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Dimers of Anthrathiophene and Anthradithiophene Derivatives: Synthesis and Characterization

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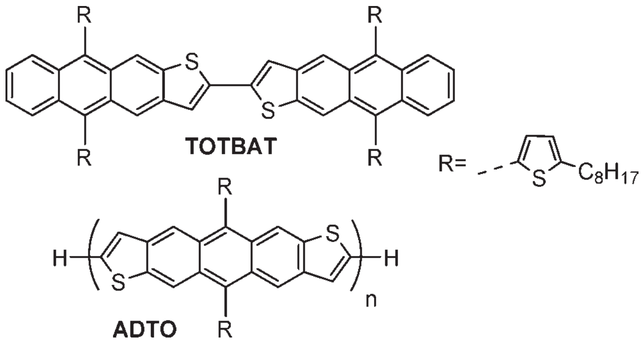
ABSTRACT



Synthesis, isolation, and characterization of derivatives of an anthrathiophene dimer (TOTBAT) and of anthradithiophene oligomers (ADTO), possessing octylthiophene units on their backbone, are described. These semiconductors are prepared through oxidative copper(II) chloride coupling. The spectroscopic properties and stability of these newly synthesized semiconductors were evaluated and supported by quantum-chemical calculations.

During the past decade, a myriad of studies has been reported in the literature on several organic semiconductors (oligothiophenes, phthalocyanines, acenes, etc.) and their use in a variety of devices such as field-effect transistors, light-emitting diodes, sensors, and photovoltaic cells.[1] Currently, fused linear (hetero)acenes represent one of the most studied categories of organic semiconductors. For example, recent publications describe the functionalization of pentacene and/or anthradithiophene cores by trialkylsilylethynyl or thienyl groups to lead to soluble semiconductors.[2] In addition, it has been shown that such substituents

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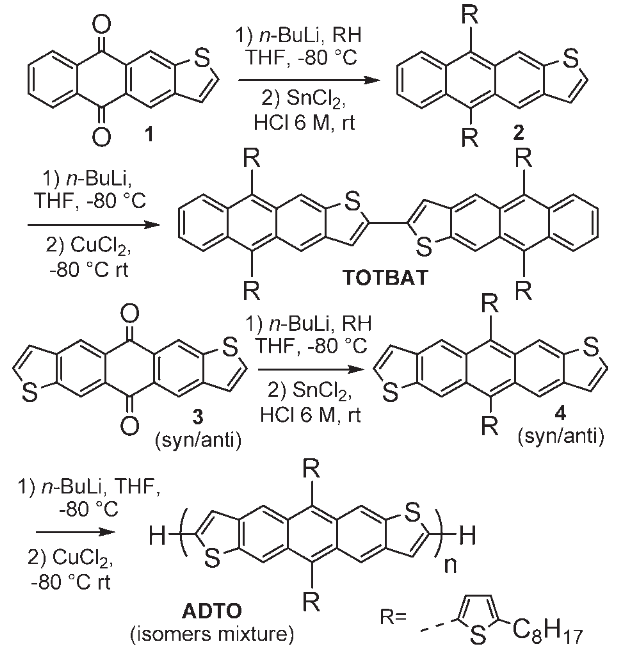
also considerably improve the stability of these derivatives toward photo-oxidation, especially in solution.[2a−c,3] Following the same strategy, Miller et al. have described a nonacene derivative which was persistent for 24 h in solution and six weeks as a solid.[4] However, while there are many studies on both synthesis and functionalization of extended fused linear (hetero)acenes,[2,4,5] only a few have been reported on their oligomerization.[6]

Herein, we describe the synthesis and characterization of the first dimer of anthrathiophene (AT) and the oligomers of anthradithiophene (ADT). AT and ADT cores have been preferred to tetracene and pentacene skeletons to form the central π-systems of the oligomers, due to their higher stability upon thermal and photoinduced decomposition.[6f,7] In order to fulfill solubility requirements and to prevent these target molecules from photodegradation, 2-octylthienyl groups were attached to positions 5,10 and 5,11 of AT and ADT backbones, respectively. The spectroscopic properties of these newly synthesized semiconductors were evaluated and supported by quantum-chemical calculations.

TOTBAT and **ADTO** were prepared as presented in Scheme 1. Synthesis of AT **2** and ADT **4** monomers was achieved with yields of respectively 54% and 17%, by reaction of anthra[2,3-*b*]thiophene-5,10-dione (**1**) and anthra[2,3-*b*:6,7-*b*′]dithiophene-5,11-dione (**3**) with the corresponding lithium intermediate of 2-octylthiophene, followed by reduction/deoxygenation using $SnCl_2$ in 6 M HCl_{aq} solution. Oxidative coupling of the lithiated derivatives of **2** and **4**, in the presence of $CuCl_2$, afforded the target products **TOTBAT** and **ADTO**, respectively. It is noteworthy that the last step involves lithiation of position 2 of the fused thienyl unit of ADT and AT skeletons, using *n*-BuLi. To the best of our knowledge, it is the first time that this kind of reaction on an ADT core is reported in the literature. At the end of the oligomerization step, water was added to the reaction mixture in order to fully precipitate the oligomers which were subsequently isolated by filtration. Thin layer chromatography in different solvents indicated that oligomers are impossible to separate. Further purification was performed by successive washes with water, methanol, and petroleum ether, to provide **TOTBAT** (red solid) and **ADTO** (dark purple solid) with yields of respectively 68% and 53%. Note that **ADTO** was produced as a mixture of isomers since its synthesis was carried out starting from a mixture of syn/anti isomers of anthra[2,3-*b*:6,7-*b*′]dithiophene-5,11-dione (**3**).

Scheme 1. Synthesis of **TOTBAT** and **ADTO**



The AT dimer and ADT oligomers possess reasonable solubilities (up to 10^{-2} M) in several common organic solvents, such as chloroform, dichloromethane, toluene, *o*-dichlorobenzene, and nitrobenzene, and were characterized by NMR and UV−visible spectroscopies.

As expected, ^{1}H NMR spectra of anthrathiophene **2** and **TOTBAT** are quite alike (Figure.SI15), except for the proton signals of the benzothiophene moiety (Figure 1). Through dimerization, the doublet centered at 7.44 ppm, assigned to proton H^3 of monomer **2**, becomes a singlet ($\delta = 7.51$ ppm) for the dimer **TOTBAT**, and the signal for H^2, observed at $\delta = 7.32$ ppm, in ^{1}H NMR spectrum of **2**, disappears. It is also noticed that peaks for H^4 and H^{11} ($\delta = 8.47$ and 8.42 ppm) in the ^{1}H NMR spectrum of compound **2** appear closer and at lower chemical shifts ($\delta = 8.36$ and 8.35 ppm) for the corresponding dimer.

On the contrary, it was difficult to obtain a highly resolved NMR spectrum for **ADTO**. Very broad signals

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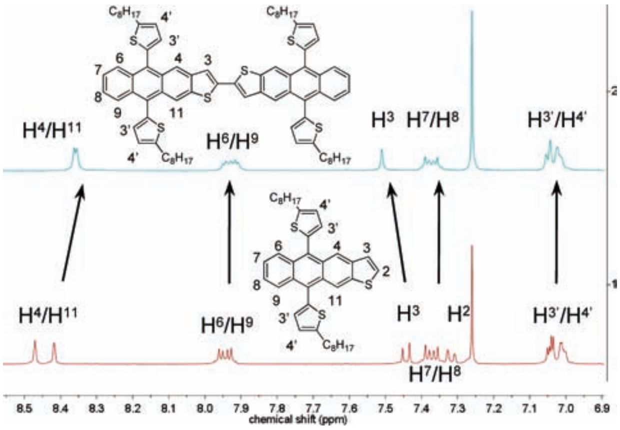

Figure 1. Comparison of the aromatic region of ^{1}H NMR spectra of **2** (1) and **TOTBAT** (2) ($CDCl_3$, 300 MHz, 25 °C).

were indeed observed upon recording the ^{1}H NMR spectrum in CD_2Cl_2 (Figure.SI16). Several attempts such as varying the solvent ($CDCl_3$, CS_2, benzene-d_6, nitrobenzene-d_5) and the temperature were performed in order to obtain a higher resolution spectrum. Unfortunately, these attempts were unsuccessful: no noticeable change in the ^{1}H NMR spectrum resolution was observed using other solvents, and degradation of the sample occurred upon increasing the temperature (40 °C). The difficulty in recording a well-defined NMR spectrum was attributed to the presence of a mixture of oligomers in solution. Indeed, **ADTO** is synthesized by oxidative coupling of lithiated species of ADT **4**. The latter has two terminal thiophenes that induce the formation of *non*-, *mono*-, and *di*lithiated intermediates which led to the formation of oligomers through the oxidative coupling. The broad signals observed for **ADTO** appear at similar chemical shifts as those for its corresponding monomer **4** (Figure.SI16). This indicates that ADT oligomers were formed. Structures of the AT dimer and ADT oligomers were confirmed by MALDI-ToF MS through the observation of isotopic patterns at m/z = 1242.5 for **TOTBAT** and at m/z = 1354.5 (dimer), m/z = 2031.7 (trimer), m/z = 2708.0 (tetramer), and m/z = 3387.2 (pentamer) for **ADTO** (Figure.SI19 and Figure.SI20). The Carothers equation (see SI) gives a number average degree of polymerization of 2.13 for **ADTO**, which indicates that the reaction affords mainly the dimer with traces of trimer, tetramer, and pentamer.[8]

Optical measurements were carried out in chloroform solutions of the compounds (Table.SI1, Figures.SI1−7) and were confronted to theoretical simulations on AT and ADT dimers. To do so, geometry optimizations have been performed at the density functional theory (DFT) level, using the B3LYP functional[9] and the 6-31G(d,p) basis set. The conjugated backbone has been imposed to be planar, and the octyl chains of the 2-octylthienyl groups were replaced by methyl chains in the geometry optimizations to reduce the computational costs. The pending thiophene units are found to be perpendicular to the conjugated core in the optimized geometry. The vertical transition energies to the lowest excited states of the isolated compounds were computed from the optimized geometries with the time-dependent density functional theory (TD-DFT) formalism,[10] using the same functional and basis set. The Gaussian 03 package was used for all calculations.[11]

Compounds **2** and **4** present typical absorption spectra profiles of AT and ADT derivatives,[6a,7] showing an intense band close to 300 nm (286(4.34) nm(eV) for **2**, 305(4.07) nm(eV) for **4**) and three additional waves located at lower energies: 410(3.02), 433(2.86), 461(2.69) nm(eV) for AT **2** and 451(2.75), 481(2.58), 516(2.40) nm(eV) for ADT **4**. Since the calculations yield a single optically coupled excited state in this energy range, the latter are assigned to vibronic satellites. **ADTO** shows a more broadened UV−visible spectrum compared to those of the monomers **2**, **4** and of the dimer **TOTBAT** (Figure.SI1). Such spectral characteristics are due to strong interactions between molecules in solution[12] and, to some extent, to the presence of low amounts (a few mole percent) of trimer, tetramer, and pentamer. Bathochromic shifts of the absorption maxima of 55(0.29) nm(eV) and of 48(0.22) nm(eV) are observed from **2** to **4** and from **TOTBAT** to **ADTO**, respectively. The calculated transition energies follow the same trends going from **2** to **4** (0.31 eV) and from the **TOTBAT** to **ADT** dimer (0.27 eV). Additionally, both oligomers present red-shifted absorption maxima compared to their monomer counterparts: 35(0.19) nm(eV) (63(0.32) nm(eV) in theory) between **2** and **TOTBAT**; 28(0.12) nm(eV) (72(0.28) nm(eV) in theory) between **4** and **ADTO**. The observed bathochromic shifts are due to the extension of the π-system.[13] The AT dimer and **ADTO** also present molar extinction coefficients (ε) higher than those of the monomers **2** and **4**, by about a factor of 2; this increase is also consistent with the quantum-chemical calculations (Figure.SI21). The synthesized compounds show fluorescence in solution (Figure.SI2). The expansion of the conjugated aromatic system leads to a red shift of the emission maximum that is in agreement with the observations made in the UV−visible studies.[13] Bathochromic shifts of 48(0.23) nm(eV) and of 57(0.22) nm(eV) are measured within the monomer (**2** and **4**) and the oligomer series (**TOTBAT** and **ADTO**) respectively. The same effect (extension of the π-system) also leads to an increase of 57(0.26) nm(eV) of the emission maximum between **2** and

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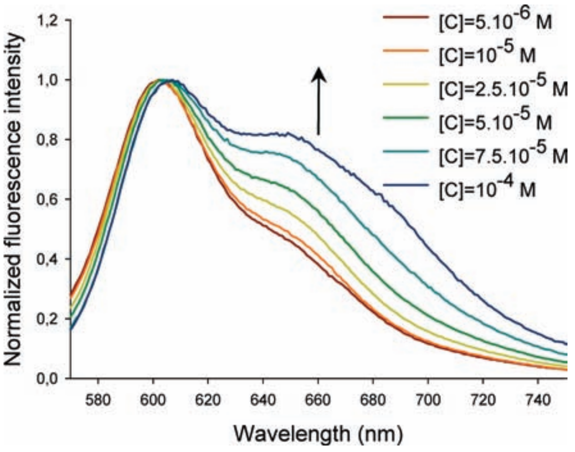

Figure 2. Evolution of the emission spectrum of **ADTO** in $CHCl_3$ upon increasing concentration from 5×10^{-6} M to 10^{-4} M.

TOTBAT as well as to a difference of 66(0.25) nm(eV) between **4** and **ADTO**. Figure 2 shows the evolution of the **ADTO** emission pattern as a function of concentration. At 5×10^{-6} M, the **ADTO** fluorescence spectrum exhibits one band at 604(2.05) nm(eV) and one shoulder around 650(1.91) nm(eV). When the solution becomes more concentrated, the intensity of the shoulder at ~650 nm increases. The change in shape of the **ADTO** spectrum is attributed to oligomer aggregation in solution and is driven by π-stacking interactions. When the same experiment was executed on **TOTBAT**, no noticeable evolution in the fluorescence spectrum was observed by varying the concentration from 5×10^{-6} M to 10^{-4} M (Figure.SI3). It can therefore be concluded that **TOTBAT** does not form aggregates in solution, in the concentration range studied.

The stability of **2**, **4**, **TOTBAT**, and **ADTO** toward photo-oxidation was investigated by monitoring the absorption decay of 10^{-5} M chloroform solutions under ambient light at room temperature (Figures.SI4−7). Taking into account an absorption decay of 50% of the lower energy bands of all synthesized compounds, the stability order observed is **2** (90 min) > **4** (30 min) > **ADTO** (15 min) > **TOTBAT** (8 min). It is noticed that the photodegradation of AT **2** follows a linear tendency whereas the absorptions of the others decrease exponentially (Figure.SI8). The AT dimer and ADT oligomers were found to be much more sensitive toward photo-oxidation than their corresponding monomers. The higher stability of **2** can be rationalized by the calculated energy of the HOMO levels among the four molecules (Table.SI1) which is the deepest in the case of compound **2**. **TOTBAT** and **ADTO** do not verify this tendency since the latter presents a higher stability, by about a factor of 2, although theoretical calculation shows that an ADT dimer has a less stable HOMO level (−4.75 eV) than the AT dimer **TOTBAT** (with a deeper HOMO at −4.91 eV). It is known that the photoinduced degradation of linear (hetero)acenes is due to the formation of an endoperoxide bridge across the most reactive central ring.[3] It has been previously established that **ADTO** tends to form aggregates in solution. This behavior is likely responsible for the better photoresistance of **ADTO** since the most reactive positions become less accessible due to aggregation. Furthermore, several isosbestic points were observed in **2** and **4** UV−vis spectra (Figures.SI4−5). This indicates the coexistence in solution of two species: the starting derivatives and their corresponding oxidized species. Such a phenomenon is however not observed for **TOTBAT**. This might imply that the photodegradation of the latter dimer occurs following a more complex mechanism. Throughout all these experiments, it was also found that freshly prepared solutions of all products stored in the dark remain stable for at least 24 h.

In conclusion, we have successfully prepared the first derivatives of an anthrathiophene dimer and of anthradithiophene oligomers. The proposed synthetic strategy involves an oxidative coupling of monolithiated AT or ADT intermediates, using $CuCl_2$ as an oligomerization agent. These newly fused heteroacene oligomers exhibit reasonable stabilities in solution without light exposure. It has been proven by optical experiments that **ADTO** tends to form aggregates in solution, rendering the ADT oligomers more resistant toward photo-oxidation than the anthrathiophene dimer **TOTBAT**.

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Supporting Information Available. Experimental procedures, optical studies, NMR, mass and theoritical spectra of new compounds are shown as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.