Synthesis and Photochromic Properties of Ladderized Poly(*p*-phenylene-*alt*-9,10-anthrylene)s

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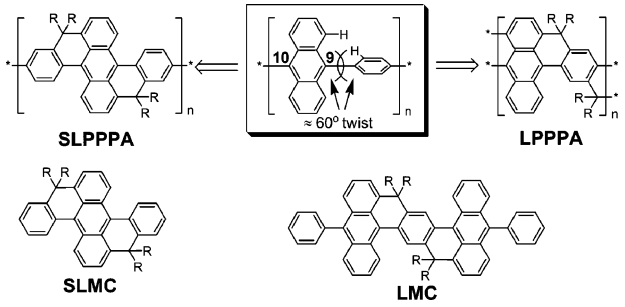
ABSTRACT: We report here the synthesis and characterization of stepladder and ladder poly(*p*-phenylene-*alt*-anthrylene)s (**SLPPPA** and **LPPPA** respectively) containing 9,10-anthrylene building groups within the main chain. The polyketone ladder polymer precursors are prepared by palladium-catalyzed Suzuki-type cross-coupling. The solution optical spectra of **SLPPPA** and **LPPPA** exhibit broad absorption bands with large Stokes shift unusual for rigid, ladder-type polymers. **SLPPPA** shows an intense yellow emission with a maximum at 584 nm while **LPPPA** is more red-shifted in emission with a maximum at 693 nm due to the planarization of the aromatic repeat units. Cyclic voltammetry studies reveal that both **SLPPPA** and **LPPPA** undergo fully reversible p- and n-doping processes. The methylene-bridged 1,4-di(10-phenylanthracen-9-yl)benzene **LMC** and the bis(methylene)-bridged 9,10-diphenylanthracene **SLMC** are also synthesized, they serve as ladder and stepladder model compounds respectively and their optical properties are discussed in comparison with the above polymers. The stepladder derivatives (**SLMC** and **SLPPPA**) are found to form endoperoxides in the presence of visible light in a thermally reversible process whereas the ladder derivatives (**LMC** and **LPPPA**) undergo irreversible photooxidation.

Introduction

Recently, much research into π-conjugated polymer materials has centered on poly-*p*-phenylene-based polymers such as stepladder-type polyphenylenes[1−4] and fully ladder-type polyphenylenes[5,6] because they possess a unique set of optoelectronic properties due to their planarized molecular structures. The optoelectronic effects of conjugated polymers (including color tuning) are highly dependent on the nature of the building blocks, the pattern in which they are linked, and the type and position of the substituents.[7,8] Anthracene derivatives have been widely studied as organic light emitters due to their high fluorescence quantum yields.[9−11] In copolymers containing 9,-10-linked anthrylene and phenylene moieties however, steric interactions with the hydrogen atoms in the *peri*-positions of the anthracene cause a strong out-of-plane twisting (Chart 1).[12] Attempts to enhance the solubility by substitution of the rings force the consecutive phenylene and 9,10-anthrylene units even further out of a common plane resulting in reduced conjugation along the chain. Therefore, utilizing methylene bridges between 9,10-anthrylene and phenylene units in the main chain can offer a simple alternative to minimize this twist along the polymer backbone and at the same time provide a site to attach solubilizing groups.

In addressing this issue, we direct our attention toward ladderized PPP-type polymers incorporating 9,10-anthrylene units as higher benzenoid building blocks, which should generate unique electronic and optical properties. While one paper has described a similar approach using 1,5-linked naphthylenes,[7] the stepladder and ladder poly(*p*-phenylene-*alt*-anthrylene)s (**SLPPPA** and **LPPPA** respectively) containing 9,10-anthrylene units within the main chain are first examples of the 9,10-linked anthrylene-based ladder-type polymers. The resulting polymers are thus relevant from both structural and spectroscopic viewpoints such as color tuning and photochromism. In addition to the synthesis and characterization of **SLPPPA** and **LPPPA**, the methylene-bridged 1,4-di(10-phenylanthracen-9-yl)benzene **LMC** and bis(methylene)-bridged 9,10-diphenylanthracene **SLMC** are described, which serve as model compounds for spectroscopic characterization of the polymers. Finally, the unique thermal and photochemical behavior of the title materials is presented.

Chart 1. Molecular Structures Planarized by Methylene Bridges between 9,10-Anthrylene and Phenylene Units in Order to Maximize the Extended π-System[a]



[a] The R groups permit solubility of the ladderized system.

Results and Discussion

Synthesis and Characterization. The synthesis of stepladder poly(*p*-phenylene-*alt*-anthrylene) containing 9,10-anthrylene building groups (**SLPPPA**) is carried out as depicted in Scheme 1. Starting from 5-bromo-2-iodobenzoic acid, 5-bromo-2-iodo-4′-decylbenzophenone (**1**) was prepared by $AlCl_3$ promoted Friedel−Crafts acylation of decylbenzene with 5-bromo-2-iodobenzoyl chloride in 85% yield. Suzuki coupling of 9,10-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene (**2**) and **1** gave 9,10-di(5-bromo-4′-decylbenzophenon-2yl)anthracene (**3**) (97%). This was converted into the corresponding anthracene diboronic ester **4** by treatment with bis(pinacolato)-diboron under $Pd(OAc)_2$/KOAc/DMF (60%) and subsequent Suzuki polycondensation of **3** and **4** generated the 9,10-anthrylene linked polyketone precursor **5** ($M_n = 6.11 \times 10^3$ g/mol and $M_w = 8.75 \times 10^3$ g/mol, PPP standard). Addition

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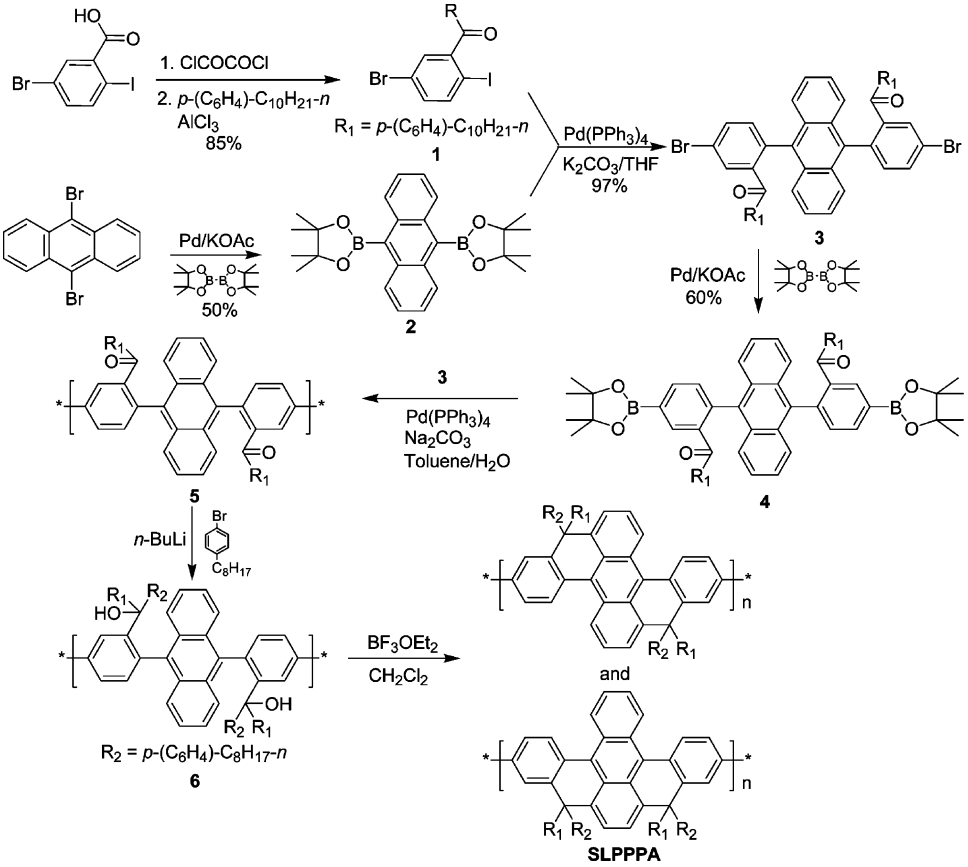
Scheme 1. Synthesis of Stepladder Poly(*p*-phenylene-*alt*-anthrylene) Containing 9,10-Anthrylene Units (SLPPPA)



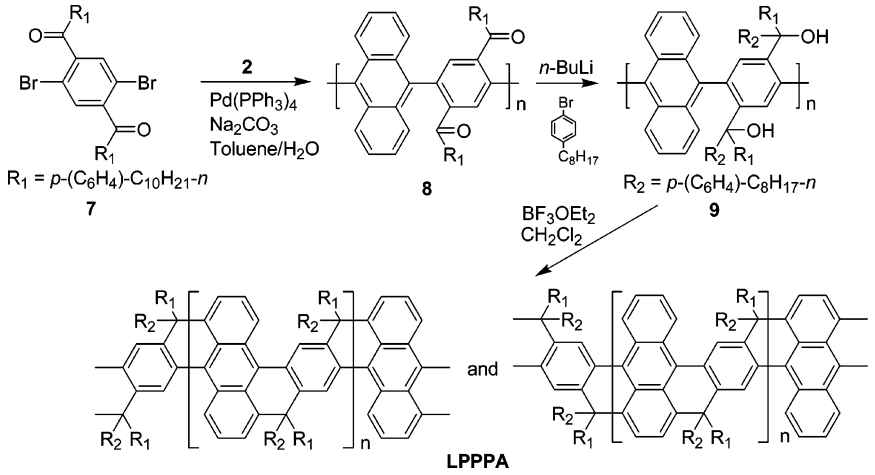
of 4-octylphenyllithium gave the corresponding polyalcohol **6** and the desired **SLPPPA** was obtained by ring closure with boron trifluoride etherate. Prior to this transformation, **5** was purified by Soxhlet extraction overnight using acetone to remove low molecular oligomeric components. **SLPPPA** is readily soluble in organic solvents like THF, toluene and dichloromethane. Gel-permeation chromatography (GPC) analysis with PPP standard shows a M_n value of 7.24×10^3 g/mol and M_w of 1.19×10^4 g/mol with a polydispersity of 1.35. To prove that the polymer analogous ring closure had gone to completion, the polymers were characterized by a combination of FT-IR and ^{13}C NMR spectroscopy. The FT-IR spectrum of **5** displays a strong absorption band at 1665 cm^{-1} due to the carbonyl group[13] and the ^{13}C NMR spectrum shows the carbon signal of the carbonyl group at $\delta = 196.5$ ppm. In the FT-IR spectrum of **SLPPPA**, the carbonyl band at 1665 cm^{-1} is not observed. An inspection of ^{13}C NMR spectrum of **SLPPPA** fails to reveal any carbonyl signals which would point toward the presence of incomplete ring closure. In view of the signal-to-noise ratio achieved we can conclude that the amount of structural defects is below 1%. Notably, the ^{13}C NMR spectrum of **SLPPPA** has a new signal at $\delta = 59.8$ ppm corresponding to the quaternary bridging carbon of the methylene bridge obtained upon cyclization. As described in Scheme 1, mixtures of two regioisomers can be formed because of the rotation between phenylene and anthrylene units in the polymer main chain. However, the ratio of the syn- and anti-ring closure reaction products cannot be determined from NMR or other spectroscopic methods.

To synthesize ladder poly(*p*-phenylene-*alt*-anthrylene) containing 9,10-anthrylene units (**LPPPA**), a precursor approach was taken as shown in Scheme 2. The precursor polyketone **8** was synthesized via Suzuki polycondensation of the anthracene diboronic ester **2** and 2′,5′-dibromo-4-decyl-4′-(4-decylbenzoyl)-benzophenone (**7**).[14] Addition of an excess of 4-octylphenyllithium produced the corresponding polyalcohol **9** which underwent facile ring closure with boron trifluoride etherate to generate the target polymer **LPPPA**. This polymer has good solubility in organic solvents. GPC analysis of this polymer exhibits a M_n value of 5.77×10^3 g/mol and M_w of 8.19×10^3 g/mol (THF, PPP standard). The completion of the ring closure is verified by FT-IR[13] and ^{13}C NMR spectroscopy as detailed earlier and one can conclude the amount of structural defects to be below 1%.

TGA thermograms of the two polymers exhibit good thermal stability up to 400 °C. Weight loss (5%) starts at 420 °C and 430 °C for **SLPPPA** and **LPPPA**. DSC analysis of the polymers shows neither a glass transition process (T_g) nor other thermal processes (such as liquid crystalline phase) from −50 to +280 °C.

Synthesis of Model Compounds (SLMC and LMC). To more precisely assess the intrinsic properties of stepladder and ladder poly(*p*-phenylene-*alt*-anthrylene)s (**SLPPPA** and **LPPPA**) containing 9,10-anthrylene linkage, it is necessary to prepare model compounds, as presented in Scheme 3. The bromination of 9-phenylanthracene in acetic acid gave 9-bromo-10-phenylanthracene (91%) which was transformed to 4,4,5,5-tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane (**10**) via lithiation and subsequent reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Suzuki coupling of **7** and **10** under palladium-catalyzed conditions generated (2,5-di(10-phenylanthracen-9-yl)-1,4-phenylene)di-4′-decylbenzophenone (**11**). The methylene-bridged 1,4-di(10-phenylanthracen-9-yl)-benzene **LMC** was synthesized in the analogous fashion as described above in 86% overall yield (2 steps). A similar procedure was adopted for the synthesis of the bis(methylene)-bridged 9,10-diphenylanthracene **SLMC** starting from 2-iodo-

Scheme 2. Synthesis of Ladder Poly(*p*-phenylene-*alt*-anthrylene) Containing 9,10-Anthrylene Units (LPPPA)

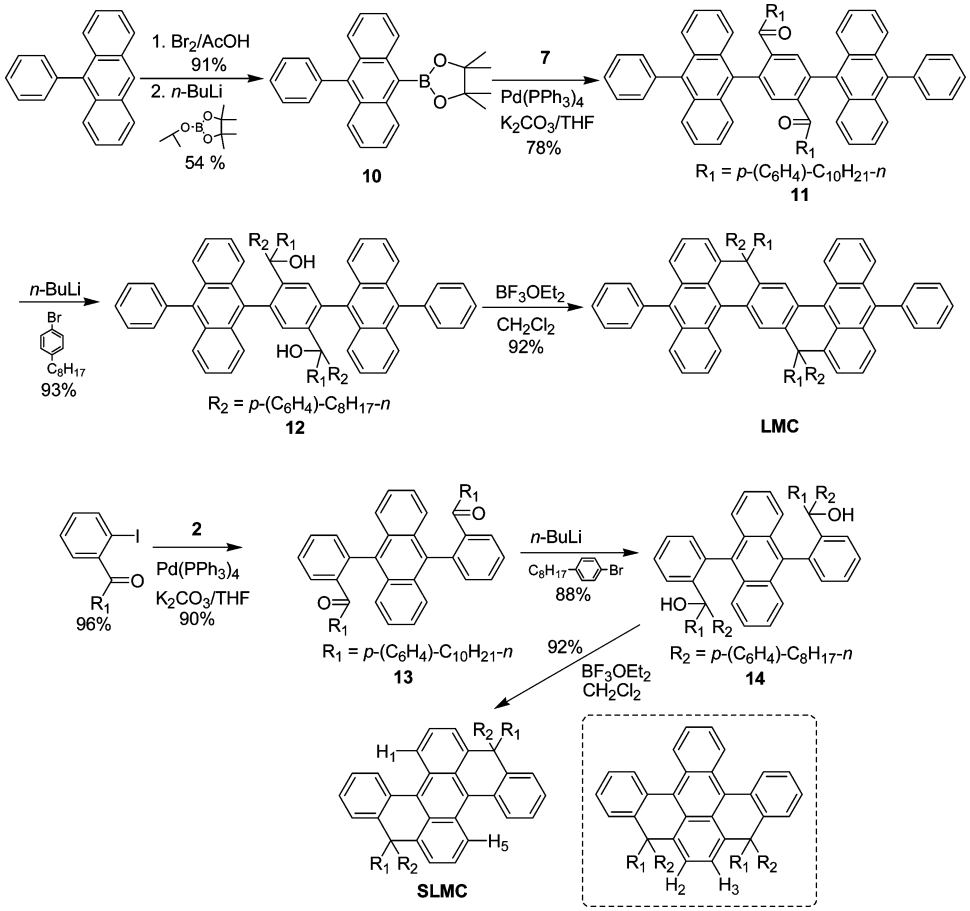


R1 = *p*-(C6H4)-C10H21-*n* **7**

8

R2 = *p*-(C6H4)-C8H17-*n* **9**

Scheme 3. Synthesis of Ladder and Stepladder Model Compounds (LMC and SLMC)



10

R1 = *p*-(C6H4)-C10H21-*n* **11**

R2 = *p*-(C6H4)-C8H17-*n* **12**

LMC

R1 = *p*-(C6H4)-C10H21-*n* **13**

R2 = *p*-(C6H4)-C8H17-*n* **14**

benzoic acid (acylation, Suzuki coupling, generation of diol, and subsequent ring closure). The cyclization of **14** can generate two regioisomers (syn and anti), analogous to the polymers. The ^{1}H NMR spectrum of **SLMC** shows a doublet of doublets at 8.52 ppm with coupling constants of 6.7 and 3.3 Hz. This signal is assigned to the two aromatic protons at the 1- and 5-positions of the anthrylene unit. If the syn-ring closed product has been formed, the protons at the 2- and 3-positions of the anthrylene unit would give a singlet, which is not observed in the ^{1}H NMR spectrum of **SLMC**. Therefore, it is concluded that the anti ring-closed isomer is formed. This result also suggests that the polymers (**SLPPPA** and **LPPPA**) contain predominantly anti ring-closed isomers.

Photophysical Properties. Figures 1 and 2 depict the UV−vis absorption and photoluminescence characteristics of the two polymers (**SLPPPA** and **LPPPA**) and their model compounds (**LMC** and **SLMC**). The absorption and PL spectral data for all compounds are also summarized in Table 1. As shown in Figures 1 and 2, **SLPPPA** in solution displays a broad absorption with a maximum around 520 nm with no vibronic features. The absorption maximum of **LPPPA** in solution is bathochromically shifted compared to that of **SLPPPA**, to 659 nm. The UV−vis and PL spectra of the ladder model compound **LMC** are also bathochromically shifted compared to the stepladder model compound **SLMC**, which suggests the notion that **LPPPA** has a more extended π-system relative to **SLP-**

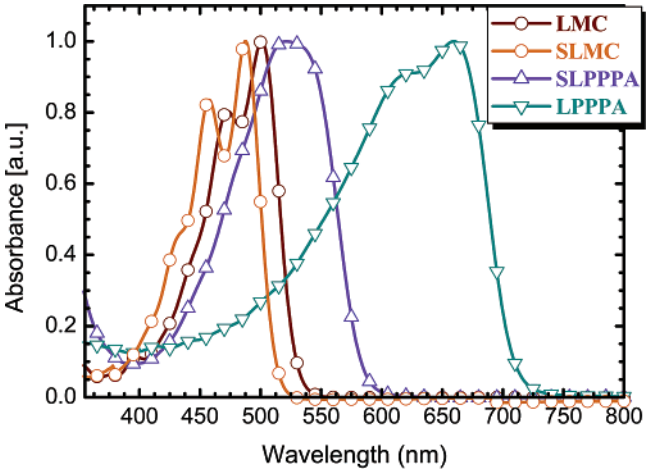


Figure 1. UV−vis spectra of **LMC**, **SLMC**, **SLPPPA**, and **LPPPA** in chloroform solution.

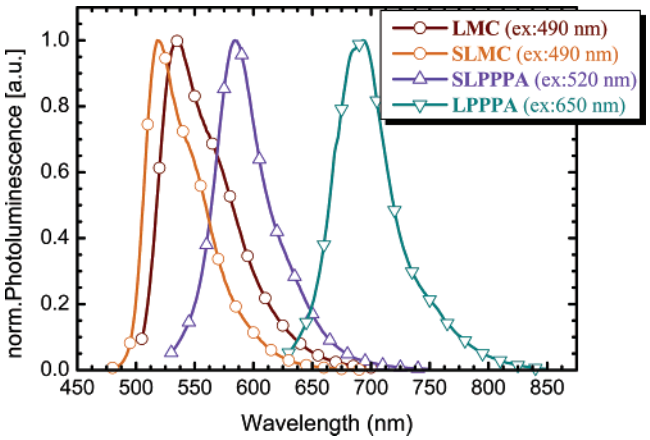


Figure 2. PL spectra of **LMC**, **SLMC**, **SLPPPA**, and **LPPPA** in chloroform solution.

PPA.[15,16] However, the large Stokes shift (ca. 64 nm for **SLPPPA** and ca. 34 nm for **LPPPA**) and the lack of any vibrational resolution are in contrast to most stepladder or ladder-type poly-*p*-phenylene-based polymers (LPPPs) which show narrow and well-resolved absorption bands. This large Stokes shift can be attributed to the deviation from the coplanarity caused by the methylene bridges between phenylene and anthrylene units. The six-membered ring containing the sp^3 carbon is not expected to be fully planarized and the attachment of bulky solubilizing groups further distorts the repeat units in the main chain due to steric hindrance. This assumption is supported by the AM1 force field simulation studies, implemented using HyperChem 6.0 (Hypercurb Inc.).[13] The simulated structure of the ladderized compound between 9,10-anthrylene and phenylene with phenyl substituents as solubilizers shows a pronounced steric stain along the main chain when compared to that of compound with methyl substituents. **SLPPPA** in solution shows a yellow emission (λ_{max} = 584 nm) whereas **LPPPA** exhibits a red emission (λ_{max} = 693 nm). The enhanced π-system induced by the methylene bridges between phenylene and 9,10-anthrylene units accounts for the observed unique optical properties.

Thermal and Photochemical Properties. It has been previously reported[17] that structurally related hydrocarbons such as perylenes and terylenes that are substituted in the bay positions exhibit considerable deviations from planarity, which results in reduced photostability. Furthermore, it has been observed that the anthracene derivatives react rapidly with oxygen to form the corresponding endoperoxides in solution which can provide interesting thermal and photochemical properties.[18−22] This prompted us to investigate the photostability of all the materials (**LMC**, **SLMC**, **SLPPPA**, and **LPPPA**).

After irradiation with sunlight in the presence of air, UV−vis absorption and PL spectra of all the compounds (**LMC**, **SLMC**, **SLPPPA**, and **LPPPA**) were taken in chloroform solution (1×10^{-5} M) to follow the course of the photooxidation (Figure 3). Both the absorption and emission intensity drop drastically upon irradiation, indicating that the anthracene chromophore has undergone chemical transformation. Field desorption mass spectrometry (FD-MS) of the irradiated model compounds (**LMC** and **SLMC**) shows an increase in mass by 32 Da, supporting the formation of the endoperoxides. On heating the stepladder derivatives (**SLMC** and **SPPPA**) at 120 °C, the initial absorption and emission spectra reappear with little loss of intensity whereas the ladder derivatives (**LMC** and **LPPPA**) display significant changes in their spectra.

It has been described[23] that two primary pathways of transformation can compete during thermolysis of aromatic endoperoxides: cycloreversion, leading to parent substrate and oxygen in a singlet or triplet state, and homolytic cleavage of the peroxidic bond, followed by rearrangement to more or less stable diepoxides or decomposition, leading to hydroxy-ketones or quinones. The relative importance of both processes depends on the structure. Therefore, it is postulated that in the 9,10-anthrylene based stepladder materials (**SLMC** and **SPPPA**), the reversibility of the photooxygenation to the endoperoxides and subsequent thermal cleavage of oxygen suggests a single photoreaction pathway involving $^1O_2$ as the sole oxidizing species (type II photooxidation)[21,23,24] whereas in the 9,10-anthrylene based ladder materials (**LMC** and **LPPPA**), the mechanism involves electron-transfer processes resulting in the anthracene cation radical (type I photooxidation)[21,25,26] as their products are irreversibly formed. After heating the endoperoxides from the **LMC** and **SLMC**, the FD-MS of **SLMC** reveals an intense peak at 1162 Da for the parent compound whereas the parent peak of **SLMC** is clearly not observed. This can support the proposed interpretation and suggest a different dissociation of endoperoxides for stepladder and ladder derivatives, respectively.

Electrochemical Properties. The redox behavior of the two polymers (**SLPPPA** and **LPPPA**) is investigated by cyclic voltammetry (CV) against Ag/Ag^+. As shown in Figure 4, the polymers exhibit clear reversibility in both the p-doping and n-doping processes. The oxidation and reduction potentials are

Table 1. Optical Data of SLPPPA, LPPPA, and the Model Compounds (LMC and SLMC)[b]

	λ_{max} (nm)			λ_{max} (nm)[a]	
compound	absorption	emission	Stokes shift (nm)	absorption	emission
LMC	472, 501	536	35	400, 423, 449 (500)	474, 529
SLMC	430, 455, 488	518	30	430, 457, 488	518
SLPPPA	520	584	64	518	580
LPPPA	620, 659	693	34	467, 501	637

[a] Absorption and emission after heating at 120 °C directly after irradiation. [b] Peaks that appear as shoulders or weak bands shown in parentheses

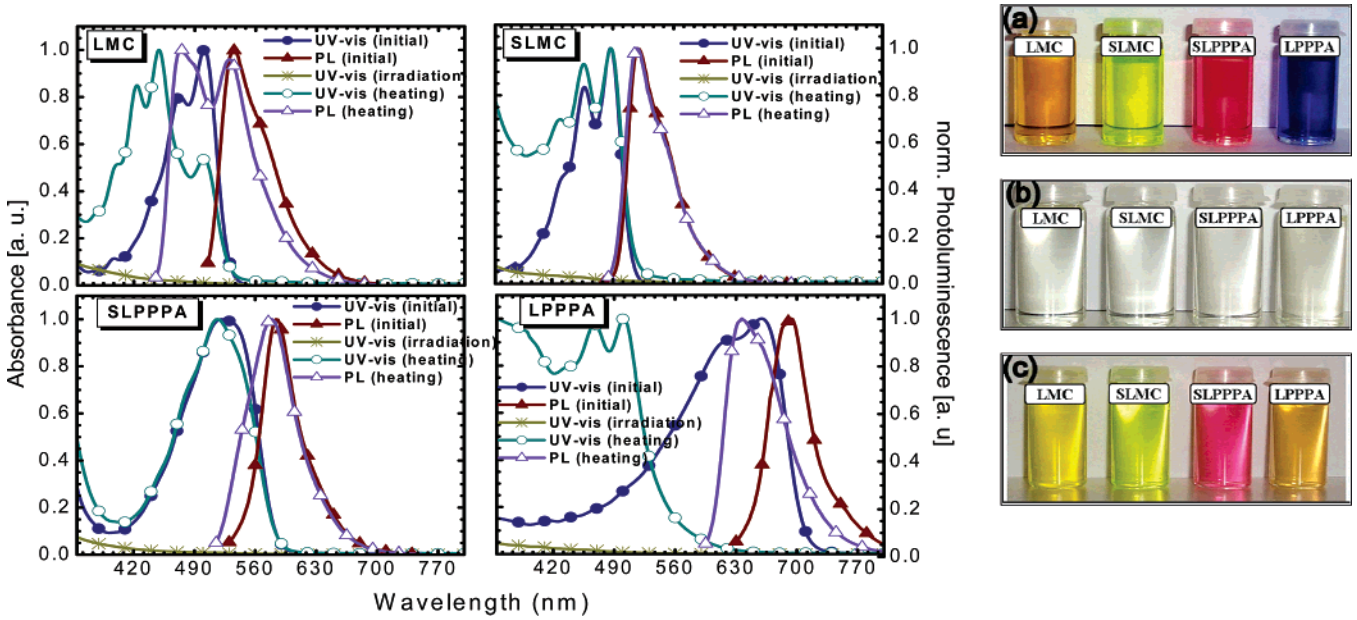


Figure 3. UV−vis and PL spectra of **LMC**, **SLMC**, **SLPPPA**, and **LPPPA** in chloroform solution (left). (a) Before and (b) after irradiation with visible light in the presence of air and (c) with heating at 120 °C directly after irradiation (right).

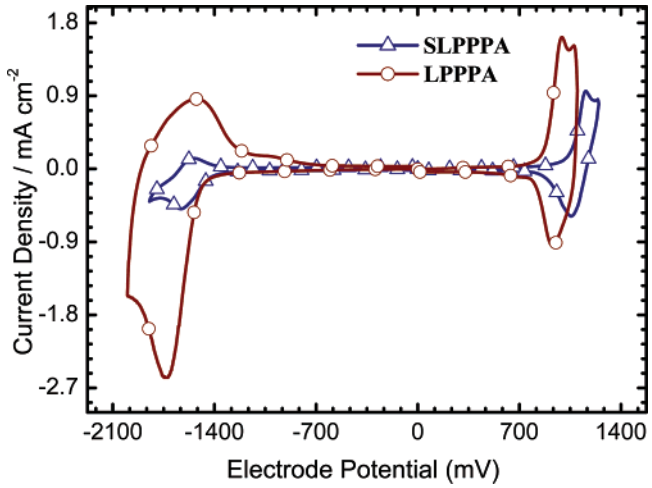


Figure 4. Cyclic voltammograms of the polymer films (**SLPPPA** and **LPPPA**) coated on platinum electrodes measured in acetonitrile containing 0.1 M Bu_4NClO_4 solution at a scan rate of 100 mV/s at room temperature.

Table 2. Electrochemical Data for SLPPPA and LPPPA[a]

polymer	E^{re}_{onset} [V]	E^{ox}_{onset} [V]	E_{HOMO} [eV]	E_{LUMO} [eV]
SLPPPA	−1.45	1.06	−5.5	−3.0
LPPPA	−1.05	0.88	−5.3	−2.9

[a] $E^{ox/re}_{onset}$ = onset oxidation/reduction potential. E_{LUMO} = lowest unoccupied molecular orbital (LUMO) energy level; E_{HOMO} = highest occupied molecular orbital (HOMO) energy level.

summarized in Table 2. Electrochemical reduction starts at about −1.38 V with a peak at E_{red} = −1.62 V vs Ag/Ag^+ for **SLPPPA** and −1.73 V for **LPPPA**. The corresponding oxidation (n-dedoping) peak is observed at −1.55 V vs Ag/Ag^+ for **SLPPPA** and −1.53 V for **LPPPA**. The electron affinity (EA) values derived from the reduction onset potentials are at 3.0 eV for **SLPPPA** and 2.9 eV for **LPPPA**.[27,28] In the oxidative region, both **SLPPPA** and **LPPPA** display reversible oxidation characterized by a peak E_{ox} = 1.15 V vs Ag/Ag^+ for **SLPPPA** and 0.99 V for **LPPPA** and the corresponding reduction (p-dedoping) peaks are observed at 1.06 and 0.93 V respectively. The estimated ionization potential (IP = E^{ox}_{onset} + 4.4 eV, HOMO levels) values are 5.5 eV for **SLPPPA** and 5.3 eV for **LPPPA**. These energy levels (HOMO and LUMO) and the observed reversible redox processes suggest that both compounds (**SLPPPA** and **LPPPA**) enhance hole and electron injections and have potential for use in hole and electron transports.

Conclusions

A series of stepladder and ladder poly(*p*-phenylene−*alt*-anthrylene)s containing 9,10-anthrylene building sets have been synthesized by Suzuki polycondensation. The resulting polymers (**SLPPP**A and **LPPPA**) are the first examples of 9,10-linked anthrylene based ladder-type polymers consisting of alternating six-membered rings prepared by polymer analogous cyclization of polyketone precursors. Through the structural manipulation of the methylene bridge at the 9,10-anthrylene unit, it is possible to tune the optical properties of the target polymers (λ_{em} = 584 nm for **SLPPPA** and λ_{em} = 693 nm for **LPPPA**). Unlike, LPPPs, a significant Stokes shift between absorption and emission is observed for both the polymers (**SLPPPA** and **LPPPA**) which is attributed to the twist of the polymer backbone along the sp^3 methylene bridges. In the photochemical studies, we have demonstrated that the photooxygenation of all materials with visible light gives the colorless endoperoxide structures. Upon thermal treatment, the stepladder derivatives (**SLMC** and **SLPPPA**) recover the initial optical properties of the starting materials (type II photooxidation) whereas the ladder derivatives (**LMC** and **LPPPA**) undergo irreversible type I photooxidation. One concludes that the structural features in conjugated polymers containing 9,10-anthrylene units can play an important role for the photoreaction pathway.

Experimental Section

General Data. Commercially available materials were used as received unless noted otherwise. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250, Bruker AMX 300 or Bruker DRX 500 MHz spectrometer and referenced to the solvent peak. Gel Permeation Chromatography (GPC) analysis against poly-*p*-phenylene and polystyrene standards was performed in THF on a Waters high pressure GPC assembly with an M590 pump, microStyragel

columns of 10^5, 10^4, 10^3, 500, and 100 Å and a refractive index detector. UV−visible absorption spectra were recorded on a Perkin-Elmer Lambda 15 spectrophotometer. Photoluminescence spectra were recorded on a SPEX Fluorolog 2 Type F212 steady-state fluorometer, using a 450 W xenon arc lamp as excitation source and a PMT R 508 photomultiplier as detector system. Thermogravimetric analysis and differential scanning calorimetry (DSC) measurements were carried out on a Mettler 500 thermogravimetric analyzer and a Mettler DSC 30 calorimeter, respectively. CV was performed on an EG&G Princeton Applied Research potentiostat, model 270 on 2 μm thick films deposited by solution-coating onto precleaned ITO as a working electrode with an area of 0.2 cm^2. After coating, the films were dried in a vacuum oven for 10 min. The measurements were carried out in acetonitrile solutions containing 0.1 M of tetrabutylammonium perchlorate as the supporting electrolyte, using Ag/AgCl as the reference electrode and a platinum wire as the counter electrode and an internal ferrocene/ferrocenium standard.

Synthesis of 5-Bromo-2-iodo-4′-decylbenzophenone (1). A flask equipped with a reflux condenser and a drying tube was charged with 5-bromo-2-iodobenzoic acid (5.0 g, 15.33 mmol) and benzene (50 mL). To this mixture were added oxalyl chloride (2.89 g, 23.0 mmol) and one drop of *N*,*N*-dimethylformamide (catalyst). The reaction mixture was heated at 80 °C overnight (bubbling observed), then the reaction was cooled and the solvent was removed in vacuo. The crude solid was dissolved in benzene (20 mL) and stirred with calcium hydride for 1 h and filtered. The solvent was removed in vacuo to give 5-bromo-2-iodobenzoyl chloride and used without further purification. To the benzoyl chloride in 20 mL of dichloromethane were added aluminum chloride (3.0 g, 23.0 mmol) and decyl benzene (6.34 g, 29.1 mmol), and the reaction was stirred at room temperature for 12 h and then quenched with aqueous 2 M HCl. The mixture was then extracted into dichloromethane and washed with brine. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 6.8 g (85%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (dd, J = 10.4 and 8.4 Hz, 3H), 7.40 (d, J = 2.3 Hz, 1H), 7.32−7.28 (m, 3H), 2.66 (t, J = 7.9 Hz, 2H), 1.69−1.58 (m, 2H), 1.37−1.21 (m, 14H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 195.53, 150.51, 146.80, 141.32, 134.35, 132.99, 131.44, 130.99, 129.24, 122.75, 90.59, 36.52, 32.24, 31.35, 29.94, 29.90, 29.79, 29.67, 23.03, 14.49. FDMS (*m*/*z*): 526.0 ($M^{+\bullet}$). Anal. Calcd for $C_{23}H_{28}$-BrIO: C, 52.39; H, 5.35; Br, 15.15; I, 24.07; O, 3.03; Found: C, 53.11; H, 5.73.

Synthesis of 9,10-Di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene (2). To a 100 mL Schlenk flask were added 9,-10-dibromoanthracene (4.20 g, 12.5 mmol), bis(pinacolato)diboron (7.75 g, 30.51 mmol), palladium acetate (0.166 g, 0.74 mmol), potassium acetate (7.34 g, 75.0 mmol) and 35 mL of anhydrous *N*,*N*-dimethylformamide. The mixture was degassed by gently bubbling argon for 30 min at room temperature. This was then heated at 70 °C under argon overnight. The cooled mixture was extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. The crude product was chromatographed on silica using 0−10% ethyl acetate in hexane as eluent. Isolated yield = 2.7 g (50%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (dd, J = 6.8 and 3.3 Hz, 4H), 7.46 (dd, J = 6.8 and 3.3 Hz, 4H), 1.58 (m, 24H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 134.91, 128.78, 125.13, 84.44, 25.18. FDMS (*m*/*z*): 430.1 ($M^{+\bullet}$). Anal. Calcd for $C_{26}H_{32}B_2O_4$: C, 72.60; H, 7.50; B, 5.03; O, 14.88; Found: C, 72.11; H, 7.73.

Synthesis of 9,10-Di(5-bromo-4′-decylbenzophenon-2yl)anthracene (3). The diboronic ester **2** (0.5 g, 1.16 mmol) and the ketone **1** (1.41 g, 2.67 mmol) were dissolved in THF (20 mL) in a 100 mL Schlenk flask, and aqueous 2 M K_2CO_3 solution (10 mL) was added to this solution, which was purged with argon for 20 min. Then tetrakis(triphenylphosphine)palladium (150 mg, 0.129 mmol) was added, and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and worked up after 2 days. The cooled mixture was extracted with diethyl ether, washed with brine and then dried over $MgSO_4$. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent and further purified by recrystallization from ethyl acetate in hexane to afford 1.1 g (97%) of the title compound as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, J = 2.0 Hz, 1H) 7.80 (m, 3H), 7.47 (m, 4H), 7.24 (m, 8H), 7.11 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.2 Hz, 2H) 6.72 (d, J = 8.2 Hz, 2H), 2.34 (m, 4H), 1.35−1.21 (m, 32H) 0.88 (t, J = 5.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 195.65, 148.12, 147.98, 143.21, 142.95, 136.94, 136.83, 134.44, 134.32, 134.08, 133.87, 133.58, 133.36, 133.08, 132.02, 131.31, 129.52, 129.29, 128.87, 127.92, 127.38, 126.63, 126.52, 125.20, 125.06, 121.74, 121.55, 35.84, 31.90, 31.18, 31.02, 29.61, 29.50, 29.44, 29.33, 29.23, 22.67, 14.10. FDMS (*m*/*z*): 974.5 ($M^{+\bullet}$). Anal. Calcd: for $C_{60}H_{64}Br_2O_2$: C, 73.76; H, 6.60; Br, 16.36; O, 3.28; Found: C, 73.29; H, 6.73.

Synthesis of 9,10-Di(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4′-decylbenzophenon-2yl)anthracene (4). To a 100 mL Schlenk flask were added the diketone **3** (0.6 g, 0.61 mmol), bis-(pinacolato)diboron (0.39 g, 1.53 mmol), palladium acetate (0.008 g, 0.037 mmol), potassium acetate (0.36 g, 3.66 mmol), and 10 mL of anhydrous *N*,*N*-dimethylformamide. The mixture was degassed by gently bubbling argon for 30 min at room temperature. The mixture was then heated at 80 °C under argon for overnight. The cooled mixture was extracted with diethyl ether, washed with brine, and then dried over $MgSO_4$. The crude product was chromatographed on silica using 0−10% ethyl acetate in hexane as eluent. Isolated yield = 0.39 g (60%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.20 (d, J = 9.0 Hz, 1H), 8.10 (dd,, J = 11.8 and 7.6 Hz, 3H), 7.46 (m, 4H) ppm 7.37 (dd, J = 16.2 and 7.5 Hz, 3H), 7.18 (m, 5H), 6.79 (d, J = 8.1 Hz 2H), 6.67 (d, J = 8.1 Hz, 2H), 2.31 (m, 4H), 1.48−1.40 (m, 32H), 1.29−1.21 (m, 24H), 0.88 (t, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 197.68, 196.84, 147.42, 147.24, 141.17, 141.02, 140.94, 136.40, 136.10, 135.85, 135.27, 135.20, 135.14, 135.08, 134.91, 134.57, 134.33, 132.13, 130.33, 129.41, 129.37, 129.28, 128.74, 128.32, 127.72, 127.13, 126.84, 126.71, 124.81, 124.69, 84.15, 35.80, 35.76, 31.87, 31.14, 31.03, 29.62, 29.57, 29.48, 29.41, 29.36, 29.29, 29.24, 24.99, 24.90, 24.82, 24.54, 24.49, 22.65, 14.08. FDMS (*m*/*z*): 1070.7 ($M^{+\bullet}$). Anal. Calcd for $C_{72}H_{88}B_2O_6$: C, 80.74; H, 8.28; B, 2.02; O, 8.96; Found: C, 80.27; H, 8.73.

Polymer 5. Monomer **3** (117 mg, 0.12 mmol), monomer **4** (128 mg, 0.12 mmol), Aliquat 336 (0.008 g, 13 mol %), 1.5 mL of aqueous 2.0 M Na_2CO_3, and 4.0 mL of toluene were taken together in a Schlenk flask and purged with argon for 15 min. To this was added tetrakis(triphenylphosphine)palladium (3.0 mg, 3.6 μmol) and the reaction heated at 85 °C under vigorous stirring for 48 h. Phenylboronic acid was then added as an end capper (2.0 mg), the reaction heated for 6 h, and then bromobenzene (5.0 mg) was added and the reaction heated again for an additional 6 h. The reaction was poured into a mixture of methanol and 2.0 M HCl (1:1, 300 mL). The precipitated product was redissolved in THF (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 24 h in acetone and again filtered and dried. Isolated yield of **5** as a dark brown polymer = 130 mg (66%). GPC analysis $M_n = 6.11 \times 10^3$ g/mol, $M_w = 8.75 \times 10^3$ g/mol, and $D = 1.43$ (against PPP standard); $M_n = 7.30 \times 10^3$ g/mol, $M_w = 1.19 \times 10^4$ g/mol, and $D = 1.63$ (against PS standard). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.20−8.11 (br m, 4H), 7.69−7.45 (br m, 8H), 7.34−7.21 (br m, 6H), 6.99−6.81 (br m, 4H), 2.45−2.31 (br m, 4H), 1.47−1.20 (br m, 32H), 0.93−0.81 (br m, 6H). ^{13}C NMR (CD_2Cl_2, 125.75 MHz): δ 196.56, 148.81, 148.71, 142.63, 139.97, 139.95, 139.77, 138.45, 138.24, 135.60, 135.44, 135.25, 134.16, 134.04, 130.35, 130.21, 129.65, 129.56, 128.63, 125.63, 125.47, 36.45, 32.51, 31.74, 30.21, 30.10, 30.01, 29.94, 29.92, 29.28, 14.47. Anal. Calcd for $C_{60}H_{64}O_2$: C, 88.19; H, 7.89; O, 3.92; Found: C, 88.67; H, 7.11.

Polymer 6. A solution of 4-octylbromobenzene (0.627 mL, 0.7 g, 2.6 mmol) in anhydrous THF (20 mL) in a 250 mL Schlenk flask was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (1.78 mL, 1.6 M, 2.86 mmol) was then added, and the mixture was stirred for 20 min. Then a solution of

the diketone polymer **5** (100 mg, 0.122 mmol) in anhydrous THF (5 mL) was added dropwise with stirring, and the solution was allowed to slowly warm to room temperature. The mixture was stirred overnight and then quenched with 2 M HCl. The crude product was extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the crude product was redissolved in THF (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and dried. Isolated yield of the yellow polymer **6** = 130 mg (89%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.75−7.31 (br m, 10H), 7.11−6.81 (br m, 20H), 2.60−2.45 (br m, 8H), 1.69−1.21 (br m, 56H), 0.95−0.81 (br m, 12H). Anal. Calcd for $C_{88}H_{108}O_2$: C, 88.24; H, 9.09; O, 2.67; Found: C, 88.69; H, 9.43.

Polymer SLPPPA. The polyalcohol **6** (0.110 mg, 91.9 μmol) was dissolved in dichloromethane (15 mL), and boron trifluoride etherate (0.736 mL) was added with stirring at room temperature. The greenish colored solution turned deep brown immediately upon addition. The mixture was stirred for 12 h and the mixture was extracted into dichloromethane and washed several times with water. The solvent was removed in vacuo, and the compound was redissolved in THF (5 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 1 day in acetone. Isolated yield of the deep red polymer **SLPPPA** = 85 mg (80%). GPC analysis: $M_n = 7.24 \times 10^3$ g/mol, $M_w = 9.78 \times 10^3$ g/mol, and $D = 1.35$ (against PPP standard); $M_n = 9.81 \times 10^3$ g/mol, $M_w = 1.45 \times 10^4$ g/mol, and $D = 1.48$ (against PS standard). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.60−8.39 (br m, 2H), 8.01−7.82 (br m, 2H), 7.62−7.31 (br m, 4H), 7.39−6.70 (br m, 20H), 2.63−2.50 (br m, 8H), 1.59−1.45 (br m, 8H), 1.35−1.21 (br m, 48H), 0.91−0.71 (br m, 12H). ^{13}C NMR ($CDCl_3$, 125.75 MHz): δ 145.07, 143.36, 142.96, 140.84, 140.68, 140.51, 140.46, 140.31, 128.74, 128.55, 127.75, 127.51, 127.36, 127.28, 127.17, 126.92, 126.80, 59.77, 35.27, 31.63, 31.02, 30.94, 29.43, 29.35, 29.24, 29.07, 22.40, 13.84. Anal. Calcd for $C_{88}H_{104}$: C, 90.98; H, 9.02; Found: C, 90.37; H, 9.43.

Polymer 8. Diboronic ester **2** (0.193 g, 0.45 mmol), diketone **7** (0.326 g, 0.45 mmol), Aliquat 336 (0.025 g, 13 mol %), 2.0 mL of aqueous 2.0 M Na_2CO_3 and 5.5 mL of toluene were taken together in a Schlenk flask and purged with argon for 15 min. To this, tetrakis(triphenylphosphine)palladium (15 mg, 0.013 mmol) was added and the reaction heated at 85 °C under vigorous stirring for 24 h. Phenylboronic acid was then added as an end capper (2.0 mg), heated for 6 h and then bromobenzene (5.0 mg) was added and heated again for an additional 6 h. The reaction was poured into a mixture of methanol and 2.0 M HCl (1:1, 300 mL) and the precipitated product was redissolved in THF (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 24 h in acetone and filtered off and dried. Isolated yield of the brown polymer **8** = 150 mg (45%). GPC analysis $M_n = 3.63 \times 10^3$ g/mol, $M_w = 5.90 \times 10^3$ g/mol, and $D = 1.62$ (against PPP standard); $M_n = 4.37 \times 10^3$ g/mol, $M_w = 8.25 \times 10^3$ g/mol, and $D = 1.89$ (against PS standard). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92−7.75 (br m, 7H), 7.67−7.30 (br m, 8H), 7.04−6.67 (br m, 3H), 2.43−2.11 (br m, 4H), 1.41−1.20 (br m, 32H), 0.91−0.82 (br m, 6H). ^{13}C NMR ($CDCl_3$, 125.75 MHz): δ 196.23, 148.60, 148.50, 148.41, 148.30, 143.12, 142.85, 137.95, 137.80, 135.10, 134.91, 134.53, 134.35, 133.85, 133.66, 133.59, 130.27, 127.91, 127.80, 127.08, 125.85, 125.74, 36.04, 35.96, 32.14, 31.26, 31.20, 29.94, 29.83, 29.74, 29.68, 29.55, 29.45, 29.38, 22.89, 14.27. Anal. Calcd for $C_{54}H_{60}O_2$: C, 87.52; H, 8.16; O, 4.32; Found: C, 87.15; H, 8.51.

Polymer 9. A solution of 4-octylbromobenzene (0.627 mL, 0.7 g, 2.6 mmol) in 10 mL of anhydrous THF (20 mL) in a 250 mL Schlenk flask was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (1.78 mL, 1.6 M, 2.86 mmol) was then added and the mixture was stirred for 20 min. Then a solution of the diketone polymer **8** (100 mg, 0.135 mmol) in anhydrous THF (5 mL) was added dropwise with stirring and the solution was allowed to slowly warm to room temperature. The mixture was stirred overnight and then quenched with 2 M HCl. The crude product was extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the crude product was redissolved in THF (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and dried. Isolated yield of the greenish polymer **9** = 120 mg (79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62−7.21 (br m, 6H), 7.17−6.79 (br m, 20H), 2.63−2.41 (br m, 8H), 1.62−1.57 (br m, 8H), 1.49−1.20 (br m, 32H), 0.95−0.82 (br m, 12H). Anal. Calcd for $C_{82}H_{104}O_2$: C, 87.80; H, 9.35; O, 2.85; Found: C, 87.32; H, 9.73.

Polymer LPPPA. The polyalcohol **9** (0.135 g, 0.12 mmol) was dissolved in dichloromethane (15 mL), and boron trifluoride etherate (0.736 mL) was added with stirring at room temperature. The greenish color solution turned deep brown immediately upon addition. The mixture was stirred for 12 h, then extracted into dichloromethane and washed several times with water. The solvent was removed in vacuo and the compound was redissolved in THF (5 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 1 day in acetone. Isolated yield of the deep blue polymer **LPPPA** = 125 mg (95%). GPC analysis $M_n = 5.77 \times 10^3$ g/mol, $M_w = 8.19 \times 10^3$ g/mol, and $D = 1.42$ (against PPP standard); $M_n = 7.55 \times 10^3$ g/mol, $M_w = 1.19 \times 10^4$ g/mol, and $D = 1.58$ (against PS standard). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91−7.71 (br m, 4H), 7.47−6.50 (br m, 20H), 2.63−2.51 (br m, 8H), 1.51−1.15 (br m, 56H), 0.93−0.72 (br m, 12H). ^{13}C NMR ($CDCl_3$, 125.75 MHz): δ 141.84, 140.18, 131.84, 131.66, 128.64, 128.61, 128.57, 128.38, 127.55, 127.50, 127.40, 126.99, 126.62, 126.57, 125.36, 124.01, 59.40, 35.04, 34.99, 31.37, 30.79, 30.67, 30.53, 29.04, 28.92, 28.84, 28.81, 22.12, 13.48. Anal. Calcd for $C_{82}H_{100}$: C, 90.72; H, 9.28; Found: C, 90.47; H, 8.99.

Synthesis of 9-Bromo-10-phenylanthracene. Bromine (3.14 g, 19.65 mmol) in acetic acid (10 mL) was added dropwise over a period of 5 min to a vigorously stirred suspension of 9-phenylanthracene (5.0 g, 19.65 mmol) in acetic acid (50 mL) at room temperature. The reaction was left to stir for 30 min during which a canary yellow precipitate formed. The solution was quenched by the addition of $Na_2S_2O_5$, extracted into diethyl ether, washed with brine, and then dried over $MgSO_4$. The crude product was chromatographed on silica using hexane as eluent and further purified by recrystallization from THF in ethanol. Isolated yield = 6.0 g (91%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.32 (d, $J = 8.9$ Hz, 2H), 7.36 (d, $J = 8.7$ Hz, 2H), 7.29 (m, 3H), 7.08 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 138.35, 137.75, 131.08, 130.99, 130.19, 128.40, 127.80, 127.69, 127.35, 126.89, 125.50, 122.70. FDMS (*m*/*z*): 333.1 ($M^{+\bullet}$). Anal. Calcd for $C_{20}H_{13}$-Br: C, 72.09; H, 3.93; Br, 23.98; Found: C, 72.29; H, 3.71.

Synthesis of 4,4,5,5-Tetramethyl-2-(10-phenylanthracen-9-yl)-dioxaborolane (10). 9-Bromo-10-phenylanthracene (3.0 g, 9.0 mmol) was dissolved in 60 mL of anhydrous THF in a 250 mL Schlenk flask and cooled to −78 °C in an acetone/dry ice bath. To this, 8.43 mL of 1.6 M *n*-butyllithium (13.5 mmol) was added slowly and stirred for 30 min. Then 3.12 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.3 mmol) was added and slowly allowed to warm to room temperature. The reaction was stirred overnight and then quenched with brine; the product was extracted into dichloromethane washed again with brine and dried. The crude product was chromatographed on silica gel using 0−10% ethyl acetate in hexane as eluent. Isolated yield = 1.85 g (54%) as a light yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.48 (d, $J =$ 8.7 Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.59−7.45 (m, 5H), 7.42 (dd, $J = 7.8$ and 1.7 Hz, 2H), 7.34 (m, 2H), 1.68−1.57 (m, 12H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 139.54, 139.11, 135.36, 131.06, 129.69, 128.36, 128.27, 127.37, 125.38, 124.79, 84.44, 25.20. FDMS (*m*/*z*): 380.1 ($M^{+\bullet}$). Anal. Calcd for $C_{26}H_{25}BO_2$: C, 82.12; H, 6.63; B, 2.84; O, 8.4; Found: C, 81.99; H, 6.23.

Synthesis of (2,5-Di(10-phenylanthracen-9-yl)-1,4-phenylene)-di-4′-decylbenzophenone (11). The boronic ester **10** (1.5 g, 3.94 mmol), **7** (1.3 g, 1.79 mmol) was dissolved in THF (20 mL) in a 100 mL Schlenk flask. Aqueous 2 M K_2CO_3 solution (10 mL) was then added and purged with argon for 20 min, then tetrakis-(triphenylphosphine)palladium (124 mg, 0.107 mmol) was added, and the reaction was heated with stirring at 85 °C. The reaction

was followed by TLC and worked up after 2 days. The cooled mixture was extracted with diethyl ether, washed with brine and then dried over $MgSO_4$. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 1.5 g (78%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (d, J = 3.7 Hz, 4H), 7.98 (s, 2H), 7.67−7.52 (m, 14H), 7.47−7.38 (m, 12H), 6.85 (d, J = 8.2 Hz, 4H), 2.51−2.40 (m, 4H), 1.30−1.21 (m, 32), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 196.20, 148.21, 142.91, 138.87, 137.90, 137.77, 134.54, 133.66, 133.21, 131.19, 130.14, 129.64, 129.17, 128.30, 127.66, 127.45, 126.54, 125.62, 124.93, 35.87, 31.86, 31.08, 29.57, 29.46, 29.39, 29.27, 22.65, 14.09. FDMS (*m*/*z*): 1071.1 ($M^{+\bullet}$). Anal. Calcd for $C_{80}H_{78}O_2$: C, 89.68; H, 7.34; O, 2.99; Found: C, 89.87; H, 7.73.

Synthesis of (4-Decylphenyl)-[4-[(4-decylphenyl)-hydroxy(4-octylphenyl)methyl]-2,5-di(10-phenylanthracen-9-yl)phenyl](4-octylphenyl)methanol (12). A solution of 4-octylbromobenzene (1.24 mL, 1.38 g, 5.13 mmol) in anhydrous THF (30 mL) in a 250 mL Schlenk flask, was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (3.3 mL, 1.6 M, 5.31 mmol) was then added, and the mixture was stirred for 20 min. Then a solution of the diketone compound **11** (1.0 g, 0.933 mmol) in anhydrous THF (20 mL) was added dropwise with stirring, and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then quenched with 2 M HCl. The crude was extracted into dichloromethane, washed with brine and dried over $MgSO_4$. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 1.3 g (93%) as orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71−7.53 (m, 19H), 7.27−7.17 (m, 10H), 6.98 (dd, J = 21.8 and 8.1 Hz, 8H),6.87−6.79 (m, 7H), 2.59−2.40 (m, 8H), 1.52−1.50 (m, 8H), 1.45−1.17 (m, 48H), 0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 145.20, 144.36, 144.02, 143.44, 143.02, 141.78, 141.34, 141.28, 140.83, 139.22, 138.96, 137.48, 137.40, 136.72, 135.85, 135.78, 135.57, 134.86, 133.68, 132.54, 131.30, 129.68, 129.62, 128.35, 127.69, 127.39, 126.99, 126.69, 124.86, 124.82, 83.56, 35.40, 31.89, 31.32, 29.63, 29.55, 29.52, 29.48, 29.44, 29.39, 29.32, 29.27, 29.22, 22.67, 14.10. FDMS (*m*/*z*): 1451.2 ($M^{+\bullet}$). Anal. Calcd for $C_{108}H_{122}O_2$: C, 89.33; H, 8.47; O, 2.20; Found: C, 90.01; H, 8.81.

Synthesis of 9,19-Di(4-decylphenyl)-9,19-di(4-octylphenyl)-5,-15-diphenyl-9,19-dihydrodinaphtho[3,2,1-*de*:3′,2′,1′-*op*]pentacene (LMC). The diol **12** (0.5 g, 0.344 mmol) was dissolved in dichloromethane (15 mL), and boron trifluoride etherate (0.2 mL) was added with stirring at room temperature. The greenish colored solution turned deep brown immediately upon addition and then became dark. The mixture was stirred for 12 h, then extracted into dichloromethane and washed with water. The solvent was removed in vacuo, the compound was redissolved in THF (5 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and purified by recrystallization from THF in ethanol. Isolated yield = 0.45 g (92%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.06 (d, J = 9.0 Hz, 2H), 7.91 (s, 2H), 7.55 (m, 9H), 7.43 (d, J = 6.5 Hz, 3H), 7.34 (dd, J = 8.7 and 7.0 Hz, 2H), 7.17 (dd, J = 14.7 and 8.0 Hz, 3H), 6.96 (dd, J = 27.3 and 4.5 Hz, 15H), 2.56 (m, 8H), 1.54 (m, 8H), 1.41−1.21 (m, 48H), 0.86 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 144.35, 142.19, 142.04, 140.78, 139.24, 137.07, 132.71, 131.87, 131.31, 131.25, 130.25, 129.50, 127.53, 127.35, 127.29, 126.99, 126.84, 126.78, 125.46, 124.74, 124.50, 124.42, 60.03, 35.54, 31.87, 31.26, 29.61, 29.57, 29.52, 29.32, 29.23, 22.66, 14.10. FDMS (*m*/*z*): 1415.3 ($M^{+\bullet}$). Anal. Calcd for $C_{108}H_{118}$: C, 91.60; H, 8.40; Found: C, 91.27; H, 8.23.

Synthesis of 2-Iodo-4′-decylbenzophenone. To 2-iodobenzoyl chloride (5.0 g, 18.7 mmol) in 20 mL of dichloromethane were added aluminum chloride (3.0 g, 23.0 mmol) and decyl benzene (6.34 g, 29.1 mmol), and the reaction was stirred at room temperature for 12 h and then quenched with aqueous 2 M HCl. The mixture was extracted into dichloromethane and washed with brine. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 8.1 g (96%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92 (dd, J = 7.9 and 0.9 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.43 (dt, J = 7.5 and 1.1 Hz, 1H), 7.28 (m, 3H), 7.16 (dt, J = 7.8 and 1.7 Hz, 1H), 2.68 (t, J = 7.7 Hz, 2H), 1.71−1.60 (m, 2H), 1.37−1.27 (m, 14H), 0.89 (t, J = 6.7 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 196.64, 149.53, 144.53, 139.49, 133.16, 130.80, 130.51, 128.60, 128.23, 127.59, 92.15, 36.02, 31.78, 30.91, 29.48, 29.44, 29.34, 29.20, 29.18, 22.57, 14.03. FDMS (*m*/*z*): 448.1 ($M^{+\bullet}$). Anal. Calcd for $C_{23}H_{29}IO$: C, 61.61; H, 6.52; I, 28.30; O, 3.57; Found: C, 61.57; H, 6.33.

Synthesis of 9,10-Di(4′-decylbenzophenon-2yl)anthracene (13). The boronic ester **2** (0.7 g, 1.63 mmol), 2-iodo-4′-decylbenzophenone (1.82 g, 4.07 mmol), and K_2CO_3 (1.1 g, 3.26 mmol) were dissolved in THF (20 mL) and water (10 mL) in a 100 mL Schlenk flask. The solution was purged with argon for 20 min, tetrakis-(triphenylphosphine)palladium (230 mg, 0.199 mmol) was added and the reaction followed by TLC and after 16 h was worked up. The cooled mixture was extracted with diethyl ether, washed with brine and then dried over $MgSO_4$. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 1.2 g (90%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (ddd, J = 15.0, 8.1, and 5.9 Hz, 6H), 7.40 (m, 4H) ppm 7.31 (dd, J = 7.2 and 1.3 Hz, 2H), 7.20 (d, J = 8.2 Hz, 3H), 7.11 (m, 4H), 7.01 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 3H), 6.61 (d, J = 8.2 Hz, 1H), 2.37−2.23 (m, 4H), 1.48−1.45 (m, 4H), 1.34−1.11 (m, 28H), 0.79 (t, J = 7.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 197.54, 147.49, 141.56, 138.05, 135.23, 134.90, 129.65, 129.61, 129.28, 127.72, 126.84, 124.68, 35.81, 35.75, 31.88, 31.18, 31.04, 29.62, 29.57, 29.47, 29.41, 29.32, 29.22, 25.16, 22.66, 14.09. FDMS (*m*/*z*): 819.0 ($M^{+\bullet}$). Anal. Calcd for $C_{60}H_{66}O_2$: C, 87.97; H, 8.12; O, 3.91; Found: C, 88.02; H, 8.32.

Synthesis of (4-Decylphenyl)[2-(10-{2-[(4-decylphenyl)hydroxy-(4-octylphenyl)methyl]phenyl}anthracen-9-yl)phenyl](4-octylphenyl)methanol (14). A solution of 4-octylbromobenzene (0.92 mL, 1.02 g, 3.78 mmol) in 20 mL of anhydrous THF (20 mL), in a 250 mL Schlenk flask, was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (2.46 mL, 1.6 M, 3.93 mmol) was then added, and the mixture was stirred for 20 min. Then a solution of the diketone **13** (597 mg, 0.728 mmol) in anhydrous THF (20 mL) was added dropwise with stirring, and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then quenched with brine. The mixture was extracted into diethyl ether, washed with brine, and dried over $MgSO_4$. The crude product obtained was purified by chromatography on silica with 0−10% ethyl acetate in hexane as eluent. Isolated yield = 0.78 g (88%) as a thick viscous greenish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (dd, J = 5.9 and 3.3 Hz, 2H), 7.38 (m, 2H), 7.27−7.19 (m, 12H), 7.00−6.91 (m, 13H), 6.89−6.71 (m, 3H), 2.51−2.43 (m, 8H), 1.58−1.45 (m, 8H), 1.34−1.11 (m, 48H), 0.79 (t, J = 7.1 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 146.61, 144.69, 143.87, 141.30, 140.85, 140.77, 139.57, 137.36, 136.82, 134.38, 129.55, 129.09, 128.87, 127.94, 127.81, 127.73, 127.66, 127.61, 127.22, 126.90, 126.71, 126.26, 125.66, 125.01, 124.23, 83.67, 35.57, 35.43, 31.91, 31.49, 31.25, 29.66, 29.61, 29.59, 29.49, 29.45, 29.33, 29.27, 22.68, 14.10. FDMS (*m*/*z*): 1199.8 ($M^{+\bullet}$). Anal. Calcd for $C_{88}H_{110}O_2$: C, 88.09; H, 9.24; O, 2.67; Found: C, 88.37; H, 9.53.

Synthesis of 8,16-Di(4-decylphenyl)-8,16-di(4-octylphenyl)-8,-16-dihydrodibenzo[*a*,*j*]perylene (SLMC). The diol **14** (0.776 g, 0.647 mmol) was dissolved in dichloromethane (15 mL), and boron trifluoride etherate (0.2 mL) was added with stirring at room temperature. The greenish colored solution turned deep brown immediately upon addition and subsequently became a dark solution. The mixture was stirred for 12 h, methanol (50 mL) was added into the solution and the solid filtered. The crude product was washed with methanol and dried. Isolated yield = 0.69 g (92%) as a thick viscous, reddish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.52 (dd, J = 6.7 and 3.3 Hz, 2H), 8.06 (d, J = 7.8 Hz, 2H), 7.35 (dt, J = 5.8 and 2.5 Hz, 5H), 7.13 (dd, J = 7.8 and 1.3 Hz, 3H), 7.21−7.11 (m, 9H), 6.99−6.75 (m, 9H), 2.57−2.41 (m, 8H), 1.57−

1.41 (m, 8H), 1.37−1.21 (m, 48H), 0.87 (t, $J = 5.7$ Hz, 12H. ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 144.93, 141.11, 139.82, 134.63, 131.17, 129.72, 129.34, 129.12, 127.74, 127.62, 127.54, 126.52, 126.19, 125.26, 60.17, 35.69, 32.16, 32.13, 31.51, 29.87, 29.76, 29.71, 29.59, 22.94, 14.37. FDMS (*m*/*z*): 1162.9 ($M^{+\bullet}$). Anal. Calcd for $C_{88}H_{106}$: C, 90.82; H, 9.18; Found: C, 90.53; H, 8.99.

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Supporting Information Available: Figures showing FT-IR spectra of **5**, **8**, **SLPPPA**, and **LPPPA** and the simulated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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