

Synthesis and Properties of Conjugated Polymers Based on Ladderized Anthanthrene Unit

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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 non-planar main chains as a consequence of high steric hinderance at the linking point. Herein, we report the synthesis of a ladderized anthanthrene unit using a sp^3 carbon bridge. Three conjugated copolymers with fluorene, isoindigo and bithiophene derivatives have been synthesise and characterized to study the effect of such ladderization on the electronic properties. The dihedral angle between the ladderized anthanthrene and the adjacent units has been significantly reduced by the formation of the sp^3 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.^[1-2] Their extended π surface, ease of functionalization and the large variety of edge topologies have allowed to prepare small molecules and polymers with a wide range of bandgaps.³⁻⁵ Moreover, their flat surface allows for strong π - π interactions in the solid state, leading to excellent morphological features for improved charge transport properties.⁶⁻⁸ Hence, PAH-based semiconductors have shown promise as the active component for different applications, including organic solar cells (OSCs),⁹⁻¹¹ field-effect transistors (OFETs)¹² and light-emitting diodes (LEDs).¹³

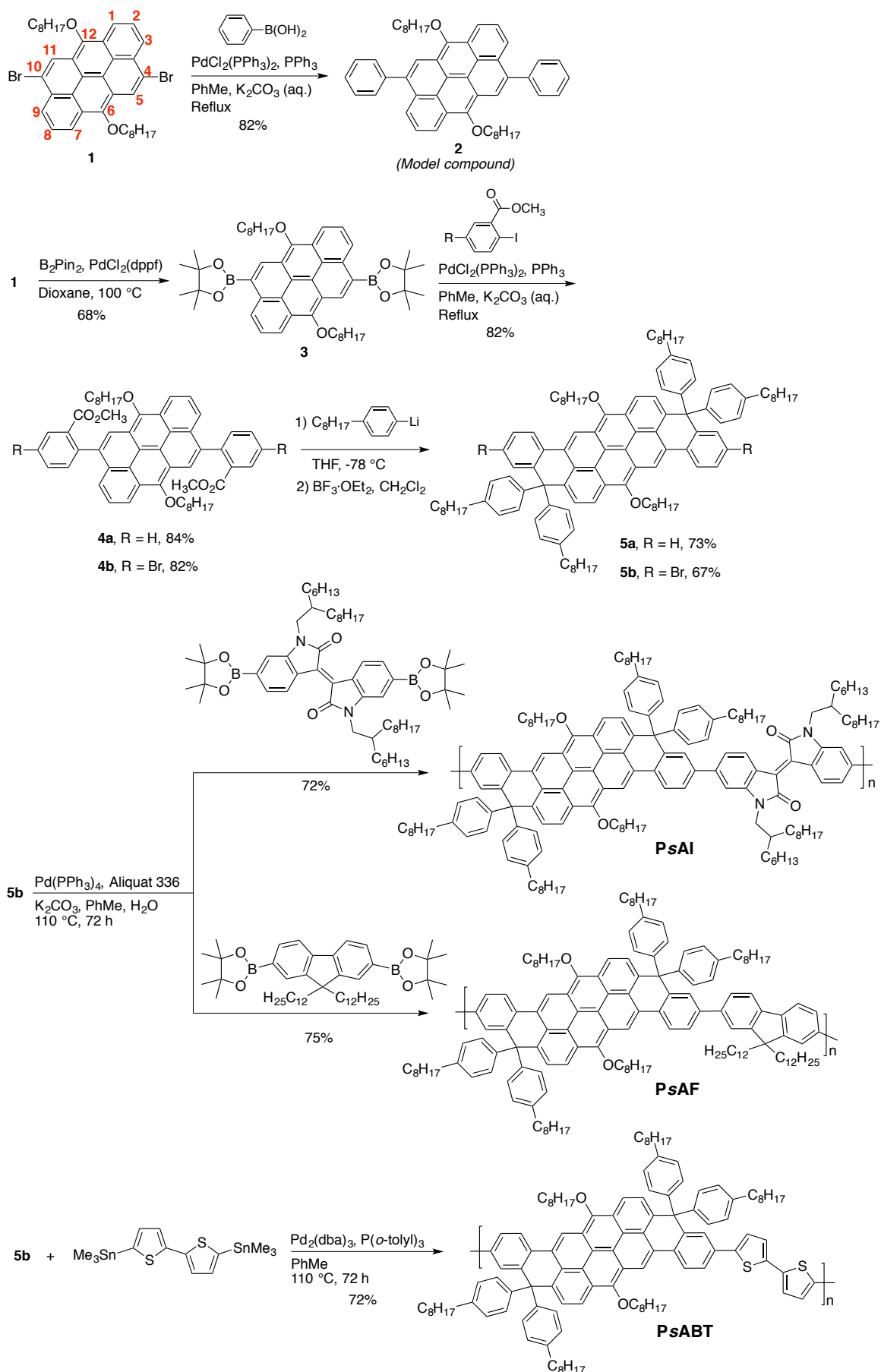
Despite their obvious advantages, a rather low number of large PAHs have been introduced into conjugated polymers for organic electronics, the main limitations being the scarce availability of functionalized PAHs and their low solubility. Recently, we and others showed that PAH 4,10-dibromoanthanthrone, a low-cost dye known as vat orange 3, is well suited for the preparation of a wide diversity of organic semiconductors.¹⁴⁻¹⁹ 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-Stephen-Sonogashira, Wittig-type reactions, and so on.^{20,21} Using these reactions, moderate bandgap conjugated polymers and small molecules for OSCs and OFETs have been prepared.^{15,16} However, the synthesis of low bandgap materials from 4,10-dibromoanthanthrone 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-bonding²² or the addition of alkyne spacers¹⁶ can help to reduce the steric hindrance and lower the bandgap, but these are not sufficient to obtain low band gap polymers.

Herein we report a new approach to reduce the dihedral angle between the anthanthrene and π -conjugated moieties attached at the 4 and 10 positions that consist of creating a sp^3 carbon

bridge at the 3 and 9 positions of the anthanthrene.^{23–26} The resulting π -extended, ladderized anthanthrene moiety was polymerized with three monomers, namely fluorene, bithiophene and isoindigo, 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-dibromoanthanthrone (compound **1**), obtained in one step from 4,10-dibromoanthanthrone,²⁰ 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 $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed intramolecular Friedel-Craft reaction²⁶ lead to compounds **5a** and **5b** in 73% and 67% yield over two steps, respectively. Compound **5b** was polymerized with bisborylated isoindigo²⁷ and fluorene²⁸ derivatives using Suzuki-Miyaura coupling to give **PsAI** and **PsAF**, respectively. After 72 hours of reaction, the polymers were precipitated in methanol, washed in a Soxhlet apparatus using methanol, hexanes and acetone successively to remove catalysts 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 π - π interactions, and to the presence of six octyl chains per ladderized anthanthrene unit.



Scheme 1. Synthesis of model compound **2** and ladderized anthanthrene-based polymers.

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 kDa (**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 the that ladderized anthanthrene is likely the most thermal-sensitive part of the polymers. The T_d values are very similar to those measured for anthanthrone-based polymers^{16,29} and thermally stable enough for the large majority of organic electronics applications.

Table 1. Characterization of polymers

Polymer	Yield (%)	M_n (g/mol) x 10 ³	M_w (g/mol) x 10 ³	PDI ^a	T_d (°C) ^b
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

^a Determined from SEC analysis. ^b Determined using thermogravimetric analysis under nitrogen at 5% weight loss.

The optical properties of the polymers were determined using UV-visible and fluorescence spectroscopy, and the results are summarized in Figures 1 and 2, and Table 2. In order to study the influence of the planarization through ladderization, a model compound (**2**, Scheme 1) was synthesized, characterized by UV-visible 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 for **5a**) while the fluorescence

band red-shifted by 31 nm. Also, the planarization yield to a decrease of the fluorescence quantum yield in solution from 71% for compound **2** to 48% for compound **5a**. Density functional theoretical (DFT) calculations (specifically ω -B97X-D/6-31+G(d,p))³⁰ have been performed on compound **2** to assess the dihedral angle (θ) between the anthanthrene core and the aryl units (Figure S2). As hypothesized, the phenyl moieties adopt a non-planar position relative to the anthanthrene unit with a dihedral angle ranging from 61-63°, with a high barrier of energy to planarity (~12 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, 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.

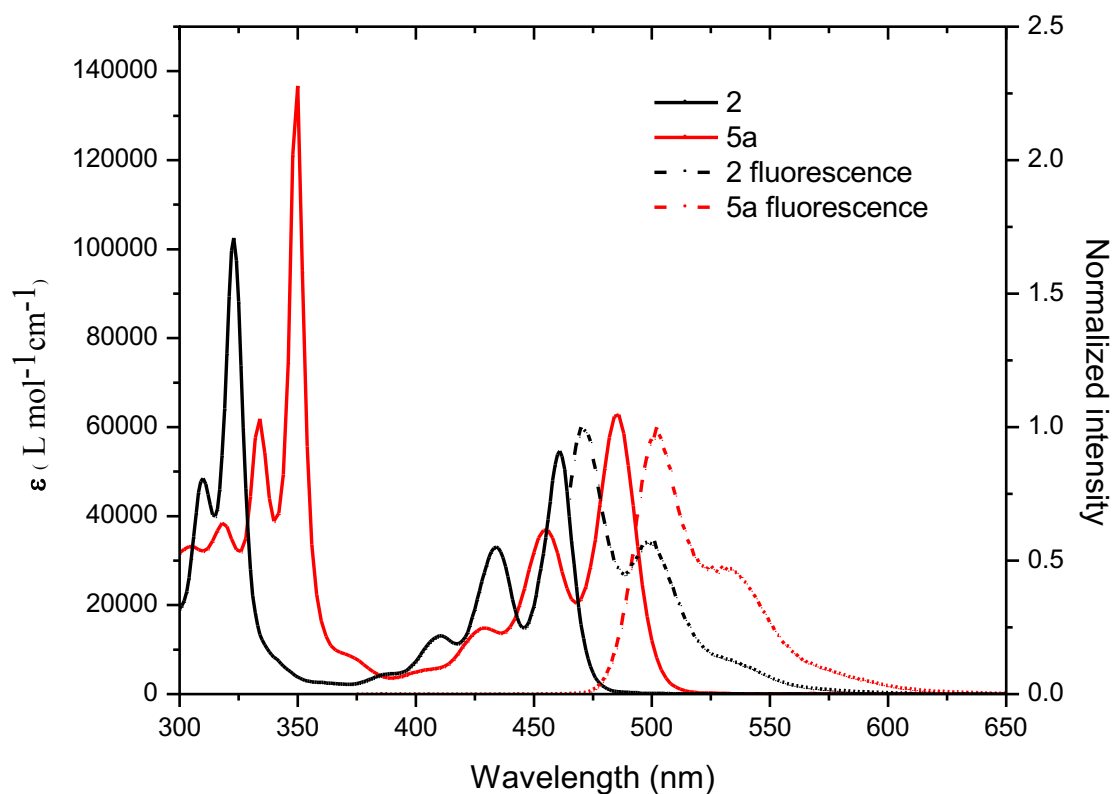


Figure 1. UV-vis spectra (CHCl_3 , solid lines) and fluorescence spectrum (CHCl_3 , dashed line) of compounds **2** and **5a**.

Table 2. Optical Properties of the model compounds and Polymers

Compound	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$E_{\text{g}}^{\text{sol}}$ (eV)	$\lambda_{\text{em}}^{\text{sol}}$ (nm)	Stokes Shift (nm)	ϕ_{F} (%)
2	461	-	2.66	470	9	71
5a	486	-	2.51	502	16	48
PsAI	488	493	2.00	-	-	-
PsAF	494	499	2.47	509	15	-
PsABT	502	511	2.43	523	21	-

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 λ_{\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 isoindigo or fluorene unit is still rather weak. The very broad absorption band centered at $\lambda = 563$ nm can be attributed to the π - π^* transition of the isoindigo unit, confirming the inefficient conjugation with the anthanthrene unit.³² **PsABT** exhibits a slightly higher λ_{\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 λ_{\max} values shifted only slightly (9 nm at most) for all three polymers. Although more study needs to be performed to understand the poor electronic interaction between the bridge anthanthrene and the various comonomers, one can argue that the presence of two bulky 4-octyloxyphenyl group at the methylene bridge induces significant steric hindrance and the linking position, preventing the moieties to adopt a coplanar conformation. Müllen and coworkers 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 sp^3 carbon bridge instead of bulky phenyl rings is an efficient way to promote planarization within the polymer backbone.²⁶

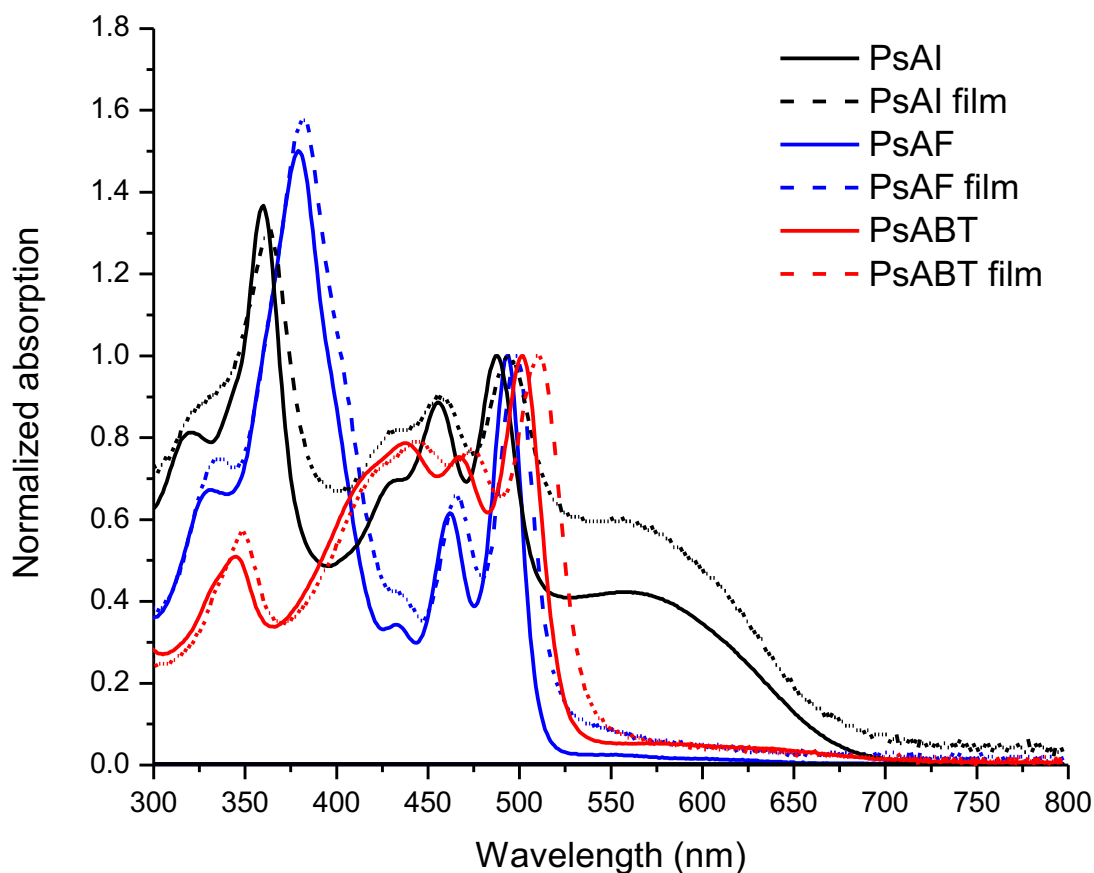


Figure 2. UV-vis spectra (CHCl_3 , solid lines; thin films, dashed lines) of the polymers.

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/AgNO_3 reference electrode in acetonitrile with tetrabutylammonium tetrafluoroborate NBu_4BF_4 0.1M as the electrolyte. The energy value 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 SI section). Despite the apparent weak electronic communication between the 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_{ox} value than **PsAI** (0.58 vs 0.64 V). Likewise, the lower E_{red} value is measured for the polymer with the more electron-deficient unit (-1.10 V). The bandgap values of all three polymers, although a little underestimated by electrochemistry, follow the same trend as observed in electronic spectroscopy (**PsAI** < **PsAF** \approx **PsABT**).

Table 3. Electrochemical Properties of the Polymers

Compound	V_{red} (V)	V_{ox} (V)	E_{g} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PsAI	-1.10	0.64	1.7	-5.3	-3.6
PsAF	-1.23	1.24	2.5	-6.0	-3.5
PsABT	-1.90	0.58	2.5	-5.3	-2.8

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⁺ level at 4.8 eV.

4. Conclusions

We showed that the bandgap of anthanthrene derivatives can be lowered by introducing a sp^3 carbon bridge between the anthanthrene and the phenyl group attached to it at the 4 and 10 positions. Although the bathochromic shift induced 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 bandgap 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 sp^3 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 bandgap and the anthanthrene derivatives.

5. Experimental Section

General. NMR analysis 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), dt (doublet of triplets) and J values are reported in hertz (Hz). The chemical shifts are reported on a ppm scale (δ) relative to the residual solvent peak. High-resolution mass spectra (HRMS) analysis were performed on an Agilent 6210 ToF-LCMS instrument (APPI ion source, Agilent Technologies, Toronto, Canada). M_n 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 Laboratories GPC220 (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 Spectrofluorimeter 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 an Ag/Ag⁺ (0.01 M of AgNO₃ in MeCN) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of 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 onset.^{33,38} The onsets potential (E') are determined at the position where the current starts to differ from the baseline.

$$E_{\text{HOMO}} = - [(E'_{\text{ox vs Ag/Ag}^+}) - (E_{\text{Ferrocene vs Ag/Ag}^+}^{1/2}) + 4.8]$$

$$E_{\text{LUMO}} = - [(E'_{\text{red vs Ag/Ag}^+}) - (E_{\text{Ferrocene vs Ag/Ag}^+}^{1/2}) + 4.8]$$

TGA spectra were recorded using a Mettler TGA/SDTA-851e/SF/1100 °C instrument equipped with a MT1 model balance. The balance is protected with a constant flow of PP nitrogen at a flow of 20 mL/min. 2 mg of samples were weighted and heated from 50 °C 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-dibromoanthanthrone has been kindly provided by Heubach GmbH as Monolite Red 316801 product. 1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoindigo was purchased from Brilliant Matters, Canada. 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-didodecylfluorene and 4,10-Dibromo-6,12-bis(octyloxy)anthanthrene were synthesized according to literature procedures.^{39–41}

Density functional theory calculations were performed with Gaussian 16 revision B0.¹⁴² using the ω B97X-D³⁰ functional and 6-31+G(d,p) basis set. To simplify the calculations, the C₈H₁₇ alkyl chains were replaced with methyl groups. The model compound **2** has four very close in energy due to the angles formed by the phenyl groups. The four geometries are shown in Figure S1, and thermochemistry computed at 298K is summarized in Table 1. Further, simplified structures of compounds **PsAI**, **PsAF** and **PsABT** were modelled at the same level of theory to study the bridging dihedral angle. The simplified structures considered are presented in Figures S2-S4.

The quantum yield (Φ) of the molecules **2** and **5a** were determined by comparing the integrated photoluminescence and absorbance intensities with a reference fluorophore

(Fluorescein ($\Phi=0.91$)⁴³). As a standard measurement, the fluorescein was dissolved in 0.1 M NaOH ($\eta=1.33$) and molecules were dissolved in THF ($\eta=1.405$) with a 10^{-6} M concentration. All samples were degassed and measured in 1 cm fluorescence cell by UV-Vis spectrometer while the absorbance values are kept below 0.1 in order to minimize re-absorption effects. The samples were then measured by PL spectrometer with constant parameters in order to get the PL emission intensity at the excitation wavelength. The quantum yield was calculated by using the following equation:

$$\Phi = \Phi_r \frac{I}{I_r} \frac{A_r}{A} \frac{n^2}{n_r^2}$$

Where Φ is the quantum yield, I is the integrated PL intensity, η is the refractive index, and A is the absorbance intensity. The subscript R refers to the reference fluorophore.

Synthesis of compound 2.

A screw-capped pressure vessel under nitrogen was charged with 4,10-dibromo-6,12-bis(octyloxy)anthanthrene (200 mg, 0.29 mmol), phenylboronic acid (106 mg, 0.87 mmol), tetrakis(triphenylphosphine)palladium(0) (34 mg, 0.03 mmol) and triphenylphosphine (15 mg, 0.06 mmol). The mixture was purged and degassed with a flow of nitrogen for 30 min. Toluene (0.1 M, 2.9 mL) and an aqueous solution of 2M K_2CO_3 (1.6 mL) were added. The mixture was heated at 110 °C for 18 hours. CH_2Cl_2 was added, and the organic layer was washed with $NaHCO_3$ aq. The organic layer was dried with $MgSO_4$ and filtered through Celite. The solvent was evaporated under reduced pressure and the crude product recrystallized from CH_2Cl_2 to afford the desired compound as an orange solid (136 mg, 69%). 1H NMR(400 MHz, chloroform-*d*) δ 8.82 (d, $J = 8.7$ Hz, 2H), 8.44 (s, 2H), 8.24 (d, $J = 8.6$ Hz, 2H), 8.14 – 8.07 (m, 2H), 7.81 – 7.76 (m, 4H), 7.66 – 7.60 (m, 4H), 7.58 – 7.52 (m, 2H), 4.40 (t, $J = 7.0$ Hz, 4H), 2.17 – 2.09 (m, 4H), 1.76 – 1.67 (m, 4H), 1.50 – 1.42 (m, 4H), 1.40 – 1.24 (m, 12H), 0.90 (t, $J = 6.4$ Hz, 6H). ^{13}C NMR (126 MHz,) δ 148.41, 139.91, 138.71, 130.19, 128.89, 127.29,

126.39, 124.74, 124.46, 123.22, 121.95, 121.41, 120.53, 119.35, 118.62, 75.25, 30.61, 29.54, 28.34, 28.10, 25.08, 21.44, 12.88. HRMS (APPI+): C₅₀H₅₂O₂ [M]⁺ 684.3967, found 684.3955

Synthesis of compound 3.

A screw-capped pressure vessel under nitrogen was charged with 4,10-dibromo-6,12-bis(octyloxy)anthanthrene (2.0 g, 2.9 mmol), bis(pinacolato)diboron (2.2 g, 8.69 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (142 mg, 0.174 mmol) and potassium acetate (1.28 g, 13.0 mmol). The mixture was purged and degassed with a flow of nitrogen for 30 min. 1,4-dioxane (0.11 M, 26.7 mL) was added. The mixture was heated at 100 °C for 18 hours. Once cooled, the mixture was poured in MeOH. The precipitate was filtered and wash with MeOH. The precipitated was solubilized in CHCl₃ and activated carbon was added. The mixture was heated until ebullition and filtered through Celite. The solvent was evaporated under reduced pressure to afford 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 (t, *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+): C₅₀H₆₇B₂O₆ [M+H]⁺ 785.5124, found 785.5171

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 2M 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 and the crude product recrystallized from CHCl₃/EtOH 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, 121.67, 121.63, 120.39, 119.99, 119.94, 76.51, 51.84, 51.74, 31.83, 30.74, 29.55, 29.32, 26.27, 22.68, 14.11. HRMS (APPI+): C₅₄H₅₆O₆ [M]⁺ 800.4077, found 800.4101

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 minutes. 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 hours 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 NH₄Cl saturated solution, 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 hours. The organic phase was washed with a NH₄Cl saturated solution and dried with MgSO₄. Purification by silica gel column chromatography

(CH₂Cl₂/hexanes 20:80 v/v) afforded the desired compound as an orange solid (142 mg, 73%). ¹H NMR(500 MHz, chloroform-*d*) δ 9.14 (s, 2H), 8.70 (d, *J* = 8.8 Hz, 2H), 8.48 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.49 (ddd, *J* = 8.1, 7.0, 1.4 Hz, 2H), 7.35 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 2H), 7.29 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.03 (s, 16H), 4.43 (t, *J* = 6.4 Hz, 4H), 2.57 – 2.52 (m, 8H), 2.22 – 2.16 (m, 4H), 1.88 – 1.81 (m, 4H), 1.61 – 1.50 (m, 12H), 1.50 – 1.42 (m, 4H), 1.40 – 1.35 (m, 6H), 1.34 – 1.23 (m, 42H), 0.94 (t, *J* = 6.8 Hz, 6H), 0.87 (t, *J* = 6.8 Hz, 12H). ¹³C NMR (126 MHz, chloroform-*d*) δ 149.70, 145.68, 143.51, 140.71, 138.49, 132.65, 131.71, 130.28, 129.24, 128.75, 127.70, 127.58, 126.86, 126.13, 124.32, 123.91, 123.77, 122.05, 120.28, 120.15, 115.20, 76.67, 59.26, 35.45, 31.91, 31.88, 31.30, 30.97, 29.76, 29.46, 29.24, 26.66, 22.74, 22.67, 14.17, 14.13. HRMS (APPI+): C₁₀₈H₁₃₂O₂ [M]⁺ 1461.0227, found 1461.0215

Synthesis of compound 5b.

A flask under nitrogen was charged with THF (0.026 M, 4 mL) and 1-bromo-4-octylbenzene (225 mg, 0.834 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 (0.57 mL, 0.92 mmol) was added dropwise to the solution. The mixture was stirred for 30 minutes. Compound **4b** (100 mg, 0.104 mmol) solubilized in a minimal amount of THF was added dropwise to the solution. The mixture was stirred for 18 hours and the temperature slowly increase to the room temperature. The solvent was evaporated under reduced pressure and the crude product was solubilized in CH₂Cl₂. The organic phase was washed with NH₄Cl saturated solution, 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 hours. The organic phase was washed with an NH₄Cl saturated solution and dried with MgSO₄. Purification by silica gel column chromatography (CH₂Cl₂/hexanes 10:90 v/v) afforded the desired compound as an orange solid

(114 mg, 67%). ¹H NMR (500 MHz, chloroform-*d*) δ 9.07 (s, 2H), 8.69 (d, *J* = 8.7 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.41 (d, 2H), 7.05 (d, *J* = 8.5 Hz, 8H), 6.99 (d, *J* = 8.1 Hz, 8H), 4.40 (t, *J* = 6.4 Hz, 4H), 2.55 (t, 8H), 2.21 – 2.13 (m, 4H), 1.95 – 1.74 (m, 4H), 1.62 – 1.49 (m, 16H), 1.48 – 1.41 (m, 4H), 1.41 – 1.20 (m, 44H), 0.93 (t, *J* = 6.8 Hz, 6H), 0.87 (t, *J* = 6.9 Hz, 12H). ¹³C NMR (101 MHz, chloroform-*d*) δ 149.90, 145.56, 144.96, 141.06, 138.11, 134.23, 131.76, 130.20, 128.69, 128.45, 127.92, 127.61, 125.78, 125.55, 124.35, 123.92, 121.97, 121.92, 120.43, 120.24, 115.48, 76.76, 59.24, 35.46, 31.93, 31.89, 31.26, 30.94, 29.73, 29.53, 29.47, 29.46, 29.26, 26.64, 22.75, 22.68, 14.17, 14.13. HRMS (APPI+): C₁₀₈H₁₃₀Br₂O₆ [M]⁺ 1616.8438, found 1616.8432

Synthesis of compound PsAI.

A screw-capped pressure vessel under nitrogen charge with compound **5b** (94 mg, 58 μmol), 1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoindigo (47 mg, 49 μmol), tetrakis(triphenylphosphine)palladium(0) (1.1 mg, 0.97 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 (120 μl) were added before sealing the tube. This reaction is heated at 110 °C for three 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, hexanes 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 (77 mg, 72%), (\overline{M}_n = 62.5 kDa, \overline{M}_w = 133.5 kDa, PDI = 2.1).

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) (1.3 mg, 1.17 μmol) and Aliquat 336 (1 drop) were pumped under vacuum and the solvents were degassed for 40 min. Toluene (1.1 ml, 0.05 M) and 2 M K_2CO_3 solution (146 μl) were added before sealing the tube. This reaction is heated at 110 °C for three 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, hexanes 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%), ($\overline{M}_n = 33.6$ kDa, $\overline{M}_w = 52.2$ kDa, PDI = 1.6).

*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, 4.94 μmol) were pumped under vacuum and the solvent were degassed for 40 min. Toluene (1.6 ml, 0.038 M) was added before sealing the tube. This reaction is heated at 110 °C for three 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, hexanes 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%), ($\overline{M}_n = 103.6$ kDa, $\overline{M}_w = 172.8$ kDa, PDI = 1.7).

Supporting Information

Supporting Information is available free of charge on the ACS Publications website: NMR spectra, cyclic voltammetry, optical properties and DFT calculations.

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