Synthesis and Properties of Conjugated Polymers Based on a Ladderized Anthanthrene Unit

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Supporting Information

ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) are interesting building blocks for the preparation of conjugated polymers due to their extended π surface and planar conformation. However, their use as comonomer in conjugated polymers often leads to nonplanar main chains as a consequence of high steric hindrance at the linking point. Herein, we report the synthesis of a ladderized anthanthrene unit using an sp3 carbon bridge. Three conjugated copolymers with fluorene, isooindigo, and biithiophene derivatives have been synthesized and characterized to study the effect of such ladderization on the electronic properties. The dihedral angle between the ladderized anthanthrene and adjacent units has been significantly reduced by the formation of the sp3 carbon bridge, thus eliminating the steric hindrance with the proton at the peri position of the anthanthrene unit and red-shifting the absorption spectrum by 25 nm.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are very useful, yet underestimated building blocks for the preparation of organic semiconductors. Their extended π surface, ease of functionalization, and large variety of edge topologies have allowed the preparation of small molecules and polymers with a wide range of band gaps. Moreover, their flat surface allows for strong π−π interactions in the solid state, leading to excellent morphological features for improved charge transport properties. Hence, PAH-based semiconductors have shown promise as the active component for different applications, including organic solar cells (OSCs), field-effect transistors (OFETs), and light-emitting diodes (LEDs).

Despite their obvious advantages, a rather low number of large PAHs have been introduced into conjugated polymers for organic electronics, the main limitations being the scarce availability of functionalized PAHs and their low solubility. Recently, we and others showed that PAH 4,10-dibromoanthanthrene, a low-cost dye known as vat orange 3, is well suited for the preparation of a wide diversity of organic semiconductors. This compound allows for functionalization at the ketone (6,12) and bromine (4,10) positions using well-known coupling methods such as Suzuki–Miyaura, Castro–Stephens–Sonogashira, Wittig-type reactions, and so on. Using these reactions, moderate band gap conjugated polymers and small molecules for OSCs and OFETs have been prepared. However, the synthesis of low band gap materials from 4,10-dibromoanthanthrene is very challenging because the protons at the peri positions (3,9) induce steric hindrance with the adjacent aryl or heteroaryl units attached at the 4 and 10 positions. Strategies including the formation of intramolecular H-bonding or the addition of alkyne spacers can help to reduce the steric hindrance and lower the band gap, but these are not sufficient to obtain low-band gap polymers.

Herein, we report a new approach to reduce the dihedral angle between anthanthrene and π-conjugated moieties attached at the 4 and 10 positions that consist of creating an sp3 carbon bridge at the 3 and 9 positions of the anthanthrene. The resulting π-extended, ladderized anthanthrene moiety was polymerized with three monomers, namely, fluorene, biithiophene, and isooindigo, and their properties were characterized using thermal analysis, optical spectroscopy, and electrochemistry. Interestingly, the elimination of steric hindrance at the peri position leads to a red shift (25 nm) of the absorption band.

2. RESULTS AND DISCUSSION

The synthetic strategy for the monomers and polymers is shown in Scheme 1. 6,12-Dioctyloxy-4,10-dibromoanthanthrene (compound 1), obtained in one step from 4,10-dibromoanthanthrene, was borylated at the 4 and 10 positions using a standard Miyaura reaction to give compound 3. Then, a two-fold Suzuki–Miyaura coupling with methyl 2-iodobenzoate or methyl 5-bromo-2-iodobenzoate provides compounds 4a and 4b, respectively. Treatment of these compounds with an excess of 4-octylphenyl lithium in THF at −78 °C followed by a BF3·OEt2-catalyzed intramolecular

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Friedel–Crafts reaction lead to compounds \( 5a \) and \( 5b \) in 73 and 67% yields over two steps, respectively. Compound \( 5b \) was polymerized with bisborylated isoindigo and fluorene derivatives using a Suzuki–Miyaura coupling to give \( \text{PsAI} \) and \( \text{PsAF} \) and \( \text{PsABT} \).
and PsAF, respectively. After 72 h of reaction, the polymers were precipitated in methanol, washed in a Soxhlet apparatus using methanol, hexanes, and acetone successively to remove catalyst residues and oligomers, and extracted using chloroform. For the synthesis of PsABT, a Stille coupling between 5,5′-trimethylstannyl-2,2′-bithiophene and compound 5b was used to provide the polymer that was purified using the purification method used for PsAI and PsAF. All three polymers are highly soluble in chloroform, THF, and aromatic solvents. The excellent solubility of these polymers can be ascribed to the presence of two substituted carbons, which prevent aggregation through \( \pi-\pi \) interactions and to the presence of six octyl chains per ladderized anthanthrene unit.

The molecular weight values were determined using size exclusion chromatography (SEC) with polystyrene standard in trichlorobenzene at 110 °C as the eluent. The results are summarized in Table 1. All three polymers exhibit high molecular weight with \( M_n \) values ranging from 33.6 (PsAF) to 103.6 kDa (PsABT), corresponding to a degree of polymerization \( (X_n) \) between 17 and 63.

The \( T_d \) values were determined using thermogravimetric analysis (TGA). In all cases, the polymers started decomposing at ca. 300 °C (5% weight loss), meaning that the ladderized anthanthrene is likely the most thermal-sensitive part of the polymers. The \( T_d \) values are very similar to those measured for anthanthrene-based polymers\(^{16,29} \) and are thermally stable enough for the large majority of organic electronics applications.

The optical properties of the polymers were determined using UV–vis and fluorescence spectroscopy, and the results are summarized in Figures 1 and 2 and Table 2. To study the influence of the planarization through ladderization, a model compound (2, Scheme 1) was synthesized, characterized by UV–vis spectroscopy, and compared to compound 5a, which differs from the monomer 5b only by the absence of bromine atoms at both ends. As expected, the planarization through ladderization shifted the absorption toward longer wavelength by 25 nm in solution (461 nm for 2 vs 486 nm for 5a), while the fluorescence band red-shifted by 31 nm. Also, the planarization yields to a decrease of the fluorescence quantum yield in solution from 71% for compound 2 to 48% for compound 5a. Density functional theory (DFT) calculations (specifically \( \omega \)-B97X-D/6-31 + G(d,p))\(^{30} \) have been performed on compound 2 to assess the dihedral angle (\( \theta \)) between the anthanthrene core and the aryl units (Figure S2). As hypothesized, the phenyl moieties adopt a nonplanar position relative to the anthanthrene unit with a dihedral angle ranging from 61–63°, with a high barrier of energy to planarity (~21 kcal/mol) due to the steric hindrance. This high barrier to planarity might explain the poor electronic communication usually observed for anthanthrene derivatives.\(^{21} \) As a consequence of their rigidity, both compounds 2 and 5a exhibit a small Stokes shift and a well-defined vibronic structure. Likewise, the polymers PsAF and PsABT also exhibit small Stokes shift, indicative of a quite rigid polymer backbone whose conformation in both ground and excited states are very similar.\(^{31} \) Additionally, DFT calculations were performed to study the dihedral angle for simplified structures of PsAI (37°), PsAF (38°), and PsABT (30°). PsAF exhibits a shallow barrier to rotation of about 2.75 kcal/mol between two structures, while PsABT is able to rotate freely with a barrier around 2.86 kcal/mol. PsAI presented convergence issues, and hence, only the minimum value is reported.

### Table 1. Characterization of Polymers

| Polymer | Yield (%) | \( M_n \) (×10^3 g/mol) | \( M_w \) (×10^3 g/mol) | PDI | \( T_d \) (°C) |
|---------|-----------|------------------------|------------------------|-----|---------------|
| PsAI    | 72        | 62.5                   | 133.5                  | 2.1 | 341           |
| PsAF    | 75        | 33.6                   | 52.2                   | 1.6 | 302           |
| PsABT   | 72        | 103.6                  | 172.8                  | 1.7 | 297           |

* Determined from SEC analysis. Determined using thermogravimetric analysis under nitrogen at 5% weight loss.

### Table 2. Optical Properties of the Model Compounds and Polymers

| Compound | \( \lambda_{max} \) sol (nm) | \( \lambda_{max} \) film (nm) | \( E_{sol} \) (eV) | \( \lambda_{sol} \) (nm) | Stokes shift (nm) | \( \phi_F \) (%) |
|----------|-----------------------------|-------------------------------|-------------------|---------------------|-------------------|-----------------|
| 2        | 461                         | 470                           | 2.66              | 9                   | 71                |
| 5a       | 486                         | 502                           | 2.51              | 16                  | 48                |
| PsAI     | 488                         | 502                           | 2.00              |                     |                   |                 |
| PsAF     | 494                         | 509                           | 2.47              | 15                  |                   |                 |
| PsABT    | 502                         | 523                           | 2.43              | 21                  |                   |                 |

Figure 1. UV–vis spectra (CHCl₃, solid lines) and fluorescence spectrum (CHCl₃, dashed lines) of compounds 2 and 5a.

Figure 2. UV–vis spectra (CHCl₃, solid lines; thin films, dashed lines) of the polymers.
All three polymers exhibit strong absorption in the UV and visible regions that extend up to 700 nm in the case of PsAI. Surprisingly, the extension of conjugation through the formation of a conjugated polymer did not have a significant effect on the $\lambda_{\text{max}}$ value for PsAF and PsAI whose absorption spectrum in solution is red-shifted by only 8 and 2 nm compared to monomer 5a, respectively. This result suggests that the electronic interaction between the anthanthrene and the isindigo or fluorene unit is still rather weak. The very broad absorption band centered at $\lambda = 563$ nm can be attributed to the $\pi$-$\pi^*$ transition of the isindigo unit, confirming the inefficient conjugation with the anthanthrene unit.32 PsABT exhibits a slightly higher $\lambda_{\text{max}}$ value (502 nm) due to the presence of the smaller thiophene unit. Going from solution to solid state does not produce a significant change in the absorption spectra as the $\lambda_{\text{max}}$ values shifted only slightly (9 nm at most) for all three polymers. Although more studies need to be performed to understand the poor electronic interaction between the bridge anthanthrene and various comonomers, one can argue that the presence of two bulky 4-octyloxyphenyl groups at the methylene bridge induces significant steric hindrance and linking position, preventing the moieties to adopt a coplanar conformation. Müller and co-workers observed a similar behavior for ladderized poly(p-phenylene-alt-9,10-anthrylene)s and reported that the use of smaller methyl groups at the sp3 carbon bridge instead of bulky phenyl rings is an efficient way to promote planarization within the polymer backbone.30

Cyclic voltammetry (CV) measurements were performed on the three polymers, and the results are summarized in Table 3 and Figures S5–S7. The polymers were deposited on a platinum electrode, and the measurements were taken relative to a Ag/AgNO3 reference electrode in acetonitrile with tetrabutylammonium tetrafluoroborate (NBu4BF4, 0.1 M) as the electrolyte. The energy values of both the HOMO and LUMO levels were determined as previously described.33

All the peaks in the anodic and cathodic regime are only partially reversible in the conditions used (see Supporting Information). Despite the apparent weak electronic communication between anthanthrene and the units attached to it as observed by electronic spectroscopy, the oxidation and reduction potential values of all three polymers are quite different, meaning that the comonomers contribute, to some extent, in both the HOMO and LUMO energy levels. In fact, PsABT, which as an electron-rich bithiophene unit, possesses a slightly lower $E_{\text{ox}}$ value than PsAI (0.58 vs 0.64 V). Likewise, the lower $E_{\text{red}}$ value is measured for the polymer with the more electron-deficient unit (−1.10 V). The band gap values of all three polymers, although a little underestimated by electrochemistry, follow the same trend as observed in electronic spectroscopy (PsAI < PsAF ≈ PsABT).

Potential values have been measured at the onsets of the oxidation and reductions peaks. The values are reported against Ag/AgNO3, at a scan rate of 50 mV·s⁻¹. With this reference electrode, the $E_{1/2}$ value for Fc/Fc’ was measured at 0.091 V. Vacuum levels were determined electrochemically with the Fc/Fc’ value at 4.8 eV.

### 3. CONCLUSIONS

We showed that the band gap of anthanthrene derivatives can be lowered by introducing an sp3 carbon bridge between anthanthrene and the phenyl group attached to it at the 4 and 10 positions. Although the bathochromic shift induce by this bridge is quite limited (25 nm), three copolymers whose properties can be modulated by the nature of the comonomers have been prepared. Interestingly, a polymer (PsAI) with a band gap value of 2.0 eV has been prepared, which is one of the lowest values reported to date for an anthanthrene-based conjugated polymers.16,34 The replacement of the 4-octyloxyphenyl group at the sp3 carbon bridge by smaller groups or the replacement of the phenyl rings at the 4 and 10 positions by aryls such as thiophene are strategies that could be envisioned to further reduced the band gap and anthanthrene derivatives.

### 4. EXPERIMENTAL SECTION

#### 4.1. General.

NMR analyses were performed on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or on an Agilent DD2 500 MHz. Peaks are identified as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and dt (doublet of triplets), and J values are reported in hertz (Hz). Chemical shifts are reported on a ppm scale (δ) relative to the residual solvent peak. High-resolution mass spectra (HRMS) analyses were performed on an Agilent 6210 TOF-LCMS instrument (APPI ion source, Agilent Technologies, Toronto, Canada). $M_h$ and $M_w$ values of polymers were measured at 110 °C by size exclusion chromatography (polystyrene as the standards) using a high-temperature Varian Polymer LaboratoriesGPC220 (RI detector) in 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as the eluent at a flow rate of 1 mL min⁻¹ and a sample concentration of 1.0 mg mL⁻¹ in TCB.35 Absorption and photoluminescence properties of the compounds were measured using a Varian diode-array spectrophotometer (model Cary 500) and Varian Cary Eclipse fluorescence spectrophotometer, respectively, with a 1 cm path length quartz cells. Cyclic voltammograms were recorded on a potentiostat (Solartron 1287) with platinum electrodes (working and counter electrodes) at a scan rate of 50 mV s⁻¹ and a Ag/Ag⁺ (0.01 M AgNO3 in MeCN) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M Bu₄NBF₄ in MeCN. Bu₄NBF₄ (98%, Aldrich) is purified using recrystallization in a mixture of water and methanol and dried at 70 °C under vacuum.36 In these conditions, for a freshly prepared reference electrode, the half-wave oxidation potential ($E_{1/2}$) of ferrocene should be around 0.091 V versus Ag/Ag⁺ as reported by Li et al.37 The HOMO and LUMO energy levels are determined from the oxidation and reduction onsets.33,38 The onset potentials ($E'_i$) are determined at the position where the current starts to differ from the baseline.

$$E_{\text{HOMO}} = \left( \frac{E'_{\text{ox vs Ag/Ag}^+}}{(E_{\text{Ferrocene vs Ag/Ag}^+})} \right) + 4.8$$

$$E_{\text{LUMO}} = \left( \frac{E'_{\text{red vs Ag/Ag}^+}}{(E_{\text{Ferrocene vs Ag/Ag}^+})} \right) + 4.8$$

TGA spectra were recorded using a Mettler TGA/SDTA 851e/SD/1100 °C instrument equipped with an MT1 model balance. The balance is protected with a constant flow of PP
nitrogen at a flow of 20 mL/min. Two milligrams of samples was weighted and heated from 50 to 600 °C at 20 °C/min.

Chemical reagents were purchased from Sigma–Aldrich Co., Canada, Oakwood Products, Inc., or Strem Chemicals, Inc. and were used as received. 4,10-Dibromoanthanthrene has been kindly provided by Heubach GmbH as a Monolite Red 316801 product. 1,1′-bis(2-hexyldecyl)-2,2′-bithiophene, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diido-decylfluorene, and 4,10-dibromo-6,12-bis(octyloxy)anthanthrene were synthesized according to literature procedures. 

Density functional theory calculations were performed with Gaussian 16 revision B0.141 using the B3LYP-D3 functional and 6-31 + G(d,p) basis set. To simplify the calculations, the C6H17 alkyl chains were replaced with methyl groups. The model compound 2 has four very close geometries in terms of energy due to the angles formed by the phenyl groups. The four geometries are shown in Figure S1, and thermochemistry energies due to the angles formed by the phenyl groups. The molecules were dissolved in THF (126 MHz) after the desired compound as a yellow solid (1.55 g, 68%). 1H NMR (400 MHz, chloroform-d): δ 9.15 (s, 2H), 9.10–9.07 (m, 2H), 8.78 (dd, J = 8.1, 0.9 Hz, 2H), 8.18 (s, J = 7.9 Hz, 2H), 4.41 (t, J = 6.4 Hz, 4H), 2.17 (dt, J = 14.3, 6.6 Hz, 4H), 1.88–1.79 (m, 4H), 1.51–1.31 (m, 16H), 0.95–0.90 (m, 6H). 13C NMR (126 MHz, chloroform-d): δ 150.25, 133.88, 133.85, 125.92, 125.72, 125.44, 124.94, 121.01, 120.73, 120.28, 83.88, 76.84, 31.96, 30.82, 29.74, 29.44, 26.50, 25.08, 22.75, 14.17. HRMS (APPI+): C50H52O2 [M + H]+ 785.5124; found, 785.5171.

4.1.3. Synthesis of Compound 4a. A screw-capped pressure vessel under nitrogen was charged with 4,10-dibromo-6,12-bis(octyloxy)anthanthrene (500 mg, 0.637 mmol), methyl 2-bromobenzoate (538 mg, 2.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (45 mg, 0.064 mmol), and triphenylphosphine (33 mg, 0.127 mmol). The mixture was purged and degassed with a flow of nitrogen for 30 min. Toluene (0.3 M, 20 mL) and an aqueous solution of 2 M K2CO3 (10 mL) were added. The mixture was heated at 110 °C for 2 days. Diethyl ether was added, and the organic layer was washed with water and dried with MgSO4. The solvent was evaporated under reduced pressure to afford the desired compound as a yellow solid (429 mg, 84%). 1H NMR (400 MHz, chloroform-d): δ 8.77 (d, J = 8.2 Hz, 2H), 8.33 (s, 2H), 8.17 (dt, J = 7.8, 1.7 Hz, 2H), 8.07–8.02 (m, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.77–7.73 (m, 2H), 7.71–7.67 (m, 2H), 7.66–7.62 (m, 2H), 4.38 (t, J = 6.6 Hz, 4H), 3.30 (d, J = 0.6 Hz, 3H), 3.26 (d, J = 0.6 Hz, 3H), 2.11 (dt, J = 14.2, 6.8 Hz, 4H), 1.73–1.65 (m, 4H), 1.47–1.40 (m, 4H), 1.38–1.26 (m, 12H), 0.89 (t, J = 6.8 Hz, 6H). 13C NMR (126 MHz, chloroform-d): δ 168.00, 167.96, 141.70, 141.65, 139.58, 132.04, 132.02, 131.93, 131.85, 130.36, 127.89, 125.93, 125.69, 124.06, 122.50, 122.17, 121.63, 120.39, 119.99, 119.74, 75.61, 51.84, 51.74, 31.38, 30.74, 29.55, 29.32, 26.27, 22.68, 14.11. HRMS (APPI+): C50H50O6 [M + H]+ 800.4077; found, 800.4101.

4.1.4. Synthesis of Compound 5a. A flask under nitrogen was charged with THF (5 mL) and 1-bromo-4-octylbenzene (269 mg, 0.999 mmol). The mixture was purged and degassed with a flow of nitrogen for 30 min. The solution was cooled at −78 °C. n-BuLi 1.6 M (0.62 mL, 1.00 mmol) was added dropwise to the solution. The mixture was stirred for 30 min. Compound 4a (100 mg, 0.125 mmol) solubilized in a minimal amount of THF was added dropwise to the solution. The
mixture was stirred for 18 h, and the temperature slowly increased to room temperature. The solvent was evaporated under reduced pressure, and the crude product was solubilized in CH2Cl2. The organic phase was washed with an NH4Cl saturated solution and dried with MgSO4 and the solvent was evaporated under reduced pressure. The product was solubilized in anhydrous CH2Cl2 in a flask under nitrogen. The solution was cooled at 0 °C. BF3·OEt2 (few drops) was added dropwise, and the solution was stirred for 2 h. The organic phase was washed with an NH4Cl saturated solution and dried with MgSO4, and the solvent was evaporated under reduced pressure. The solvent was evaporated under reduced pressure, and the crude product slowly increased to room temperature. The solvent was evaporated under reduced pressure, and the product was precipitated in cold MeOH and directly filtered, and dried under vacuum at 60 °C for 24 h to obtain the desired polymer. Yield (77 mg, 72%), (Mn = 62.5 kDa, Mw = 133.5 kDa, PDI = 2.1).

4.1.7. Synthesis of PsAF. A screw-capped pressure vessel under nitrogen charge with compound 5b (100 mg, 49.8 μmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-didodecylfluorene (44 mg, 49.8 μmol), tetrakis(triphenylphosphine)palladium(0) (1.1 mg, 1.17 μmol), and Aliquat 336 (1 drop) were pumped under vacuum, and the solvents were degassed for 40 min. Toluene (1 mL, 0.05 M) and 2 M K2CO3 solution (146 μL) were added before sealing the tube. This reaction is heated at 110 °C for 3 days. Once cooled to room temperature, the polymer was precipitated in cold MeOH and directly filtered in an extraction thimble. The residue was purified by Soxhlet extraction in methanol, acetone, and hexane and was recovered in chloroform. The solvent was evaporated, and the product was precipitated in MeOH, filtered, and dried under vacuum at 60 °C for 3 days. Once cooled to room temperature, the polymer was precipitated in cold MeOH and directly filtered in an extraction thimble. The residue was purified by Soxhlet extraction in methanol, acetone, and hexane and was recovered in chloroform. The solvent was evaporated, and the product was precipitated in MeOH, filtered, and dried under vacuum at 60 °C for 24 h to obtain the desired polymer. Yield (86 mg, 75%), (Mn = 33.6 kDa, Mw = 52.2 kDa, PDI = 1.6).

4.1.8. Synthesis of PsABT. A screw-capped pressure vessel under nitrogen charge with compound 5b (100 mg, 61.7 μmol), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (30.4 mg, 61.7 μmol), tris(dibenzylideneacetone)dipalladium(0) (1.1 mg, 1.23 μmol), and tri(o-tolyl)phosphine (1.5 mg, 9.49 μmol) were pumped under vacuum, and the solvent was degassed for 40 min. Toluene (1.6 mL, 0.038 M) and a 2 M K2CO3 solution (146 μL) were added before sealing the tube. This reaction is heated at 110 °C for 3 days. Once cooled to room temperature, the polymer was precipitated in cold MeOH and directly filtered in an extraction thimble. The residue was purified by Soxhlet extraction in methanol, acetone, and hexane and was recovered in chloroform. The solvent was evaporated, and the product was precipitated in MeOH, filtered, and dried under vacuum at 60 °C for 24 h to obtain the desired polymer. Yield (72 mg, 72%), (Mn = 103.6 kDa, Mw = 172.8 kDa, PDI = 1.7).

ASSOCIATED CONTENT

Supporting Information

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NMR spectra, cyclic voltammetry, optical properties, and DFT calculations (PDF)

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