

Synthesis of Poly(1,4-naphthylenevinylenes): Metathesis Polymerization of Benzobarrelenes[†]

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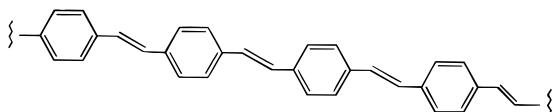
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ABSTRACT: The syntheses of hexyl- and undecyl-substituted benzobarrelenes **10a,b** are described. These molecules readily undergo ring-opening metathesis polymerization (ROMP) to generate the corresponding ring-opened polymers **11a,b**. Polymers **11a,b** can be conveniently converted into alkyl-substituted poly(1,4-naphthylenevinylenes) (PNVs), **13a,b**, by oxidizing them using DDQ (2,3-dichloro-5,6-dicyanoquinone). Both **13a** and **13b** are soluble in organic solvents and are shown by NMR and UV/vis spectroscopy to be fully conjugated. Strong fluorescence is observed for these new materials. Thin films can be prepared by spin-coating chloroform solutions of the conjugated polymers on glass slides. After being doped with an acetonitrile solution of nitrosonium tetrafluoroborate, these polymer films become highly conductive. The conductivities of **13a,b**, 6 and 15 S cm⁻¹, respectively, are over 2 orders of magnitude higher than that of the insoluble PNV previously prepared by a different precursor route.

Introduction

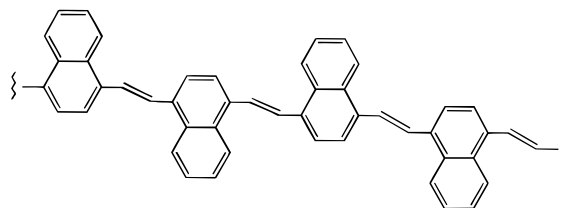
Conjugated organic polymers exhibit many interesting electrical and optical properties and have potential for use in practical devices.¹ One of the most interesting conjugated polymers is poly(*p*-phenylenevinylene) (PPV),



which is composed of alternating phenylene and vinylene units. This material is an organic semiconductor that can become conductive upon oxidative or reductive doping.² Poly(phenylenevinylene) also demonstrates photo- and electroluminescent properties,³ as well as large third-order nonlinear optical activity.⁴ However, because of its rigid planar structure, PPV is insoluble and difficult to process. To overcome this problem, precursor routes have been developed. This strategy involves the preparation of a soluble, processable precursor polymer that can be converted to the desired conjugated form.⁵ Recently, a metal carbene catalyzed "living" ring-opening metathesis polymerization (ROMP) was utilized to make PPV via such a precursor route (Scheme 1).⁶ In this process, a barrene derivative **1**

a soluble precursor polymer, **3**. Thermal elimination of acetate from **3** at temperatures above 200 °C led to the formation of PPV. By using well-defined metal–carbene complexes to catalyze the polymerization,⁷ it was possible to control the molecular weight and the molecular weight distribution of the precursor polymer and ultimately the structure and properties of the conjugated polymer.

A related process can be used to prepare poly(1,4-naphthylenevinylene) (PNV), a polymer that, in spite of its potential for use in electrooptical devices, has received little attention.⁸ In the structure of PNV, an additional phenyl ring is fused to the backbone of PPV.



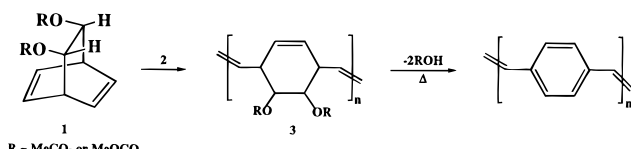
We now report the synthesis and ROMP of benzobarrene derivatives to generate alkyl-substituted PNVs, a new class of soluble and highly conductive materials.

Results and Discussion

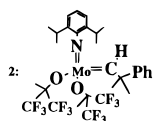
A. Preparation of Benzobarrene Monomers.

Benzobarrene, **4**, represents an interesting class of strained bicyclic olefins, which can be synthesized from hexachlorobenzene in two steps (Scheme 2).⁹ Although this route is efficient for the preparation of benzobarrene, efforts to extend this method to the synthesis of benzobarrene derivatives bearing alkyl substituents on the phenyl ring have failed. Alkyl substituents are required to increase the solubility of the resulting poly(arylenevinylenes). The tetrachloro-substituted benzobarrene, **5**, was inert to alkyl Grignard reagents in the presence of either nickel or palladium catalysts.¹⁰ All other ways to prepare benzobarrene either involved many synthetic steps or gave very low yields.¹¹ In order to obtain the desired benzobarrene derivatives, a new synthesis was recently developed.¹² This method involved the addition of a substituted benzyne

Scheme 1



R = MeCO- or MeOCO-

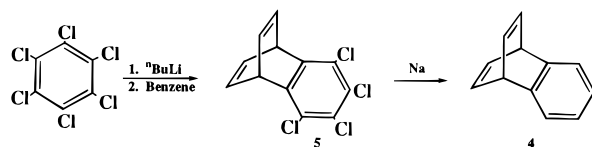


was synthesized and polymerized by a molybdenum bis(hexafluoro-*tert*-butoxy)carbene catalyst, **2**, to generate

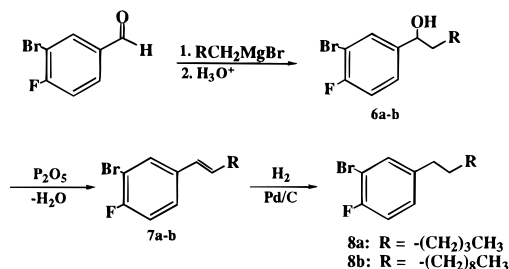
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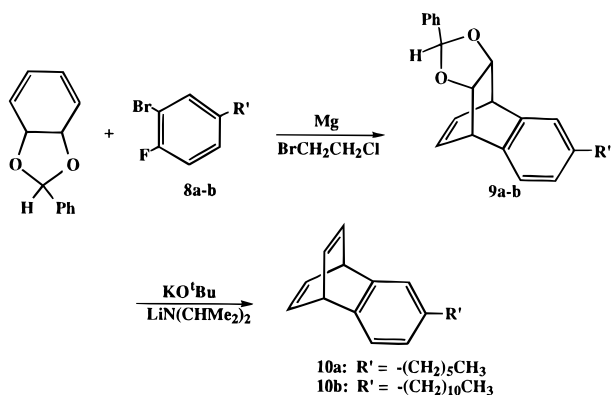
Scheme 2



Scheme 3



Scheme 4



to a cyclohexadienediol derivative, followed by a base-promoted thermal fragmentation. To make long chain alkyl-substituted benzobarrelenes, alkyl-substituted benzyne precursors were prepared (Scheme 3).

When commercially available 3-bromo-4-fluorobenzaldehyde was reacted with Grignard reagents, the alcohols **6a,b** were obtained in high yields. Dehydration of **6a,b** in THF solution with P_2O_5 at 60 °C generated **7a,b**, which were then hydrogenated to **8a,b**. The overall yield obtained from the aldehyde to the desired alkyl-substituted aromatics was 90%. The reaction of **8a,b** with 1,2-(benzylidenedioxy)-3,5-cyclohexadiene and magnesium in the presence of an initiator, 1-bromo-2-chloroethane, produced **9a,b**. Since none of the catalysts would polymerize the acetals **9a,b**, alkyl-substituted benzobarrelenes **10a,b** were prepared by the base-promoted thermal elimination of benzoate from **9a,b** (Scheme 4).

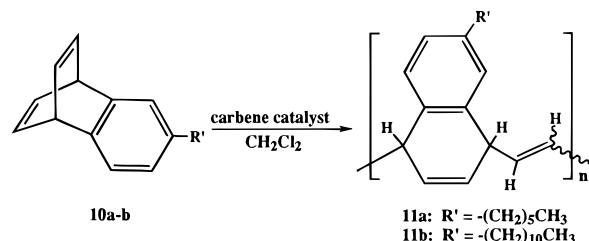
B. Ring-Opening Metathesis Polymerization of Benzobarrelenes. The strained benzobarrelenes were readily polymerized using a metal-carbene ROMP catalyst. In methylene chloride, benzobarrelene was polymerized by **2** to yield a white precipitate, which was not soluble in any organic solvents. This indicates a very rigid structure for the ring-opened polymer of benzobarrelene. In order to make soluble benzobarrelene polymers and soluble conjugated PNVs, the alkyl chain substituted benzobarrelenes **10a,b** were polymerized.

Polymerization of **10a** and **10b** by a molybdenum carbene catalyst in methylene chloride produced a viscous solution after several hours. When the reaction was complete, the polymers **11a** and **11b** were precipi-

Table 1. Selected NMR Data of **10a,b** and **11a,b**

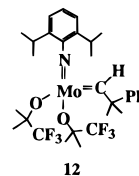
	¹ H NMR signals, δ		
	bridge head proton	olefin proton	¹³ C NMR signals, δ bridge head carbon
10a	4.93 (m, 2H)	6.91 (t, $J = 3.6$ Hz, 4H)	49.14, 48.73
11a	cis: 4.36	cis: 6.05, 5.96, 5.38	cis: 38.12 (m)
	trans: 3.95	trans: 5.86, 5.53	trans: 43.45, 43.16
10b	4.89 (m, 2H)	6.88 (t, $J = 3.6$ Hz, 4H)	49.15, 48.74
11b	cis: 4.62	cis: 6.03, 5.93, 5.36	cis: 37.86 (m)
	trans: 3.93	trans: 5.86, 5.54	trans: 43.44, 43.22

Scheme 5



tated with methanol and separated by centrifuging the resulting suspension (Scheme 5). When **2** was used as the catalyst, a mixture of cis:trans isomers was obtained; the cis/trans ratio was in the range of 1:3 to 1:7 depending on the concentration of the monomers and the monomer to catalyst ratio.

When **10b** was polymerized by the molybdenum bis-(trifluoro-*tert*-butoxy) carbene catalyst, **12**, however, the trans isomer was obtained exclusively. The factors that

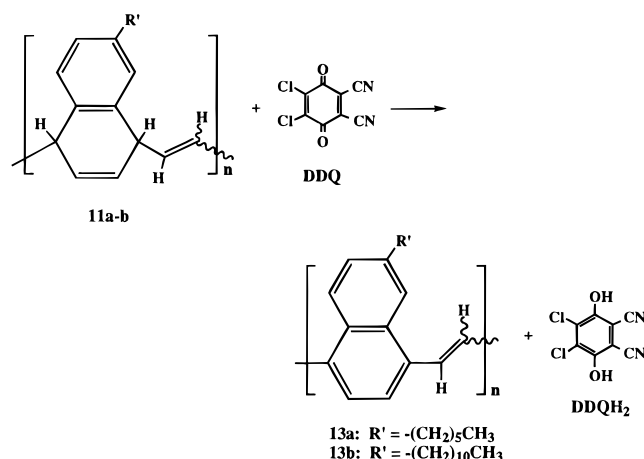


control the stereochemistry of the polymers formed by this class of catalysts remain under investigation. While the all-trans polymer is soluble, it was not used for further study because it became insoluble upon oxidation to its fully conjugated form.

Table 1 lists selected ¹H and ¹³C NMR resonances for **10a,b** and **11a,b**. The signals due to the bridgehead carbons and protons in monomers **10a,b** were shifted upfield in polymers **11a,b** because of the release of the strain. In the ¹³C NMR spectrum of **11a**, two groups of signals were observed for the tertiary sp³ carbons in the six member rings of the polymer. The peaks at 43.45 and 43.16 ppm were assigned to the trans isomer, and the multiplet at 37.86 ppm was assigned to the cis isomer by analogy to polynorbornene.¹³ The cis:trans ratio of **11a** (vide supra) was determined by the intensity of the methine proton signals at 4.66 (cis) and 3.95 (trans) ppm in the ¹H NMR spectrum. The ¹H and ¹³C NMR spectra of **11b** were similar to those of **11a**.

Molecular weights of the polymers were determined by gel permeation chromatography (GPC, methylene chloride). When a 0.25 M solution of **10a** was polymerized by **2** (0.013 equiv), GPC of the polymer obtained, **11a**, showed $M_n = 4900$, $M_w = 26\,600$, and PDI = 5.4. GPC of the polymer **11b**, obtained from 0.42 M **10b** and **2** (0.02 equiv), showed $M_n = 11\,700$, $M_w = 59\,800$, and PDI = 5.10. The broad polydispersity observed for these polymers may be due to termination of the growing chain by the highly active triallylic β-hydrogen in the

Scheme 6



propagating carbene or could also be due to initiation being slow relative to propagation.

Thermogravimetric analysis (TGA) of **11a** in the presence of air indicated that the polymer was stable up to 258 °C. From 258 to 376 °C polymer **11a** lost 5% of its mass, and by 474 °C the total mass lost was 63%. Under argon, TGA showed that **11a** was stable up to 241 °C. From 241 to 386 °C it lost 9% of its mass, and by 462 °C it lost 79% of its original mass. TGA of polymer **11b** in the presence of air showed that it was stable up to 264 °C. From 264 to 381 °C the polymer lost 7% of its mass, and by 472 °C it lost 76% of its original mass. Under argon, TGA showed **11b** was stable up to 251 °C. From 251 to 359 °C it lost 6% of its mass, and by 500 °C it lost 88% of its original mass. These TGA results demonstrate that it is difficult to thermally convert **11a** or **11b** to its oxidized conjugated form (0.84% weight loss) without further degradation of the polymer.

C. Preparation of the Conjugated Polymers by Oxidation of the Precursor Polymers. Precursor polymers **11a,b** were readily oxidized by DDQ (2,3-dichloro-5,6-dicyanoquinone) at room temperature.¹⁴ When a yellow solution of DDQ was added to a pale yellow solution of a precursor polymer, a dark red slurry formed immediately. After the reaction was complete, methanol was added to precipitate the oxidized polymer, **13a** or **13b** (Scheme 6). DDQH₂ (2,3-dichloro-5,6-dicyanodihydroquinone) produced from reduction of DDQ is not very soluble in methylene chloride but can be dissolved by methanol, so it was removed by repeatedly dissolving the polymer in methylene chloride, or chloroform, and then precipitating it in methanol.

GPC (methylene chloride) of **13a** showed $M_n = 2\,000$, $M_w = 5\,000$, and PDI = 2.5. Although the polymer was soluble in methylene chloride before it was dried, it could not be completely dissolved even with sonication after being dried under vacuum or in air. Therefore, the GPC data obtained for **13a** (dried) only reflected the molecular weight of the polymer which dissolved in methylene chloride. Polymer **13b** was found to be completely soluble in methylene chloride after sonication. This is probably because **13b** has a longer flexible alkyl chain than **13a**. GPC (methylene chloride) showed $M_n = 9\,900$, $M_w = 47\,100$, and PDI = 4.8. Under argon, TGA of **13a** showed that the polymer was stable up to 258 °C. From 258 to 387 °C it lost 4% of its mass, and by 519 °C it lost 64% of its original mass. TGA of **13b** under argon showed that the polymer began decompos-

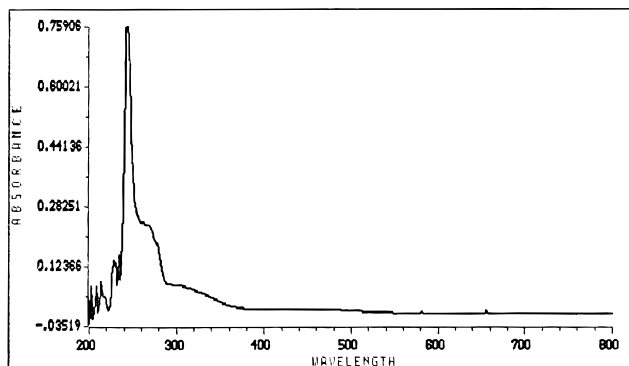


Figure 1. UV/vis spectrum of **10a** in chloroform.

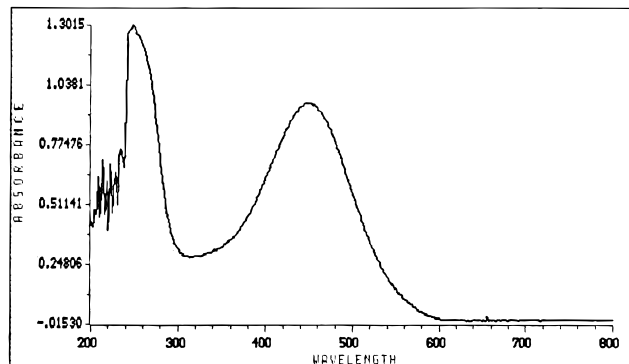


Figure 2. UV/vis spectrum of **11a** in chloroform.

ing at 369 °C and by 500 °C it lost 83% of its original mass.

Both **13a** and **13b** are soluble in chloroform and chlorobenzene upon sonication. The ¹H NMR spectra of the polymers in deuterated chloroform shows the disappearance of the methine proton signals of the precursor polymers, indicating >95% completion of the oxidation. All of the olefin proton signals observed in the precursor polymers are shifted to the aromatic region in the fully conjugated polymers.

The UV/vis spectrum of **13a** displays a strong absorbance at 448 nm, which demonstrates the formation of an extended π -conjugation in the oxidized polymer after the dehydrogenation of **11a** (Figures 1 and 2). The UV/vis spectrum of **13b** shows a similar absorbance at 450 nm. When excited at 440 nm, the fluorescence emission spectra of **13a** and **13b** show strong signals at 583 and 572 nm, respectively. By visual observation, solutions of the conjugated polymers glow yellow orange under UV irradiation. The FT-IR (KBr pellet) spectra of **13a,b** show strong signals at 956 cm⁻¹, corresponding to the ethylene out-of-plane bending mode. These signals indicate that trans isomers dominate in the conjugated polymers. Figure 3 is the FT-IR spectrum of **13a** (KBr pellet).

Thin films of **13a,b** were prepared by spin-coating chloroform solutions of the polymers on glass slides. These films were then doped using a solution of nitrosonium tetrafluoroborate in acetonitrile. When immersed into the dopant solution, the color of the films immediately turned dark green from red-orange, suggesting that the polymers were oxidized. The doped conjugated polymers showed excellent conductivities of 6 S cm⁻¹ for doped **13a** and 15 S cm⁻¹ for doped **13b**.¹⁵

For comparison, previous reports describe the preparation of poly(1,4-naphthylenevinylene) via the precursor route shown in Scheme 7.^{8a-f}

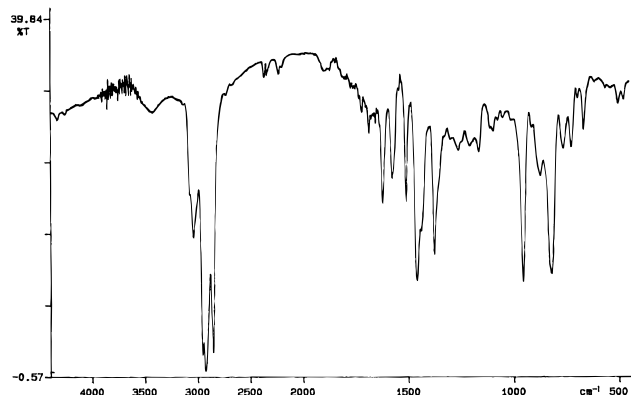
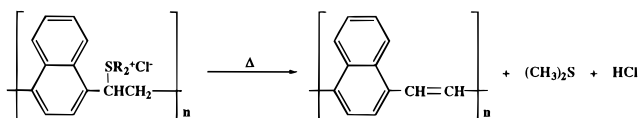


Figure 3. FT-IR spectrum of **13a** (KBr pellet).

Scheme 7



This process, which requires a thermal elimination carried out at 300 °C, resulted in insoluble PNV. Doped polymers prepared by this route have been reported with conductivities of 0.032 S cm⁻¹ by doping with AsF₅^{8a} and 3 S cm⁻¹ by electrochemical doping.^{8d} One possible explanation for the increased conductivity of the soluble polymers presented here is that the route used avoids the high-temperature thermal elimination, which may cause cross-linking or degradation of the polymer which could decrease the polymer's conductivity.

Conclusions

Poly(1,4-naphthylenevinylenes) have been synthesized from benzobarrelenes using metal-carbene-catalyzed ring-opening metathesis polymerization. The introduction of alkyl substituents to the backbone of the rigid, planar PNV structure renders the polymer soluble in common organic solvents, which allows the polymer to be characterized by routine spectroscopic methods such as ¹H NMR, ¹³C NMR, and UV/vis. The PNVs obtained show strong fluorescence, and thin films can be conveniently prepared from solutions of the conjugated polymers. After doping, these polymer films exhibit excellent conductivity. The synthesis of PNVs described here not only produces soluble and processable conducting materials under very mild conditions but also avoids the high-temperature cross-linking or degradation that may be involved in the previously reported precursor route. Alkyl-substituted PNVs represent a new class of soluble conducting polymers whose solubility and conductivity make them very attractive materials. Practical applications of these materials are currently being explored and the synthesis of PNVs bearing different functional groups is also being carried out.

Experimental Section

General Data. NMR spectra were recorded on a QE Plus-300 MHz (300.1 MHz ¹H; 75.33 MHz ¹³C) spectrometer. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Elemental analyses were performed by Oneida Research Corp. or Mid-West Microlab. High-resolution mass spectra were obtained from the UC Riverside Mass Spectrometry Facility. UV/vis spectra were recorded on a HP Vectra ES/12 spectrometer. Thermogravimetric analyses were carried out using a TGA 7 thermogravimetric analyzer.

Gel permeation chromatography (GPC) utilized an AM Gel Linear 10 column and a Knauer differential refractometer. Emission spectra were recorded on an SLM 8000 C spectrofluorometer. Conductivity was measured with a standard four-point probe using a Princeton Applied Research (PAR) model 173 potentiostat and a PAR model 175 universal programmer. The thickness of thin films was measured with a Sloan Dektak 3030 profilingmeter. Ether was dried with sodium benzophenone. THF, hexane, and benzene were dried by passing through activated alumina columns. Grignard reagents, 3-bromo-4-fluorobenzaldehyde, lithium diisopropylamide, potassium *tert*-butoxide, and DDQ were purchased from Aldrich and used without further purification.

Preparation of 1-(3-Bromo-4-fluorophenyl)undecanol, 6b. Under argon, decylmagnesium bromide (1.0 M ether solution, 100.8 mL) was added to a dry ether solution of 3-bromo-4-fluorobenzaldehyde (20.1 g, 0.099 mol, 0.99 M) at 0 °C over 20 min. After the addition was complete, the reaction mixture was stirred at 0 °C for an additional 30 min and then at room temperature for 2 h. An aqueous solution of HCl (1.82 M, 100 mL) was then added to quench the reaction at 0 °C, and a white precipitate was formed. The mixture was extracted with ether (3 × 200 mL) and dried over Na₂SO₄. After filtration and removal of the solvent, the resulting product was dissolved in benzene and dried under vacuum. A yellow oil, **6b**, was obtained in quantitative yield. ¹H NMR (CDCl₃): δ 7.55 (dd, *J* = 9, 1 Hz, 1H), 7.23 (m, 1H), 7.08 (t, *J* = 9 Hz, 1H), 4.64 (m, 1H), 1.70 (m, 2H), 1.26 (br, 16H), 0.88 (t, *J* = 7 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 158.1 (d, *J*_{C-F} = 981.6 Hz), 142.2 (d, *J*_{C-F} = 14.1 Hz), 130.8, 126.3 (d, *J*_{C-F} = 28.2 Hz), 116.1 (d, *J*_{C-F} = 88.2 Hz), 108.8 (d, *J*_{C-F} = 84 Hz), 73.24, 39.08, 31.85, 29.55, 29.49, 29.42, 28.28, 25.56, 22.63, 14.03. Exact mass (EI) *m/e* calcd for C₁₇H₂₆BrFO: 344.1151. Obsd: 344.1159.

Preparation of 2-Bromo-1-fluoro-4-(1-undecenyl)benzene, 7b. Under argon, a hexane (dry) solution of **6b** (34.11 g, 0.099 mol, 0.40 M) was added, over 3.5 h via an addition funnel, to a round bottom flask containing P₂O₅ (47 g, 0.33 mol) in refluxing hexane (dry, 250 mL). The resulting reaction mixture was refluxed for another 20 min. After filtration and removal of the solvent, ¹H NMR spectroscopy showed the formation of **7b** with <5% impurity. The crude product was used for the next reaction without further purification. ¹H NMR (CDCl₃): δ 7.52 (dd, *J* = 9 Hz, 1 Hz, 1H), 7.20 (m, 1H), 7.02 (t, *J* = 9 Hz, 1H), 6.20 (m, 2H), 2.19 (q, *J* = 7 Hz, 2H), 1.45 (br m, 2H), 1.27 (br, 12H), 0.88 (t, *J* = 7 Hz, 3H). ¹³C NMR (CDCl₃): δ 157.9 (d, *J*_{C-F} = 981 Hz), 135.6 (d, *J*_{C-F} = 16.2 Hz), 132.4 (d, *J*_{C-F} = 6.6 Hz), 130.5, 127.3, 126.2 (d, *J*_{C-F} = 27.3 Hz), 116.2 (d, *J*_{C-F} = 89.7 Hz), 109.0 (d, *J*_{C-F} = 86.7 Hz), 32.97, 31.93, 29.62, 29.56, 29.51, 29.38, 29.26, 22.72, 14.11. Exact mass *m/e* calcd for C₁₇H₂₄BrF: 326.1045. Obsd: 326.1049.

Preparation of 2-Bromo-1-fluoro-4-undecylbenzene, 8b. A mixture of **7b** (0.094 mol) and 10% Pd/C (398 mg) in ethyl acetate (200 mL) was stirred under a hydrogen balloon for >12 h and filtered through Celite. The solvent was then removed under vacuum. The resulting orange oil was distilled between 141 °C/140 mTorr and 148 °C/130 mTorr to yield a colorless oil, **8b** (yield 95%). The isolated yield of **8b** based upon 3-bromo-4-fluorobenzaldehyde was 90%. ¹H NMR (CDCl₃): δ 7.35 (dd, *J* = 9, 1 Hz, 1H), 7.05 (m, 1H), 7.00 (t, *J* = 9 Hz, 1H), 2.55 (t, *J* = 9 Hz, 2H), 1.58 (br m, 2H), 1.29 (br, 16H), 0.89 (t, *J* = 7 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 157.3 (d, *J*_{C-F} = 972 Hz), 140.2 (d, *J*_{C-F} = 17.1 Hz), 133.0, 128.6 (d, *J*_{C-F} = 26.7 Hz), 115.9 (d, *J*_{C-F} = 87.9 Hz), 108.5 (d, *J*_{C-F} = 81.6 Hz), 34.89, 31.97, 31.41, 29.69, 29.61, 29.48, 29.41, 29.18, 22.74, 14.12. Exact mass (EI) *m/e* calcd for C₁₇H₂₆BrF: 328.1202. Obsd: 328.1211.

Preparation of 6-Undecyl-1,2,3,4-tetrahydro-2,3-(benzylidenedioxy)-1,4-ethenonaphthalene, 9b. In a drybox, a THF (dry, 30 mL) solution of **8b** (12.6 g, 0.038 mol) and 1-bromo-2-chloroethane (5.75 g, 0.040 mol) was loaded into a 50 mL syringe. Using a syringe pump, this solution was added over 3 h to a THF (dry, 50 mL) solution of 1,2-(benzylidenedioxy)-3,5-cyclohexadiene (3.79 g, 0.019 mol) and magnesium

(4.5 g, 0.185 mol) at 60 °C (oil bath temperature). During the addition, gas was evolved. After the addition was complete, the reaction mixture was continuously heated at 60 °C for 12 h. The solvent was then removed under vacuum. The resulting residue was loaded onto a plug of silica gel (175 mL) and eluted with 1200 mL of ether. After removal of ether, a yellow solid was obtained. The product was recrystallized by partially dissolving in warm pentane and cooling at -50 °C for 12 h. Filtration of the cold mixture afforded light yellow crystals of **9b** (4.91 g, 60% yield based upon 1,2-(benzylidenedioxy)-3,5-cyclohexadiene). ¹H NMR (CDCl₃): δ 7.54 (m, 2H), 7.39 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.10 (s, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.62 (m, 2H), 5.80 (s, 1H), 4.34 (s, 2H), 4.26 (s, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.59 (br, 2H), 1.27 (br, 16H), 0.89 (t, *J* = 6.6 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 141.3, 140.4, 137.6, 136.5, 133.3, 133.0, 129.7, 128.3, 127.5, 126.2, 125.1, 124.6, 106.0, 79.80, 79.75, 45.34, 44.88, 35.77, 31.91, 31.65, 29.67, 29.63, 29.58, 29.51, 29.43, 29.35, 22.69, 14.13. Exact mass (EI) *m/e* calcd for C₃₀H₃₈O₂ + H⁺: 431.2950. Obsd: 431.2964. Anal. Calcd for C₃₀H₃₈O₂: C, 83.68; H, 8.89. Found: C, 83.48; H, 8.84.

Compounds **6a**, **7a**, **8a**, and **9a** were prepared and characterized in the manner described for compounds **6b**, **7b**, **8b**, and **9b**, respectively.

Preparation of 6-Undecyl-1,4-dihydro-1,4-ethenonaphthalene, 10b. Under argon, a slurry of lithium diisopropylamide (LDA, 7.70 g, 71.8 mmol) in diethyl ether (dry, 50 mL) was added to a mixture of **9b** (2.03 g, 4.68 mmol) and potassium *tert*-butoxide (7.91 g, 70.5 mmol) in diethyl ether (dry, 50 mL) at 60 °C (oil bath temperature) over 5 h. After the addition was complete, the reaction mixture was kept at 60 °C for another hour. The resulting dark brown slurry was cooled with an ice bath, and water (4 mL) was added to quench the reaction. The mixture was then filtered through a plug of silica gel (100 mL) and eluted with 800 mL of ether. After removal of ether, the residue was loaded onto a silica gel column (7 in. × 2 in.) and eluted with hexane. The product was collected from 335 to 1300 mL. The solvent was removed to give a light yellow liquid, **10b** (1.18 g, 81.6% yield). ¹H NMR (CDCl₃): δ 7.06 (d, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.88 (t, *J* = 3.6 Hz, 4H), 6.77 (d, *J* = 6.9 Hz, 1H), 4.89 (m, 2H), 2.51 (t, *J* = 7.8 Hz, 2H), 1.55 (p, *J* = 7.1 Hz, 2H), 1.27 (br, 16H), 0.89 (t, *J* = 6.6 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 147.5, 144.8, 139.8, 139.5, 138.2, 122.9, 122.7, 121.7, 49.15, 48.74, 35.64, 31.91, 31.68, 29.67, 29.63, 29.59, 29.53, 29.48, 29.34, 22.69, 14.13. Exact mass (EI) *m/e* calcd for C₂₃H₃₂: 308.2504. Obsd: 308.2505. Anal. Calcd for C₂₃H₃₂: C, 89.54; H, 10.46. Found: C, 89.47; H, 10.43.

6-Hexyl-1,4-dihydro-1,4-ethenonaphthalene, 10a, was prepared as described for **10b**. ¹H NMR (CDCl₃): δ 7.10 (d, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 6.91 (t, *J* = 3.6 Hz, 4H), 6.73 (d, *J* = 7.2 Hz, 1H), 4.93 (m, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.61 (p, *J* = 7.4 Hz, 2H), 1.34 (br, 6H), 0.93 (t, *J* = 6.6 Hz, 3H). ¹³C{¹H} NMR (CDCl₃): δ 147.5, 144.8, 139.8, 139.5, 138.1, 122.9, 122.7, 121.7, 49.14, 48.73, 35.64, 31.74, 31.64, 29.15, 22.60, 14.11. Exact mass (EI) *m/e* calcd for C₁₈H₂₂: 238.1722. Obsd: 238.1717.

Preparation of Precursor Polymer 11a. In a drybox, to a methylene chloride solution (2.6 mL) of **10a** (314 mg, 1.32 mmol) was added a solution of **2** (12.8 mg, 1.67 × 10⁻² mmol) in methylene chloride (2.6 mL). The resulting yellow solution was stirred at room temperature for 5 h, during which a brown color developed and the solution became viscous. After the polymerization was complete, as shown by ¹H NMR spectroscopy, methanol was added to precipitate out the polymer. The precipitate was isolated by centrifuging the suspension and further purified by redissolving the polymer in methylene chloride and precipitating it with methanol two more times. After being dried under vacuum, **11a** was obtained as a pale yellow tacky solid in quantitative yield. ¹H NMR (CDCl₃, all peaks were broad): δ 7.13, 7.04, 6.05 (cis), 5.96 (cis), 5.86, 5.53, 5.38, 4.36 (cis), 3.95, 2.59, 1.62, 1.33, 0.91. ¹³C{¹H} NMR (CDCl₃): δ 140.9 (m), 135.9 (m), 133.7 (m), 132.3 (m), 128.8 (br), 127.9 (m), 126.6, 43.45 and 43.16 (trans), 38.12 (cis, m), 35.64 (m), 31.76, 31.46, 29.25, 29.12, 22.64, 14.16. UV/vis (chloroform): λ_{max}/nm = 244. IR (KBr, pellet): ν/cm⁻¹ = 3022

(s), 2926 (s), 2854 (s), 1614 (w), 1573 (w), 1498 (s), 1461 (s), 1378 (m), 1081 (w), 1028 (w), 965 (s), 891 (w), 820 (m), 790 (m), 724 (m). Anal. Calcd for (C₁₈H₂₂)_n: C, 90.70; H, 9.30. Found: C, 90.21; H, 9.22.

Preparation of Precursor Polymer 11b. In a drybox, to a solution of **10b** (1.038 g, 3.36 mmol) in methylene chloride (dry, 7.3 mL) was added a methylene chloride solution (0.8 mL) of **2** (51 mg, 6.68 × 10⁻² mmol). The resulting yellow solution was stirred at room temperature for 11 h, during which the solution turned cloudy orange and viscous and a clump of white precipitate formed. After addition of two drops of methanol to quench the polymerization, the reaction solution was added into more methanol to precipitate the polymer. The polymer was isolated and further purified as described for **11a**. After being dried under vacuum, **11b** was obtained as a yellow-brown tacky solid in quantitative yield. ¹H NMR (CDCl₃, all peaks were broad): δ 7.09, 6.03, 5.93, 5.86, 5.54, 5.36, 4.62, 3.93, 2.57, 1.60, 1.28, 0.89. ¹³C NMR (CDCl₃): δ 140.9 (m), 135.8 (m), 133.7 (m), 132.3 (m), 128.7 (m), 127.9 (m), 126.6 (m), 43.44, 43.22, 37.86 (m), 31.93, 31.73, 31.56, 29.68, 29.39, 22.70, 14.14. UV/vis (chloroform): λ_{max}/nm = 236. IR (KBr, pellet): ν/cm⁻¹ = 3032 (s), 2924 (s), 2852 (s), 1665 (w), 1614 (m), 1573 (m), 1499 (s), 1464 (s), 1378 (s), 1154 (w), 1080 (m), 1025 (m), 964 (s), 890 (m), 819 (s), 789 (s), 722 (s), 647 (w), 495 (m). Anal. Calcd for (C₂₃H₃₂)_n: C, 89.54; H, 10.46. Found: C, 89.29; H, 10.46.

Preparation of Hexyl-Substituted PNV, 13a. In air, to a methylene chloride solution (5 mL) of **11a** (131.8 mg) was added a solution of DDQ (119 mg) in methylene chloride (9 mL). A dark red slurry formed immediately. In 0.5 h, the slurry was added into excess methanol, generating a deep red polymer precipitate. The polymer was isolated by centrifuge separation and further purified by dissolving the polymer in chloroform and precipitating it with methanol. After being dried under vacuum, **13a** was obtained in 84% yield. ¹H NMR (CDCl₃, all peaks were broad): δ 8.24, 8.08, 8.02, 7.94, 7.47 (the peaks in the aromatic region overlap, 7H), 2.82 (2H), 1.73 (2H), 1.33 (8H), 0.89 (3H). ¹³C{¹H} NMR (CDCl₃): δ 140.9 (m), 131.8 (m), 130.1 (br), 128.6 (m), 127.7 (m), 123.9 (m), 123.0 (m), 36.46, 31.77, 31.62, 29.12, 22.64, 14.12. UV/vis (chloroform): λ_{max}/nm = 248, 448. Emission spectrum (chloroform, excited at 440 nm): λ_{max}/nm = 583 (s). IR (KBr, pellet): ν/cm⁻¹ = 3038 (m), 2954 (s), 2926 (s), 2854 (s), 1622 (m), 1574 (m), 1510 (m), 1457 (s), 1377 (s), 956 (s), 821 (s). Anal. Calcd for (C₁₈H₂₀)_n: C, 91.47; H, 8.53; Found: C, 88.20; H, 8.29; N, 0.43. The presence of nitrogen, as shown by the analysis indicates that ca. 5% of DDQH₂ probably exists either as an impurity or chemically bonded to the polymer.

Preparation of Undecyl-Substituted PNV, 13b. To a solution of **11b** (199.5 mg) in methylene chloride (20 mL) was added a methylene chloride solution (10 mL) of DDQ (139.7 mg). A dark red slurry formed immediately. In 3 h, the slurry was added into excess methanol, which generated a deep red polymer precipitate. The polymer was isolated by centrifuge separation and further purified by dissolving the precipitate in chloroform and precipitating it with methanol (a trace amount of NaCl-methanol solution was found to facilitate the precipitation of the polymer and was therefore added to the mother liquor). After being dried under vacuum, **13b** was obtained in 90% yield. ¹H NMR (CDCl₃, all of the peaks were broad): δ 8.29, 8.02, 7.47, 2.82, 1.73, 1.23, 0.88. ¹³C{¹H} NMR (CDCl₃): δ 141.0 (m), 134.9 (m), 131.9 (m), 130.1 (m), 129-128.6 (m), 127.7 (m), 124.0 (m), 123.1 (m), 36.45 (br), 31.91, 31.70, 29.67, 29.36, 27.69, 14.13. UV/vis (chloroform): λ_{max}/nm = 253, 444. Emission spectrum (chloroform, excited at 440 nm): λ_{max}/nm = 572 (s). IR (KBr, pellet): ν/cm⁻¹ = 3038 (m), 2954 (s), 2926 (s), 2854 (s), 1622 (m), 1574 (m), 1510 (m), 1457 (s), 1377 (s), 956 (s), 821 (s).

Doping the Conjugated Polymers 13a,b. The red-orange thin films of polymers **13a,b** were obtained by spin-coating their saturated chloroform solution on glass slides. In a drybox, when the thin films were immersed into a glass dish containing a solution of nitrosonium tetrafluoroborate (~300-400 mg) in acetonitrile (30 mL), the red-orange films immediately turned dark green. In 10 s, the films were removed from the dopant solution and rinsed with acetonitrile. The

doped films were dried under vacuum. The thickness of the films was ca. 500–2000 nm.

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References and Notes

- (1) (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (b) Bredas, J. L.; Silbey, R. *Conjugated Polymers: the novel science and technology of highly conducting and nonlinear optically active materials*; Kluwer Academic Publishers: Boston, 1991. (c) Kiess, H. G., Ed. *Conjugated Conducting Polymers*; Springer-Verlag: New York, 1992.
- (2) (a) Han, C. C.; Elsenbaumer, R. L. *Synth. Met.* **1989**, *30*, 123. (b) Reynolds, J. R.; Pomerantz, M. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: Basel, 1991; Vol. 2, Chapter 4.
- (3) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
- (4) (a) Kaino, T.; Kobayashi, H.; Kubodera, T.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Appl. Phys. Lett.* **1989**, *54*, 1619. (b) Kaino, T.; Kubodera, K. I.; Tomura, S.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Electron. Lett.* **1987**, *23*, 1095.
- (5) (a) Wessling, R. A. *J. Polym. Sci., Polym. Symp. Ed.* **1985**, *72*, 55. (b) Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3241. (c) Antoun, S.; Karasz, F. E.; Lenz, R. W. *J. Polym. Sci., Part A* **1988**, *26*, 1809. (d) Lahti, P. M.; Sarker, A.; Garay, R. O.; Lenz, R. W.; Karasz, F. E. *Polymer* **1994**, *35*, 1312.
- (6) Conticello, V. P.; Gin, D. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 9708.
- (7) For reviews about olefin metathesis and ROMP, see: (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983. (b) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (c) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.
- (8) For references on poly(1,4-naphthylenevinylene) see: (a) Antoun, S.; Gagnon, D. K.; Karasz, F. E.; Lenz, R. W. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 503. (b) Ohmori, Y.; Muro, K.; Onada, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **1992**, *31*, L646–L648. (c) Stenger-Smith, J. D.; Sauer, T.; Wegner, G.; Lenz, R. W. *Polymer* **1990**, *31*, 1632–1636. (d) Onada, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Yoshino, K. *J. Phys. D: Appl. Phys.* **1991**, *24*, 1658–1664. (e) Onada, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Amakawa, K.; Yoshino, K. *J. Phys. D: Appl. Phys.* **1991**, *24*, 1152–1157. (f) Onoda, M.; Uchida, M.; Ohmori, Y.; Yoshino, K. *Jpn. J. Appl. Phys.* **1993**, *32*, 3895–3899. For a reference on poly(2,6-naphthylenevinylene), see: (g) Capistran, J. D.; Gagnon, D. R.; Antoun, S.; Lenz, R. W.; Karasz, F. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 282. For a reference about other poly(arylenevinylene)s, see: (h) Sarker, A.; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 65.
- (9) Hales, N. J.; Heaney, H.; Hollinshead, J. H.; Singh, P. *Org. Synth.* **1979**, *59*, 71.
- (10) For a review on nickel and palladium complex catalyzed cross-coupling reactions of organometallic reagents with organic halides, see: Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.
- (11) (a) Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*, 3071. (b) Friedman, L.; Lindow, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 2329. (c) Kirahonoki, K.; Takano, Y. *Tetrahedron* **1969**, *25*, 2417. (d) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1988**, *53*, 5799. (e) Balci, M.; Cakmak, O.; Harmandar, M. *Tetrahedron Lett.* **1985**, *26*, 5469.
- (12) Pu, L.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 1351.
- (13) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983; p 202.
- (14) For a review on the application of DDQ in organic synthesis, see: Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.
- (15) Conductivities were calculated using the equation

$$\sigma = \frac{\ln 2}{\pi d} \frac{i}{V}$$

where σ is the conductivity and d is the film thickness.

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