

A Zirconocene-Coupling Route to Substituted Poly(*p*-phenylenedienylene)s: Band Gap Tuning via Conformational Control

Brett L. Lucht, Shane S. H. Mao, and T. Don Tilley*

Contribution from the Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

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Abstract: A series of substituted poly(*p*-phenylenediyne)s (**1a–f**) was synthesized by the palladium-catalyzed cross-coupling condensation of terminal dialkynylalkanes with substituted diiodobenzenes. Polymerizations were conducted with 1,4-diiodo-5-hexoxy-2-methoxybenzene or 1,4-diiodo-5-hexyl-2-methylbenzene and with 1,6-hexadiyne, 1,7-heptadiyne, or 1,8-octadiyne. Thus, six different poly(*p*-phenylenediyne)s (**1a–f**, $[\text{ArC}\equiv\text{C}(\text{CH}_2)_n\text{C}\equiv\text{C}]_m$; Ar = 5-hexoxy-2-methoxyphenylene or 5-hexyl-2-methylphenylene, and $n = 2, 3$, or 4) were obtained. Intramolecular zirconocene couplings of **1a–f** afforded zirconacyclopentadiene-containing polymers **2a–f**. These metal-containing polymers were then cleanly hydrolyzed to the substituted poly(*p*-phenylenedienylene)s (**3a–f**, $[\text{ArCH}=\text{C}(\text{CH}_2)_n\text{C}=\text{CH}]_m$; Ar = 5-hexoxy-2-methoxyphenylene or 5-hexyl-2-methylphenylene, and $n = 2, 3$, or 4). Variation of the polymer structure allows for manipulation of the absorption and emission maxima over the ranges of 316–524 nm and 437–619 nm, respectively. The optical properties of model compounds **9a–f**, $(\text{ArHC}=\text{C}(\text{CH}_2)_n\text{C}=\text{CHAr})_n$; Ar = phenyl or 2,5-dimethoxy-4-methylphenyl, and $n = 2, 3$, or 4) are very similar to those for polymers **3a–f**. The structures of **9c** (Ar = 2,5-dimethoxy-4-methylphenyl, $n = 2$) and **9d** (Ar = phenyl, $n = 4$) were determined by single-crystal X-ray crystallography. Molecules of **9c** are almost completely planar, while molecules of **9d** are twisted and have poor π -orbital overlap. The conformation of the diene unit in polymers **3a–f** and the model compounds **9a–f** are largely responsible for the observed variations in optical properties. Finer tuning of the optical properties for poly(*p*-phenylenedienylene)s may be achieved via synthesis of copolymers from mixtures of 1,6-heptadiyne and 1,7-octadiyne. The optical properties of the resulting copolymers represent weighted averages for the corresponding homopolymers. Investigation of the photophysical properties of polymers retaining some of the diyne units suggest that defects play a major role in defining the emissive properties of the poly(*p*-phenylenedienylene)s described here.

Introduction

In recent years there has been considerable interest in the synthesis and properties of conjugated polymers, which combine the processibility and mechanical properties of polymers with the optoelectronic properties of inorganic semiconductors.¹ They have attracted interest in materials science for many potential applications, including rechargeable battery electrodes, electrochromic devices, chemical and optical sensors, light emitting diodes (LEDs), and nonlinear optical materials.¹ The development of specific functions for charge-transporting polymers relies on manipulation of the polymer's electronic properties via chemical modifications. For example, the synthesis of light-emitting polymers which produce a specific color is a challenging endeavor which requires tuning of the polymer's band

gap and redox potentials.^{1i,2–4} The tuning of band gaps for conjugated polymers has primarily been achieved via manipulation of the polymer's conjugation lengths,^{1i,2–4} for example, via introduction of backbone substituents which result in conformational disruption of more delocalized structures,² or by breaking the conjugation length at regular intervals with a spacer

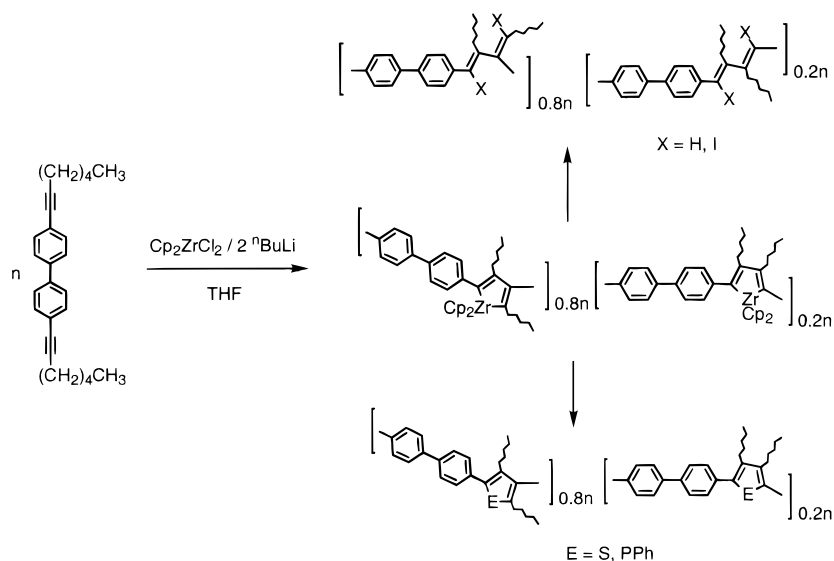
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Scheme 1

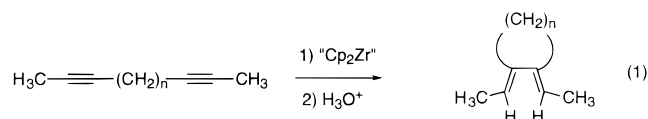


group.³ One of the largest ranges for optical tunability, 305–595 nm for absorption λ_{max} values, was achieved by varying substituents on polythiophenes.^{2a} In addition, the role of polymer defects on the optoelectronic properties of conjugated polymers is very important.⁵ However, many of the conjugated polymers of interest are insoluble, making the characterization or detection of defects by spectroscopic means difficult.⁶

We have been exploring an organometallic approach to the synthesis of conjugated polymers, based on the zirconocene-coupling of diynes.^{7,8} This approach allows for chemical modification of the polymers' electronic properties, based on the "modular" exchange of groups in the polymer backbone. Initial attempts to produce π -conjugated polymers from 4,4'-di(alkynyl) biphenyl derivatives resulted in primarily cross-conjugated structures and nonregioselective couplings (Scheme 1).^{8c} Nonetheless, it was shown that the polymer properties could be varied via conversions of zirconacyclopentadiene backbone units to a variety of functionalities (dienes, thiophenes,

phospholes, and aromatic groups).^{8e,9,10} Due to their irregular and crossconjugated structures, these polymers possess relatively wide band gaps and display emission bands varying from 398 to 470 nm and quantum yields for emission ranging from zero to ca. 30%.

In this paper, we describe the use of regioselective zirconocene-couplings in the preparation of fully conjugated polymers. This approach takes advantage of regioselective, ring-closing diyne couplings which employ flexible diyne spacer groups (eq 1).^{7a} High isolated yields (70–90%) have been



reported for diynes with $n = 2, 3$, and 4 . The method reported here for the synthesis of conjugated poly(*p*-phenylenedienylene)s is outlined in eq 2.¹¹ First, poly(arylenediyne)s were prepared using palladium-catalyzed cross coupling,¹² according to methodology that has previously been employed in the synthesis of conjugated poly(*p*-phenyleneethynylene)s from aryldiynes and dihaloaryls.¹³ The poly(arylenediyne)s were then transformed

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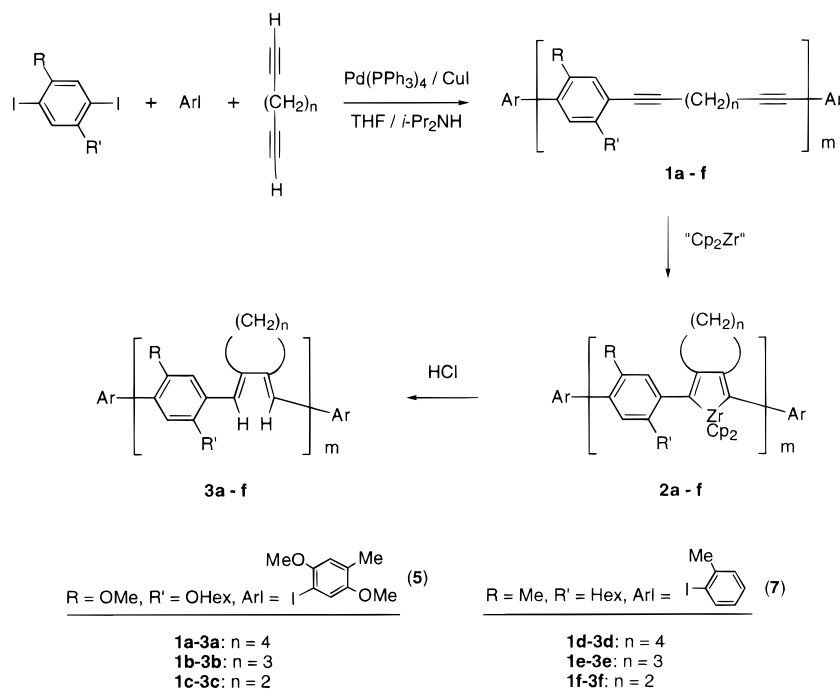
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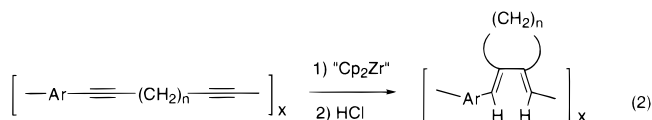
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Scheme 2



via intramolecular zirconocene coupling and hydrolysis to poly(arylenediene)s (eq 2). Variation of substituents on the arene ring and diene allows for tuning of the optical absorption and emission energies for the polymers. Also, copolymerizations with combinations of different diynes result in polymers with optical properties that are the weighted average for the two homopolymers.



While the method outlined in eq 2 may lead to a variety of interesting polymers, this strategy will inherently lead to polymer defects for nonquantitative transformations involving the polymer backbone. For the reactions described here, these conversions are nearly quantitative, as judged by spectroscopic characterization of the polymers and comparisons with related reactions of small molecules.^{7,8} However, incomplete conversions present possibilities for the synthesis of additional polymers with interesting “hybrid” properties, and conjugated polymers with breaks in the conjugation lengths (defects) have been found to exhibit both increased quantum yields and higher solubilities.^{5a}

Results and Discussion

Synthesis and Characterization of Polymers. The general procedure employed for synthesis of poly(*p*-phenylenediene)s is outlined in Scheme 2. An initial attempt to employ this method, using 1,4-diiodobenzene and 1,7-octadiyne, resulted in formation of an insoluble polymer. For this synthetic scheme, polymers **1** must have reasonably high solubilities in THF at -78°C to allow for complete conversion to polymers of type **2**. Soluble polymers of type **1** were obtained by employing asymmetrically substituted arene monomers such as 2-methoxy-

5-hexoxy-1,4-diiodobenzene (**4**).¹⁴ While condensations of 1,7-octadiyne with **4** yield polymers with superior solubility properties, the molecular weight and solubility of the polymers proved difficult to reproduce due to the stringent need for a 1:1 stoichiometry for the two bifunctional monomers.¹⁵ This problem was circumvented with use of 2,5-dimethoxy-4-methyliodobenzene (**5**) as an end-capping agent. The addition of low concentrations (5–20%) of **5** to polymerizations of 1,7-octadiyne and **4** resulted in the synthesis of polymers with reproducible molecular weights and solubilities.¹⁶

The polycondensations of 1,7-octadiyne, 1,6-heptadiyne, and 1,5-hexadiyne with **4** and 0.1 equiv of **5** were carried out with $\text{Pd(PPh}_3)_4/\text{CuI}$ catalyst in a mixture of THF and diisopropylamine. The reaction time was typically 12–16 h at room temperature although shorter reaction times can be used when the reaction temperature is raised to 50°C . The polymers remained soluble during the reaction and were isolated as pale yellow-brown solids by precipitation from methanol. Polymers **1a–c** were purified by washing chloroform solutions with dilute NH_4OH and water, followed by reprecipitation from methanol. The latter procedure results in a substantially reduced yield (by almost 50%); however, it was found that transformations of **1a–c** to **3a–c** could be carried out with the crude polymers. The molecular weights of polymers **1a–c**, as determined by gel permeation chromatography (GPC; polystyrene standards; $M_n = 4500\text{--}5500$; $\text{PDI} = 1.7\text{--}5.5$), are similar to the theoretical values expected for condensation polymerizations with addition of 10% of an end cap ($n = 20$, $M_n = 6000$)¹⁵ and are consistent with the number average molecular weights determined by end-group analysis (4700–5400; ^1H NMR spectroscopy). Nonetheless, it is difficult from the spectroscopic data to conclude that

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Table 1. Optical Properties of Poly(phenylenedienylene)s

polymer	λ_{max} (nm) absorption	λ_{max} (nm) excitation	λ_{max} (nm) emission	color	ϵ_{max}^a
3a	368	368	489	yellow	6 900
3b	472	390	546	red	7 900
3c	524	420	619	purple	20 000
3d	316	314	437	colorless	19 000
3e	414	365	495	orange	9 500
3f	438	375	556	red	14 000

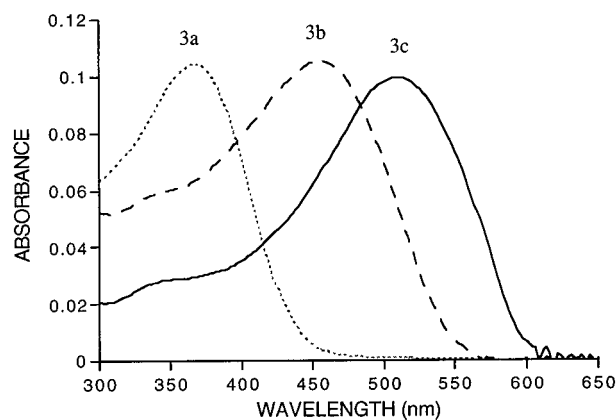
^a ϵ_{max} = the molar absorptivity per repeat unit of the polymer.

quantitative end-capping has occurred. Polymers **1a–c** are completely soluble in THF, toluene, and chloroform. The ^{13}C NMR spectra for these polymers contain four resonances for the alkynyl groups, representing environments involving both *o*-OMe and *o*-OHx substituents. The IR spectra of **1a–c** contain weak alkyne stretches at 2232–2235 cm^{-1} , which are consistent with unsymmetrically substituted carbon–carbon triple bonds. Palladium-catalyzed cross coupling can result in the formation of alkyne–alkyne coupling products in addition to the desired products, but such couplings are minimized by using palladium(0) catalysts such as $\text{Pd}(\text{PPh}_3)_4$.^{12g} We observed no evidence for alkyne–alkyne coupling by ^1H NMR spectroscopy.

In a similar manner, treatment of 1,4-diiodo-2-methyl-5-hexylbenzene (**6**) with 1,7-octadiyne, 1,6-heptadiyne, or 1,5-hexadiyne in the presence of $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$ produced the soluble polymers **1d–f**. The degree of polymerization was controlled by addition of 0.1 equiv of 2-iodotoluene (**7**). Polymer molecular weights determined by GPC (M_n = 4200–5500; PDI = 2.1–2.5) are consistent with both the theoretical prediction (n = 20; 5400) and values determined by end-group analysis (4800–5200). Four well-resolved alkynyl resonances, and broad resonances for the main-chain methylene carbons, are observed in the ^{13}C NMR spectrum, consistent with unsymmetrically substituted aryl rings. The IR spectra contain weak alkyne absorbances at 2226–2229 cm^{-1} .

Solutions of **1a–f** in THF were added dropwise over 5 min to a fresh solution of “zirconocene”, generated by the addition of *n*-BuLi to Cp_2ZrCl_2 in THF at -78°C .^{7b} Warming to room temperature afforded deeply colored solutions of the zirconium-containing polymers (**2a**: red; **2b**: green; **2c**: blue; **2d**: yellow-orange; **2e**: red; **2f**: violet). These conversions are highly sensitive to the amount of added *n*-BuLi, such that significant deviations from the ideal stoichiometry of 1.95 equiv per equiv of Cp_2ZrCl_2 led to impure materials. Also, **2a–f** decompose to black inhomogeneous mixtures when stirred in solution at room temperature for > 8 h. Therefore these polymers were not isolated or characterized in solution but were converted directly to the corresponding polymers **3a–f** by addition of excess 6 M HCl.

Polymers **3a–f** exhibit colors that are highly dependent on the number of methylene units in the polymer-fused rings (Table 1) and are soluble in toluene, chloroform, and THF. The molecular weights of **3a–f**, as determined by GPC (M_n = 5400–6300; PDI = 3–6), are consistent with expected theoretical values (n = 20, 6000). End-group analyses were generally not possible since the broad polymer resonances obscured peaks for the end groups. Subtle, apparent differences in the molecular weights of polymers **1a–f** vs **3a–f**, as determined by GPC, presumably reflect changes in the polymer structures and not the overall degree of polymerization. The ^{13}C aromatic and vinyl resonances are extremely broad and difficult to distinguish, while the alkoxy side chain and aliphatic ring resonances are sharp and well resolved. Polymers **3a–e** exhibit three major

**Figure 1.** Absorption spectra for polymers **3a** (···), **3b** (---), **3c** (—).

resonances between 6.0 and 8.0 ppm attributed to the vinyl and aryl protons. However, **3f** has several other small resonances in this region, which may represent defects in the polymer arising from incomplete conversion of diyne to diene units. The IR spectra for all polymers **3a–f** contain no evidence for alkynyl absorbances, indicating relatively efficient conversion of alkyne to alkene functionalities.

The resulting molecular weights for **1a–f** and **3a–f** are highly dependent on the amount of added capping group. Syntheses of **3b** with higher (0.2 equiv) or lower (0.05 equiv) amounts of **5** resulted in molecular weights (GPC) which were consistent with the theoretical values (0.05 equiv: M_n/M_w = 12 000/50 000; 0.1 equiv: 5300/19 000; 0.2 equiv: 2400/9600). The lower-molecular-weight polymers were found to be substantially more soluble, while the optical properties (vide infra) did not vary significantly with molecular weight.

Optical Properties of Polymers. The photophysical properties of polymers **3a–f** in dilute deoxygenated THF solutions were investigated. Absorption data are summarized in Table 1, and Figure 1 presents absorption spectra for polymers **3a–c**. The absorption spectra have a strong dependence on both the size of the polymer-fused ring and on the nature of substituents on the aryl ring. A red-shift in the absorption maximum as the ring size decreases ($4 > 5 > 6$) in both the alkoxy- (**3c** > **3b** > **3a**) and alkyl- (**3f** > **3e** > **3d**) substituted polymers indicates an increase in π -delocalization along the polymer backbone. These changes in electronic properties undoubtedly reflect variations in the average conjugation lengths, as determined by dihedral angles along the chain. Electron donation from alkoxy substituents on polymers **3a–c** results in an auxochromic red shift of 52–76 nm relative to the alkyl-substituted polymers **3d–f**.¹⁷

Emission and excitation spectra were acquired on dilute deoxygenated THF solutions of polymers **3a–f** with optical absorption maxima between 0.07 and 0.13. Emission spectra for polymers **3a–f** are independent of the excitation wavelength but highly dependent on the structure of the polymer (Table 1). The photoluminescence quantum yields, determined relative to a quinine bisulfate standard, are fairly low (<0.01) for all polymers **3a–f**.¹⁸ The low quantum yields are somewhat surprising, but increasing the rigidity of conjugated polymers is known to result in a decrease in photoluminescence efficiency.¹⁹ Excitation spectra for polymers **3a** (Figure 2) and

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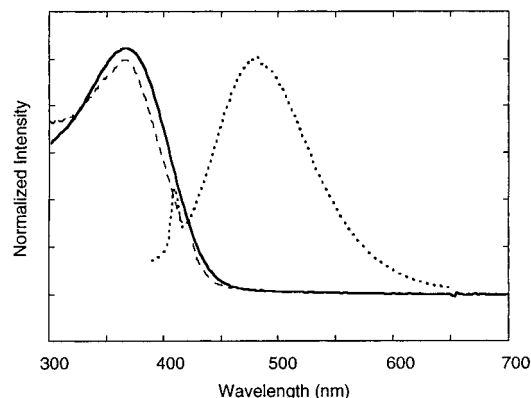


Figure 2. Absorption (—), emission (···), and excitation (---) spectra of **3a**. The sharp peak in the emission spectrum results from Raman scattering.

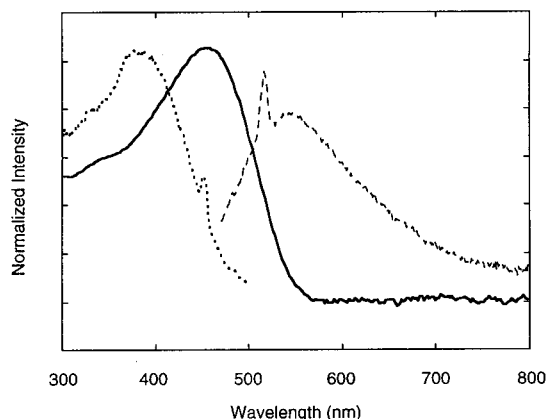


Figure 3. Absorption (—), emission (---), and excitation (···) spectra of **3b**. The sharp peaks in the emission and excitation spectra result from Raman scattering.

3d reproduce the corresponding absorption spectra; however, excitation spectra for polymers **3b** (Figure 3), **3c**, **3e**, and **3f** do not. The excitation spectra indicate that emissions from polymers **3b**, **3c**, **3e**, and **3f** result from excitation into the high energy shoulder of the absorption band. We do not fully understand the observed differences in absorption and excitation spectra, but we believe that they are caused by the presence of defects in some of the polymers (vide infra). Emission from short oligomers was ruled out by photophysical investigations of fractionated polymers. However, we cannot at this time exclude the possibility that emission results from discrete, short-conjugation sequences within the polymer backbone.²⁰ Also, since the excitation spectra do not fully reproduce the absorption spectra for **3b**, **3c**, **3e**, and **3f**, values for the photoluminescence quantum yields of these polymers are not very readily interpreted.

Synthesis and Characterization of Model Compounds. To investigate the origin of the diverse colors and optical properties for polymers **3a–f**, appropriate model compounds were synthesized. The red-shifts for the polymers' absorptions and emissions (**3c** > **3b** > **3a**) vary inversely with the size of the fused ring and is therefore in agreement with the conformational properties of 1,2-dimethylenecycloalkanes which have been studied by computational methods, photoelectron spectroscopy, microwave spectroscopy, and NMR spectroscopy.²¹ In addition, several X-ray crystallographic determinations of vitamin D

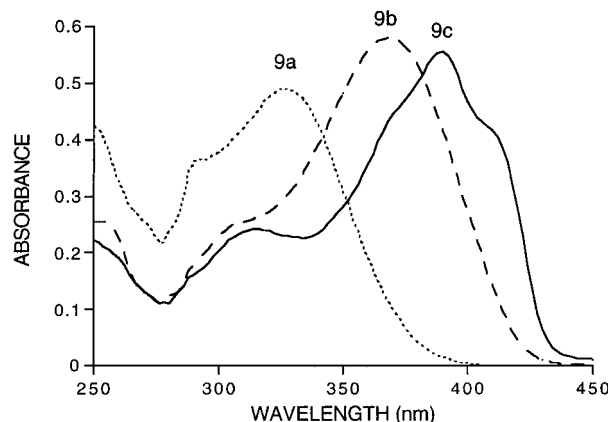
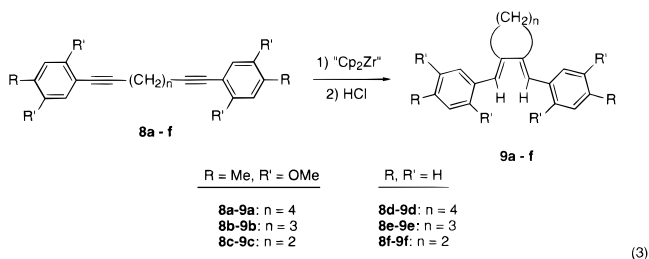


Figure 4. Absorption spectra for compounds **9a** (···), **9b** (---), **9c** (—).

derivatives containing an exocyclic cyclohexadiene group have been conducted.²² The data suggest that 1,2-dimethylenecyclobutane has a planar conformation while 1,2-dimethylenecyclohexane has a chair conformation with torsion angles of approximately 55–60° for the diene system. In polymers **3a–f**, steric interactions between the fused ring and aryl substituents may also play an important role in determining conjugation between the aryl and diene π -systems.

The 1,4-diphenylbutadiene compounds **9a–f** were synthesized via the three-step procedure shown in eq 3. Diynes **8a–f** were obtained in high yield as crystalline solids or oils by palladium-catalyzed cross-couplings. Intramolecular zirconocene couplings of **8a–f** in THF afforded deep red solutions of the zirconacyclopentadienes, which were hydrolyzed with concentrated HCl to give the diene products **9a–f** as crystalline products from 1:1 pentane/OEt₂. The chemical structures of **9a–f** were confirmed by ¹H and ¹³C NMR, IR, and high-resolution mass spectroscopy. In general, spectroscopic properties for these compounds are very similar to those for the corresponding polymers **3a–f**.



Optical Properties of Model Compounds. We investigated the photophysical properties of **9a–f** in dilute, deoxygenated chloroform solutions. A strong bathochromic shift of the absorption maxima for both the substituted (**9a–c**, Figure 4) and unsubstituted (**9d–f**) 1,4-diaryldienes is associated with a decrease in the size of the backbone-fused ring (Table 2). In

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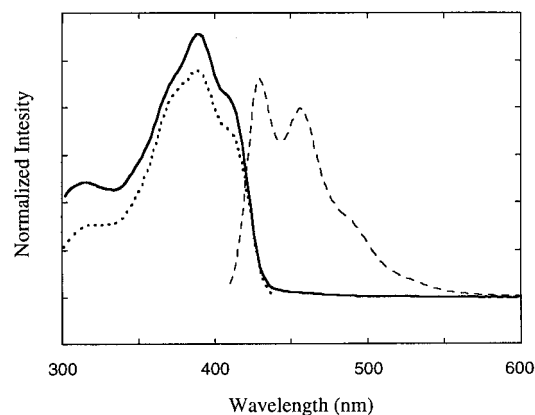
(21) (a) Hofmann, H.; Cimraglia, R. *J. Org. Chem.* **1990**, 55, 2151. (b) Hemmersbach, P.; Klessinger, M.; Bruckmann, P. *J. Am. Chem. Soc.* **1978**, 100, 6344. (c) Avairah, T. K.; Cook, R. L.; Malloy, T. B. *J. Mol. Spectrosc.* **1975**, 54, 231. (d) Asmus, P.; Klessinger, M. *Tetrahedron* **1974**, 30, 2477. (e) Pfeffer, H. U.; Klessinger, M. *Org. Magn. Reson.* **1977**, 9, 121.

(22) (a) Hodgkin, D. C.; Rimmer, B. M.; Dunitz, J. D.; Trueblood, K. N. *J. Chem. Soc.* **1963**, 4945. (b) Knobler, C.; Romers, C.; Braun, P. B.; Hornstra, J. *Acta Crystallogr., Sect. B* **1972**, 28, 2097. (c) Trinh-Toan; DeLuca, H. F.; Dahl, L. F. *J. Org. Chem.* **1976**, 41, 3476. (d) Trinh-Toan; Ryan, R. C.; Simon, G. L.; Calabrese, J. C.; Dahl, L. F.; De Luca, H. F. *J. Chem. Soc., Perkin Trans.* **1977**, 2, 393. (e) Hull, S. E.; Leban, I.; Main, P.; White, P. S.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1976**, 32, 2374.

Table 2. Optical Properties of 1,4-Diphenyldienes

compd	λ_{max} (nm) absorption	λ_{max} (nm) emission	Φ^a	ϵ_{max}^b
9a	326	448	0.011	13 000
9b	368	455	0.032	21 000
9c	372, 388, 408	429, 456, 484	0.29	40 000
9d	294	379	0.003	29 000
9e	334	410	0.004	33 000
9f	328, 346, 364	383, 407, 430	0.007	45 000

^a Φ = photoluminescence quantum yield. ^b ϵ_{max} = the molar absorptivity.

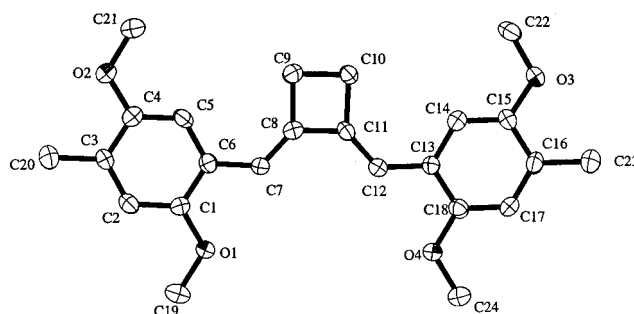
**Figure 5.** Absorption (—), emission (---), and excitation (···) spectra of **9c**.

addition, alkoxy substitution results in an auxochromic red shift of 30–40 nm for all model compounds. Therefore, trends in the absorption characteristics of the model compounds **9a–f** are very similar to those observed for polymers **3a–f**, except for two primary differences. The first is that cyclobutanes **9c** and **9f** exhibit fine structure in their absorption spectra, as observed for *trans*-1,4-diphenylbutadiene.²³ The second difference is the bathochromic shift for the absorption maxima for polymers **3a–f** relative to the respective molecular species, which corresponds to greater conjugation lengths for the polymers. Additionally, polymers **3b**, **3c**, **3e**, and **3f** are substantially more red shifted (74–106 nm) than polymers **3a** and **3d** (22–42 nm) with respect to their model compounds. This is consistent with the assumption that π -orbital overlap is more efficient in polymers with smaller fused rings.

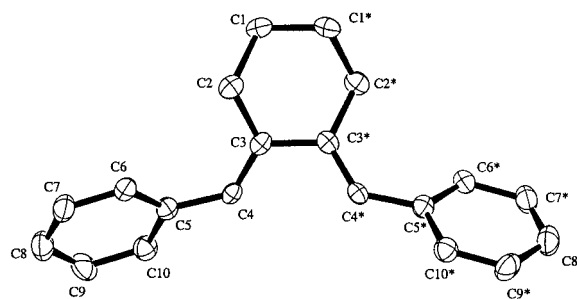
Emission and excitation spectra were acquired on dilute chloroform solutions of **9a–f** with optical absorbances of 0.07–0.13. The emission spectra of **9a–f** are independent of excitation wavelength and exhibit shifts in energies that parallel the absorption spectra (Table 2), with the emission energies shifting to longer wavelengths as the fused ring size decreases. Emission spectra are Stokes-shifted by 55–122 nm relative to the corresponding absorption spectra, and the magnitude of this shift varies directly with the size of the fused ring (6 > 5 > 4). Model compounds **9a**, **9b**, **9d**, **9e**, and **9f** have low photoluminescence quantum yields (<0.03), but **9c** exhibits a quantum yield of 0.29. This is at least partially consistent with a combination of the expected effects of increased rigidity and alkoxy-substitution,²⁴ but the origins of these differences are currently not fully understood. Excitation spectra of **9a**, **9b**, **9c** (Figure 5), and **9d–f** reproduce the absorption spectra, confirming that emission correlates with the absorption band.

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A



B

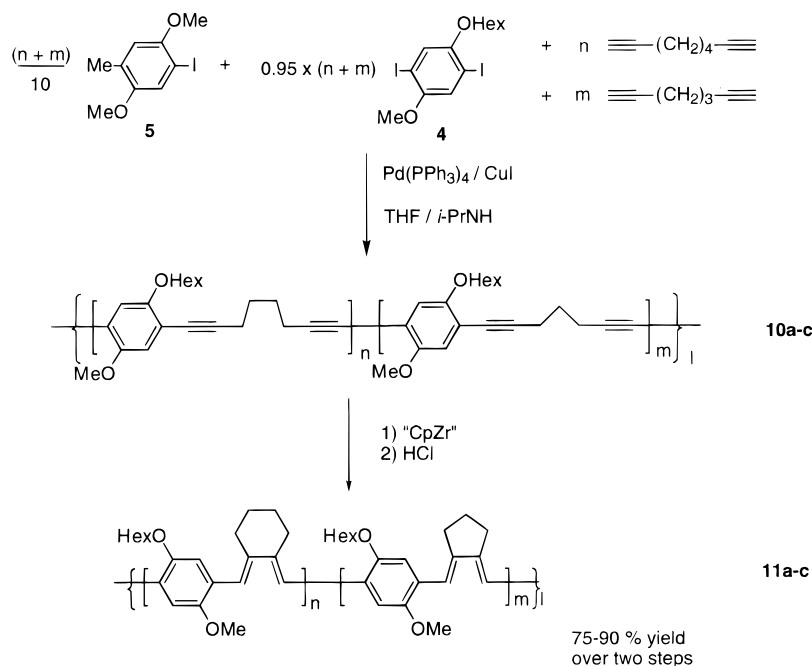
Figure 6. X-ray crystallographic structures of model compounds **9c** (A) and **9d** (B).

Structural Analyses of 9c and 9d. The molecular structures of **9c** and **9d** (Figure 6) were determined to establish relationships between structural conformations and the corresponding electronic properties. Most of the metrical parameters for these compounds are unexceptional, and the most significant conformational differences may be described in terms of dihedral angles. For **9c**, the C(5)–C(6)–C(7)–C(8) and C(7)–C(8)–C(11)–C(12) dihedral angles of 1.3° and 2.6°, respectively, describe an essentially planar (and highly conjugated) molecule. The angle between the two least-squares planes of the aryl rings is only 3.0°. The related dihedral angles for **9d**, C(6)–C(5)–C(4)–C(3) and C(4)–C(3)–C(3*)–C(4*), are 30.9° and 42.4°, respectively, resulting in much less π -orbital overlap and electron delocalization for this compound.

Random Copolymers. The above results describe the tuning of electronic properties for conjugated polymers via variations in two structural parameters: the conformation of a diene unit and the nature of the aromatic ring substitutions. In principle, a finer tuning of electronic properties may be achieved by combining different monomer types in various ratios into random copolymers. By preparing copolymers incorporating both five- and six-membered fused rings, we have achieved smooth variations in electronic properties for the resulting polymers. To prepare random copolymers with optical properties that are the weighted average of two homopolymers, two primary requirements need to be satisfied. The conjugation must be extended over more than one repeat unit of the polymer, and the rates of polymerization for the different monomers must be very similar. The polymers described here meet both of these requirements. First, polymers **3a–f** have significant conjugation lengths, as indicated by the red shift in the absorption maxima of the polymers with respect to those for the model compounds **9a–f**. Also, the polymerization rates for 1,7-octadiyne, 1,6-heptadiyne, and 1,5-hexadiyne are very similar. This allows for a random distribution of monomer units, since no kinetic preference exists for homopolymerizations.

The synthesis of random copolymers employs a procedure

Scheme 3

**Table 3.** Optical Properties of Copolymers

polymer	% <i>n</i>	% <i>m</i>	λ_{max} (nm) absorption	λ_{max} (nm) emission	absorbance band width (nm) ^a
3a	100	0	368	489	110
11a	75	25	378	497	150
11b	50	50	418	514	140
11c	25	75	448	533	120
3b	0	100	472	546	140

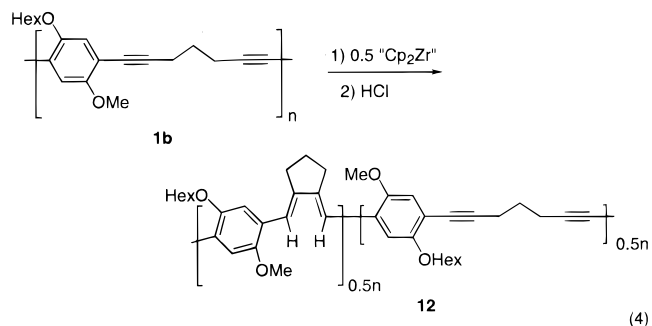
^a The full width at half-maximum intensity of the absorption spectrum.

analogous to that used for the homopolymers, as shown in Scheme 3. Treatment of **4** with various ratios of 1,7-octadiyne and 1,6-heptadiyne in the presence of Pd(PPh₃)₄/CuI provided polymers **10a–c**. Intramolecular zirconocene coupling of **10a–c**, followed by hydrolysis with HCl, resulted in formation of the random copolymers **11a–c**. The polymer resulting from a 50:50 mixture of 1,7-octadiyne and 1,6-heptadiyne (**11b**) exhibits an absorption maximum at 418 nm and an emission maximum at 514 nm. Both of these values are very close to the average absorption and emission maxima for the corresponding homopolymers **3a** and **3b**. Significantly, the bandwidths of the copolymers are very similar to those for the homopolymers, indicating the presence of uniquely defined chromophores (Table 3). Polymerizations with other diyne ratios yielded copolymers **11a** and **11c**, with absorption and emission maxima that are close to the weighted average for the two homopolymers (Table 3). As shown in Figure 7, there is a linear correlation between the 1,7-octadiyne/1,6-heptadiyne ratio and the absorption maxima. Based on these results, we anticipate that it should be straightforward to prepare poly(phenylenedienylene)s with absorption and emission maxima which take on any value in the 316–524 and 437–619 nm ranges, respectively.

Role of Polymer Defects. The preparation of conjugated polymers via a multistep process involving the chemical conversion of one polymer structure to another is potentially susceptible to less than quantitative conversions and incorporation of defects into the backbone. Conversions of **8a–f** to **9a–f** are quantitative by NMR spectroscopy. The conversions of

1a–e to **3a–e** also appear to be quantitative by ¹H NMR spectroscopy. Furthermore, the lack of alkyne IR absorbances in polymers **3a–f** suggests that the alkyne-to-alkene conversion is at least 95% complete. The only polymer that exhibits evidence for polymer defects by ¹H NMR spectroscopy (in the aromatic region) is **3f**. Several small resonances in the spectrum for **3f** may represent defects that arise from incomplete conversion of diyne to diene units.

Polymers **3a–e** have absorption spectra that are fairly symmetric with only a single maximum, while **3f** has two absorption maxima—a primary one at 438 nm and a second, lower intensity band at higher energy (380 nm) which is very similar to the excitation maximum (375 nm) for this polymer. We therefore propose that the absorption feature at 380 nm and the excitation maximum for **3f** both result from defects in the polymer.



While NMR and IR data suggest that polymers **3a–e** are defect-free, the excitation spectra of polymers **3b**, **3c**, **3e**, and **3f** suggest that polymer defects (resulting from incomplete conversion of diyne units) may be responsible for the observed emissions. Treatment of **1b** with less than 1.0 equiv of zirconocene (0.5 equiv) under previously described conditions results in formation of the "highly defective" copolymer **12** (eq 4). Polymer **12** exhibits an alkyne stretch at 2230 cm^{−1} in the infrared spectrum, with approximately half of the intensity of the alkyne stretch for **1b**. Additionally, the absorption spectrum of **12** is intermediate between those for **1b** and **3b** (Figure 8).

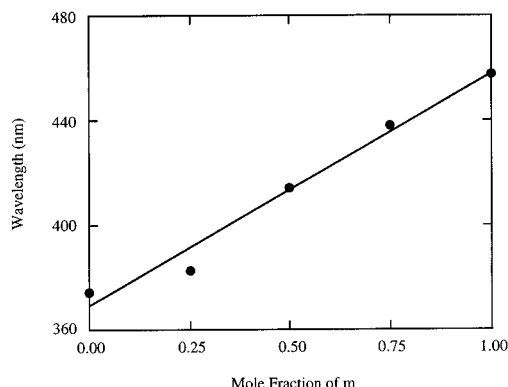


Figure 7. Plot of the absorption maxima vs mole fraction of *m* for random copolymers see Scheme 3.

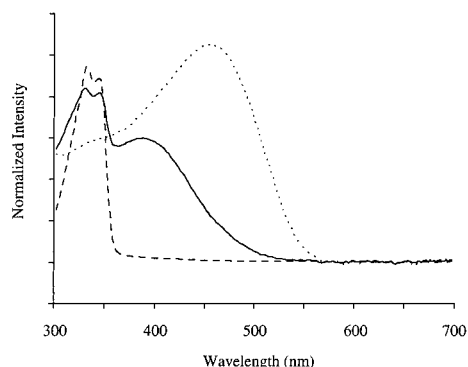


Figure 8. Absorption spectra of **1b** (---), **3b** (···), and **12** (—).

The emission spectrum of **12** has maxima at 364, 371, 469, and 489 nm. The two shorter wavelength emissions (364 and 371 nm) correspond to emissions from segments which are similar to **1b** (the emission spectrum of **1b** has two maxima at 360 and 368 nm). The longer wavelength emissions (469 and 489 nm) are consistent with segments which have been converted to dienes. The excitation spectra of both **1b** and **12** accurately reproduce the absorption spectra. However, the excitation spectrum of **12** resembles that for **3b**, with both featuring excitation maxima at 390 nm. This suggests that emission from **3b** results primarily from polymer defects. Also, since emission and excitation spectra for polymers **3b**, **3c**, **3e**, and **3f** are dependent upon the size of the fused ring, the emitting chromophores in each case are associated with both alkyne and diene fragments. Given the apparent influence of defects on determining emission properties, it may seem somewhat surprising that the emission energies vary considerably from one diene polymer to another (see Table 1). This implies that the excitons decay from defects with somewhat different structures, which could occur if the emitting (defect) chromophores include at least an alkyne-arene-diene unit. The fluorescence quantum yields for polymers **1b** and **12** are 0.035 and 0.021, respectively, almost an order of magnitude larger than the quantum yield observed for **3b**. Note that defects in conjugated polymers are known to result in higher fluorescence quantum yields due to inhibition of the migration of excitons to quenching sites.⁵

Conclusions

The results presented here demonstrate that poly(*p*-phenylenedienylene)s are readily accessible via zirconocene-coupling routes, which provide means for fine control over polymer electronic properties. The optical tunability operates primarily via conformational properties of exocyclic diene units in the

polymer; however, aryl substituent effects are also important. This conformational control of the polymer backbone via the incorporation of exocyclic dienes represents a new approach for tuning the optical properties of conjugated polymers. In addition to the formation of polymers with a single type of exocyclic diene, random copolymers with both five- and six-membered fused rings allow for further fine-tuning of the polymer band gap. This suggests that the optical absorption and emission maxima can be tuned to any wavelength within the ranges of 316–524 nm and 437–619 nm, respectively. Further investigation of the photophysical properties of poly(*p*-phenylenedienylene)s suggests that polymer emissions may be associated with imperfections in the polymers that result from incomplete conversion of the alkyne groups. This further supports the view that polymer defects can play a vital role in determining the optoelectric properties of conjugated polymers. We anticipate that polymerization reactions of the type described here will be useful for the synthesis of a variety of new conjugated polymers, since both the palladium- and zirconocene-coupling steps are compatible with many arenes and heteroarenes. Future reports will describe the use of solubilizing diynes for the preparation of poly(arylenedienylene)s.²⁵

Experimental Section

General Procedures. All procedures were carried out in a nitrogen-filled Vacuum Atmospheres drybox or in Schlenk-type glassware interfaced to a vacuum line. Reagents used in this study were purchased from commercial sources and purified, dried, and deoxygenated as necessary. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium/benzophenone ketyl. Benzene-*d*₆ was purified by vacuum distillation from Na/K alloy. Elemental analyses were performed by the UCB Microanalytical Laboratory. IR spectra were recorded on a Mattson Infinity FT-IR spectrometer. NMR spectra were recorded on a Bruker AMX (300 MHz) or a Bruker AMX (400 MHz) NMR spectrometer. Molecular weights of the polymers were determined by gel permeation chromatography (GPC; Waters Company; Detector: Differential Refractometer R401; Waters 501 HPLC pump; Waters 745 Data Module) with THF as eluting solvent and polystyrene standards.

Emission spectra were collected by using an Instruments SA/Jobin Yvon-Spex Fluoromax photon-counting fluorimeter equipped with a Xe arc lamp excitation source and a Hamamatsu R928P photomultiplier tube operating at –900 Vdc. Data were collected on thoroughly deoxygenated solutions (THF for polymers, CHCl₃ for model compounds) having an optical density of 0.07–0.13 (1.0 cm path length) at the excitation wavelength. Background measurements on the solvent blanks revealed no signals other than the expected Raman lines of the neat solvent. The excitation energy for photoluminescence spectra was 10 nm lower than the absorption maximum, and excitation spectra were acquired at the emission maximum. All quantum yield measurements were carried out at a single excitation wavelength (350 nm). Spectra were corrected using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220M tungsten quartz lamp). All subsequent manipulations were carried out with the corrected spectra.

Relative quantum yield (Φ) values are reported relative to a 1.0 N H₂SO₄ solution of quinine bisulfate ($\Phi = 0.546$)¹⁶ and calculated according to the equation

$$\Phi_u = \Phi_s \left(\frac{I_u}{I_s} \right) \left(\frac{A_s}{A_u} \right) \left(\frac{\eta_u}{\eta_s} \right)^2$$

where Φ_u is the radiative quantum yield of the sample, Φ_s is the radiative quantum yield of the standard, I_u and I_s are the integrated emission intensities of the sample and standard, respectively, A_u and A_s are the absorbances of the sample and standard, respectively, at the excitation wavelength (350 nm), and η_u and η_s are the indexes of

(25) Lucht, B. L.; Tilley, T. D. unpublished results.

refraction of the sample and the standard solutions. Multiple measurements on each sample indicated a precision of ca. 10% for our reported values of Φ .

Polymer 1a. A 100 mL Schlenk flask was charged with **4** (1.0 g, 2.2 mmol), **5** (0.06 g, 0.2 mmol), Pd(PPh₃)₄ (0.13 g, 0.11 mmol), CuI (0.04 g, 0.21 mmol), *i*-Pr₂NH (7.0 mL), and THF (15.0 mL). To this solution under N₂ was added 1,7-octadiyne (0.24 g, 2.3 mmol) in 0.5 mL of THF. The resulting solution was allowed to stir at room temperature for 16 h. During this period, a substantial amount of white precipitate formed. The reaction mixture was then added slowly to rapidly stirring methanol (300 mL) to precipitate the crude polymer **1a** in near quantitative yield. The polymer was further purified by washing a chloroform (50 mL) solution with dilute NH₄OH and then H₂O, evaporating the chloroform solution to dryness by rotoevaporation, redissolving the polymer in THF, and finally precipitating the polymer by adding the THF solution to rapidly stirring methanol (300 mL). This yields **1a** (44%, 0.30 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (br, 3 H, CH₃), 1.31 (br, 4 H, CH₂), 1.45 (br, 2 H, CH₂), 1.74 (br, 2 H, CH₂), 1.81 (br, 4 H, CH₂), 2.53 (br, 4 H, CH₂), 3.80 (br, 3 H, OCH₃), 3.92 (t, J = 6.6 Hz, 2 H, CH₂O), 6.81 (s, 1 H, CH), 6.84 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.03 (CH₃), 19.40 (multiple resonances, CH₂), 22.63 (CH₂), 25.66 (CH₂), 27.8 (multiple resonances, CH₂), 29.26 (CH₂), 31.55 (CH₂), 56.32 (OCH₃), 65.59 (OCH₂), 77.2 (multiple resonances, C \equiv C), 95.11 (multiple resonances, C \equiv C), 113.13, 113.92, 115.38, 117.59, 153.54, 153.80 (C₆H₂). M_n/M_w = 5400/30 000 by GPC. IR (film, KBr, cm⁻¹): 2940, 2861, 2232 (C \equiv C), 1501, 1464, 1403, 1273, 1204, 1039, 862.

Polymer 1b. This compound was prepared by a procedure identical to that for **1a**, using 1,6-heptadiyne (2.1 g, 2.3 mmol) instead of 1,7-octadiyne. This yields **1b** (41%, 0.28 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, J = 7.0 Hz, 3H, CH₃), 1.32 (br, 4H, CH₂), 1.47 (br, 2H, CH₂), 1.79 (mult, 2 H, CH₂), 1.94 (mult, 2 H, CH₂), 2.65 (br, 4 H, CH₂), 3.81 (s, 3 H, OCH₃), 3.94 (t, J = 3.94, 2 H, CH₂O) 6.85 (s, 1 H, CH), 6.87 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 13.86 (CH₃), 18.93 (multiple resonances, CH₂), 22.48 (CH₂), 25.55 (CH₂), 27.88 (CH₂), 29.13 (CH₂), 31.41 (CH₂), 56.15 (CH₃O), 69.42 (CH₂O), 77.20 (C \equiv C), 94.47 (C \equiv C), 112.9, 113.7, 115.2, 117.4, 128.4, 153.4, 163.6 (C₆H₂). M_n/M_w = 5300/19 000 by GPC. IR (film, KBr, cm⁻¹) 2948, 2903, 2867, 2835, 2232 (C \equiv C stretch), 1502, 1465, 1403, 1273, 1229, 1038, 862.

Polymer 1c. This compound was prepared by a procedure identical to that for **1a**, using 1,5-hexadiyne (0.19 g, 2.4 mmol) instead of 1,7-octadiyne and (0.11 g, 0.4 mmol) of **5** to yield a lower molecular weight polymer with better solubility. This yields **1c** (42%, 0.29 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (br, 3 H, CH₃), 1.31 (br, 4 H, CH₂), 1.45 (br, 2 H, CH₂), 1.75 (br, 2 H, CH₂), 2.80 (br, 4 H, ring CH₂), 3.78 (s, 3 H, CH₃O), 3.90 (t, J = 6.51, 2 H, CH₂O), 6.85 (s, 1 H, CH), 6.88 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.04 (CH₃), 20.19 (CH₂), 22.62 (CH₂), 25.64 (CH₂), 29.21 (CH₂), 31.54 (CH₂), 56.36 (CH₃O), 69.72 (CH₂O), 77.73 (C \equiv C), 93.77 (C \equiv C), 113.07, 113.89, 115.62, 117.98, 153.59, 153.79 (C₆H₂). M_n/M_w = 2600/4600 by GPC. IR (film, KBr, cm⁻¹) 2936, 2861, 2235 (C \equiv C stretch), 1501, 1464, 1403, 1273, 1203, 1039, 863.

Polymer 1d. A 100 mL Schlenk flask was charged with **6** (1.0 g, 2.3 mmol), 2-iodotoluene (**7**, 0.4 g, 0.2 mmol), Pd(PPh₃)₄ (0.13 g, 0.11 mmol), CuI (0.04 g, 0.21 mmol), *i*-Pr₂NH (7.0 mL), and THF (15.0 mL). To this solution under N₂ was added 1,7-octadiyne (0.25 g, 2.4 mmol) in 0.5 mL of THF. The resulting solution was allowed to stir at room temperature for 16 h. During this period, a substantial amount of white precipitate formed. The reaction mixture was then added slowly to rapidly stirring methanol (300 mL) to precipitate the crude polymer **1d** in near-quantitative yield. The polymer was further purified by washing a chloroform (50 mL) solution with dilute NH₄OH and then H₂O, evaporating the chloroform solution to dryness by rotoevaporation, redissolving the polymer in THF, and finally precipitating the polymer by adding the THF solution to rapidly stirring methanol (300 mL). This yields **1d** (48%, 0.32 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (br, 3 H, CH₃), 1.31 (br, 6 H, CH₂), 1.60 (br, 2 H, CH₂), 1.82 (br, 4 H, CH₂), 2.34 (s, 3 H, CH₃), 2.53 (br, 4 H, CH₂), 2.68 (t, J = 5.4 Hz, 2 H, CH₂), 7.18 (s, 1

H, CH), 7.20 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.15 (CH₃), 19.20 (CH₂), 20.03 (CH₂), 22.64 (CH₃), 27.98 (CH₂), 29.19 (CH₂), 30.61 (CH₂), 31.76 (CH₂), 34.03 (CH₂), 79.76, 79.96 (C \equiv C), 93.81, 94.45 (C \equiv C), 122.51, 122.93, 131.87, 132.90, 136.88, 141.76 (C₆H₂). M_n/M_w = 4600/12 000 by GPC. IR (film, KBr, cm⁻¹) 3020, 2927, 2857, 2226 (C \equiv C), 1492, 1456, 1437, 1327, 896, 734.

Polymer 1e. This compound was prepared by a procedure identical to that for **1d**, using 1,6-heptadiyne (0.23 g, 2.5 mmol) instead of 1,7-octadiyne and (0.09 g, 0.4 mmol) of 2-iodotoluene (**7**) to yield a lower molecular weight polymer with better solubility. This yields **1e** (42%, 0.28 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.87 (br, 3 H, CH₃), 1.30 (br, 6 H, CH₂), 1.59 (br, 2 H, CH₂), 1.92 (br, 2 H, CH₂), 2.34 (s, 3 H, CH₃), 2.65 (br, 2 H, CH₂), 2.67 (br, 4 H, CH₂), 7.18 (s, 1 H, CH), 7.19 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.12 (CH₃), 18.89 (CH₂), 20.01 (CH₂), 22.61 (CH₃), 28.17 (CH₂), 29.19 (CH₂), 30.63 (CH₂), 31.76 (CH₂), 34.03 (CH₂), 80.02, 80.19 (C \equiv C), 93.16, 93.89 (C \equiv C), 122.46, 122.94, 131.91, 132.89, 136.90, 141.84 (C₆H₂). M_n/M_w = 2000/3000 by GPC. IR (film, KBr, cm⁻¹) 2952, 2927, 2857, 2227 (C \equiv C stretch), 1492, 1456, 1436, 1028, 892, 693.

Polymer 1f. This compound was prepared by a procedure identical to that for **1d**, using 1,5-hexadiyne (0.20 g, 2.5 mmol) instead of 1,7-octadiyne and 2-iodotoluene (0.09 g, 0.4 mmol), to yield a lower molecular weight polymer with better solubility. This yields **1f** (40%, 0.25 g) as a light yellow-brown gummy solid. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, J = 5.1 Hz, 3 H, CH₃), 1.28 (br, 6 H, CH₂), 1.56 (br, 2 H, CH₂), 2.33 (s, 3 H, CH₃), 2.68 (t, J = 6.0, 2 H, CH₂), 2.78 (s, 4 H, CH₂), 7.20 (s, 1 H, CH₂), 7.24 (s, 1 H, CH₂). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.08 (CH₃), 19.91 (CH₂), 20.11 (CH₂), 22.56 (CH₃), 28.89 (CH₂), 30.44 (CH₂), 31.65 (CH₂), 33.82 (CH₂), 80.32, 80.53 (C \equiv C), 92.48, 93.06 (C \equiv C), 122.32, 122.78, 131.92, 132.79, 137.04, 141.92 (C₆H₂). M_n/M_w = 2300/3500 by GPC. IR (film, KBr, cm⁻¹) 3020, 2953, 2925, 2856, 2230 (C \equiv C stretch), 1492, 1456, 1437, 1337, 1254, 895.

Polymer 3a. A 100 mL Schlenk flask was charged with Cp₂ZrCl₂ (1.0 g, 3.4 mmol) and 30 mL of dry THF. The resulting solution was cooled to -78 °C in a dry ice acetone bath, and *n*-BuLi (4.0 mL, 1.6 M, 6.4 mmol) was added dropwise over 5 min. The solution was allowed to stir for 15 min at -78 °C, and then crude **1a** (0.72 g, 2.3 mmol of diyne units) in 10 mL of dry THF was slowly added via cannulae over 5 min. The reaction mixture was allowed to stir under N₂, while the bath slowly warmed to room temperature (3–4 h) and then was allowed to stir for an additional 1 h at room temperature. The conversion is very sensitive to a modest excess of *n*-BuLi, and the product (**2a**) will decompose if stirred at room temperature for > 8 h. **2a** was not isolated but was converted directly to **3a** by addition of HCl (15 mL, 6 M). The reaction mixture was then added slowly to rapidly stirring methanol (400 mL) to precipitate crude polymer **3a**. The polymer was purified by washing with methanol and then pentane. This yields **3a** (88%, 0.65 g) as a bright yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 0.87 (br, 3 H, CH₃), 1.32 (br, 4 H, CH₂), 1.45 (br, 2 H, CH₂), 1.68 (br, 4 H, ring CH₂), 1.76 (br, 2 H, CH₂), 2.65 (br, 4 H, ring CH₂), 3.81 (br, 3 H, OCH₃), 3.95 (br, 2 H, OCH₂), 6.72 (s, 2 H, CH), 6.81 (s, 2 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.05 (CH₃), 22.62 (CH₃), 25.78, 26.43, 29.42, 30.57, 31.61, (all CH₂), 56.23 (OCH₃), 69.79 (OCH₂), 113.36, 115.96, 119.49, 125.85, 127.01, 143.75, 150.47, 151.32 (aromatic and alkene). M_n/M_w = 6200/23 000 by GPC. Anal. Calcd for C₄₃₈H₅₈₂O₄₄: C, 80.28; H, 8.97. Found: C, 79.92; H, 9.03. IR (film, KBr, cm⁻¹) 2930, 2857, 1493, 1463, 1404, 1205, 1037, 880.

Polymer 3b. This compound was prepared by a procedure identical to that for **3a**, using **1b** (0.68 g, 2.3 mmol of diyne units) instead of **1a**. This yields **3b** (92%, 0.63 g) as a red solid. ¹H NMR (400 MHz, CDCl₃): δ 0.91 (br, 3 H, CH₃), 1.37 (br, 4 H, CH₂), 1.53 (br, 2 H, CH₂), 1.85 (br, 2 H, ring CH₂), 1.87 (br, 2 H, CH₂), 2.81 (br, 4 H, ring CH₂), 3.88 (s, 3 H, OCH₃), 4.01 (br, 2 H, OCH₂), 7.04 (s, 2 H, CH), 7.33 (s, 1 H, CH), 7.37 (s, 1 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 14.12 (CH₃), 22.73 (CH₃), 25.07 (CH₂), 25.95 (CH₂), 29.50 (CH₂), 31.71 (CH₂), 32.18 (CH₂), 56.15 (OCH₃), 69.68 (OCH₂), 111.59, 113.81, 114.03, 126.71, 127.02, 144.41, 150.84, 151.33 (aromatic and

alkene). $M_n/M_w = 6400/22\,000$ by GPC. Anal. Calcd for $C_{418}H_{542}O_{44}$: C, 80.05; H, 8.73. Found: C, 76.67; H, 8.45. IR (film, KBr, cm^{-1}) 2951, 2930, 2866, 1492, 1462, 1409, 1203, 1037, 881.

Polymer 3c. This compound was prepared by a procedure identical to that for **3a**, using **1c** (0.68 g, 2.4 mmol of diyne units) instead of **1a**. This yields **3c** (88%, 0.60 g) as a purple solid. 1H NMR (400 MHz, $CDCl_3$): δ 0.91 (br, 3 H, CH_3), 1.30 (br, 4 H, CH_2), 1.52 (br, 2 H, CH_2), 1.84 (br, 2 H, CH_2), 3.16 (br, 4 H, ring CH_2), 3.85 (s, 3 H, OCH_3), 3.98 (br, 2 H, OCH_2), 6.97 (s, 2 H, CH), 7.08 (s, 1 H, CH), 7.10 (s, 1 H, CH). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 14.04 (CH_3), 22.61 (CH_3), 25.86 (CH_2), 29.39 (CH_2), 30.72 (CH_2), 31.65 (CH_2), 56.19 (OCH_3), 69.61 (OCH_2), 109.68, 111.56, 111.72, 125.81, 126.45, 143.65, 150.65, 151.06 (aromatic and alkene). $M_n/M_w = 3200/7700$ by GPC. Anal. Calcd for $C_{208}H_{262}O_{24}$: C, 79.39; H, 8.41. Found: C, 79.52; H, 8.69. IR (film, KBr, cm^{-1}) 2952, 2932, 2861, 1495, 1464, 1413, 1285, 1206, 1040, 873, 802.

Polymer 3d. This compound was prepared by a procedure identical to that for **3a**, using **1d** (0.64 g, 2.3 mmol of diyne units) instead of **1a**. This yields **3d** (90%, 0.58 g) as a colorless solid. 1H NMR (400 MHz, $CDCl_3$): δ 0.89 (br, 3 H, CH_3), 1.33 (br, 6 H, CH_2), 1.58 (br, 2 H, CH_2), 1.65 (br, 4 H, ring CH_2), 2.31 (s, 3 H, CH_3), 2.50 (br, 4 H, ring CH_2), 2.62 (br, 2 H, CH_2), 6.56 (br, 1 H, CH), 6.61 (br, 1 H, CH), 7.04 (br, 2 H, CH). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 14.11 (CH_3), 19.73 (CH_2), 22.68 (CH_3), 26.81 (CH_2), 29.27 (CH_2), 30.50 (CH_2), 30.92 (CH_2), 31.79 (CH_2), 33.26 (CH_2), 122.10, 130.32, 131.29, 133.75, 134.94, 135.58, 138.59, 142.61 (aromatic and alkene). $M_n/M_w = 4300/29\,000$ by GPC. Anal. Calcd for $C_{434}H_{574}$: C, 89.99; H, 10.01. Found: C, 86.44; H, 9.31. IR (film, KBr, cm^{-1}) 2927, 2856, 1488, 1456, 1260, 1060, 913, 815.

Polymer 3e. This compound was prepared by a procedure identical to that for **3a**, using **1e** (0.64 g, 2.4 mmol of diyne units) instead of **1a**. This yields **3e** (84%, 0.55 g) as an orange solid. 1H NMR (400 MHz, $CDCl_3$): δ 0.88 (br, 3 H, CH_3), 1.32 (br, 6 H, CH_2), 1.60 (br, 2 H, CH_2), 1.79 (br, 2 H, ring CH_2), 2.39 (br, 3 H, CH_3), 2.73 (br, 6 H, CH_2 and ring CH_2), 7.07 (br, 1 H, CH), 7.12 (br, 1 H, CH), 7.26 (br, 2 H, CH). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 14.11 (CH_3), 19.85 (CH_2), 22.72 (CH_3), 25.09 (CH_2), 29.36 (CH_2), 31.20 (CH_2), 31.83 (CH_2), 32.21 (CH_2), 33.52 (CH_2), 116.39, 129.41, 130.33, 133.58, 135.01, 134.40, 138.64, 144.21 (aromatic and alkene). $M_n/M_w = 2400/6300$ by GPC. Anal. Calcd for $C_{414}H_{534}$: C, 90.21; H, 9.79. Found: C, 82.25; H, 9.40. IR (film, KBr, cm^{-1}) 2953, 2927, 2856, 1699, 1456, 1054, 904.

Polymer 3f. This compound was prepared by a procedure identical to that for **3a**, using **1f** (0.60 g, 2.4 mmol of diyne units) instead of **1a**. This yields **3f** (92%, 0.57 g) as a red solid. 1H NMR (400 MHz, $CDCl_3$): δ 0.91 (br, 3 H, CH_3), 1.34 (br, 6 H, CH_3), 1.63 (br, 2 H, CH_2), 2.40 (br, 3 H, CH_3), 2.56 (br, 2 H, CH_2), 3.15 (br, 4 H, ring CH_2), 6.85 (br, 2 H, CH), 7.21 (br, 1 H, CH), 7.28 (br, 1 H, CH). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 14.13 (CH_3), 19.53, 19.83, 19.89 (all CH_3), 22.70 (CH_3), 29.22 (CH_2), 30.63 (CH_2), 30.81 (CH_2), 31.22 (CH_2), 31.77 (CH_2), 33.23 (CH_2), 114.12, 126.89, 128.05, 129.01, 133.38, 135.12, 138.38, 144.02 (aromatic and alkene). $M_n/M_w = 4200/9400$ by GPC. Anal. Calcd for $C_{204}H_{254}$: C, 90.52; H, 9.48. Found: C, 87.29; H, 9.55. IR (film, KBr, cm^{-1}) 2954, 2925, 2856, 1489, 1457, 886.

2-Methoxy-5-hexoxy-1,4-diiodobenzene (4). This compound was synthesized from 1-*n*-hexoxy-4-methoxybenzene, via a modified literature procedure.¹⁶ A 1000 mL flask was charged with 30 g of 1-*n*-hexoxy-4-methoxybenzene (144 mmol), 32 g of I_2 (126 mmol), 7.2 g of HIO_3 (41 mmol), 30 mL of H_2SO_4 , 50 mL of H_2O , and 300 mL of CH_3COOH . The reaction mixture was heated at 70 °C for 12 h, followed by neutralization with a saturated NaOH solution until pH > 6. The reaction mixture was extracted with pentane (3 \times 200 mL) and washed with saturated aqueous $Na_2S_2O_3$ (2 \times 250 mL) to remove the residual I_2 . Removal of solvent from the combined extracts gave a white solid, which was recrystallized from methanol to give 50.4 g of **4** as white crystals (76% yield). 1H NMR (400 MHz, C_6D_6): δ 0.89 (t, 3H, $J = 6.8$, CH_3), 1.25 (m, 6H, CH_2), 1.50 (m, 2H, CH_2), 2.96 (s, 3H, OCH_3), 3.30 (t, 2H, $J = 6.8$, CH_2O), 6.94 (s, 1H, C_6H_2), 7.05 (s, 1H, C_6H_2). ^{13}C { 1H } NMR (400 MHz, C_6D_6): 14.26 (CH_3), 22.93, 25.96, 29.31, 31.72 (CH_2), 56.29 (OCH_2), 69.84 (OCH_3), 85.93, 86.58, 121.58, 122.91, 153.27, 153.59 (aromatic). Anal. Calcd for

$C_{13}H_{18}O_2I_2$: C, 33.93; H, 3.95. Found: C, 33.87; H, 3.92. IR (KBr, cm^{-1}) 2963, 2936, 2859, 1485, 1462, 1434, 1350, 1214, 1055, 1020, 996, 941, 850, 774.

2,5-Dimethoxy-4-methylidobenzene (5). This compound was prepared from 1,4-dimethoxy-3-methylbenzene, via a modified literature procedure.¹⁶ A 1000 mL flask was charged with 12.0 g of 1,4-dimethoxy-3-methylbenzene (79 mmol), 13.0 g of I_2 (50 mmol), 1.8 g of HIO_3 (8.5 mmol), 300 mL of CH_3COOH , 80 mL of H_2O , and 20 mL of H_2SO_4 . The reaction mixture was heated at 70 °C for 12 h and treated as described above. Recrystallization from methanol gave 19.9 g of **5** as white crystals (91% yield). 1H NMR (400 MHz, $CDCl_3$): δ 2.19 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.68 (s, 1H, C_6H_2), 7.17 (s, 1H, C_6H_2). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 16.5 (CH_3), 56.1 (OCH_3), 57.0 (OCH_3), 81.4, 114.0, 121.0, 127.9, 152.2, 152.5 (aromatic). Anal. Calcd for $C_9H_{11}O_2I$: C, 38.87; H, 3.99. Found: C, 38.97; H, 3.94. IR (KBr, cm^{-1}) 3003, 2959, 2919, 2840, 1494, 1467, 1440, 1368, 1280, 1212, 1047, 1030, 853, 778, 707.

1,4-Diiodo-2-methyl-5-hexylbenzene (6). This compound was prepared from 1-hexyl-4-methylbenzene, via a modified literature procedure.²⁶ A 1000 mL flask was charged with 50.0 g of 1-hexyl-4-methylbenzene (283 mmol), 50.0 g of I_2 (200 mmol), 10 g of HIO_3 (57 mmol), 350 mL of CH_3COOH , 50 mL of H_2O , and 30 mL of H_2SO_4 . The reaction mixture was heated at 70 °C for 4 days and treated as described above. Recrystallization from methanol gave 71.3 g of **6** as white crystals (59% yield). 1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 3H, $J = 6.8$, CH_3), 1.31 (mult, 6H, CH_2), 1.53 (mult, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.58 (t, 2H, $J = 6.5$, CH_2), 7.59 (s, 1H, C_6H_2), 7.64 (s, 1H, C_6H_2). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 14.09 (CH_3), 22.58 (CH_3), 26.87, 28.95, 30.18, 31.59, 39.79 (CH_2), 100.09, 100.86, 138.82, 139.70, 140.68, 144.77 (aromatic). Anal. Calcd for $C_{13}H_{18}I_2$: C, 36.45; H, 4.25. Found: C, 36.58; H, 4.22. IR (KBr, cm^{-1}) 2950, 2921, 2847, 1459, 1343, 1039, 878, 768.

1,8-bis-(2',5'-dimethoxy-4'-methylphenyl)-1,7-octadiyne (8a). A 500-mL round-bottom flask was charged with 2,5-dimethoxy-4-methylidobenzene (**5**, 5.0 g, 18 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.10 mmol), CuI (0.04 g, 0.21 mmol), *i*- Pr_2NH (50 mL), and THF (100 mL). To the solution was added 1,7-octadiyne (0.98 g, 9.2 mmol) dropwise over 5 min. The reaction mixture was stirred at room temperature for 18 h. During this period, a substantial amount of white precipitate formed. Addition of pentane (200 mL) to the reaction mixture was followed by washing with dilute HCl, H_2O , saturated $NaHCO_3$, and H_2O . The pentane was removed by rotoevaporation, and the residual oil was dissolved in warm methanol and recrystallized at -40 °C to yield white crystals (3.2 g, 87% yield): mp = 117–119 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.83 (t, $J = 5.9$, 4H, CH_2), 2.20 (s, 6 H, CH_3), 2.54 (t, $J = 7.0$, 4 H, CH_2), 3.76 (s, 6 H, CH_3O), 3.82 (s, 6 H, CH_3O), 6.66 (s, 2 H, C_6H_2), 6.83 (s, 2 H, C_6H_2). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 16.6 (CH_2), 19.4 (CH_3), 28.1 (CH_2), 55.9, 56.5 (CH_3O), 77.2, 93.3 ($C\equiv C$), 110.2, 114.1, 115.0, 127.8, 151.3, 154.0 (C_6H_2). HRMS m/z calcd 406.2144; found 406.2136. IR (Nujol, KBr, cm^{-1}) 2954, 2924, 2855, 1502, 1210, 1042, 862.

1,7-Bis-(2',5'-dimethoxy-4'-methylphenyl)-1,6-heptadiyne (8b). This compound was prepared by a procedure identical to that for **8a**, using 1,6-heptadiyne (0.92, 4.4 mmol) instead of 1,7-octadiyne. The product was isolated as a light yellow solid after recrystallization from methanol (3.0 g, 85% yield): mp = 98–101 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.85 (q, $J = 6.8$, 2H, CH_2), 2.27 (s, 6 H, CH_3), 2.76 (t, $J = 6.4$, 4 H, CH_2), 3.83 (s, 6 H, CH_3O), 3.85 (s, 6 H, CH_3O), 6.73 (s, 2 H, C_6H_2), 6.96 (s, 2 H, C_6H_2). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 16.6 (CH_2), 19.1 (CH_3), 28.2 (CH_2), 55.8 (OCH_3), 56.5 (OCH_3), 77.4, 92.7 ($C\equiv C$), 110.1, 114.0, 115.0, 127.9, 151.3, 153.9 (C_6H_2). HRMS m/z calcd 392.1988; found 392.1984. IR (Nujol, KBr, cm^{-1}) 2954, 2924, 2854, 1512, 1499, 1396, 1282, 1225, 1209, 1042, 869, 843, 796.

1,6-Bis-(2',5'-dimethoxy-4'-methylphenyl)-1,5-hexadiyne (8c). This compound was prepared by a procedure identical to that for **8a**, using 1,5-hexadiyne (0.72 g, 9.2 mmol) instead of 1,7-octadiyne. The product was isolated as a light yellow solid after recrystallization from methanol (2.5 g, 72% yield): mp = 131–133 °C. 1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 6 H, CH_3), 2.81 (s, 4 H, CH_2CC), 3.73 (s, 6 H,

CH₃O), 3.81 (s, 6 H, CH₃O), 6.66 (s, 2 H, C₆H₂), 6.84 (s 2H, C₆H₂). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 16.6 (CH₂), 20.3 (CH₃), 55.8, 56.6 (CH₃O), 77.9, 91.9 (C≡C), 110.1, 114.2, 115.2, 128.1, 151.4, 154.0 (C₆H₂). HRMS *m/z* calcd 378.1831; found 378.1828. IR (Nujol, KBr, cm⁻¹) 2995, 2933, 2848, 2830, 1502, 1465, 1395, 1209, 1044, 862.

1,8-Diphenyl-1,7-octadiyne (8d). A 500-mL round-bottom flask was charged with iodobenzene (10.0 g, 49 mmol), Pd(PPh₃)₄ (0.11 g, 0.10 mmol), CuI (0.04 g, 0.21 mmol), *i*-Pr₂NH (100 mL), and THF (200 mL). To this solution was added 1,7-octadiyne (2.7 g, 25 mmol) dropwise over 5 min. The reaction was allowed to stir at room temperature for 18 h. During this period, a substantial amount of white precipitate formed. Addition of pentane (200 mL) to the reaction mixture was followed by washing with dilute HCl, H₂O, saturated NaHCO₃, and H₂O. The pentane was removed by rotoevaporation, and the residual oil was dissolved in warm methanol and recrystallized at -40 °C to yield white crystals (4.8 g, 76% yield): mp = 31–33 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.78 (m, 4 H, CH₂), 2.49 (m, 4 H, CH₂), 7.28 (m, 6 H, C₆H₅), 7.45 (m, 4 H, C₆H₅). ¹³C {¹H} NMR (100.7 MHz, CDCl₃): δ 19.06, 27.93 (CH₂), 80.98, 89.86 (C≡C), 123.99, 127.59, 128.23, 131.60 (C₆H₅). HRMS *m/z* calcd 258.1409; found 258.1412. IR (Nujol, KBr, cm⁻¹) 3055, 2942, 2862, 2230 (C≡C stretch), 1598, 1490, 1441, 1330, 1070, 914, 756, 691.

1,7-Diphenyl-1,6-heptadiyne (8e). This compound was prepared by a procedure identical to that for **8d**, using 1,6-heptadiyne (2.3 g, 25 mmol) instead of 1,7-octadiyne. After column chromatography (silica gel, hexane) the product was isolated as a light yellow oil (4.3 g, 72% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.97 (q, *J* = 5.2, 2H, CH₂), 2.66 (t, *J* = 7.0, 4 H, CH₂), 7.33 (mult, 6 H, C₆H₅), 7.50 (mult, 4H, C₆H₅). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 18.8, 28.08 (CH₂), 81.41, 89.33 (C≡C), 123.95, 127.76, 128.34, 131.70 (C₆H₅). HRMS *m/z* calcd 244.1252, found 244.1245. IR (Nujol, KBr, cm⁻¹) 2954, 2924, 2855, 2225 (C≡C stretch), 1499, 1396, 1282, 1225, 1209, 1042, 918, 869, 718, 695.

1,6-Diphenyl-1,5-hexadiyne (8f). This compound was prepared by a procedure identical to that for **8d**, using 1,5-hexadiyne (2.0 g, 25 mmol) instead of 1,7-octadiyne. The product was isolated as a light yellow solid after recrystallization from methanol (3.8 g, 67% yield): mp = 49–50 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.66 (s, 4 H, CH₂), 7.27 (mult, 6 H, C₆H₅), 7.41 (mult, 4 H, C₆H₅). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 19.81 (CH₂), 81.57, 83.35 (C≡C), 123.63, 127.78, 128.22, 131.65 (C₆H₅). Anal. Calcd for C₁₈H₁₄: C, 93.86; H 6.14; found C, 93.43; H, 6.04. HRMS *m/z* calcd 230.1096, found 230.1092. IR (Nujol, KBr, cm⁻¹) 3055, 2911, 2840, 2450 (C≡C stretch), 1488, 1441, 1275, 1071, 917, 755, 693.

(*E,E*)-1,2-Bis[(2',5'-dimethoxy-4'-methylphenyl)methylene]cyclohexane (9a). A 100 mL Schlenk flask was charged with Cp₂ZrCl₂ (0.29 g, 1.0 mmol) and 30 mL of dry THF. The solution was cooled to -78 °C in a dry ice acetone bath, and *n*-BuLi (1.2 mL, 1.6 M, 1.9 mmol) was added dropwise over 5 min. The solution was allowed to stir for 15 min at -78 °C, and then **8a** (0.38 g, 0.94 mmol) in 10 mL of dry THF was slowly added via cannulae over 5 min. The reaction was allowed to stir under N₂ while the bath slowly warmed to room temperature (3–4 h), after which it was stirred for an additional 1 h at room temperature. The zirconacyclopentadiene was not isolated but was converted directly to **9a** by addition of HCl (15 mL, 6 M). Addition of Et₂O (40 mL) to the reaction mixture was followed by washing with dilute HCl, H₂O, saturated NaHCO₃, and H₂O. The Et₂O was removed by rotoevaporation leaving a residual oil. The oil was recrystallized from 1:1 Et₂O/pentane to yield 81% of **9a** (0.31 g, 0.76 mmol): mp = 124–126 °C. ¹H NMR (400 MHz, CDCl₃): 1.66 (m, 4 H, CH₂), 2.25 (s, 6 H, CH₃), 2.62 (m, 4 H, CH₂), 3.80 (s, 6 H, OCH₃), 3.81 (s, 6 H, OCH₃), 6.69 (s, 2 H, CH), 6.17 (s, 2 H, CH), 6.76 (s, 2 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 16.4 (CH₃), 26.4 (CH₂), 30.5 (CH₂), 56.1 (OCH₃), 56.3 (OCH₃), 113.4, 113.9, 119.5, 124.8, 126.0, 143.7, 151.0, 151.6 (C₆H₂ and C=C). HRMS *m/z* calcd 408.2301; found 408.2295. IR (Nujol, KBr, cm⁻¹) 2928, 2856, 1501, 1398, 1302, 1209, 1045, 875.

(*E,E*)-1,2-Bis[(2',5'-dimethoxy-4'-methylphenyl)methylene]cyclopentane (9b). This compound was prepared by a procedure identical to that for **9a**, using **8b** (0.50 g, 1.3 mmol) instead of **8a**. The oil was recrystallized from 1:1 Et₂O/pentane to yield 77% of **9b** (0.41 g, 1.0

mmol): mp = 141–143 °C. ¹H NMR (400 MHz, CDCl₃): 1.83 (m, 2H, CH₂), 2.25 (s, 6 H, CH₃), 2.74 (m, 4 H, CH₂), 3.81 (s, 6 H, OCH₃), 3.83 (s, 6 H, OCH₃), 6.71 (s, 2 H, CH), 6.94 (s, 2 H, CH), 7.24 (s, 2 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 16.4 (CH₃), 25.0 (CH₂), 32.0 (CH₂), 56.1 (OCH₃), 56.3 (OCH₃), 111.9, 113.8, 113.9, 125.4, 126.0, 143.6, 151.2, 151.3 (C₆H₂ and C=C). HRMS *m/z* calcd 394.2144; found 394.2146. IR (Nujol, KBr, cm⁻¹) 2954, 2924, 2855, 1503, 1401, 1207, 1045.

(*E,E*)-1,2-Bis[(2',5'-dimethoxy-4'-methylphenyl)methylene]cyclobutane (9c). This compound was prepared by a procedure identical to that for **9a**, using **8c** (0.50 g, 1.3 mmol) instead of **8a**. The oil was recrystallized from 1:1 Et₂O/pentane to yield 85% of **9c** (0.42 g, 1.1 mmol): mp = 137–141. ¹H NMR (400 MHz, CDCl₃): 2.24 (s, 6H, CH₃), 3.14 (s, 4 H, CH₂), 3.81 (s, 6 H, OCH₃), 3.84 (s, 6 H, OCH₃), 6.71 (s, 2 H, CH), 6.93 (s, 2 H, CH), 7.05 (s, 2 H, CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 16.4 (CH₃), 30.4 (CH₂), 55.9 (OCH₃), 56.5 (OCH₃), 109.6, 111.3, 114.4, 124.5, 126.2, 142.7, 150.9, 151.7 (C₆H₂ and C=C). EIMS: M⁺ = 380. HRMS *m/z* calcd 380.1987; found 380.1978. IR (Nujol, KBr, cm⁻¹) 2954, 2924, 2855, 1508, 1403, 1289, 1225, 1208, 1045, 871, 850.

(*E,E*)-1,2-Bis(phenylmethylene)cyclohexane (9d). A 100 mL Schlenk flask was charged with Cp₂ZrCl₂ (1.0 g, 3.4 mmol) and 30 mL of dry THF. The solution was cooled to -78 °C in a dry ice acetone bath and *n*-BuLi (4.0 mL, 1.6 M, 6.5 mmol) was added dropwise over 5 min. The solution was allowed to stir for 15 min at -78 °C, and then **8d** (0.83 g, 3.2 mmol) in 10 mL dry THF was slowly added via cannulae over 5 min. The reaction was allowed to stir under N₂ while the bath slowly warmed to room temperature (3–4 h), and stirring was continued for an additional 1 h at room temperature. The zirconacyclopentadiene was not isolated but was converted directly to **9d** by addition of HCl (15 mL, 6 M). Addition of Et₂O (40 mL) to the reaction mixture was followed by washing with dilute HCl, H₂O, saturated NaHCO₃, and H₂O. The Et₂O was removed by rotoevaporation leaving a residual oil. The oil was recrystallized from 1:1 Et₂O/pentane to yield 81% of **9d** (0.68 g, 2.6 mmol): mp = 125–127 °C. ¹H NMR (400 MHz, CDCl₃): 1.66 (m, 4 H, CH₂), 2.65 (m, 4 H, CH₂), 6.64 (s, 2 H, CH), 7.23 (m, 4 H, C₆H₅), 7.34 (m, 6 H, C₆H₅). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 26.27 (CH₂), 29.96 (CH₂), 124.13, 126.34, 128.05, 129.46, 137.98, 144.47 (C₆H₅ and C=C). IR (Nujol, KBr, cm⁻¹) 3021, 2940, 2866, 1420, 921, 863, 699.

(*E,E*)-1,2-Bis(phenylmethylene)cyclopentane (9e). This compound was prepared by a procedure identical to that for **9d**, using **8e** (0.75 g, 3.1 mmol) instead of **8d**. The oil was recrystallized from 1:1 Et₂O/pentane and then sublimed to yield 84% of **9e** (0.64 g, 2.6 mmol): mp = 149–151 °C. ¹H NMR (400 MHz, CDCl₃): 1.85 (m, 2 H, CH₂), 2.78 (m, 4 H, CH₂), 6.99 (s, 2 H, CH), 7.22 (m, 2 H, C₆H₅), 7.36 (m, 4 H, C₆H₅), 7.43 (m, 4 H, C₆H₅). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 25.1 (CH₂), 32.0 (CH₂), 119.15, 126.41, 128.30, 128.87, 138.32, 144.37 (C₆H₅ and C=C). HRMS *m/z* calcd 246.1409; found 246.1406. Anal. Calcd for C₁₉H₁₈: C, 92.62; H, 7.38. Found C, 92.37; H, 7.36. IR (Nujol, KBr, cm⁻¹) 3052, 3025, 2953, 2924, 2855, 1485, 1446, 1175, 1077, 919, 866, 741, 695.

(*E,E*)-1,2-Bis(phenylmethylene)cyclobutane (9f). This compound was prepared by a procedure identical to that for **9d**, using **8f** (1.5 g, 6.5 mmol) instead of **8d**. The oil was recrystallized from 1:1 Et₂O/Pentane to yield 80% of **9f** (1.2 g, 5.2 mmol): mp = 125–128. ¹H NMR (400 MHz, CDCl₃): 3.14 (s, 4 H, CH₂), 6.34 (s, 2 H, CH), 7.19 (m, 2 H, C₆H₅), 7.32 (m, 8 H, C₆H₅). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 30.65 (CH₂), 117.50, 126.59, 127.80, 128.53, 137.42, 143.75 (C₆H₅ and C=C). HRMS *m/z* calcd 232.1252; found 232.1253. IR (Nujol, KBr, cm⁻¹) 3079, 3057, 3020, 2962, 2922, 1446, 908, 855, 744, 689, 512.

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Supporting Information Available: Tables of positional and thermal parameters, bond lengths, angles, and torsional angles and figures for the crystal structures of **9c** and **9d** and absorption, excitation, and emission spectra for polymers **3c–f**

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