*, 1415–1418.
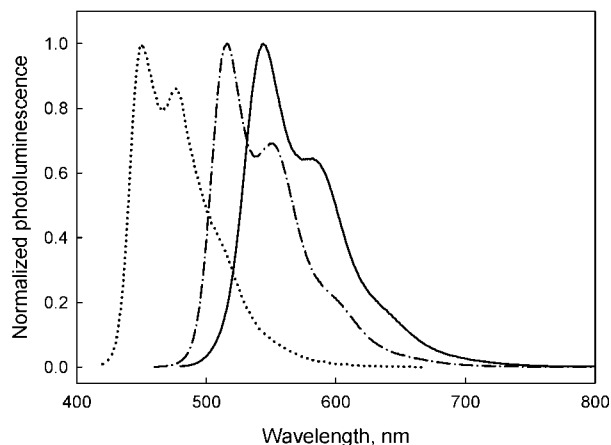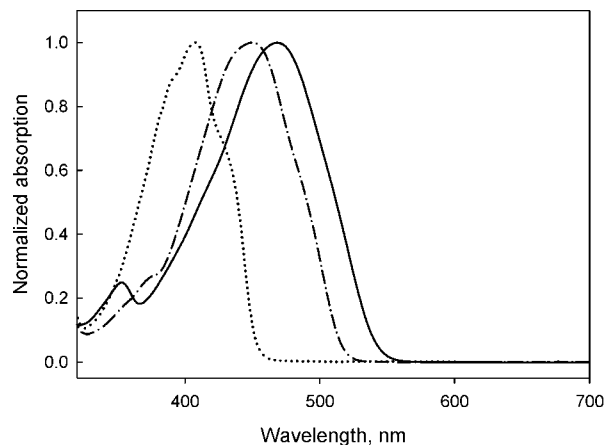
FIGURE 1. Normalized absorption and photoluminescence spectra of **Oct-2T** (dotted line), **Oct-4T** (dashed-dotted line), and **Oct-6T** (solid line) in CH_2Cl_2.

E_{pa}^2, while the difference $\Delta E_{pa} = E_{pa}^2 - E_{pa}^1$ decreases from **Oct-4T** (180 mV) to **Oct-6T** (140 mV) due to the smaller Coulombic repulsion in the dicationic state as chain length increases. Replacement of *n*-octyl chains of **Oct-4T** by *p*-tolyl groups in **Tol-4T** leads to a positive shift of 40 mV and 70 mV of the E_{pa}^1 and E_{pa}^2 values, respectively (Figure S6, Supporting Information).

The absorption and emission spectra of **4T** are shown in Figure S7, Supporting Information. A broad absorption band attributed to a $\pi-\pi^*$ transition is observed at $\lambda_{max} = 442$ nm, while the emission spectrum exhibits a more resolved vibronic structure with the most populated 0–0 transition at 512 nm, a less intense peak at 545 nm, and a shoulder at 595 nm. Similar spectra are observed for **Oct-4T** and **Tol-4T**, although substitution of the indeno[1,2-*b*]thiophene heterocycle leads to a slight red shift of absorption and emission maxima (Table 1).

The UV–vis spectrum of compound **13** shows an absorption maximum at 379 nm, and the ~63 nm blue shift compared to **4T** agrees well with the restricted conjugation imposed by the twisted structure of the molecule (Figure S7, Supporting Information).

Figure 1 shows the absorption and emission spectra of oligothiophenes of the octyl series. As expected, increasing the length of the π-conjugated system from two to six thiophene rings leads to a progressive red shift of the maximum of absorption associated with the reduction of the HOMO–LUMO gap (ΔE). The latter can be estimated from the absorption edges in the UV–vis spectra of **Oct-2T** ($\Delta E = 2.7$ eV), **Oct-4T** ($\Delta E = 2.4$ eV), and **Oct-6T** ($\Delta E = 2.3$ eV).

Theoretical Calculations. Theoretical calculations on **4T** and a reference compound fluorene-thiophene-thiophene-fluorene (**FTTF**) (Chart 2), which has recently demonstrated great potential as active material in OFETs,[37,38] have been performed at the ab initio density functional level with the Gaussian 03 program. Becke's three-parameter gradient corrected functional (B3LYP) with a polarized 6-31G(d,p) basis was used for all full geometry optimizations. In both cases, the oligothiophene chain adopts an *anti* conformation. As expected, **4T** presents a more planar structure than **FTTF**. While the dihedral angles between the thiophene rings of the central bithiophene core are comparable for **4T** (13°) and for **FTTF** (10°), the dihedral angles between the terminal indeno[1,2-*b*]thiophene unit (14°) or the terminal fluorene unit (25°) and the vicinal thiophene ring differ significantly (Figure 2). This difference results in a decrease of the calculated ΔE from 3.18 eV for **FTTF** to 2.74 eV for **4T**,
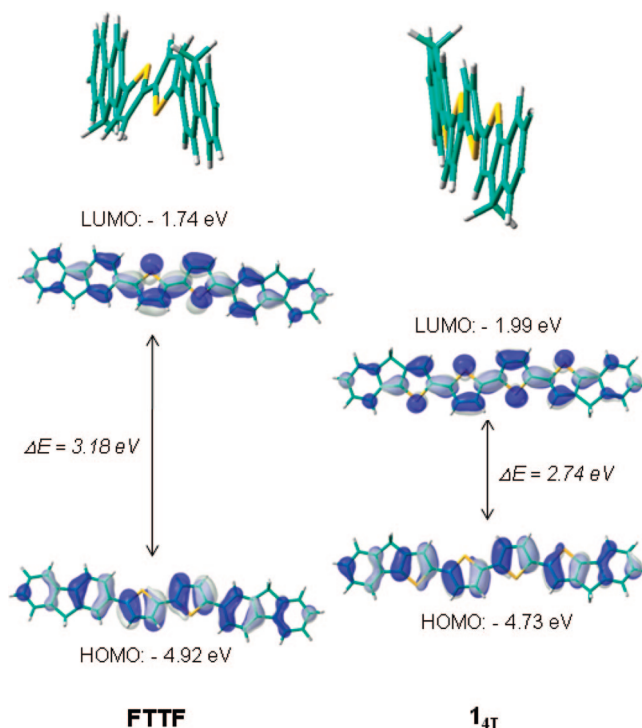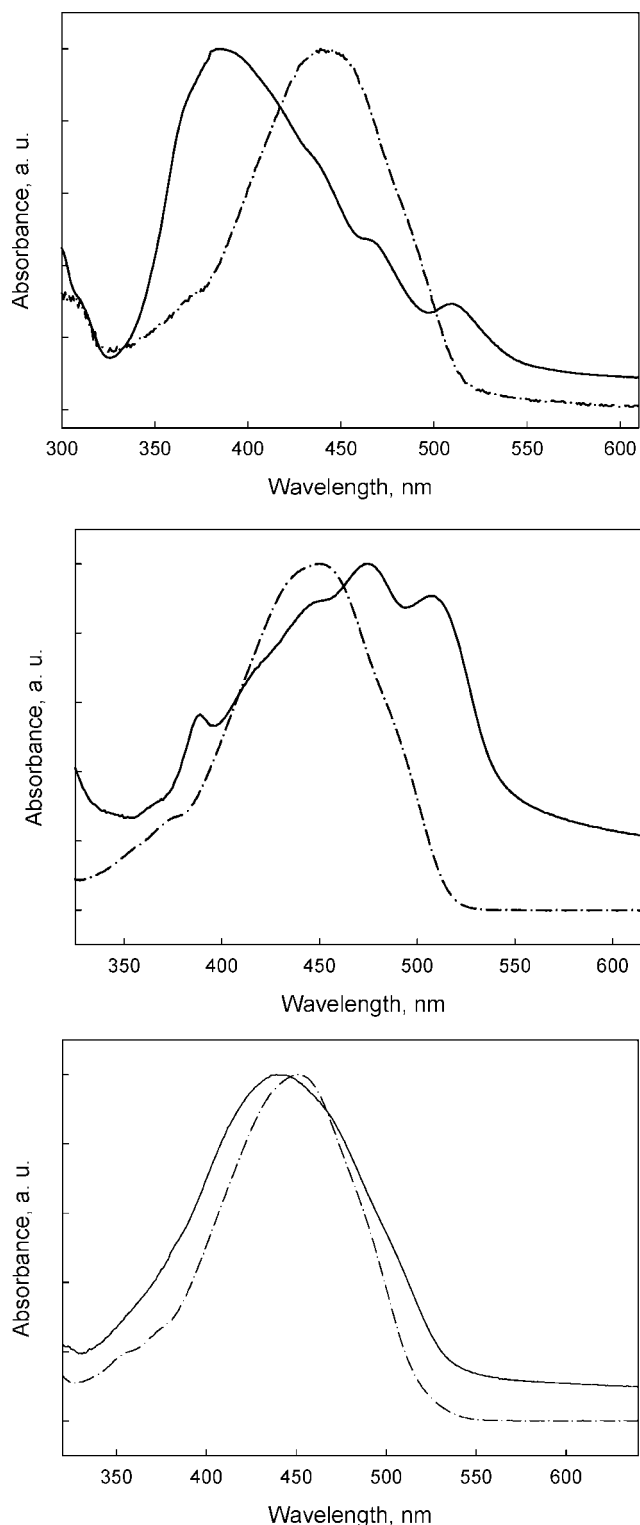

FIGURE 2. Optimized structures and energy levels of HOMO and LUMO of **FTTF** and **4T**.

which stems from the concomitant +0.19 eV increase of the HOMO level and −0.25 eV decrease of the LUMO level. Interestingly, the LUMO level is more affected than the HOMO level. The HOMO and LUMO of both molecules show typical aromatic and quinoid characters, respectively, with an extension of π-conjugation over the whole conjugated backbone.

Film Characterizations. Films of **4T**, **Oct-4T**, and **Tol-4T** have been grown on glass by sublimation of **4T**, **Oct-4T**, or **Tol-4T** under high vacuum. The absence of degradation of the molecules during vacuum sublimation was confirmed by checking the UV–vis absorption spectrum of the redissolved films.
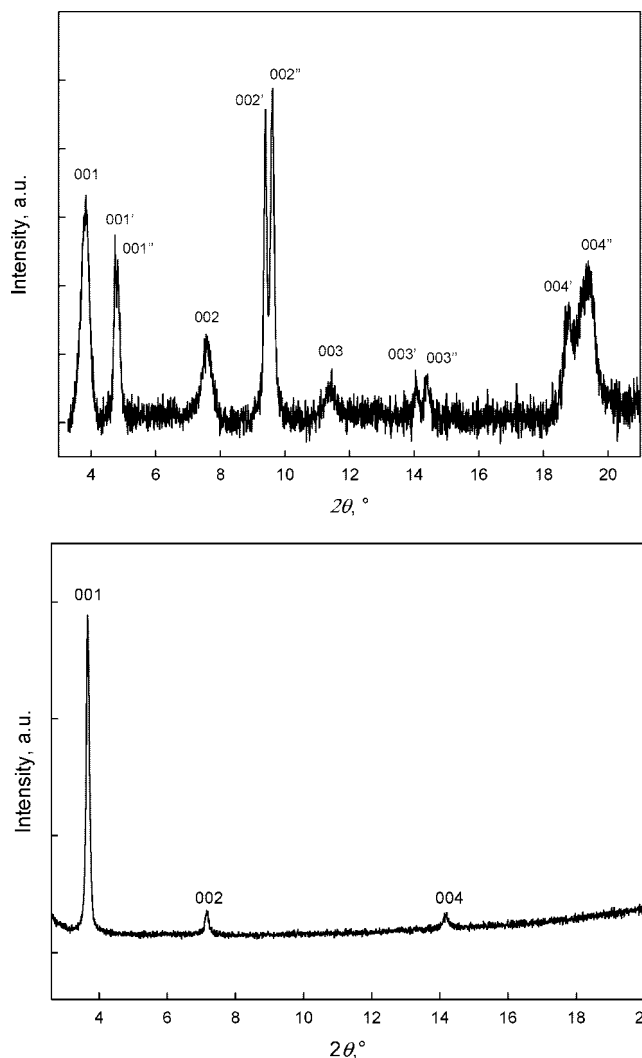
Although **4T**, **Oct-4T**, and **Tol-4T** show similar UV–vis spectra in solution, those of the corresponding thin films exhibit three drastically different behaviors. Thus, comparison of the solution and the solid-state spectra of **4T** reveals a 57 nm blue shift of λ_{max} and the appearance of a weak electronic transition at 510 nm for the film (Figure 3, top). As already observed for

FIGURE 4. X-ray diffraction diagrams of films of 50 nm thickness of **4T** (top) and **Oct-4T** (bottom) on glass.

The solid-state optical spectrum of **Oct-4T** shows a well-resolved vibronic structure. However, in contrast to **4T**, a red shift in absorbance typical of the formation of *J* aggregates[52] and a broadening of the absorption band of **Oct-4T** are observed in the solid state (Figure 3, middle), suggesting weaker intermolecular π-interactions and a different molecular arrangement. On the other hand, the similarity of the UV−vis spectrum of **Tol-4T** obtained in solution or as film indicates limited π-intermolecular interactions in the solid state (Figure 3, bottom).

In addition, the quenching of the fluorescence for the film of **4T** and the persistence of fluorescence properties for films of **Oct-4T** and **Tol-4T** (Figure S9, Supporting Information) agree well with the expected weaker intermolecular π-interactions in the two latter cases.

Films of 50 nm thickness of **4T**, **Oct-4T**, and **Tol-4T** have been analyzed by X-ray diffraction in reflection mode. The XRD diagram of a film of **Tol-4T** shows the absence of diffraction peaks indicating an amorphous character (Figure S10, Supporting Information). By contrast, films of **4T** and **Oct-4T** show a

FIGURE 3. Absorption spectra of **4T** (top), **Oct-4T** (middle), and **Tol-4T** (bottom) as films on glass (solid line) or in CH_2Cl_2 (dashed-dotted line).

other oligothiophenes,[1,19,20,21a,c,22,51] this behavior results from a Davydov splitting of the singlet excited state that is generally associated with strongly interacting π-conjugated systems in the solid state.

(51) Roncali, J.; Frère, P.; Blanchard, P.; de Bettignies, R.; Turbiez, M.; Roquet, S.; Leriche, P.; Nicolas, Y. *Thin Solid Films* **2006**, *511−512*, 567–575.
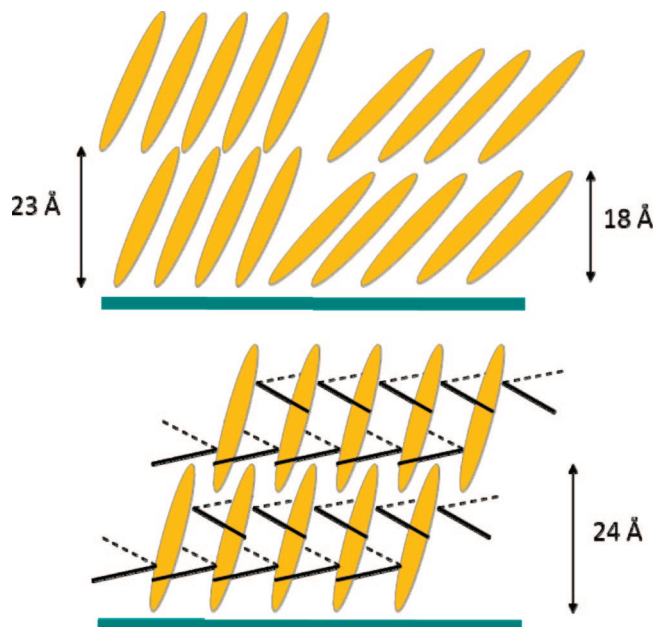
(52) (a) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973–2011. (b) Dautel, O. J.; Wantz, G.; Almairac, R.; Flot, D.; Hirsch, L.; Lère-Porte, J.-P.; Parneix, J.-P.; Serein-Spirau, F.; Vignau, L.; Moreau, J. J. E. *J. Am. Chem. Soc.* **2006**, *128*, 4892–4901.
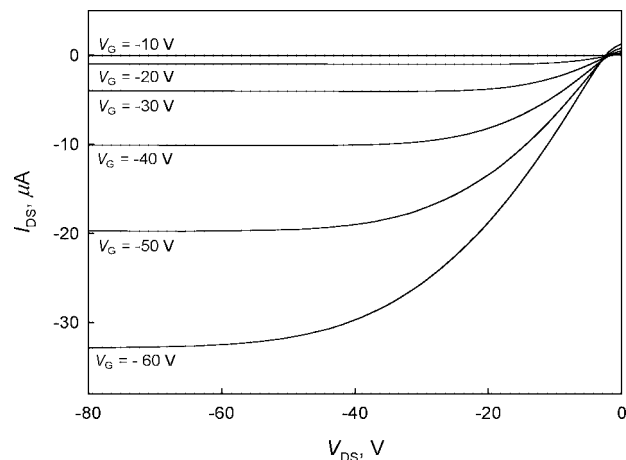
FIGURE 5. Possible structures for films of **4T** (top) and **Oct-4T** (bottom).

FIGURE 6. I_{DS} versus V_{DS} characteristics at different V_G values for an OFET based on an evaporated layer of **4T**, channel length $L = 50$ μm and channel width $W = 5$ mm.

crystalline character and are highly ordered as evidenced by sharp diffraction peaks (Figure 4). The XRD diagram for **4T** exhibits various peaks among them three different first order diffraction peaks (*001*), (*001'*), and (*001''*) at 2θ values of 3.83°, 4.76°, and 4.84°, which correspond to the respective *d*-spacings of 23.0, 18.5, and 18.2 Å ($\lambda_{Cu-\alpha} = 1.5406$ Å). Assuming a fully extended linear structure for **4T** with all vicinal thiophene rings in an *anti* conformation, the MM2 minimized length of **4T** was estimated to 25 Å. Hence, these results suggest that three crystalline domains coexist in the film where the long axis of molecules **4T** is tilted relative to the normal of the surface with the angle values of 23°, 42°, and 43°. Figure 5 (top) represents a schematic description of the film structure of **4T**.

The XRD diagram of a film of **Oct-4T** shows one intense diffraction peak (*001*) at $2\theta = 3.65°$ and two weak peaks corresponding to higher orders of diffraction. These peaks lead to a molecular layer of 24.2 Å of thickness. Using the molecular length calculated for **4T**, molecules **Oct-4T** adopt a quasivertical orientation relative to the surface with an estimated tilt angle of 15° with, however, weaker intermolecular π-interactions due to the presence of the *n*-octyl chains, (Figure 5, bottom) in agreement with UV−vis results.

OFET Fabrication and Measurements. TGA and DSC measurements (see Supporting Information) showed that quaterthiophenes **4T**, **Oct-4T**, and **Tol-4T** presented high thermal stability compatible with a sublimation process. On this basis, top-contact OFETs were made by deposition of a film of 50 nm thickness of **4T**, **Oct-4T**, and **Tol-4T** onto a substrate kept at 20 °C of a heavily doped silicon with a 200 nm thick SiO_2 layer as dielectric, and the devices were completed by gold top contact source and drain electrodes.

Devices realized from the octyl (**Oct-4T**)- and tolyl (**Tol-4T**)-substituted quaterthiophenes did not show any field-effect behavior, as could be expected from the already discussed weak intermolecular interactions. Figure 6 presents the drain current versus drain-source voltage (I_{DS}/V_{DS}) curves at different gate voltages (V_G) of an OFET based on **4T**. The drain current increases with increasing negative gate voltage, as expected for

a *p*-type semiconductor. A field-effect mobility μ of 2.2×10^{-2} cm^2 V^{-1} s^{-1} corresponding to an average of eight devices was obtained at a drain voltage of −80 V. The transfer characteristics and the $\log(I_{DS})$ versus V_G curve (Figure S11, Supporting Information) give an average threshold voltage V_T of −16.9 V and an average on/off ratio of 2.2×10^4, respectively. Using similar conditions, Bao et al. have reported a field-effect mobility of $2-3 \times 10^{-2}$ cm^2 V^{-1} s^{-1} with on/off ratios of 10^5-10^6 for OFETs based on **FTTF**.[37]

Conclusion

Quaterthiophene derivatives **4T**, **Oct-4T**, and **Tol-4T** based on a central 2,2′-bithiophene core with two terminal 4,4-unsubstituted or 4,4-disubstituted indeno[1,2-*b*]thiophene heterocycles have been synthesized using Stille or Miyaura−Suzuki couplings. While complete characterization of the unsubstituted derivative **4T** of the series was prevented because of its lack of solubility in common organic solvents, the introduction of *n*-octyl chains or *p*-tolyl groups at the 4-positions of the indeno[1,2-*b*]thiophene moiety led to more soluble compounds **Oct-4T** and **Tol-4T**. Moreover, a detailed study of the synthesis of quaterthiophene **Oct-4T** has evidenced the formation of byproduct such as bithiophene **Oct-2T** and sexithiophene **Oct-6T** resulting from homocoupling reactions. These side reactions that make the purification of insoluble derivative **4T** difficult led us to adopt an alternative synthetic route involving a soluble precursor for the synthesis of **4T**.

Optical and X-ray diffraction results show that sublimed films of **4T** and **Oct-4T** are highly crystalline with molecules adopting a quasivertical orientation on the substrate, whereas films of **Tol-4T** are amorphous. Strong $\pi-\pi$ intermolecular interactions in the case of **4T** allow for the realization of OFET with interesting hole-mobilities and on/off ratios, while such interactions are hindered by the presence of the *n*-octyl chains of **Oct-4T**.

Work focused on the development of new conjugated systems based on the indenothiophene building block and combining solubility and strong intermolecular interactions is now underway and will be reported in future publications.

Experimental Section

Devices Preparation and Characterization. Organic FETs were prepared by evaporation of **4T**, **Oct-4T**, and **Tol-4T** under a vacuum

of 6×10^{-7} mbar and subsequent deposition of a 50 nm thick organic layer at a rate of 0.2 nm s^{-1} onto Si n++ wafer with a 200 nm thick SiO$_2$ layer (ACM) with a substrate temperature of 20 °C. As source and drain top contacts, 50 nm of Au were evaporated through a homemade shadow mask, defining a channel of 5000 μm width and 50 μm length. The characterization was carried out in a glovebox using an Agilent 4155C semiconductor parameter analyzer. The contacts were obtained by W tips (Signatone). For evaluation of the mobility (μ) in the saturation regime, the following equation was used:

$$I_{DS}(\text{sat}) = (W/2L)\mu C_i (V_G - V_T)^2 \qquad (1)$$

where I_{DS} is the drain current, V_G is the gate voltage, V_T is the extrapolated threshold voltage, μ is the field-effect mobility, L and W are the channel length and width, respectively, and C_i is the insulator capacitance per unit area.

2-Iodo-4H-indeno[1,2-b]thiophene (6). A solution of N-iodosuccinimide (2.7 g, 12.7 mmol) in DMF (60 mL) was added dropwise to a solution of **5** (2 g, 11.6 mmol) in DMF (60 mL) cooled to 0 °C and protected from the daylight. The reaction mixture was stirred for 1 h at 0 °C and then allowed to reach room temperature. Water (450 mL) was added, and the resulting white precipitate was filtered and washed with water (2 × 50 mL) giving, after drying, **6** (3.06 g, 88% yield) as white powder. Mp 91–92 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.69 (s, 2H), 7.21 (t, 1H, $^3J =$ 7.5 Hz), 7.29 (s, 1H), 7.32 (t, 1H, $^3J =$ 7.5 Hz), 7.44 (d, 1H, $^3J =$ 7.5 Hz), 7.48 (d, 1H, $^3J =$ 7.5 Hz). MS (70 eV, EI) m/z (I%) = 298 (M$^{+\bullet}$, 100), 171 (55).

2-Bromo-4H-indeno[1,2-b]thiophene (7). A solution of N-bromosuccinimide (1.08 g, 6.1 mmol) in DMF (30 mL) was added dropwise to a solution of **5** (1 g, 5.8 mmol) in DMF (30 mL) cooled to 0 °C and protected from the daylight. The resulting solution was stirred for 1 h at 0 °C and then was allowed to reach room temperature. The mixture was concentrated under reduced pressure. After dilution with Et$_2$O (50 mL), the solution was washed with water (3 × 50 mL), dried over MgSO$_4$, and concentrated to give a residue that was purified by chromatography over silica gel (cyclohexane) to give **7** as light-yellow crystals (1.41 g, 97% yield). Mp 58–59 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.69 (s, 2H), 7.12 (s, 1H), 7.22 (t, 1H, $^3J =$ 7.4 Hz), 7.32 (t, 1H, $^3J =$ 7.5 Hz), 7.43 (d, 1H, $^3J =$ 7.4 Hz), 7.48 (d, 1H, $^3J =$ 7.3 Hz). MS (70 eV, EI) m/z (I%) = 252 (M$^{+\bullet}$, 90), 250 (M$^{+\bullet}$, 100), 171 (90).

2-Tributylstannyl-4H-indeno[1,2-b]thiophene (8). Under a N$_2$ atmosphere, a solution of n-BuLi 1.6 M in hexanes (2.85 mL, 4.56 mmol) was added dropwise to a solution of **7** (1.10 g, 4.38 mmol) in anhydrous Et$_2$O (125 mL) cooled to −78 °C. After 0.5 h of stirring at this temperature, Bu$_3$SnCl 96% (1.77 mL, 6.26 mmol) was added, and the reaction mixture was then allowed to warm slowly to room temperature. After dilution with Et$_2$O (150 mL), the mixture was washed successively with a saturated aqueous solution of NH$_4$Cl (40 mL) and brine (2 × 100 mL). The organic phase was separated by decantation and concentrated under reduced pressure. The residue was diluted with EtOAc (40 mL), and a saturated aqueous solution of NaF (30 mL) was added leading, after 20 min of stirring, to the precipitation of Bu$_3$SnF, which was separated by filtration. The filtered solution was washed with brine (50 mL), dried over MgSO$_4$, and concentrated to dryness. The obtained oil (2.03 g) was sufficiently pure (>90%) and hence was used in the next step without further purification. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.91 (t, 9H, $^3J =$ 7.2 Hz), 1.08–1.25 (m, 6H), 1.34–1.39 (m, 6H), 1.56–1.65 (m, 6H), 3.68 (s, 2H), 7.15 (s, 1H), 7.16 (t, 1H, $^3J =$ 7.4 Hz), 7.30 (t, 1H, $^3J =$ 7.4 Hz), 7.46 (d, 1H, $^3J =$ 7.0 Hz), 7.48 (d, 1H, $^3J =$ 7.4 Hz).

5,5′-Bis(4H-indeno[1,2-b]thien-2-yl)-3,3′-bis(trimethylsilyl)-2,2′-bithiophene (13). A mixture of 3,3′-bis(trimethylsilyl)-5,5′-dibromo-2,2′-bithiophene **12**^{23h} (1 g, 2.14 mmol) and stannyl derivative **8** (2.53 g, 5.41 mmol) in the presence of AsPh$_3$ (0.35 g, 1.14 mmol) and CuI (0.10 g, 0.53 mmol) in anhydrous toluene (60

mL) was degassed with N$_2$ for 10 min before addition of Pd$_2$dba$_3$ (015 g, 0.16 mmol). The reaction mixture was refluxed for 18 h under a N$_2$ atmosphere. After concentration under reduced pressure, the residue was filtered on silica gel (eluent, CH$_2$Cl$_2$). Further purification was performed by a first column chromatography on silica gel with a mixture cyclohexane/CH$_2$Cl$_2$ 9:1 as eluent and another one with cyclohexane as solvent (R_f = 0.37). Finally, a preparative thick layer chromatography on silica gel led to **13** (0.43 g, 31% yield) as a yellow solid. Mp 193–194 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.19 (s, 18H), 3.71 (s, 4H), 7.18 (s, 2H), 7.21 (t, 2H, $^3J =$ 7.5 Hz), 7.23 (s, 2H), 7.34 (t, 2H, $^3J =$ 7.3 Hz), 7.47 (d, 2H, $^3J =$ 7.5 Hz), 7.49 (d, 2H, $^3J =$ 7.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 0.06, 34.3, 118.8, 119.8, 124.93, 124.99, 127.0, 128.7, 138.78, 138.81, 139.1, 140.3, 142.2, 143.5, 145.6, 147.7. MS MALDI-TOF 650 [M$^{+\bullet}$]. UV−vis (CH$_2$Cl$_2$): $\lambda_{max} =$ 379 nm.

5,5′-Bis(4H-indeno[1,2-b]thien-2-yl)-2,2′-bithiophene (4T). Miyaura−Suzuki Coupling. A solution of Na$_2$CO$_3$ (1.3 g, 12 mmol) in water (10 mL) and Aliquat 336 (480 mg, 1.2 mmol) was added to a mixture of diboronic ester **9**^{46} (500 mg, 1.2 mmol) and iodo derivative **6** (720 mg, 2.4 mmol) in toluene (15 mL). This mixture was degassed with N$_2$ for 15 min before addition of a catalytic amount of Pd(PPh$_3$)$_4$ (87 mg, 75 μmol) and subsequent refluxing for 48 h. The reaction mixture was then poured into MeOH (100 mL) leading to the formation of a brown precipitate, which was filtered and washed successively with toluene, an aqueous solution of HCl 5%, water, hot MeOH (4 × 75 mL) and hot acetone (3 × 75 mL). After drying, the brown precipitate was subjected to successive Soxhlet extractions with hexane (5 h), acetone (15 h), dichloromethane (15 h), toluene (24 h), and finally chlorobenzene (2 × 48 h). The orange precipitate observed in the toluenic extract was filtered to give 75 mg of compound **4T** as demonstrated by MALDI-TOF mass spectrometry and UV−vis spectroscopy. In addition the extracts obtained from chlorobenzene were concentrated and the resulting residue was triturated with acetone and filtered, washed with acetone and hexane, and dried to afford 120 mg of compound **4T**, accompanied by traces of **6T** as observed by MALDI-TOF mass spectrometry (ca. 32% of overall yield). Note that some amount of **2T** as slightly yellow powder (65 mg) resulting from homocoupling of compound **6** was obtained by evaporation of the dichloromethane extracts and further purification by dissolution in hot CHCl$_3$ and precipitation using EtOH.

Stille Coupling between 7 and 10. A mixture of 5,5′-bis(tributylstannyl)-2,2′-bithiophene **10**^{47} (1 g, 1.34 mmol) and bromo derivative **7** (0.84 g, 3.35 mmol) in anhydrous toluene (30 mL) was degassed with N$_2$ for 10 min before addition of Pd(PPh$_3$)$_4$ (150 mg, 0.13 mmol). The reaction mixture was refluxed for 16 h under a N$_2$ atmosphere. At room temperature, the resulting orange precipitate was filtered, successively washed with toluene and pentane and dried to give 0.53 g of orange powder. The same sequence of Soxhlet extractions as Miyaura−Suzuki coupling was carried out on the orange powder leading to 80 mg of **4T** obtained from the precipitate of the toluenic extracts while the extracts of chlorobenzene gave 220 mg of **4T**, accompanied by traces of **6T** as observed by MALDI-TOF mass spectrometry (ca. 44% of overall yield).

Stille Coupling between 8 and 11. A mixture of 5,5′-dibromo-2,2′-bithiophene **11**^{48} (0.27 g, 0.83 mmol) and stannyl derivative **8** (1.02 g, 2.21 mmol) in anhydrous toluene (30 mL) was degassed with N$_2$ for 10 min before addition of Pd(PPh$_3$)$_4$ (100 mg, 0.09 mmol). The reaction mixture was refluxed for 21 h under a N$_2$ atmosphere. At room temperature, the resulting orange precipitate was filtered, successively washed with toluene and pentane and dried to give 0.35 g of orange powder. The same sequence of Soxhlet extractions as Miyaura−Suzuki coupling was carried out leading to 50 mg of **4T** obtained from the precipitate of the toluenic extracts while the extracts of chlorobenzene gave 150 mg of **4T**, accompanied by traces of **6T** as observed by MALDI-TOF mass spectrometry (ca. 48% of overall yield).

Elimination of Trimethylsilyl Groups of 13. A solution of *n*-Bu$_4$NF 1 M in THF (1 mL) was added to a solution of **13** (100 mg, 0.15 mmol) in pyridine (10 mL) and the reaction mixture was stirred at 20 °C for 20 h. The resulting precipitate was filtered, washed successively with water (3 × 50 mL), acetone (3 × 50 mL) and Et$_2$O (2 × 50 mL) and dried affording **4T** (40 mg, 51% yield).

4T: Mp 356 °C. ^{1}H NMR analysis was prevented due to the lack of solubility of **4T** in CDCl$_3$, pyridine-d$_5$, THF-d$_8$, DMSO-d$_6$, DMF-d$_7$, benzene-d$_6$ and chlorobenzene-d$_5$ at 20 °C. However, one singlet was observed for the two methylene bridges at 3.72 ppm in hot CDCl$_3$ (55 °C) or at 3.80 ppm in hot DMSO-d$_6$ (90 °C) (see Supporting Information). MS MALDI-TOF 506 [M$^{+•}$]. ESI$^+$ HRMS: cald for C$_{30}$H$_{18}$S$_4$ 506.02914; found 506.0293. UV–vis (CH$_2$Cl$_2$): λ_{max} = 442 nm.

2T: Mp 124–125 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.72 (s, 4H), 7.21 (t, 2H, ^3J = 7.5 Hz), 7.25 (s, 2H), 7.33 (t, 2H, ^3J = 7.5 Hz), 7.47 (d, 2H, ^3J = 7.5 Hz), 7.49 (d, 2H, ^3J = 7.5 Hz). ^{13}C NMR: **2T** was too insoluble in CDCl$_3$, pyridine-d$_5$ and DMSO-d$_6$ to obtain a ^{13}C NMR spectrum. MS MALDI-TOF 342 [M$^{+•}$]. ESI$^+$ HRMS: cald for C$_{22}$H$_{14}$S$_2$ 342.05369; found 342.0535. UV–vis (CH$_2$Cl$_2$): λ_{max} = 380 nm (sh), 397 nm, 417 nm (sh).

4,4-Dioctyl-4*H*-indeno[1,2-*b*]thiophene (14). Potassium hydroxide (2.5 g) was added to a mixture of **5** (2.4 g, 13.9 mmol), 1-bromooctane (5.97 g, 11 mmol) and potassium iodide (70 mg, 0.4 mmol) in DMSO (60 mL) cooled to 0 °C. The resulting solution was allowed to reach room temperature overnight. Water (100 mL) was slowly poured into the reaction mixture previously cooled to 0 °C. The mixture was extracted with Et$_2$O (2 × 80 mL), and the combined organic extracts were washed with water, brine, an aqueous saturated solution of NH$_4$Cl, dried over MgSO$_4$ and concentrated under vacuum. The residual 1-bromooctane was distilled using a Kugelrohr apparatus. The resulting brown oil was purified by chromatography of silica gel (eluent: Petroleum Ether) to give **14** as a colorless oil (3.4 g, 60% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.72–0.85 (m, 4H), 0.84 (t, 6H, ^3J = 7.3 Hz), 1.06–1.25 (m, 20 H), 1.84 (dt, 2H, ^2J = 13.0 Hz, ^3J = 4.8 Hz), 1.94 (dt, 2H, ^2J = 13.0 Hz, ^3J = 4.8 Hz), 6.97 (d, 1H, ^3J = 4.8 Hz), 7.18 (dt, 1H, ^3J = 7.4 Hz, ^4J = 1 Hz), 7.24–7.30 (m, 3 H), 7.40 (d, 1H, ^3J = 7.4 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1, 22.6, 24.1, 29.2, 29.3, 30.1, 31.8, 39.0, 53.8, 118.6, 121.5, 122.6, 124.9, 126.7, 127.1, 138.2, 141.1, 153.9, 155.4. MS (70 eV, EI) *m/z* (I%) = 396 (M$^{•+}$, 100%). Anal. Calcd for C$_{27}$H$_{40}$S: C, 81.74; H, 10.16. Found: C, 81.71; H, 10.42.

2-Iodo-4,4-dioctyl-4*H*-indeno[1,2-*b*]thiophene (15). A solution of *N*-iodosuccinimide (580 mg, 2.6 mmol) in DMF (30 mL) was added dropwise to a solution of **14** (1 g, 2.5 mmol) in DMF (20 mL) cooled to 0 °C and protected from the daylight. The resulting solution was stirred for 1 h at 0 °C, and then allowed to reach room temperature. Water (400 mL) was added and the resulting mixture was extracted with CH$_2$Cl$_2$ (4 × 100 mL). The organic layers were gathered, washed with water (4 × 60 mL), dried over magnesium sulfate and concentrated. A chromatography on silica gel (eluent: cyclohexane) afforded **15** (1.2 g, 92% yield) as a colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.66–0.77 (m, 4H), 0.84 (t, 6H, ^3J = 7.2 Hz), 1.05–1.32 (m, 20 H), 1.76–1.91 (m, 4 H), 7.13 (s, 1H), 7.19 (t, 1H, ^3J = 7.5 Hz), 7.24 (t, 1H, ^3J = 7.5 Hz), 7.25 (d, 1H, ^3J = 7.5 Hz), 7.33 (d, 1H, ^3J = 7.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.3, 22.8, 24.2, 29.4, 29.4, 30.1, 31.9, 39.0, 54.5, 74.3 (C–I), 118.9, 122.8, 125.5, 127.0, 131.2, 137.8, 146.4, 153.0, 156.0. MS (70 eV, EI) *m/z* (I%) = 522 (M$^{•+}$, 100).

2-Trimethylstannyl-4,4-dioctyl-4*H*-indeno[1,2-*b*]thiophene (16). A solution of *n*-BuLi 2.5 M in hexanes (1.75 mL) was added dropwise to a solution of **15** (2.1 g, 4.02 mmol) in anhydrous Et$_2$O (50 mL) under inert atmosphere at −70 °C. The reaction mixture was then allowed to reach 0 °C and then cooled to −50 °C before addition of a solution of trimethyltin chloride (920 mg, 4.62 mmol) in anhydrous Et$_2$O (10 mL). The reaction mixture was allowed to reach room temperature and was diluted with Petroleum Ether (100 mL).

A saturated aqueous solution of NH$_4$Cl was added to the mixture and, after vigorous stirring for 0.5 h, the organic phase was separated by decantation, dried over MgSO$_4$ and concentrated. The viscous oil was dissolved in EtOAc (50 mL) and was vigorously stirred for 0.5 h after addition of a saturated aqueous solution of NaF to get rid of the unreacted trimethyltin chloride. The resulting precipitate was filtered over celite which was rinsed with EtOAc. The filtrated solution was washed with brine (50 mL), water (50 mL), dried over MgSO$_4$ and concentrated. The resulting oil (1.80 g) consisted of a mixture of *ca*. 80% of **16** and *ca*. 20% of **14** as determined by ^{1}H NMR. This crude product was used in the next step without further purification.

5,5′-Bis(4,4-dioctyl-4*H*-indeno[1,2-*b*]thien-2-yl)-2,2′-bithiophene (Oct-4T). Miyaura–Suzuki Coupling between 15 and 9. A solution of Na$_2$CO$_3$ (0.65 g, 6 mmol) in water (5 mL) was added to a mixture of boronic ester **9**[46] (0.25 g, 0.6 mmol), compound **15** (630 mg, 1.2 mmol) and Aliquat 336 (240 mg, 0.6 mmol) in toluene (10 mL). This mixture was degassed with N$_2$ for 0.5 h before addition of Pd(PPh$_3$)$_4$ (50 mg, 45 μmol) and subsequent refluxing for 65 h under a N$_2$ atmosphere. Water (100 mL) was added and the reaction mixture was extracted with Petroleum Ether (3 × 100 mL). The organic phases were gathered, washed with an aqueous solution of HCl 1 M (100 mL), brine (100 mL), dried over MgSO$_4$ and concentrated under reduced pressure. Chromatography on silica gel (eluent: Petroleum Ether) led to a fraction corresponding to **Oct-2T** as a yellow oil (R$_f$ = 0.62, 80 mg, 27% yield) and to a fraction corresponding to **Oct-4T** as an orange-red powder (R$_f$ = 0.49, 140 mg, 24% yield).

Stille Coupling between 16 and 11. Pd(PPh$_3$)$_4$ (120 mg, 0.11 mmol) was added to a N$_2$ degassed solution of **16** (1.80 g, 80% pure, 2.6 mmol) and dibromobithiophene **11**[48] (360 mg, 1.1 mmol) in toluene (50 mL). The reaction mixture was refluxed for 24 h, and then water (60 mL) was added at room temperature. The mixture was diluted with Petroleum Ether (50 mL), washed with brine (50 mL), dried over MgSO$_4$ and concentrated. The viscous red oil was purified by chromatography on silica gel (eluent: Petroleum Ether) to give **Oct-4T** as an orange-red solid (R$_f$ = 0.49, 690 mg, 66% yield). Compound **Oct-6T** (R$_f$ = 0.27, 120 mg, 16% yield) was also isolated as bright red powder.

Oct-2T: ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.71–098 (m, 8H), 0.82 (t, 12H, ^3J = 7.2 Hz), 1.06–1.30 (m, 40H), 1.85 (m, 4H), 1.94 (m, 4H), 7.09 (s, 2H), 7.18 (t, 2H, ^3J = 7.5 Hz,), 7.26 (m, 4 H), 7.36 (d, 2H, ^3J = 7.5 Hz). MS MALDI-TOF 790 [M$^{+•}$]. UV–vis (CH$_2$Cl$_2$): λ_{max} = 391 nm (sh), 408 nm, 427 nm (sh).

Oct-4T: Mp 101–102 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.75–0.92 (m, 8 H), 0.83 (t, 12H, ^3J = 7.2 Hz), 1.11–1.26 (m, 40H), 1.85 (dt, 4H, ^2J = 13.0 Hz, ^3J = 4.6 Hz), 1.94 (dt, 4H, ^2J = 13.0 Hz, ^3J = 4.6 Hz), 7.04–7.14 (m, 6H), 7.20 (t, 2H, ^3J = 7.5 Hz), 7.25–7.30 (m, 4H), 7.39 (d, 2H, ^3J = 7.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1, 22.7, 24.2, 29.32, 29.35, 30.1, 31.8, 39.0, 54.4, 118.2, 118.7, 122.5, 123.7, 124.2, 125.3, 126.9, 135.5, 137.4, 138.0, 139.1, 140.4, 153.4, 156.1. MS MALDI-TOF 954 [M$^{+•}$]. UV–vis (CH$_2$Cl$_2$): λ_{max} = 450 nm. Anal. Calcd for C$_{62}$H$_{82}$S$_4$: C, 77.93; H, 8.65. Found: C, 77.72; H, 8.72.

Oct-6T: Mp 147–148 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.73–0.93 (m, 8H), 0.83 (t, 12H, ^3J = 7.2 Hz), 1.08–1.26 (m, 40H), 1.86 (dt, 4H, ^2J = 13.0 Hz, ^3J = 4.6 Hz), 1.94 (dt, 4H, ^2J = 13.0 Hz, ^3J = 4.6 Hz), 7.04–7.15 (m, 10H), 7.20 (t, 2H, ^3J = 7.5 Hz), 7.25–7.30 (m, 4H), 7.39 (d, 2H, ^3J = 7.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.2, 22.7, 24.2, 29.3, 29.4, 30.1, 31.9, 39.0, 54.4, 118.2, 118.7, 122.6, 123.7, 124.3, 124.5, 124.5, 125.3, 127.0, 135.3, 135.9, 136.2, 137.6, 138.0, 139.1, 140.4, 153.5, 156.1. ESI$^+$ HRMS: calcd for C$_{62}$H$_{82}$S$_4$ 1118.50538; found 1118.5036. UV–vis (CH$_2$Cl$_2$): λ_{max} = 470 nm.

2-Trimethylstannyl-4,4-di-*p*-tolyl-4*H*-indeno[1,2-*b*]thiophene (19). A solution of *n*-BuLi 1.6 M in hexanes (1.2 mL, 1.92 mmol) was added dropwise to a solution of **18** (0.77 g, 1.78 mmol) in anhydrous THF (35 mL) cooled to −75 °C under an inert atmosphere. After 0.5 h of stirring at this temperature, a solution

of Me$_3$SnCl 1 M in THF (2.2 mL, 2.2 mmol) was added to the reaction mixture, which was then allowed to warm to room temperature and stirred for 12 h. After dilution with Et$_2$O (150 mL), the reaction mixture was washed with a saturated aqueous solution of NH$_4$Cl (100 mL) and concentrated under reduced pressure. The residue was diluted with EtOAc (30 mL) and a saturated aqueous solution of NaF (25 mL) was added. This mixture was stirred for 20 min and filtered on celite, and the filtered solution was washed with a saturated aqueous solution of NaCl (15 mL), dried over MgSO$_4$, and concentrated to dryness. The resulting oil (0.77 g) consisted of a mixture of ca. 70% of **19** and ca. 30% of **17** as determined by ^{1}H NMR. This crude product was used in the next step without further purification.

5,5′-Bis(4,4-di-*p*-tolyl-4*H*-indeno[1,2-*b*]thien-2-yl)-2,2′-bithiophene (Tol-4T). A mixture of 5,5′-dibromo-2,2′-bithiophene **11** (0.19, 0.59 mmol) and stannyl derivative **19** (0.77 g, 80% pure, 1.20 mmol) in anhydrous toluene (30 mL) was nitrogen degassed for 15 min before addition of Pd(PPh$_3$)$_4$ (0.17 g, 0.15 mmol). The reaction mixture was refluxed for 21 h under an inert atmosphere. After concentration under reduced pressure, the resulting residue was subjected to two successive column chromatographies on silica gel (eluent, cyclohexane/CH$_2$Cl$_2$ 90:10) to give a orange-red solid, which was further recrystallized from a mixture of CH$_2$Cl$_2$ and EtOH leading to **Tol-4T** as an orange-red crystalline powder (0.27 g, 53% yield). Mp 212−214 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.30 (s, 12H), 7.03 (d, 2H, ^3J = 4.1 Hz), 7.05 (d, 8H, ^3J = 8.2 Hz), 7.07 (d, 2H, ^3J = 4.1 Hz), 7.08 (s, 2H), 7.13 (d, 8H, ^3J = 8.3 Hz), 7.17 (dt, 2H, ^3J = 7.6 Hz, ^4J = 1.1 Hz), 7.28 (dt, 2H, ^3J = 7.5 Hz, ^4J = 0.8 Hz), 7.34 (d, 2H, ^3J = 7.5 Hz), 7.42 (d, 2H, ^3J = 7.4 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 21.0, 63.2, 119.4, 119.5, 124.0, 124.2, 124.3, 124.5, 125.09, 126.14, 127.6, 127.8, 129.1, 135.7, 136.5, 136.96, 137.01, 140.0, 140.1, 141.6, 153.3, 156.4. MS (70 eV, EI) m/z (I%) = 866 (M$^{+\cdot}$, 100), 433 (80). ESI$^+$ HRMS: calcd for C$_{58}$H$_{42}$S$_4$ 866.21694; found 866.2168. UV−vis (CH$_2$Cl$_2$): λ_{max} = 452 nm.

Supporting Information Available: Synthetic procedures for compounds **2**−**5**, **17**, and **18**; thermal stability data for **4T**, **Oct-4T**, and **Tol-4T**; MALDI-TOF mass spectra of **4T**; cyclic voltammograms of **2T** and **Tol-4T**; absorption and emission spectra of **Tol-4T**; emission spectrum of a film of **Oct-4T**; transfer characteristic and log(I_{DS}) vs V$_G$ plot of an OFET based on **4T**; ^{1}H and ^{13}C NMR spectra of new compounds; and crystallographic data for **Tol-4T** presented in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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